



“Gheorghe Asachi” Technical University of Iasi, Romania



## OPTIMIZATION OF SOME CATIONS FOR REMOVAL OF ARSENIC FROM GROUNDWATER BY ELECTROCOAGULATION PROCESS

Mehmet Kobya<sup>1</sup>, Emrah Sık<sup>2</sup>, Erhan Demirbas<sup>3\*</sup>, Aysegül Yagmur Goren<sup>4</sup>,  
Mehmet Salim Oncel<sup>1</sup>

<sup>1</sup>Department of Environmental Engineering, Gebze Institute of Technology, Gebze, Turkey

<sup>2</sup>TÜBİTAK Marmara Research Center, Environmental and Cleaner Production Institute, Gebze, Turkey

<sup>3</sup>Department of Chemistry, Gebze Institute of Technology, Gebze, Turkey

<sup>4</sup>Department of Environmental Engineering, İzmir Institute of Technology, İzmir, Turkey

### Abstract

This study dealt with investigation of arsenic removal from groundwater using electrocoagulation (EC) method in a batch mode by the Box-Behnken experimental design method. Effects of some cations like Ca, Fe, Mg, Mn and operating time on the removal were explored by an air injected EC reactor. The combined effects of these variables were analyzed by the quadratic model for predicting the highest removal efficiency of arsenic from groundwater. The arsenic removal efficiency was found to be dependent on increase with operating time and concentrations of Ca, Mg, Fe and lower concentration of Mn. When operating variables were considered as minimum operating cost and maximum removal efficiency, the optimum operating parameters were determined to be 132 mg/L of  $C_{Ca}$ , 55 mg/L of  $C_{Mg}$ , 4.5 mg/L of  $C_{Fe}$ , 4.5 mg/L of  $C_{Mn}$  and operating time of 3 min to meet the target concentration of <10 µg/L. Values of removal efficiency and operating cost at the optimum conditions were 95.1% and 0.041 \$/m<sup>3</sup>.

*Key words:* arsenic removal, cations effects, electrocoagulation, groundwater, reactor design

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### 1. Introduction

Groundwater and surface water contamination through arsenic is one of the major environmental problems in the present time because many people are exposed to excessive amounts of arsenic through contaminated drinking water (Camacho et al., 2011; Mandal and Suzuki, 2002; Mondal et al., 2013). Arsenic contamination in groundwater has been found to occur due to geothermally-influenced groundwater, mineral dissolution (e.g., pyrite oxidation), desorption in the oxidising environment, and reductive desorption and dissolution (Smedley and Kinniburgh, 2002). Argentina, Bangladesh, China, India, Mexico, Mongolia, Thailand and Taiwan where a large proportion of groundwater is contaminated with arsenic in the range 50 - 3200 µg/L (Ali et al., 2012;

Ravenscroft, 2009). Turkey is one of the countries under the threat of arsenic pollution since concentrations of arsenic in groundwater and surface water vary from 0.5 to 10700 µg/L in the last ten years (Altas et al., 2011; Colak, 2003; Gemici et al., 2008; Gunduz et al., 2010; Dogan and Dogan, 2007; Simsek, 2013).

Arsenic in groundwater occurs in two oxidation states As(III) (arsenite) and As(V) (arsenate). As(III) is more mobile in groundwater and 25-60 times more toxic than As(V). In each case, the removal efficiency is influenced by the chemical form of the arsenic present in the water, usually as As(V) or As(III) (Vaclavikova et al., 2008). Exposure to high levels of arsenic can cause problems such as skin lesions, neurological effects, hyperkeratosis, obstetric problems, diseases of the respiratory system and

\* Author to whom all correspondence should be addressed: e-mail: erhan@gyte.edu.tr; Phone: +90 2626053010; Fax: +90 2626053005

melanosis (Bhattacharjee et al., 2013; Col et al., 1999; Rahman et al., 2009). Based on the above adverse health effects, World Health Organization (WHO) and US Environmental Protection Agency (USEPA) recommended the new maximum contaminant level (MCL) of arsenic in drinking water to 10 µg/L (USEPA, 2001; WHO, 1996). A number of treatment methods such as adsorption, precipitation/coprecipitation, membrane filtration, coagulation, ion exchange resins were conducted to study the arsenic removal (Chen et al., 1999; Heather et al., 2010; Vaclavikova et al., 2008). In addition, USEPA has identified best available technologies for removing arsenic (%) from drinking water; technologies likely to be used by small systems (activated alumina: 95%, enhanced lime softening: 90%), other technologies (ion-exchange: 95%, coagulation-assisted microfiltration: 90%, enhanced coagulation/filtration: 95%, oxidation/filtration including greensand filtration: 80%, reverse osmosis: 95%, electrodialysis: 85%) (USEPA, 2000). These methods were reported to be effective mainly for the removal of As(V). Therefore, a pre-oxidation step with Cl<sub>2</sub>, KMnO<sub>4</sub> and HOCl was usually required, in order to achieve efficient removal As(III) (Guan et al., 2009; Sorlini and Gialdini, 2010). Thus, there is an urgent need for the development of a simple, economical and efficient removal technology for both As(III) and As(V).

In recent years, electrocoagulation (EC) process has been shown to be a promising and alternative method for treatment of groundwater containing arsenic because of higher removal efficiency, removing to trace levels, reduced amount of sludge, no addition of chemical for pre-oxidation of As(III) to As(V), simple in operation, compact treatment facility, and relatively cost-effective (Ali et al., 2012; Flores et al., 2013; Garcia-Lara and Montero-Ocampo, 2010; Hansen et al., 2007; Kobyta et al., 2011, 2013, 2014; Lakshmanan et al., 2010; Parga et al., 2005; Vasudevan and Oturan, 2014; Vasudevan et al., 2010; Wan et al., 2011). In the literature, plate and rod types of Al or Fe electrodes for removal of arsenic from waters were generally used in the EC reactors (Garcia-Lara and Montero-Ocampo, 2010; Kobyta et al., 2011; Lakshmanan et al., 2010; Wan et al., 2011). Moreover, changing of these electrodes in the reactors was time consuming and has a limited surface area. In the earlier studies, the EC reactors using Fe ball anodes were applied successfully for removal of arsenic from groundwater (Kobyta et al., 2014; Sik et al., 2013).

In this study, the new designed EC reactor (Fig. 1) with an air injection unit including iron ball anodes was used for the removal. The new EC reactor needs to be optimised for different types of groundwater samples since their compositions contain different amounts of anions (phosphate, sulfate, carbonate, silicate, fluoride, etc.) and cations (iron, manganese, calcium, magnesium, etc.) which could have some effects on the removal of arsenic from groundwater. Therefore, this study focused concentration effects of

some cations and operating time on the arsenic removal. Full three-level Box-Behnken experimental design was used as a design framework for second-order response surface modeling to evaluate the influence of important process variables on the efficiency of arsenic removal from groundwater. The interactions between these parameters were also studied and optimized.

## 2. The removal of arsenic with Fe electrode in the EC process

The EC process operates on the principle that the cations produced electrolytically from iron anodes enhance the coagulation of contaminants from an aqueous medium. The EC process generates coagulants in situ by dissolving iron from the anodes (Eqs. 1 and 5). H<sub>2(g)</sub> bubbles produced at the cathode carry the pollutant to the top of the solution where it is removed (Eqs. 2 and 6). In EC process, the sacrificial Fe anodes were used to continuously produce monomeric and polymeric Fe species such as Fe(OH)<sup>2+</sup>, Fe(OH)<sub>2</sub><sup>+</sup>, Fe<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, Fe(H<sub>2</sub>O)<sub>2</sub><sup>+</sup>, Fe(H<sub>2</sub>O)<sub>5</sub>OH<sup>2+</sup>, Fe(H<sub>2</sub>O)<sub>4</sub>OH<sub>2</sub><sup>+</sup>, Fe(H<sub>2</sub>O)<sub>8</sub>OH<sub>2</sub><sup>4+</sup>, Fe<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>OH<sub>4</sub><sup>2+</sup>, and Fe(OH)<sub>4</sub><sup>-</sup> (Gomes et al., 2007; Kobyta et al., 2014). These positive charged species led to coagulation by neutralizing the negatively charged species such as H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup> and AsO<sub>4</sub><sup>3-</sup> which were moved to the anodes by electrophoretic motion. In addition, the rate of the oxidation of Fe<sup>2+</sup> ions in solution depended on the availability of dissolved oxygen in the solution (Eq. 4). The oxidation of Fe<sup>2+</sup> was slow at pH 6.5 and hydroxides produced at the cathode were not used up which resulted in a pH increase. At 6.5 ≥ pH ≤ 8.5, Fe(OH)<sub>3(s)</sub> led to a pH decrease. The Fe<sup>2+</sup> produced during the EC underwent complete oxidation to form Fe(OH)<sub>3(s)</sub> at pH ≥ 6.5. Therefore, removal rate of arsenic was better as pH ≥ 6.5. Lakshmanan et al. (2009, 2010) indicated that at pH 8.5, Fe<sup>2+</sup> was completely oxidized and resulted in Fe(OH)<sub>3(s)</sub>. As Fe(OH)<sub>3(s)</sub> was amphoteric, some Fe(OH)<sub>4</sub><sup>-</sup> formation was likely at pH 8.5 since OH<sup>-</sup> ions were consumed to form iron hydroxide complexes. Typically, at the cathode the solution becomes alkaline with time. The applied current forced OH<sup>-</sup> ion migration towards the cathode and combine with hydroxide ions (Eqs. 3 and 7).

Mechanism 1:

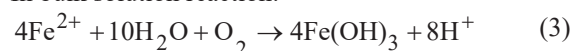
Anode reaction:



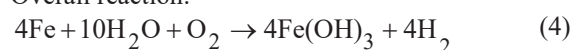
Cathode reaction:



In bulk solution reaction:



Overall reaction:



Mechanism 2:

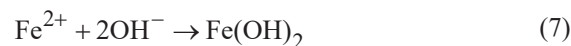
Anode reaction:



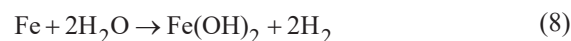
Cathode reaction:



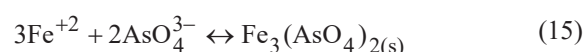
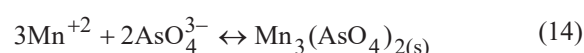
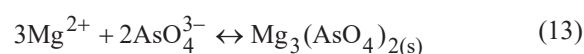
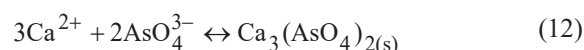
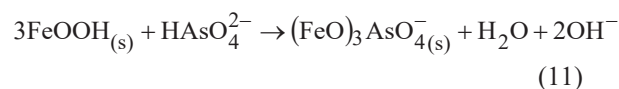
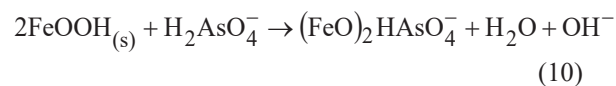
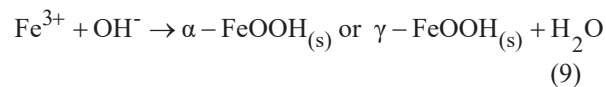
In bulk solution reaction:



Overall reaction:



In the EC process, both As(V) and As(III) were strongly sorbed by  $\text{Fe}^{3+}$  oxides such as amorphous  $\text{Fe}(\text{OH})_{3(s)}$ , hydrous ferric oxide (HFO) goethite ( $\alpha\text{-FeOOH}$ ) and lepidocrocite ( $\gamma\text{-FeOOH}$ ) during the process (Balasubramanian et al., 2009; Garcia-Lara and Montero-Ocampo, 2010; Hansen et al., 2007; Kobya et al., 2011). For pH values common in groundwater, the predominate As(V) species in solution were  $\text{H}_2\text{AsO}_4^{-}$  between pH 2.2 and 6.9, and  $\text{HAsO}_4^{2-}$  between pH 6.9 and 11.5.  $\text{H}_3\text{AsO}_3^0$  predominated up to pH 9.2, and  $\text{H}_2\text{AsO}_3^{-}$  from pH 9.2-12 (Welch and Stollenwerk, 2003). The arsenic removal occurred by ligand exchange, arsenate displaced a hydroxyl group of  $\text{FeOOH}$  giving rise to an insoluble surface complex (Eqs. 9-11). As(III) since As(V) species in the solution were adsorbed by the  $\text{Fe}(\text{OH})_3$  and HFO colloids. Arsenate anion bound to HFO may form naturally occurring arsenate minerals  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$  (scorodite) and  $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  (symplectite) as the dominant solid phase (Balasubramanian et al., 2009). Therefore, arsenic was removed by compound formation or surface complex adsorption or both (Eqs. (9-11)) and co-precipitation (Eqs. 12-15) (Mcneill and Edwards, 1997).



### 3. Material and methods

#### 3.1. Groundwater characteristics

Groundwater for the EC experiments was obtained from a well situated in the province of Kocaeli, Turkey and stored in 5 tones high-density polyethylene container. Characterizations of the groundwater were shown in Table 1. The groundwater sample was prepared daily by dissolving sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) for As(V) and sodium arsenite  $\text{NaAsO}_2$  for As(III). Magnesium, calcium, iron and manganese stock solutions were prepared from  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{FeSO}_4$  and  $\text{MnCl}_2$ .

**Table 1.** Characteristics of groundwater

Parameters	Value
pH	7.5
Conductivity (mS/cm) at 20 °C	1.1-1.3
Dissolved $\text{O}_2$ (mg/L)	8.95
Alkalinity ( $\text{CaCO}_3$ , mg/L)	260
TDS (mg/L)	528
$\text{Ca}^{2+}$ (mg/L)	152
$\text{Mg}^{2+}$ (mg/L)	15
SiO <sub>2</sub> -Si (mg/L)	10
Cl <sup>-</sup> (mg/L)	127
SO <sub>4</sub> <sup>2-</sup> (mg/L)	94
NO <sub>3</sub> <sup>-</sup> (mg/L)	24

#### 3.2. The air injected EC reactor

The new EC reactor with an air injection unit was designed for removal of arsenic from groundwater (Fig. 1). The reactor consisted of a round bottom base unit (150 mm in diameter and 45 mm in thickness) having a number of round holes in 2 mm diameter drilled with equidistant and a direct air is supplied underneath with a compressor. An air feed diffuser was attached underneath the base unit. A cylindrical shaped Plexiglas (245 mm×100 mm×5 mm) was fixed to the base unit. Another cylindrical shaped titanium cathode (250 mm×70 mm×1 mm) with 5 mm in diameter holes drilled in equidistant (10 mm intervals) all over the length was placed inside the Plexiglas cylinder (250 mm×60 mm×5 mm). Second Plexiglas cylinder with 2 mm in diameter drilled holes over the length was placed inside the cathode and filled with iron ball anodes (2-8 mm in size up to 8 cm height in the reactor). The titanium cylinder as cathode was connected to the negative outlet of a DC power supply (Agilent 6675A model). A stainless steel rod (260 mm in length and 2mm in diameter) for connection to applied electrical current was immersed in the center of iron ball anodes and connected to the positive outlet of the DC power supply. The anodes have higher surface areas due to its shape and size.

A volume of 0.80 L of the groundwater containing 200 µg/L of total As (100 µg/L of As (III) and 100 µg/L of As(V) in equal volume was placed into the EC reactor for each run. Current and voltage were held constant at desired values and the experiment was started.

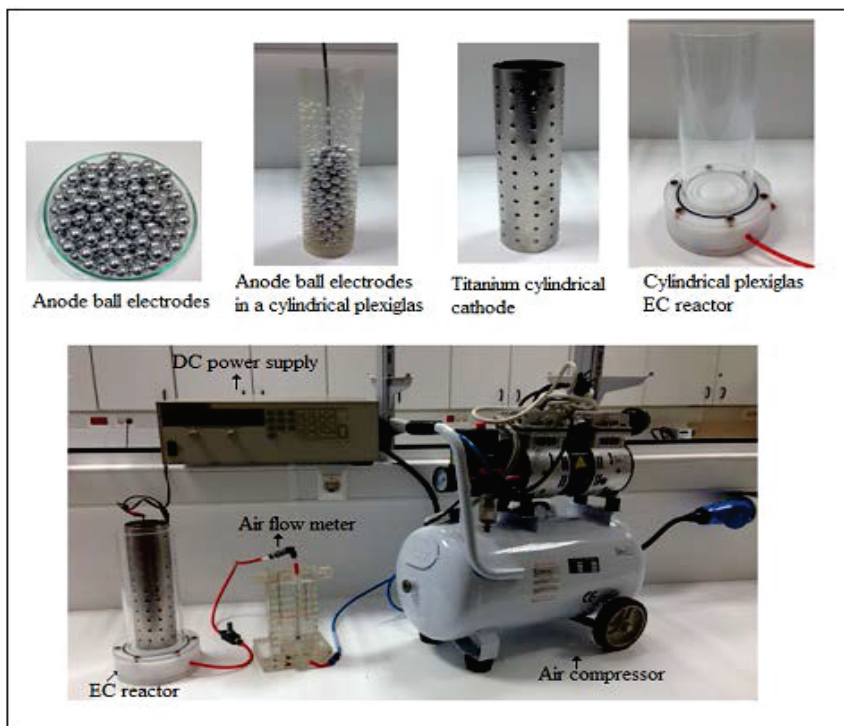


Fig. 1. An air fed EC reactor

The samples taken from the EC reactor at different operating times were filtered using a 0.45 μm Millipore membrane and arsenic concentration was measured. At the end of the run, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried and reweighed. All experiments were carried out at room temperature.

Eq. (16) was used to calculate for removal efficiencies of arsenic ( $y_1, \%$ ).

$$y_1 = \frac{(C_i - C_f)}{C_i} \cdot 100 \quad (16)$$

where  $C_i$  and  $C_f$  are the initial and final concentrations of arsenic.

### 3.3. Experimental design and data analysis

Response surface methodology (RSM) uses an experimental design to fit a model by least squares technique. RSM usually contains three steps: (i) design and experiments, (ii) response surface modeling through regression and (iii) optimization. The main objective of RSM is to determine the optimum operational conditions of the process or to determine a region that satisfies the operating specifications (Kobyia et al., 2009; Smith and Edwards, 2005). RSM makes it possible to represent independent process parameters in quantitative form as (Eq. 17):

$$y = f(x_1, x_2, x_3, \dots, x_n) \pm \varepsilon \quad (17)$$

where  $y$  is the response (yield),  $f$  is the response function,  $\varepsilon$  is the experimental error, and  $x_1, x_2,$

$x_3, \dots, x_n$  are independent parameters. By plotting the expected response of  $y$ , a surface, known as the response surface is obtained. The form of  $f$  is unknown and may be very complicated. Thus, RSM aims at approximating  $f$  by a suitable lower-ordered polynomial in some region of the independent process variables. If the response can be well modeled by a linear function of the independent variables, the function in Eq. (17) can be written as (Eq. 18):

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \varepsilon \quad (18)$$

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} x_i x_j + \varepsilon \quad (19)$$

For statistical calculations, the variables  $X_i$  were coded as  $x_i$  according to Eq. (20):

$$x_i = \frac{X_i - X_i^x}{\Delta X_i} \quad (20)$$

where  $x_i$  is the coded value of the  $i$ th independent variable,  $X_i$  the actual value of the  $i$ th independent variable,  $X_i^x$  the actual value of the  $i$ th independent variable at the center point, and  $\Delta X_i$  is the value of step change.

Thus, each response  $y$  can be represented by a mathematical equation that correlates the response surface. The Box-Behnken experimental design method (Design Expert 8.0 trial version) was used to determine the effects of Ca, Mg, Fe, Mn concentrations and operating time on the arsenic removal and to find the combination of variables



resulting in maximum arsenic removal efficiency. Forty-six experiments from the design procedure were conducted for the removal by the EC process. Five important operating parameters for the air injected EC process were selected as the independent variables namely, initial calcium ( $C_{Ca}$ : 125-325 mg/L), magnesium ( $C_{Mg}$ : 15-55 mg/L), iron ( $C_{Fe}$ : 0.5-4.5 mg/L), manganese concentrations ( $C_{Mn}$ : 0.5-4.5 mg/L) and operating time ( $t_{EC}$ , 2.0-8.0 min). The experimental design involved five operating variables, each at three levels and coded (-1), (0), and (+1) for low, middle and high, respectively.

The earlier studies had shown that the following terms; operating time, current, air flow rate and column of anode height in the reactor affected significantly the removal process (Masue et al., 2007). On the other hand, it was checked that changing pH value of groundwater at 6-9 didn't affect the removal efficiency as expected. Therefore, some parameters such as pH, current, air flow rate, anode ball size and anode height in the reactor were kept constant. Effects of cations ( $x_1$ :  $C_{Ca}$  (mg/L),  $x_2$ :  $C_{Mg}$  (mg/L),  $x_3$ :  $C_{Fe}$  (mg/L),  $x_4$ :  $C_{Mn}$  (mg/L) and  $x_5$ : operating time (min)) as independent variables were examined for the removal of arsenic at pH 7.5, 200 µg/L of As, 0.15 A, ball size of 7.5 mm, air flow rate of 6 L/min and column height of 5 cm. The independent experimental variables and responses for removal of arsenic from 46 runs were presented in Table 2. The responses in Table 2 were arsenic removal efficiency ( $y_1$ , %) and effluent concentrations (Table 2(a)), energy consumption ( $y_2$ , kWh/m<sup>3</sup>), electrode consumption ( $y_3$ , kg Fe/m<sup>3</sup>), operating cost ( $y_4$ , \$/m<sup>3</sup>) and amount of arsenic removed per mg iron electrode or amount of arsenic removed per Coulomb ( $y_5$ : µg As/mgFe or µg As/C) (Table 2(b)).

### 3.4. Analytical methods

The hydride generation procedure coupled with ICP optical emission spectrometer (PerkinElmer ICP-OES Optima 7000 DV) was used to determine the total arsenic concentrations in the samples. Total arsenic determination required reducing using KI and ascorbic acid to convert As(V) to As(III) prior to the arsine formation step. NaBH<sub>4</sub> instantaneously converted As(III) to arsine gas (AsH<sub>3</sub>) at room temperature, while the reduction of As(V) to arsine (AsH<sub>3</sub>) occurred relatively slow. The chemical analysis of the groundwater (pH, alkalinity, presence of arsenic, iron and phosphate) was carried out according to the standard methods (Korbahti et al., 2007).

Chemical analysis of drinking water was performed by the standard methods like chloride, nitrate and sulphate ions by an ion chromatography (Shimadzu HIC-20A), alkalinity by a titration method, phosphate by a spectrophotometer (Perkin Elmer lambda 35 UV/Vis) and conductivity, pH and dissolved O<sub>2</sub> by Hach Lange HQ40d, dissolved iron, magnesium, manganese and arsenic by ICP-OES, respectively.

All the chemical reagents were of analytical grade. All the experiments were repeated three times and the average data were reported. In this study, energy and electrode material costs were taken into account as major cost items in the calculation of the operating cost ( $y_4$ , \$/m<sup>3</sup>) (Koby et al., 2009; Martinez-Villafane et al., 2009). Costs of electrical energy ( $y_2$ ; kWh/m<sup>3</sup>), electrode consumptions ( $y_3$ ; kg Fe/m<sup>3</sup>) and operating cost were calculated from Eqs. (21-23).

$$y_2 \text{ (kWh/m}^3\text{)} = \frac{U \cdot i \cdot t_{EC}}{v} \quad (21)$$

$$y_3 \text{ (kg/m}^3\text{)} = \frac{i \cdot t_{EC} \cdot M_{Fe}}{z \cdot F \cdot v} \quad (22)$$

$$y_4 \text{ (\$/m}^3\text{)} = ay_2 + by_3 \quad (23)$$

where  $U$  is cell voltage (V),  $i$  is current (A),  $t_{EC}$  is the operating time (s) and  $v$  is the volume (m<sup>3</sup>) of the groundwater in the EC reactor,  $M_w$  are molecular mass of iron (56.8 g/mole),  $z$  is number of electron transferred ( $z_{Fe} = 2$ ),  $a$  is electrical energy price (0.072 \$ kWh/h),  $b$  is and electrode material price (0.85 \$/kgFe) in June 2013 and  $F$  is Faraday's constant (96487 C/mole). Amount of removed arsenic per mg iron was given in Eq. (24).

$$y_5 \text{ (}\mu\text{g As /mgFe)} = (C_i - C_f) \cdot v \cdot \left( \frac{i \cdot t_{EC} \cdot M_{Fe} \cdot 10^3}{z_{Fe} \cdot F} \right) \text{ or}$$

$$y_5 \text{ (}\mu\text{g As/ C)} = (C_i - C_f) \cdot v / i \cdot t_{EC} \quad (24)$$

## 4. Results and discussion

### 4.1. Response surface methodology

The Box-Behnken experimental design was used for statistical design of experiments and data analysis. Initial calcium, magnesium, iron, manganese concentrations and operating time at each three levels were optimized. Initial arsenic concentration in the groundwater was 200 µg/L and minimum removal efficiency of 95% was needed in the EC process to reach the permissible effluent concentration for the discharge purposes.

In this section, effects of interactions of independent variables mainly metal cations and operating time on the removal efficiency from groundwater with respect to allowable removal efficiency of arsenic were evaluated. Firstly, interactions of  $C_{Mn}$  with respect to  $C_{Ca}$ ,  $C_{Fe}$ ,  $C_{Mg}$  and  $t_{EC}$  were considered. There were positive effects observed for removal of arsenic with the following interactions; as concentrations of Mn from 0.5 mg/L to 4.5 mg/L and Ca from 125 mg/L to 325 mg/L increased at the constant operating conditions ( $C_{Mg}$ =35 mg/L,  $C_{Fe}$ =2.5 mg/L and  $t_{EC}$ =5 min), then the removal efficiency of arsenic increased from 91.33% to 97.56% (run 46 in Table 2(a)). Operating cost ( $y_4$ ) and dissolved amount of Fe (mg) from Fe anode balls

electrochemically and removed amount of As per Coulomb charge ( $y_5$ ) were calculated at this operating conditions as 0.11  $\$/m^3$  and 11.99  $\mu g$  As/mg Fe (2.78  $\mu g$  As/C). The similar results were obtained with interactions of  $C_{Fe}$  and  $C_{Mn}$  at runs 12 and 42 in Table 2(a). Arsenic removal efficiencies at constant operating conditions ( $C_{Ca}=225$  mg/L,  $C_{Mg}=35$  mg/L and  $t_{EC}=5$ ) were 95.39% (0.5 mg/L of Mn) and 98.36% (4.5 mg/L of Mn) with low Fe concentration (0.5 mg/L). Values of  $y_4$  and  $y_5$  at these operating conditions were 0.119  $\$/m^3$  and 11.72  $\mu g$  As/mg Fe (2.71  $\mu g$  As/C).

There was also a positive effect on the removal when Fe concentration was 4.5 mg/L. Electrochemically dissolved Fe anode balls and Fe in the groundwater caused formation of Fe oxyhydroxides during the EC process which led to increase the arsenic removal efficiency.

In addition,  $C_{Mn}$  and  $t_{EC}$  interactions gave positive results for higher removal efficiency of arsenic. Operating time was increased from 2 min to 8 min and Mn concentration was decreased from 4.5 mg/L to 0.5 mg/L at the constant operating conditions ( $C_{Ca}=225$  mg/L,  $C_{Mg}=35$  mg/L and  $C_{Fe}=2.5$  mg/L).

**Table 2 (a).** The independent experimental variables and responses for removal of arsenic in the EC process

Run	$x_1 : C_{Ca}$ (mg/L)		$x_2 : C_{Mg}$ (mg/L)		$x_3 : C_{Fe}$ (mg/L)		$x_4 : C_{Mn}$ (mg/L)		$x_5 : t_{EC}$ (min)	$C_f$ ( $\mu g/L$ )	$y_i : R_e$ (%)
	$C_{o,Ca}$	$C_{f,Ca}$	$C_{o,Mg}$	$C_{f,Mg}$	$C_{o,Fe}$	$C_{f,Fe}$	$C_{o,Mn}$	$C_{f,Mn}$			
1	225	196.3	15	13.8	2.5	0.37	4.5	1.93	5	21.74	89.13
2	225	206.3	15	14.2	4.5	1.68	2.5	1.02	5	18.82	90.59
3	225	196.6	55	36.5	2.5	0.71	0.5	0.17	5	19.39	90.31
4	225	190.3	15	13.7	2.5	0.56	2.5	1.04	8	8.48	95.75
5	325	223.3	35	24.9	2.5	0.81	0.5	0.13	5	17.35	91.33
6	225	183.9	15	13.4	2.5	0.61	2.5	1.14	2	57.05	71.48
7	125	108.7	35	25.1	2.5	1.15	4.5	1.71	5	25.09	87.46
8	225	204.4	55	39.1	2.5	1.29	2.5	0.98	8	16.17	91.92
9	225	206.0	35	27.6	4.5	0.92	2.5	0.91	8	4.33	97.84
10	225	185.0	55	35.1	0.5	0.57	2.5	0.92	5	17.08	90.46
11	225	193.4	35	27.0	2.5	1.34	2.5	1.08	5	22.62	88.69
12	225	188.9	35	25.3	4.5	1.81	0.5	0.15	5	9.23	95.39
13	225	193.7	35	24.8	0.5	0.60	2.5	1.11	8	11.07	94.47
14	225	201.1	35	26.6	0.5	0.49	4.5	1.90	5	16.26	91.87
15	225	189.6	35	25.0	2.5	1.27	2.5	0.81	5	20.60	89.70
16	325	218.2	15	13.1	2.5	0.92	2.5	0.98	5	20.52	89.74
17	125	105.4	15	13.8	2.5	1.06	2.5	0.89	5	23.92	88.04
18	325	205.9	55	35.1	2.5	0.99	2.5	0.87	5	13.25	93.38
19	325	213.8	35	27.4	0.5	0.43	2.5	1.11	5	18.31	90.85
20	225	190.5	35	25.2	2.5	1.04	4.5	1.60	8	17.62	91.19
21	125	115.1	35	27.1	4.5	1.69	2.5	1.03	5	16.35	91.83
22	225	199.4	35	25.9	0.5	0.37	2.5	1.10	2	47.15	76.43
23	125	101.3	35	25.8	2.5	1.11	2.5	0.84	8	9.43	95.29
24	225	202.7	35	27.7	2.5	1.72	2.5	1.15	5	19.41	90.30
25	225	212.6	35	28.3	2.5	2.40	2.5	1.26	5	18.44	90.78
26	225	196.1	35	26.5	2.5	0.97	0.5	0.98	8	6.39	96.81
27	325	216.7	35	27.3	2.5	0.95	2.5	1.09	2	42.72	78.64
28	225	203.2	35	27.3	2.5	0.82	2.5	1.26	5	20.15	89.93
29	225	193.3	55	36.4	4.5	1.30	2.5	0.94	5	8.55	95.73
30	225	196.5	35	26.5	2.5	1.03	2.5	0.95	5	27.52	86.24
31	225	185.4	35	26.0	2.5	0.38	4.5	1.99	2	35.54	82.23
32	225	209.3	35	28.2	4.5	1.94	2.5	1.24	2	34.97	82.52
33	125	114.4	35	27.4	2.5	1.77	2.5	1.17	2	46.96	76.52
34	225	210.0	15	14.3	0.5	0.59	2.5	1.20	5	28.25	85.88
35	325	243.1	35	28.4	4.5	1.82	2.5	0.85	5	8.91	95.55
36	225	203.5	55	38.5	2.5	0.79	2.5	1.05	2	36.95	81.53
37	225	214.5	55	39.3	2.5	0.51	4.5	2.18	5	12.59	93.71
38	225	185.4	35	26.2	0.5	0.38	0.5	0.15	5	29.73	85.14
39	125	109.9	35	26.2	0.5	0.44	2.5	1.01	5	26.98	86.51
40	225	191.7	15	14.8	2.5	1.12	0.5	0.15	5	17.65	91.18
41	325	242.2	35	29.8	2.5	0.62	2.5	1.16	8	7.60	96.20
42	225	194.4	35	27.1	4.5	2.51	4.5	1.54	5	3.29	98.36
43	125	109.4	35	27.3	2.5	0.76	0.5	0.16	5	20.32	89.84
44	225	203.0	35	26.4	2.5	1.01	0.5	0.10	2	57.80	71.10
45	125	111.3	55	39.4	2.5	0.57	2.5	1.10	5	10.23	94.89
46	325	204.5	35	27.9	2.5	0.36	4.5	1.65	5	4.88	97.56

Table 2 (b). The responses of the model and parameters for removal of arsenic in the EC process

Run	U (V)	Faraday (F/m <sup>3</sup> )	pH <sub>f</sub> (-)	W <sub>sludge</sub> (kg/m <sup>3</sup> )	y <sub>2</sub> : ENC (kWh/m <sup>3</sup> )	y <sub>3</sub> : ELC (kg/m <sup>3</sup> )	y <sub>4</sub> : OC (\$/m <sup>3</sup> )	y <sub>5</sub> : q <sub>e</sub>	
								(µg As/mg Fe)	(µg As/C)
1	8.3	0.583	7.48	0.0081	0.13016	0.01750	0.1175	10.95	2.54
2	8.1	0.583	7.80	0.0129	0.12672	0.01649	0.1115	11.13	2.58
3	6.8	0.583	7.46	0.0235	0.10672	0.01754	0.1132	11.09	2.57
4	7.6	0.933	7.58	0.0246	0.18975	0.02755	0.1821	7.35	1.70
5	9.5	0.583	7.94	0.0159	0.14844	0.01730	0.1199	11.22	2.60
6	7.7	0.233	7.56	0.0381	0.04819	0.00660	0.0441	21.95	5.08
7	6.9	0.583	7.71	0.0915	0.10781	0.01760	0.1138	10.74	2.49
8	6.5	0.933	7.77	0.0908	0.16275	0.02710	0.1746	7.06	1.63
9	7.4	0.933	7.74	0.0836	0.18575	0.02730	0.1800	7.51	1.74
10	8.3	0.583	7.98	0.0679	0.12938	0.01730	0.1163	11.11	2.57
11	8.2	0.583	7.77	0.0049	0.12859	0.01820	0.1209	10.90	2.52
12	8.3	0.583	7.76	0.0105	0.12891	0.01780	0.1188	11.72	2.71
13	6.7	0.933	7.88	0.0103	0.16750	0.02780	0.1792	7.25	1.68
14	7.2	0.583	7.34	0.0086	0.11234	0.01660	0.1093	11.29	2.61
15	7.0	0.583	7.41	0.0083	0.10891	0.01810	0.1166	11.02	2.55
16	7.1	0.583	7.67	0.0229	0.11063	0.01650	0.1085	11.02	2.55
17	10.6	0.583	7.81	0.0388	0.16563	0.01850	0.1295	10.82	2.50
18	6.6	0.583	7.74	0.0325	0.10234	0.01790	0.1143	11.47	2.66
19	7.2	0.583	7.68	0.0766	0.11250	0.01840	0.1189	11.16	2.58
20	7.2	0.933	7.72	0.0686	0.17975	0.02840	0.1847	7.00	1.62
21	9.1	0.583	7.80	0.0473	0.14219	0.01710	0.1176	11.28	2.61
22	7.9	0.233	7.69	0.0694	0.04956	0.00690	0.0460	23.47	5.43
23	10.2	0.933	8.04	0.0486	0.25500	0.02740	0.1937	7.32	1.69
24	8.0	0.583	7.80	0.0208	0.12516	0.01780	0.1181	11.09	2.57
25	7.3	0.583	7.92	0.0063	0.11438	0.01859	0.1202	11.15	2.58
26	7.3	0.933	7.47	0.0294	0.18175	0.02850	0.1856	7.43	1.72
27	7.2	0.233	7.55	0.0234	0.04513	0.00710	0.0462	24.15	5.59
28	7.4	0.583	7.69	0.0235	0.11563	0.01810	0.1179	11.05	2.56
29	7.1	0.583	7.69	0.0185	0.11047	0.01790	0.1159	11.76	2.72
30	7.4	0.583	7.84	0.0058	0.11516	0.01805	0.1175	10.59	2.45
31	8.0	0.233	7.58	0.0041	0.04994	0.00736	0.0485	25.26	5.85
32	7.8	0.233	7.63	0.0081	0.04900	0.00780	0.0507	25.34	5.87
33	10.2	0.233	8.03	0.0143	0.06375	0.00751	0.0519	23.50	5.44
34	7.8	0.583	7.15	0.0257	0.12188	0.01759	0.1164	10.55	2.44
35	6.9	0.583	7.42	0.0709	0.10844	0.01728	0.1122	11.74	2.72
36	7.0	0.233	7.45	0.0321	0.04400	0.00701	0.0455	25.04	5.80
37	6.9	0.583	7.51	0.0812	0.10703	0.01746	0.1129	11.51	2.67
38	7.2	0.583	7.74	0.0098	0.11219	0.01740	0.1135	10.46	2.42
39	9.9	0.583	7.93	0.0192	0.15516	0.01740	0.1217	10.63	2.46
40	7.7	0.583	7.71	0.0238	0.11969	0.01830	0.1197	11.20	2.59
41	6.8	0.933	7.84	0.0642	0.17050	0.02550	0.1675	7.39	1.71
42	7.2	0.583	7.75	0.0085	0.11297	0.01750	0.1142	12.08	2.80
43	9.1	0.583	7.58	0.0182	0.14219	0.01790	0.1219	11.04	2.56
44	7.7	0.233	7.61	0.0059	0.04831	0.00750	0.0489	21.84	5.06
45	9.0	0.583	7.72	0.0250	0.14063	0.01680	0.1158	11.66	2.70
46	6.9	0.583	7.85	0.0167	0.10844	0.01690	0.1102	11.99	2.78

So the removal efficiency was increased to 96.81% with operating cost of 0.186 \$/m<sup>3</sup> (run 26 in Table 2(a)). Secondly, interactions of C<sub>Fe</sub> with respect to C<sub>Ca</sub>, C<sub>Mn</sub>, C<sub>Mg</sub> and t<sub>EC</sub> were considered. As concentrations of Fe from 0.5 mg/L to 4.5 mg/L and Ca from 125 mg/L to 325 mg/L increased at the constant operating conditions (C<sub>Mg</sub>=35 mg/L, C<sub>Fe</sub>=2.5 mg/L and t<sub>EC</sub>=5 min), the removal efficiency of arsenic increased from 90.85% to 95.55% (run 35 in Table 2(a)). Values of y<sub>4</sub> and y<sub>5</sub> at these conditions were 0.112 \$/m<sup>3</sup> and 11.74 µg As/mg Fe (2.72 µg As/C). As Fe concentration was 4.5 mg/L and of Mg concentration was 55 mg/L, the removal efficiency at

C<sub>Ca</sub>=225 mg/L, C<sub>Mn</sub>=2.5 mg/L and t<sub>EC</sub>=5 min was 95.73% with operating cost of 0.116 \$/m<sup>3</sup> (run 29). C<sub>Fe</sub> and t<sub>EC</sub> interactions also gave positive result for removal efficiency of arsenic. As operating time and Fe concentration at the operating conditions (C<sub>Ca</sub>=225 mg/L, C<sub>Mg</sub>=35 mg/L and C<sub>Mn</sub>=2.5 mg/L) were 8 min and 4.5 mg/L, the removal efficiency was 97.84% with operating cost of 0.180 \$/m<sup>3</sup> (run 9 in Table 2(a)). Thirdly, interactions of C<sub>Ca</sub> with respect to C<sub>Fe</sub>, C<sub>Mn</sub>, C<sub>Mg</sub> and t<sub>EC</sub> were considered. Arsenic removal efficiencies were determined for higher than 95% when Ca concentration and operating time were higher. As seen runs 23 and 41 in Table 2(a), the

arsenic removal efficiencies were increased from 95.29% at 125 mg/L of Ca to 96.20% at 325 mg/L of Ca with the constant operating conditions ( $C_{Mg}=35$  mg/L,  $C_{Fe}=2.5$  mg/L,  $C_{Mn}=2.5$  mg/L and 8 min). The removal efficiency was observed to increase slightly with increasing of concentration of Ca and operating time. Values of  $y_4$  and  $y_5$  at these conditions were calculated as 0.167  $\$/m^3$  and 7.39  $\mu\text{g As/mg Fe}$  (1.71  $\mu\text{g As/C}$ ). The most important parameters in the EC process are applied current and operating time which control dissolution of anode material. This part study was carried out at constant applied current ( $i=0.15$  A and  $j$  (current density)= $0.07595$  A/m<sup>2</sup>). Interactions of cation concentrations and operating time for the removal efficiency of arsenic were indicated that arsenic removal efficiencies were increased to 96.20% within 8 min of operating time at the constant operating conditions ( $C_{Ca}=325$  mg/L,  $C_{Mg}=35$  mg/L,  $C_{Fe}=2.5$  mg/L and  $C_{Mn}=2.5$  mg/L; run 41 in Table 2(a)). Interactions of  $C_{Mg} \times t_{EC}$  on the removal efficiency were shown that arsenic removal efficiency was 95.75% at 8 min when the constant operating conditions ( $C_{Mg}=15$  mg/L,  $C_{Ca}=225$  mg/L,  $C_{Fe}=2.5$  mg/L and  $C_{Mn}=2.5$  mg/L) were applied in the EC process (Run 4 in Table 2(a)). >95 removal efficiency was observed at low Mg concentration and high operating time with operating cost of 0.182  $\$/m^3$ . Increasing concentrations of Ca, Mg and iron from the

independent variables and operating time had more positive effect on the response parameters (Fig. 4). Other physical parameters such as voltage change, Faraday (F/m<sup>3</sup>), final pH, amount of sludge generated (kg/m<sup>3</sup>), electrode (kg/m<sup>3</sup>) and energy (kWh/m<sup>3</sup>) consumptions and operating cost ( $\$/m^3$ ) for each run were presented in Table 2(b).

Actual values were measured as response data for a particular run, and the predicted values were obtained from the model and generated by using the approximating functions. It was seen in Fig. 2 that the data points lied close to the diagonal line and the developed model was adequate for the prediction of each response. Values of experimental and model  $R^2$  and Adj  $R^2$  for the responses were in the range 0.86-0.99. This showed that responses obtained from the model were consistent with the experimental.

The relationship between five independent variables and responses was established well with the quadratic model. The quadratic regression model for removal efficiency of arsenic ( $y_1$ ), energy consumption ( $y_2$ ), electrode consumption ( $y_3$ ), operating cost ( $y_4$ ) and  $y_5$  (arsenic removal capacity per dissolved iron anode) in terms of coded factors was presented as Eqs. (25-30).

Positive and negative signs in front of the terms refer to a synergistic effect and antagonistic effect, respectively.

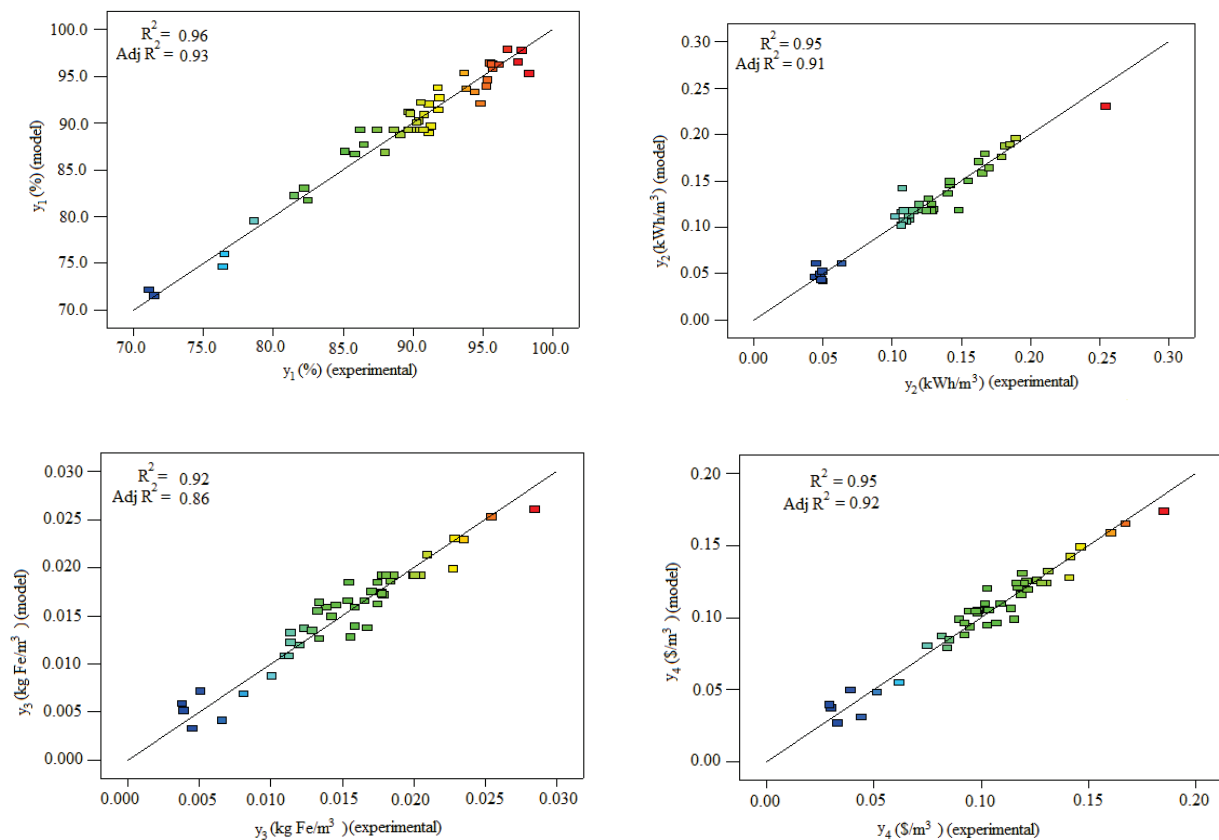


Fig. 2. Comparison of model-actual values for the removal efficiencies of arsenic



$$y_1 (\%) = 89.27 + 1.46x_1 + 1.91x_2 + 2.89x_3 + 1.28x_4 + 8.69x_5 - 0.68x_1x_2 - 0.15x_1x_3 + 2.16x_1x_4 - 0.30x_1x_5 + 0.14x_2x_3 + 1.36x_2x_4 - 3.47x_2x_5 - 0.94x_3x_4 - 0.68x_3x_5 - 4.19x_4x_5 + 1.23x_1^2 + 0.40x_2^2 - 1.66x_3^2 + 1.10x_4^2 - 4.13x_5^2 \quad (25)$$

$$y_2 (\text{kWh/m}^3) = 0.12 - 0.017x_1 - 6.83 \cdot 10^{-3}x_2 + 2.46 \cdot 10^{-4}x_3 - 4.98 \cdot 10^{-3}x_4 + 0.068x_5 + 4.18 \cdot 10^{-3}x_1x_2 + 2.23 \cdot 10^{-3}x_1x_3 - 1.41 \cdot 10^{-3}x_1x_4 - 0.016x_1x_5 - 5.94 \cdot 10^{-3}x_2x_3 - 2.54 \cdot 10^{-3}x_2x_4 - 5.50 \cdot 10^{-3}x_2x_5 - 4.02 \cdot 10^{-3}x_3x_4 + 4.71 \cdot 10^{-3}x_3x_5 - 9.06 \cdot 10^{-4}x_4x_5 + 0.013x_1^2 - 4.36 \cdot 10^{-4}x_2^2 + 3.14 \cdot 10^{-4}x_3^2 - 2.05 \cdot 10^{-3}x_4^2 - 2.55 \cdot 10^{-3}x_5^2 \quad (26)$$

$$y_3 (\text{kg Fe/m}^3) = 0.019 + 2.14 \cdot 10^{-3}x_1 - 1.97 \cdot 10^{-4}x_2 + 1.19 \cdot 10^{-3}x_3 + 7.72 \cdot 10^{-4}x_4 + 6.93 \cdot 10^{-3}x_5 - 1.10 \cdot 10^{-3}x_1x_2 + 2.45 \cdot 10^{-3}x_1x_3 + 2.98 \cdot 10^{-3}x_1x_4 + 2.26 \cdot 10^{-3}x_1x_5 + 1.40 \cdot 10^{-3}x_2x_3 - 1.01 \cdot 10^{-3}x_2x_4 - 2.49 \cdot 10^{-3}x_2x_5 - 1.38 \cdot 10^{-3}x_3x_4 + 8.25 \cdot 10^{-4}x_3x_5 - 4.49 \cdot 10^{-3}x_4x_5 - 1.78 \cdot 10^{-3}x_1^2 - 2.38 \cdot 10^{-3}x_2^2 - 3.29 \cdot 10^{-3}x_3^2 - 2.80 \cdot 10^{-4}x_4^2 - 3.52 \cdot 10^{-3}x_5^2 \quad (27)$$

$$y_4 (\$/\text{m}^3) = 0.12 + 8.17 \cdot 10^{-3}x_1 - 2.34 \cdot 10^{-3}x_2 + 6.34 \cdot 10^{-3}x_3 + 3.15 \cdot 10^{-3}x_4 + 0.05x_5 - 5.04 \cdot 10^{-3}x_1x_2 + 0.013x_1x_3 + 0.016x_1x_4 + 8.93 \cdot 10^{-3}x_1x_5 + 6.29 \cdot 10^{-3}x_2x_3 - 5.78 \cdot 10^{-3}x_2x_4 - 0.014x_2x_5 - 8.05 \cdot 10^{-3}x_3x_4 + 5.27 \cdot 10^{-3}x_3x_5 - 0.024x_4x_5 - 6.92 \cdot 10^{-3}x_1^2 - 0.013x_2^2 - 0.017x_3^2 - 1.87 \cdot 10^{-3}x_4^2 - 0.019x_5^2 \quad (28)$$

$$y_5 (\mu\text{g As/mgFe}) = 10.67 + 0.25x_1 + 0.44x_2 + 0.38x_3 + 0.25x_4 - 8.19x_5 - 0.25x_1x_2 - 0.25x_1x_3 + 0.25x_1x_4 - 0.25x_1x_5 - 0.25x_2x_3 + 0.25x_2x_4 - 1.0x_2x_5 - 0.5x_3x_5 - 1.0x_4x_5 + 0.042x_1^2 - 0.042x_2^2 + 0.21x_3^2 + 0.042x_4^2 + 4.46x_5^2 \quad (29)$$

$$y_5 (\mu\text{g As/C}) = 3.17 + 0.057x_1 + 0.10x_2 + 0.12x_3 + 0.087x_4 - 2.39x_5 - 0.029x_1x_2 - 5.5 \cdot 10^{-3}x_1x_3 + 0.077x_1x_4 - 0.042x_1x_5 + 4.9 \cdot 10^{-3}x_2x_3 + 0.048x_2x_4 - 0.24x_2x_5 - 0.033x_3x_4 - 0.12x_3x_5 - 0.28x_4x_5 + 0.041x_1^2 + 6.1 \cdot 10^{-3}x_2^2 + 0.074x_3^2 + 0.034x_4^2 + 1.29x_5^2 \quad (30)$$

There were negative effects from interactions between  $x_1$  and  $x_2$ ,  $x_1$  and  $x_3$ ,  $x_1$  and  $x_5$ ,  $x_2$  and  $x_5$ ,  $x_3$  and  $x_4$ ,  $x_3$  and  $x_5$ ,  $x_4$  and  $x_5$  on the removal efficiency. Especially more negative effects were observed for  $x_5$ ,  $x_4$  and  $x_5$  on the removal efficiency (Eq. 25 and Fig. 3) whereas  $x_1$  and  $x_4$ ,  $x_2$  and  $x_4$  showed positive interaction effects on the removal. There were negative ( $x_1$ ) and positive ( $x_5$ ) effects on energy consumption (Eq. 26) and the rest had very little effects on it (Table 2).  $x_2$  had negative and  $x_1$ ,  $x_3$ ,  $x_4$  and  $x_5$  had positive effects on electrode consumption (Eq. 27). According to the Faraday's law,  $i$  and  $x_5$  in the EC process had some effect on  $y_3$  which increased as  $i$  and  $x_5$  were increased. The main variables had also a positive effect on  $y_4$ . Effects of independent variables for the removal in the EC process were evaluated with results from perturbation graph (Fig. 3). Perturbation graph gave interaction of independent experimental variables. The highest effects on the removal efficiency of arsenic were observed with increasing iron concentration and operating time. The

removal efficiency also increased slightly with increasing concentrations of Ca, Mn and Mg ions after the center point. Operating cost increased with operating time. Concentrations of Fe, Ca and Mg ions increased slowly to the center point and little changes were observed after the center point (Fig. 3).

The adequacy of the model was justified through analysis of variance (ANOVA). Only terms found statistically significant were included in the model. The ANOVA results for the response parameters were shown in Table 3.  $F$ -values from the ANOVA were 30.45, 23.07, 15.02, 25.90, 180.67 and 470.12 for removal efficiency of arsenic, energy consumption, electrode consumption, operating cost and capacity of arsenic removal for iron ball anodes, respectively. Values of  $Prob > F$  were less than 0.0001 showed that the model terms were significant. The  $R^2$  coefficient gave the proportion of the total variation in the response variable accounted for the predictors ( $x$ 's) included in the model. A high  $R^2$  coefficient ensured a satisfactory adjustment of the quadratic model to the

experimental data. The values of  $R^2$  and adjusted  $R^2$  were varied from 0.92 to 0.99 and from 0.86 to 0.99. The coefficient of variance ( $CV$ ) is the ratio of the standard error of estimate to the mean value of observed response (as percentage) and considered to be reproducible when it is not greater than 10 %. In this work, the  $CV$ s for  $y_1$  and  $y_4$  were 1.97 and 13.48. Adequate precision ( $AP$ ) compares the range of the predicted values at the design points to the average prediction error. A ratio of  $AP > 4$  is desirable. For the present study,  $AP$  values for the EC process were 22.2, 20.7, 16.4, 21.6, 45.7 and 73.2 for the responses ( $y_1$ - $y_5$ ) which indicated an adequate signal. Statistical data for the model verification of the cations were illustrated in Table 4. Contour plots were showing the interaction effects of the cations concentrations and operating time on the removal efficiency of arsenic (Fig. 4). As shown in Fig. 4, operating time had positive effects for removal of arsenic from the groundwater as well as higher concentrations of  $Ca^{2+}$ ,  $Fe^{2+}$   $Mg^{2+}$  and lower concentration of  $Mn^{2+}$ . These results were consistent with the work of Smith and Edwards (2005).

Fig. 5 showed also that the removal efficiency increased significantly with increasing concentrations of Ca, Mn and Mg and operating time during the EC process. When the calcium concentration was 125 mg/L, final arsenic concentration reached below the permissible level (10  $\mu$ g/L) at 12 min. The final concentration of arsenic decreased to 10  $\mu$ g /L limit level at 10 min, 8 min and 4 min when Mg concentrations were 15, 35 and 55 mg/L. Removal efficiency of arsenic was higher as iron concentration

was increased from 0.5 mg/L to 4.5 mg/L in groundwater due to strong affinity between iron and arsenic. The arsenic removal efficiency was strongly dependent on the initial iron concentration and Fe/As ratio. Moreover,  $Ca^{2+}$  and  $Mg^{2+}$  multivalent ions decreased electrical double layer thickness and surface negative charge reduced on the flocs thus aggregation increased as a result provided for higher removal efficiency of arsenic (Guan et al., 2009).

4.2. Confirmation experiments

Some additional confirmation experiments were conducted for the validity of the statistical experimental design. The observed values of removal efficiencies and operating costs were close to those predicted values obtained from the model (Fig. 6). This also testified that the model approach was appropriate for optimizing the operational conditions for removal of arsenic from groundwater ( $R^2 > 0.96$ ).

4.3. Optimization of operating conditions

Optimization process variables and responses with five criteria for removal of arsenic from groundwater were presented in Table 5. As can be seen in Table 5, the optimized parameters were determined as 132 mg/L of  $C_{Ca}$ , 55 mg/L of  $C_{Mg}$ , 4.5 mg/L of  $C_{Fe}$ , 4.5 mg/L of  $C_{Mn}$ , operating time of 3 min; removal efficiency of 95.1% and operating cost of 0.041  $\$/m^3$ , when operating variables were in range, minimum OC, maximum removal efficiency and the target concentration of 9.9  $\mu$ g/L in the EC process.

Table 3. ANOVA results for the response parameters

Responses	$R^2$	Adj $R^2$	SD	CV	PRESS	F-value	Prob>F	AP
$y_1$ (%)	0.96	0.93	1.760	1.97	274.89	30.45	<0.001	22.2
$y_2$ (kWh/m <sup>3</sup> )	0.95	0.91	0.014	11.18	0.0180	23.07	<0.001	20.7
$y_3$ (kg Fe/m <sup>3</sup> )	0.92	0.86	0.002	13.48	0.0004	15.02	<0.001	16.4
$y_4$ ( $\$/m^3$ )	0.95	0.92	0.010	9.70	0.0090	25.90	<0.001	21.6
$y_5$ ( $\mu$ gAs / mgFe)	0.99	0.99	0.600	4.87	32.40	180.67	<0.001	45.7
$y_5$ ( $\mu$ gAs / C)	0.99	0.99	0.110	2.94	1.120	470.12	<0.001	73.2

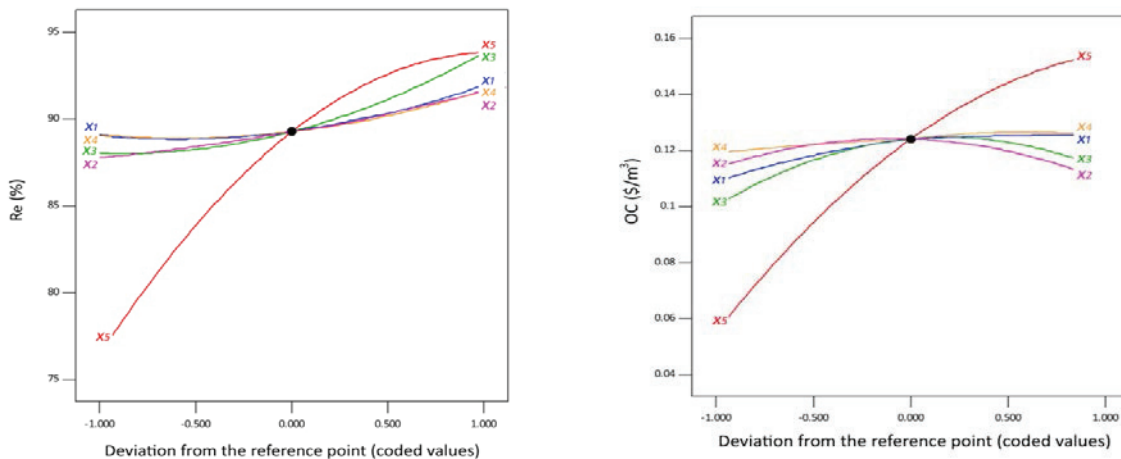
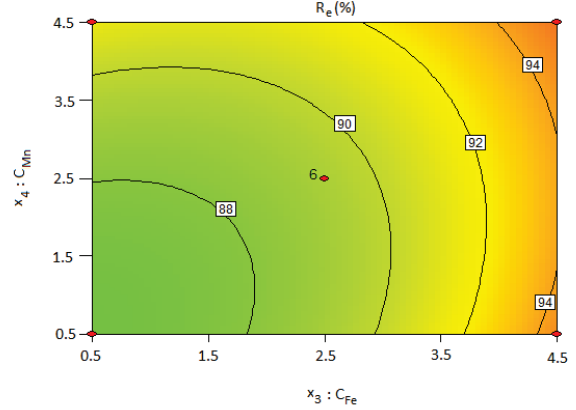
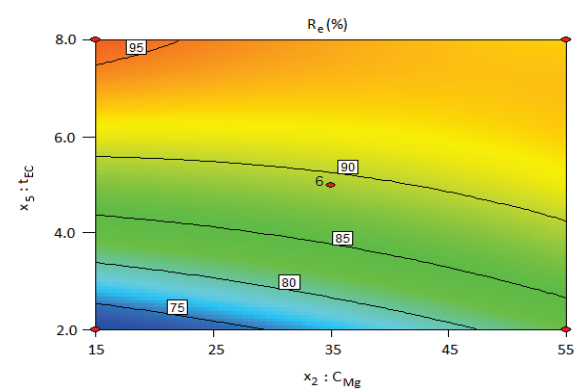
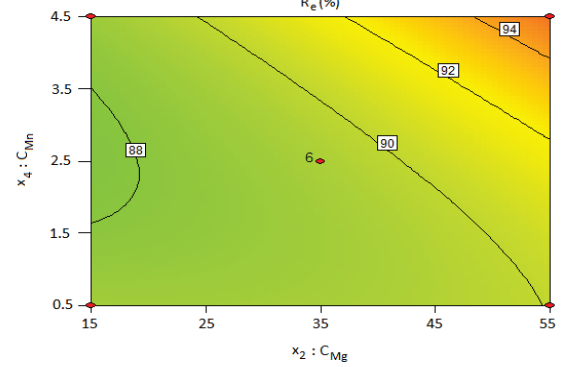
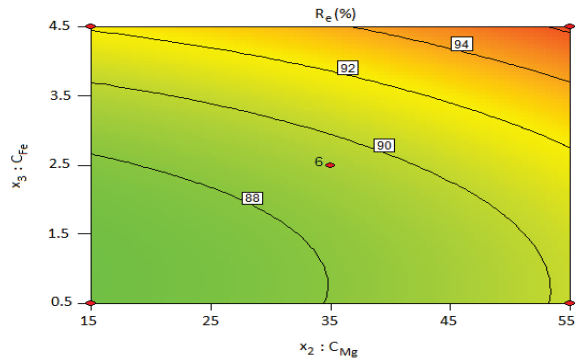
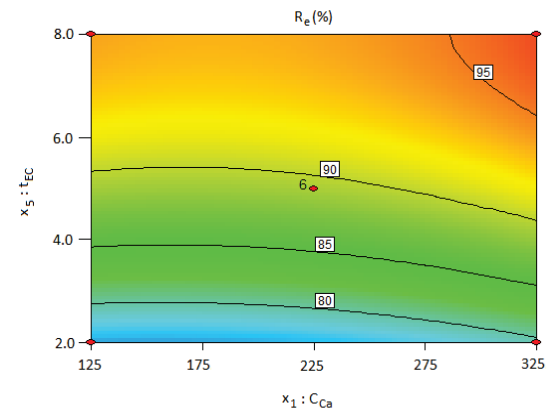
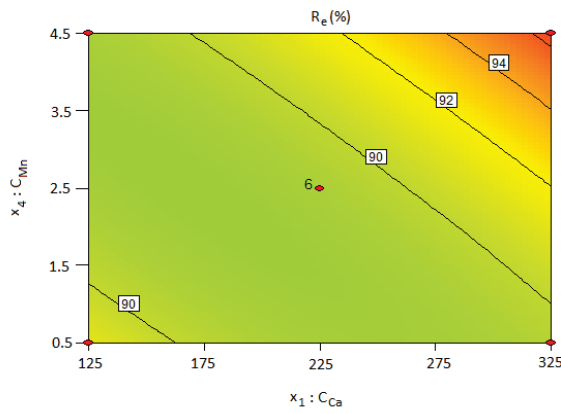
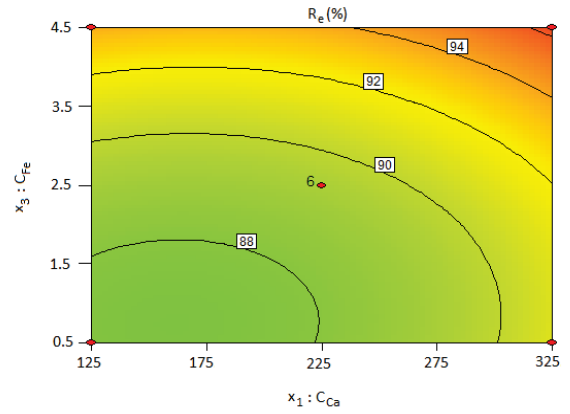
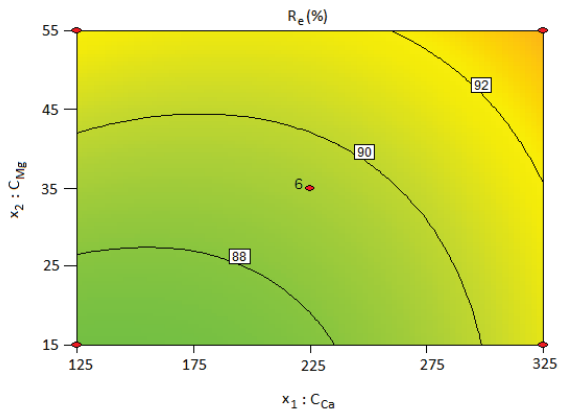


Fig. 3. Perturbation graphs of the arsenic removal with respect to independent variables

Optimization of some cations for removal of arsenic from groundwater by electrocoagulation process



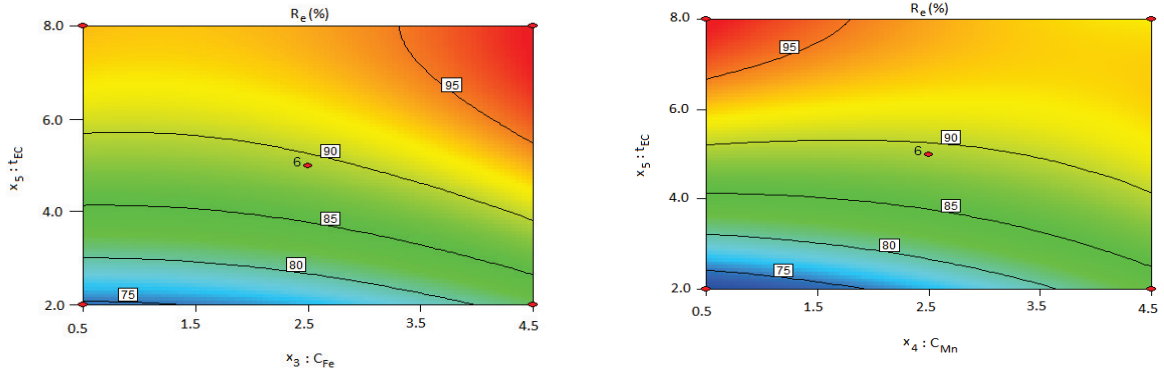


Fig. 4. Contour plots showing the interactive effects of the cations and operating time on the removal efficiency of arsenic from groundwater

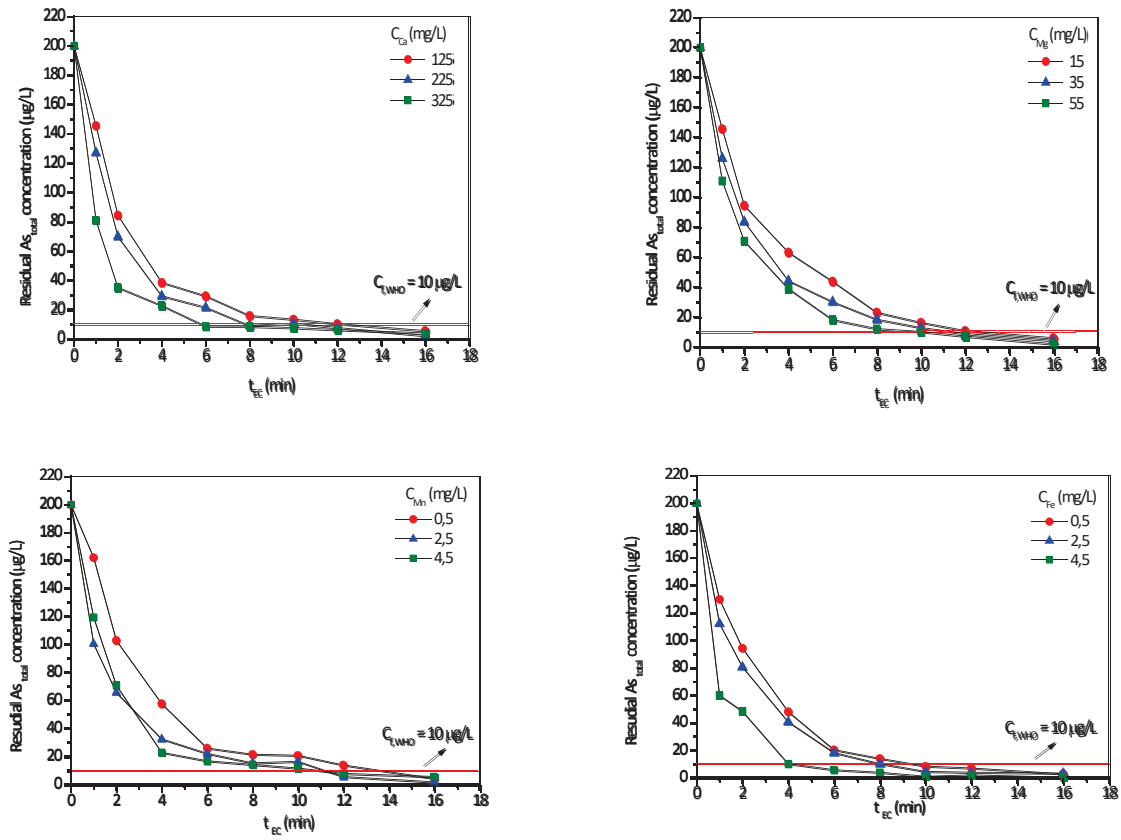


Fig. 5. Removal of arsenic in the presence of Ca, Mg, Fe, Mn ions in the EC process

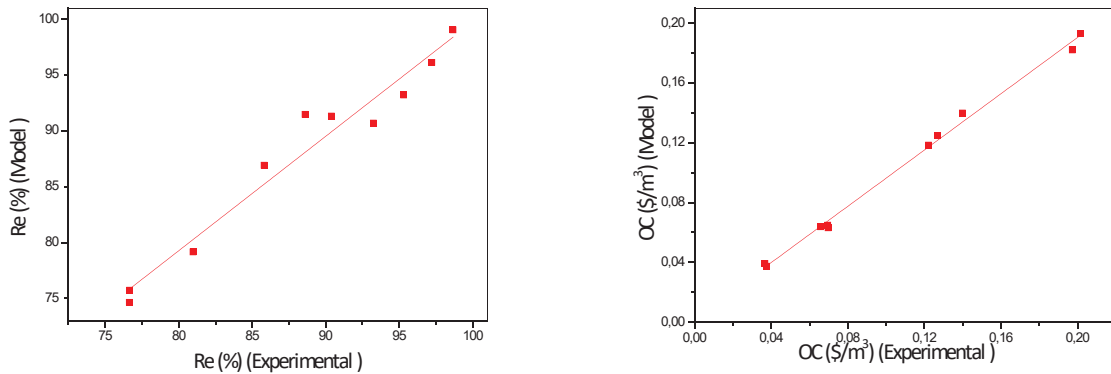


Fig. 6. The model and experimental values for conformation experiments



**Table 4.** Statistical data for the model verification of the cations

Responses	R <sup>2</sup>	Standard deviation (%)	Prob>F
C <sub>f</sub> (µg/L)	0.95	0.08	<0.001
R <sub>e</sub> (%)	0.95	0.08	<0.001
ENC (kWh/m <sup>3</sup> )	0.91	0.09	<0.001
ELC (kg/m <sup>3</sup> )	0.99	0.01	<0.001
OC (\$/m <sup>3</sup> )	0.99	0.02	<0.001
q <sub>e</sub> (µg As/mg Al)	0.99	0.02	<0.001
q <sub>e</sub> (µg As/C)	0.99	0.02	<0.001

**Table 5.** Optimization process variables and responses on the removal of arsenic using iron ball anodes (Desirability: 0.99)

Criteria and target	Optimization process variables and responses									
	C <sub>Ca</sub> (mg/L)	C <sub>Mg</sub> (mg/L)	C <sub>Fe</sub> (mg/L)	C <sub>Mn</sub> (mg/L)	t <sub>EC</sub> (min)	C <sub>f</sub> (µg/L)	R <sub>e</sub> (%)	OC (\$/m <sup>3</sup> )	q <sub>e</sub>	
									(µg As/ mg Fe)	(µg As/C)
Variables and responses (in range)	225	15	2.5	2.5	8.0	8.4	95.8	0.159	7.7	2.2
Variables and responses (in range), C <sub>f</sub> =9.9 µg/L	196.5	34.3	3.2	1.8	7.0	9.9	95.1	0.152	7.7	2.2
R <sub>e</sub> (maksimum), OC (minimum) and C <sub>f</sub> =9.9 µg/L	132	55	4.5	4.5	3.0	9.9	95.1	0.041	21.8	6.3
Cations concentration (maximum), t <sub>EC</sub> and responses (in range)	325	55	4.5	4.2	2.4	3.30	98.4	0.765	25.3	7.3
Cations concentration (minimum), t <sub>EC</sub> and responses (in range)	125	15	0.6	0.5	6.7	5.6	97.2	0.126	8.8	2.5

## 5. Conclusions

In this study, forty-six experiments were carried out to optimize the design of experiment for the arsenic removal in the EC process. Interactions of five different parameters were considered. Analysis of variance for all variables had confirmed the predicted models by the experimental design within 95% confidence level (R<sup>2</sup>: 0.95, Adj-R<sup>2</sup>: 0.92) which ensured a satisfactory adjustment of the quadratic model with the experimental data.

Higher concentrations of calcium, magnesium, iron and lower concentration of manganese ions from the independent variables and higher operating time had positive effects on the response parameters which resulted in higher removal efficiency of arsenic. The final effluent pH for the EC process at the optimum operating conditions was 7.6 and fell into the limit values set by discharge standards of water pollution control regulations.

Maximum removal efficiency of arsenic and minimum operating cost at the optimized conditions were determined to be 95.1% and 0.041 \$/m<sup>3</sup>. The removal mechanism in the EC process might be involved with adsorption and co-precipitation. The results showed that electrocoagulation could be effectively used for the removal of arsenic from groundwater.

## Nomenclature

EC electrocoagulation  
 WHO the World Health Organization  
 DO dissolved oxygen

## RSM

response surface methodology  
 X<sub>1</sub> initial calcium concentration C<sub>Ca</sub> (mg/L)  
 X<sub>2</sub> initial magnesium concentration C<sub>Mg</sub> (mg/L)  
 X<sub>3</sub> initial iron concentration C<sub>Fe</sub> (mg/L)  
 X<sub>4</sub> initial manganese concentration C<sub>Mn</sub> (mg/L)  
 X<sub>5</sub> operating time (min)  
 y<sub>1</sub> removal efficiency of arsenic (%)  
 y<sub>2</sub> energy consumption (kWh/m<sup>3</sup>)  
 y<sub>3</sub> electrode consumption (kg Fe/m<sup>3</sup>)  
 y<sub>4</sub> operating cost (\$/m<sup>3</sup>)  
 y<sub>5</sub> arsenic removal capacity per dissolved mg iron anode (µg As/mgFe)

ICP-OES inductive coupled plasma with optical emission spectrometer

R<sup>2</sup> regression correlation coefficient values

Adj R<sup>2</sup> adjusted regression correlation coefficient values

AP adequate precision

CV the coefficient of variance

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