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Techno-economic evaluation of simultaneous arsenic and fluoride removal from synthetic groundwater by electrocoagulation process: optimization through response surface methodology

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ABSTRACT

In the present work, electrocoagulation process has been used to treat arsenic and fluoride containing synthetic water using aluminium electrode. Box–Behnken design, a subnet of response surface methodology, was employed to fix the experimental conditions and Design Expert software was used to evaluate the interaction and effects of different process parameters such as initial pH, current density and run time on removal of arsenic and fluoride as well as the operating cost. Initial concentration of arsenic and fluoride was fixed at 550 µg/l and 12 mg/l, respectively, for all the experiments. High R^2 values of three responses (arsenic removal: 0.998, fluoride removal: 0.984 and operating cost: 0.996) ensures a satisfactory adjustment of developed quadratic model with the experimental data. Under the optimum conditions, initial pH: 7, current density: 10 A/m^2 and run time: 95 min, the predicted arsenic and fluoride removal is found to be 98.64 and 84.80%, respectively, whereas the operating cost is found to be 0.354 USD/m^3. Further, the experimental values of arsenic removal (98.51%), fluoride removal (88.33%) and operating cost (0.343 USD/m^3) are found to be in good agreement with the predicted values. The present electrocoagulation process is able to reduce the arsenic and fluoride concentration below 10 µg/l and 1.5 mg/l, respectively, which are maximum contaminant level of these elements in drinking water according to WHO. EDX analysis of sludge confirms the occurrence of arsenic and fluoride in produced sludge and FTIR spectra suggest that arsenic is also removed in the form of As(III). Real groundwater sample collected from Kaudikasa Village, Rajnandgaon District, Chhattisgarh, India and having As: 512 µg/l, F: 6.3 mg/l was also treated under optimum conditions of the present study and the concentration of arsenic and fluoride became below WHO drinking water norms.

Keywords: Electrocoagulation; Groundwater; Arsenic removal; Fluoride removal; Operating cost; Response surface methodology

1. Introduction

Over the past decades, elevated concentration of arsenic and fluoride in groundwater has posed a serious threat to living beings around the world. Arsenic and fluoride contamination in groundwater occurs mainly through natural sources such as volcanic activity, weathering of minerals associated to the bed rocks of aquifers with some contribution of

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anthropogenic sources such as wastewater streams of fertilizer, pesticide, semiconductor, metallurgy and electroplating industries [1–4]. Prolong exposure of arsenic via drinking water leads to several acute and chronic health effects such as skin lesions, skin cancer, bladder cancer and lung cancer [5]. Although fluoride is essential for dental and skeleton health in small concentration; however, the excessive intake of fluoride via drinking water may cause mottling of teeth and skeleton fluorosis, etc. [6–8]. Co-occurrence of arsenic and fluoride in drinking water can result more devastating situation. It is reported that co-exposure of arsenic and fluoride can show more impact on the integrity of the genetic material of cells than the individual exposure [9]. It may also be possible that co-exposure of these could lead to both arsenicosis and endemic fluorosis [10]. Around 140 million people are exposed to arsenic contaminated water worldwide [11]. Some important arsenic effected countries in the world are Mexico, India, Taiwan, Mongolia, Chile, Argentina, the USA and Bangladesh [12]. Considering the health impact of arsenic, World Health Organization (WHO) has set the maximum arsenic recommended contaminant level of 10 μg/l for drinking water [13]. Similarly, many countries around the globe, such as India, Egypt, Bangladesh, China, Mexico and Kenya, have areas where fluorosis is endemic (>1.5 mg/l) [14,15]. It is estimated that around hundred million people suffer from high fluoride contamination in groundwater worldwide [16]. It is reported that ~2–8 million people are suffered from arsenic and fluoride borne diseases due to consumption of both arsenic and fluoride contaminated groundwater in Chaco-Pampean plain of Argentina [17]. In addition to this, several researchers reported the co-existence of arsenic and fluoride in groundwater of Mexico, Mongolia, Italy, China, Pakistan and India (Uttar Pradesh, Assam, Punjab, Chhattisgarh, West Bengal) [18–25]. Very recently in 2015, high arsenic and fluoride concentration has been reported in the groundwater of Rajnandgaon District of Chhattisgarh in India [26]. Hence, it is important to remove these contaminants from groundwater.

From literature it reveals that many approaches are being investigated for arsenic and fluoride removal from contaminated water. The most commonly used techniques are adsorption onto activated carbon/alumina/iron oxide/soil/bio-adsorbents, coagulation, electrodialysis, ion exchange, etc. [27–35]. All these methods have their own limitations. The coagulation technique possesses high chemical cost and sludge disposal issue, electrodialysis and ion exchange are expensive processes and require high maintenance. Adsorption process requires pre-treatment of adsorbent for arsenic and fluoride removal [36,37]. Apart from this, the important drawback of the adsorption process is that the adsorbent gets exhausted soon and considerable time is needed for its regeneration. Further, regeneration steps leads to secondary pollution generation because arsenic and fluoride containing aqueous solution is discarded as a waste [38]. Thus, a new technique is required which can overcome the drawback of the conventional processes and be technologically feasible.

Electrocoagulation technique is getting more attention in recent years as it has high removal efficiency [39–45]. This process produces coagulants in situ by dissolving electrodes in the cell, which helps the removal of the pollutants producing negligible secondary pollutants [46,47]. Major phenomena taking place during the electrocoagulation process are anode oxidation, reduction of water at cathode, electrolytic reaction at electrode surface and removal of pollutants through bridge coagulation/adsorption, sweep coagulation, charge neutralization and co-precipitation, sedimentation, or floatation [48–51]. Some important reactions of electrocoagulation process using Al as electrode are shown through Eqs. (1)–(4) [52].

$$\text{Reaction at anode: } Al \rightarrow Al^{3+} + 3e^- \tag{1}$$

$$\text{Reaction at cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

Reaction in aqueous solution at alkaline condition:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3(s) \tag{3}$$

Reaction in aqueous solution at acidic condition:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+ \tag{4}$$

Efficiency of electrocoagulation process is highly dependent on the nature of electrode, electrode area, current density, solution pH, run time, etc. [53], whereas presence of electrolytes and inter electrode distance can also influence the efficiency [54]. Presence of co-occurring ions may significantly increase or decrease removal efficiency depending on the nature of the ions. However, it has been reported that NaCl concentration above 0.8 g/l does not increase the efficiency much [55,56]. Further, inter-electrode distance of 1 cm has been suitably used for electrocoagulation of arsenic/fluoride from water by many researchers [45,55–57].

A good number of reports are available on the removal of arsenic and fluoride from contaminated water through electrocoagulation [52,58–62]. In most of these literatures, individual removal of arsenic and fluoride has been studied and effects of process parameters such as run time, current density and pH on the percentage removal of arsenic or fluoride has been reported. Although different types of electrodes, like Fe, Al and Ti, have been used [40,52,62–64], it is reported that Fe electrode can give more arsenic removal than fluoride removal, whereas reverse trend is observed with Al electrode [1,65,66]. Ti electrode is found to be costly [67]. There is only one literature on the simultaneous removal of arsenic and fluoride from water through integrated electrooxidation and electrocoagulation process [63]. In this study, initial concentrations of arsenite and fluoride were 1 and 4.5 mg/l, respectively. However, in real groundwater the concentration of arsenic is found less (<500 μg/l) and fluoride concentration is found high (even >10 mg/l in some places) as compared to concentration used by them [26,38,68]. There is few literature on the techno-economic evaluation of the arsenic/fluoride removal by electrocoagulation process [52,60,61]. However, there is hardly any report on the techno-economic evaluation for the simultaneous removal of arsenic and fluoride.

To understand the effect of process parameters on contaminant removal through conventional experimental methods more number of experimentation is required, which is time consuming and costly in term of chemicals requirement. Moreover, the interaction of process parameters and its combined effects on % removal are not well addressed due to the lack of inadequate experimental design in conventional methods [69–71]. Response surface methodology (RSM) has been found a useful tool to overcome the issues related with conventional methods of study. RSM is a mathematical and statistical technique tool used for designing of experiments, models building, evaluating the effects of process variables and to find the optimum conditions for specific responses. Several researchers have used RSM to optimize the process variable for contaminants removal by electrocoagulation method [61,72–76]. Further, in order to explore the suitable mechanism for the removal of arsenic and fluoride in electrocoagulation, the produced sludge can be analysed for SEM, EDX and FTIR analysis.

The present work is performed to techno-economically optimize the process variables for simultaneous removal of arsenic and fluoride through RSM approach. The aims of the present study are (i) to optimize the process variables such as initial pH, current density and run time for simultaneous removal of arsenic and fluoride from synthetic groundwater along with the operating cost using electrocoagulation process with the help of RSM using Box–Behnken design (BBD), (ii) to develop input–output model for electrocoagulation process, (iii) to validate the developed model and (iv) characterization of sludge to elucidate the mechanism of removal.

2. Materials and methods

2.1. Materials

All chemicals of analytical grade were used for the experiments. Stock solutions of As(III) and fluoride were prepared by sodium arsenite ($NaAsO_2$) and sodium fluoride (NaF) in distilled water, respectively. Desired concentration of solution was prepared by diluting the above stock solutions. Desired initial pH of solution before electrocoagulation, was adjusted using 5 N NaOH and 1 N HCl solution.

2.2. Experimental setup

A Perspex reactor having dimension of 0.15 m × 0.10 m × 0.12 m with working volume of 1.4 l was used to perform the electrocoagulation experiments in batch mode. Four aluminium electrodes (97.4% purity) with total effective surface area of 512 cm^2 were used. These electrodes were connected to DC power supply (0–30 V and 0–10A) in monopolar mode. Distance between each electrode was maintained constant at 1 cm [45,55–57].

2.3 Procedure

Before each run, the electrodes were abraded with sand paper and then cleaned with dilute nitric acid and deionized water. After cleaning, electrodes were dried at 105˚C in oven to remove the moisture. Similarly, at the end of the each run, electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried and reweighed. In batch electrocoagulation experiments solution composed of fix concentration of 550 μg/l As(III) and 12 mg/l fluoride was treated at different experimental conditions in a reactor with continuous stirring at 500 rpm by magnetic stirrer. To increase the ionic strength of solution 1gm of sodium chloride (NaCl concentration 714.3 mg/l) was added into each working solution as supporting electrolyte [61,64] as it is reported that further addition of sodium chloride does not influence the defluoridation much [77]. The selection of sodium chloride salts is based on its ability to improve the solution conductivity as well as the ability of chloride ions to rupture the passive films of aluminium electrodes [61,64]. After pre-determined run time, the power supply and stirring both was stopped and sample was taken out immediately and filtered through Whatman filter (0.45 micron) to analyse the arsenic and fluoride concentration. All experiments were performed twice and the average value is reported. The removal of contaminants in percentage is calculated from Eq. (5):

$$\text{Removal } (\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{5}$$

where C_i and C_f are the initial and final concentrations of contaminants in solution, respectively.

Visual MINTEQ simulation program was used for single-component speciation of As(III), fluoride and aluminium at different initial pH (1–14) putting the fixed temperature value of 25°C. The total cost for operating the electrocoagulation process includes cost of chemicals, electrode, electricity, maintenance, sludge disposal and fixed cost [60]. For the preliminary economic evaluation of operating cost, the electrode material cost and electricity charges were taken into account (Eq. (6)):

$$\text{Operating cost} = a \times C_{\text{electrodes}} + b \times C_{\text{energy}} \tag{6}$$

where $C_{\text{electrodes}}$ (kg Al/m^3) and C_{energy} (Kwh/m^3) are the consumption of quantities for the treatment of arsenic and fluoride contaminant water, while a and b are the coefficient for Indian market in the year 2015, respectively.

Coefficient a: Wholesale electrode material price = 1.77 USD/kg Al [78].

Coefficient b: Industrial electricity price = 0.06 USD/kwh^{-1} [79].

Energy consumption in electrocoagulation process was calculated by Eq. (7):

$$\text{Energy consumption} \left(\frac{\text{Kwh}}{\text{m}^3}\right) = \frac{\text{voltage} \times \text{current} \times \text{runtime}}{\text{working volume of reactor}} \tag{7}$$

In the present work, the constant current was maintained throughout the experiments by controlling the voltage. The small changes in voltage with time are also considered in cost estimation by taking its average value. Cost of electrode material was considered in terms of material loss in electrocoagulation process by subtracting the initial weight and final weight of anode electrode before and after electrocoagulation process [61]. Removal efficiency of electrocoagulation process depends on pH, current density and run time [61,65,76]. It is well known that in electrocoagulation, the amount of generated adsorbent in solution is proportional to the product of run time and current (according to Faraday law). This means using very high current density (when electrode area is constant) large amount of adsorbents can be generated within less time or the same amount of adsorbent can be generated using less current density for longer time period. However, the pollutants have their own removal kinetics and require certain time for removal. Further, when the concentration of pollutants are very less, the driving force for adsorption is also becomes very less, which gives slower removal rate. Thus, the study on individual effects of time and current density is considered. Experimentation with real groundwater sample collected from Kaudikasa Village, Rajnandgaon District, Chhattisgarh, India and having As: 512 μg/l, F: 6.3 mg/l was also conducted under optimum conditions to assess the performance of the present process.

2.4. Analysis

The analysis of arsenic was carried out by an inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer, model-ELAN-DRC-e) according to standard method USEPA 200.8 [80]. The arsenic detection limit of the instrument was 0.026 μg/l with an accuracy of 98 ± 1%. The fluoride detection was done by ion-selective electrode (Orlab India, model-OR930) from solution containing aliquot and TISAB buffer in 1:1 volume ratio. The fluoride detection limit was 0.02 mg/l with an accuracy of ±1. TISAB buffer solution was used to eliminate the other ion interferences in fluoride analysis. TISAB was made by continuous mixing of 58 g of NaCl, 57 ml of glacial acetic acid and 4 g of 1,2-cyclohexylene diamine tetra acetic acid (CDTA). Till the solution pH reached to 5.3–5.5, 6 N NaOH solution was added drop wise to it. The sludge produced in electrocoagulation was analysed for field emission scanning electron microscopy (FE-SEM, FEI, model-Quanta 200 FEG). For sample preparation, the dried sludge sample was coated with gold in presence of argon. Energy-dispersive X-ray analysis was an integrated feature of the scanning electron microscope. An infrared spectrum of produced sludge was taken by Thermo FTIR (model-Nicolet 6700). Around 10 mg of dried sludge was dispersed in 100 mg of spectroscopic grade KBr to record IR spectra in the wavenumber range of 4,000–500 cm^{-1}.

2.5. BBD and data analysis

Box and Behnken proposed some three-level designs for fitting response surfaces [81]. BBD is a spherical, revolving RSM design; it consists of a central point and the middle points of the edges of the cube circumscribed on the sphere [82]. Number of experiments in BBD was calculated from Eq. (8):

$$N = 2K(K-1) + C \tag{8}$$

where N, K and C represents the number of experiments, number of factors and number of central points, respectively.

The relationship between response Y, factors x_1, x_2, …, x_k and residual error ε are given in Eq. (9):

$$Y = f(x_1, x_2, \ldots x_k) + \varepsilon \tag{9}$$

BBD design generally uses the manual regression method to developed model relationship of experimental data and to identify relevant model terms such as linear terms, square terms and linear by linear interaction terms. The quadratic response model can be represented by Eq. (10):

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_{ii}^2 + \sum \beta_{ij} x_i x_j + \varepsilon \tag{10}$$

where x_i and x_j are the variables; β_0, β_i, β_{ii} and β_{ij} are constant, interaction coefficient of linear, quadratic and the second-order terms, respectively [83].

In the present study, Box–Behnken experimental design with three factors (initial pH: A, current density: B, runtime: C) at three levels (−1, 0, +1) were used to identify the experimental conditions to optimize and investigate the effects of process variables on three responses (Y_1: Arsenic removal (%), Y_2: fluoride removal (%) and Y_3: operating cost). Range of operating conditions was selected based on the previous work reported in literature [14,52,63,74,84,85]. The domain ranges and the coded levels for the factors investigated in the present study are given in Table 1. According to BBD, total 17 numbers of experiments were performed. The details of BBD experimental metrics and their results are listed in Table 2.

Table 1
Experimental range and level of variables

		Range and coded level		
Factor, unit	Symbol	−1	0	+1
Initial pH	A	3	7	11
Current density (A/m^2)	B	10	35	60
Run time (min)	C	10	65	120

3. Results and discussion

3.1. Development of electrocoagulation models

Removal efficiency of electrocoagulation process depends on pH, current density and run time, while the operating cost of electrocoagulation process depends mainly on current density and run time. For

Table 2
BBD and experimental results

S. no.	Initial pH	Current Density (A/m^2)	Run time (Min)	Arsenic removal (%)	Fluoride removal (%)	Operating cost (USD/m^3)	Final pH
1	7	10	10	39.41	54.16	0.050	8.8
2	11	60	65	97.82	81.98	2.557	9.8
3	7	35	65	95.12	84.61	1.254	9.7
4	3	35	120	98.87	87.67	2.358	8.8
5	7	60	10	68.12	77.47	0.434	9.0
6	7	10	120	98.83	87.83	0.524	9.0
7	3	35	10	49.52	92.60	0.226	5.9
8	7	35	65	94.25	83.41	1.170	9.4
9	7	35	65	96.11	84.86	1.207	9.5
10	7	60	120	99.01	76.02	4.896	9.3
11	11	10	65	89.19	71.01	0.329	9.5
12	7	35	65	96.02	84.89	1.213	9.6
13	11	35	10	56.42	60.21	0.203	9.8
14	3	10	65	84.19	97.10	0.285	5.0
15	7	35	65	95.98	82.19	1.189	9.4
16	3	60	65	95.82	97.10	2.375	9.0
17	11	35	120	98.77	83.33	2.155	9.7

all three responses, linear, two-factor interactions, quadratic and cubic models were analysed by Design Expert software (Design-Expert 7.0.0), in which the quardratic model was suggested as best one on the basis of *p*-value. The low *p*-value for all three models implies that atleast one of the terms in each model has a significant effect on the response. Moreover, analysis of variance (ANOVA) results listed in Table 3 also confirm the terms and their interaction effects on responses. The developed quadratic models correlating process variables and response Y_1 (arsenic removal, %), Y_2 (fluoride removal, %) and Y_3 (operating cost, USD/m^3) are presented in coded form by Eqs. (11)–(13), respectively.

$$\begin{aligned} Y_1 = 95.50 &+ 1.73 \times A + 6.14 \times B + 22.75 \times C \\ &- 0.75 \times A \times B - 1.75 \times A \times C - 7.13 \times B \times C \\ &- 2.09 \times A^2 - 1.65 \times B_2 - 17.51 \times C^2 \end{aligned} \tag{11}$$

$$\begin{aligned} Y_2 = 83.99 &- 9.74 \times A + 2.81 \times B + 6.30 \times C + 2.74 \\ &\times A \times B + 7.01 \times A \times C - 8.78 \times B \times C \\ &+ 4.94 \times A^2 - 2.14 \times B^2 - 7.98 \times C^2 \end{aligned} \tag{12}$$

$$\begin{aligned} Y_3 = &+1.19 + 0.000 \times A + 1.13 \times B + 1.13 \times C \\ &+ 0.034 \times A \times B - 0.045 \times A \times C + 1.00 \times B \\ &\times C + 0.21 \times B^2 + 0.058 \times C^2 \end{aligned} \tag{13}$$

The adequacy of developed models between the three factors and responses of electrocoagulation process were examined based on *F*-value, *p*-value, R^2, adjusted R^2, predicted R^2 and adequate precision. A good and suitable model should have high *F*-value, low *p*-value ($p < 0.05$) and the difference between adjusted R^2 and predicted R^2 should be <0.2. The value of desirable adequate precision, which is the ratio of signal to noise, should also be >4.

In the present case, the ANOVA results listed in Table 3, show that for all the three models *F*-values and R^2 values fall within 48.855–387.437 and 0.984–0.998, respectively, where as the *p*-value is <0.0001. The difference betweeen adjusted R^2 and predicted R^2 is also in desirable range (<0.2) and the adequate precisions are also high and in range of 24.517–59.184. Hence, it can be conclude that the quadratic models correlating three responses with process variables are best suited to explain the experimental data of electrocoagulation process. Fig. 1(a)–(c) indicate a good agreement between observed experimental values and model predicted values of response Y_1, Y_2 and Y_3, respectively. Furthermore, it is also elucidated from Fig. 1(a) and (b) that some experimental and predicted values of arsenic and fluoride removal are found to be ≥98.18 and 87.50%, respectively, which results residual concentrations of arsenic and fluoride below 10 μg/l and 1.5 mg/l (WHO limits for drinking water norms), respectively [13]. From this observation, it seems that electrocoagulation process has capability to remediate the arsenic and fluoride contaminant synthetic water, which is also confirmed using real groundwater sample collected from Kaudikasa Village, Rajnandgaon District, Chhattisgarh, India.

From Table 3, it is observed that current density (*B*), run time (*C*), interaction of current density and runtime (*BC*) as well as square term of run time (C^2) are highly significant factor ($p < 0.0001$) for arsenic removal. Further, initial pH (*A*), interaction of initial pH and run time (*AC*), square term of initial pH (A^2) and current density (B^2) are found significant factor although interaction of initial pH and current density (*AB*) is not significant due to high *p*-value of 0.2921.

As seen from Table 3 for fluoride removal, initial pH (*A*), run time (*C*), interaction of current density and run time (*BC*) are highly significant factor (*p*-value < 0.0001) as compared to other significant linear, quadratic and interaction term of current density (*B*) and run time (*C*), excluding square term of current density (B^2) as the p value is more (0.0818).

In case of operating cost as shown in Table 3, current density (*B*), runtime (*C*) and interaction of current density and runtime (*BC*) are found highly significant to this response. While, initial pH (*A*), interaction of initial pH and current density (*AB*), interaction of initial pH and run time (*AC*) as well as square term of run time (C^2) are found insignificant other than square term of current density (B^2), as the *p*-values of 0.0136.

3.2. Analysis of response surfaces

Data extracted manually from Desisgn Expert software are used to draw Fig 2(a), (b), and (c), and explain the effects of initial pH, run time and current density on three responces. From Fig. 2(a), it is evident that the percentage removal of arsenic increases with increase in initial solution pH from 3 to 7 and decreases thereafter slightly upto initial pH value of 11. A good amount of arsenic (~96%) is also removed at lower initial pH value of 3. At lower pH the As(III) species predominantly exists as neutral species as evident from Fig 3(a) and dissolved aluminium exists as positively charged species (Fig. 3(b)), and hence, this pH is not favourable for chemisorption of As(III).

Table 3
ANOVA results for arsenic removal, fluoride removal and operating cost

Source	Sum of squares	df	Mean square	F-value	P	
Arsenic removal (%)						
Model	6,045.279	9	671.697	387.437	<0.0001	Significant
A initial pH	23.805	1	23.805	13.731	0.0076	
B current density	301.965	1	301.965	174.175	<0.0001	
C run time	4,140.955	1	4,140.955	2,388.518	<0.0001	
AB	2.250	1	2.250	1.298	0.2921	
AC	12.250	1	12.250	7.066	0.0326	
BC	203.490	1	203.490	117.374	<0.0001	
A^2	18.467	1	18.467	10.652	0.0138	
B^2	11.418	1	11.418	6.586	0.0372	
C^2	1,290.469	1	1,290.469	744.357	<0.0001	
Residual	12.136	7	1.734			
Lack of fit	9.556	3	3.185	4.939	0.0785	Not significant
Pure error	2.579	4	0.645			
Total	6,057.415	16				
R^2 = 0.998, R^2 (adj.) = 0.995, R^2 (pred.) = 0.974, Adeq. precision = 59.184						
Fluoride removal (%)						
Model	2,052.548	9	228.061	48.855	<0.0001	Significant
A initial pH	759.330	1	759.330	162.664	<0.0001	
B current density	63.113	1	63.113	13.520	0.0079	
C run time	317.646	1	317.646	68.046	<0.0001	
AB	30.085	1	30.085	6.445	0.0387	
AC	196.701	1	196.701	42.137	0.0003	
BC	308.354	1	308.354	66.055	<0.0001	
A^2	102.918	1	102.918	22.047	0.0022	
B^2	19.255	1	19.255	4.125	0.0818	
C^2	268.363	1	268.363	57.489	0.0001	
Residual	32.677	7	4.668			
Lack of fit	27.149	3	9.049	6.549	0.0505	Not significant
Pure error	5.528	4	1.382			
Total	2,085.224	16				
R^2 = 0.984, R^2 (adj.) = 0.964, R^2 (pred.) = 0.787, Adeq. precision = 24.517						
Operating cost (USD/m^3)						
Model	24.655	8	3.0819	166.522	<0.0001	Significant
A initial pH	0.000	1	0.000	0.000	1.0000	
B current density	10.292	1	10.292	556.111	<0.0001	
C run time	10.170	1	10.170	549.5121	<0.0001	
AB	0.005	1	0.005	0.257	0.6257	
AC	0.008	1	0.008	0.438	0.5268	
BC	3.976	1	3.976	214.835	<0.0001	
B^2	0.184	1	0.184	9.928	0.0136	
C^2	0.014	1	0.014	0.757	0.4096	
Residual	0.148	8	0.019			
Lack of fit	0.144	4	0.036	36.605	0.0021	Significant
Pure error	0.004	4	0.001			
Total	24.803	16				
R^2 = 0.994, R^2 (adj.) = 0.988, R^2 (pred.) = 0.942, Adeq. precision = 46.874						

Inspite of this fact, high removal of arsenic at initial pH 3 is possible because of the increase in solution pH with run time and current density. In the present case, it is observed that under the experimental conditions, using initial pH of 3, the final solution pH attains a value within 5–9 as evident in Table 2. Above pH 7, the neutral As(III) starts to convert to negatively charged species, and at pH 9, it predominantly exists as negatively charged species. The positively charged nature of dissolved aluminium gradually decreases with an increase in solution pH, and above the pH value of 8 it exists predominantly as negatively

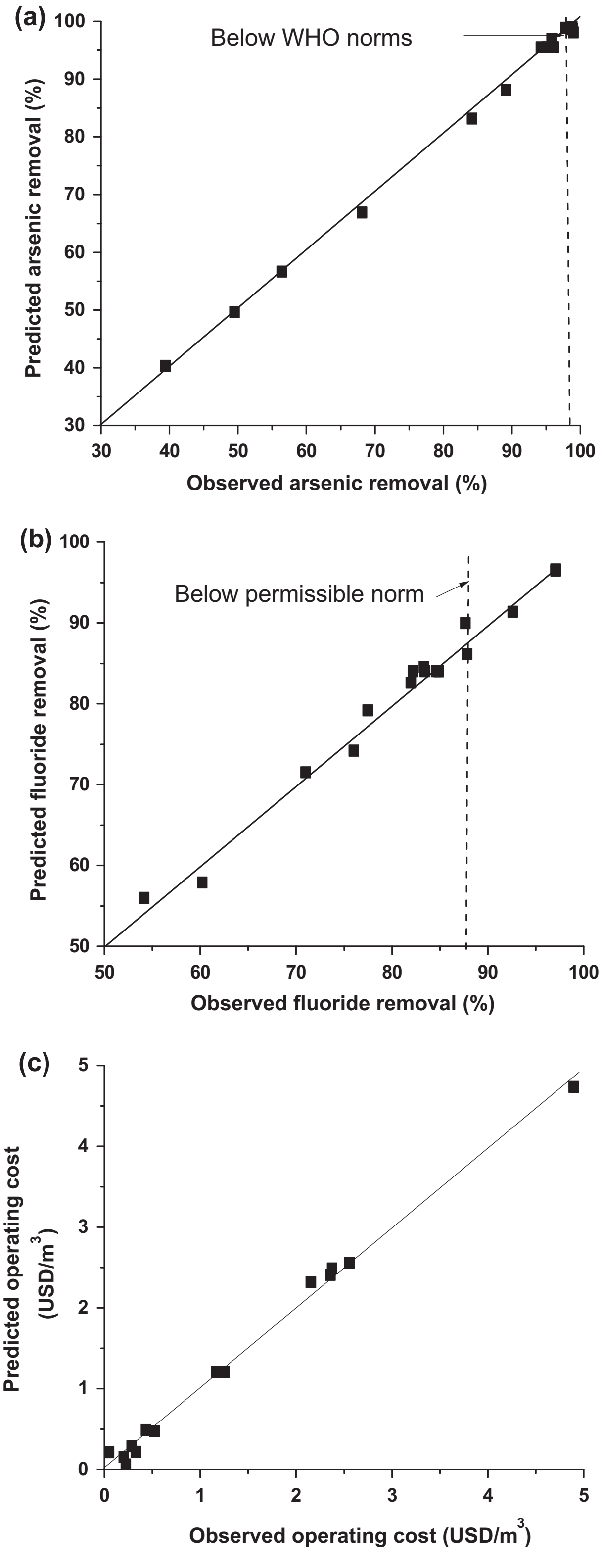

Fig. 1. Plots for the predicted and observed values of (a) arsenic removal, (b) fluoride removal, (c) operating cost.

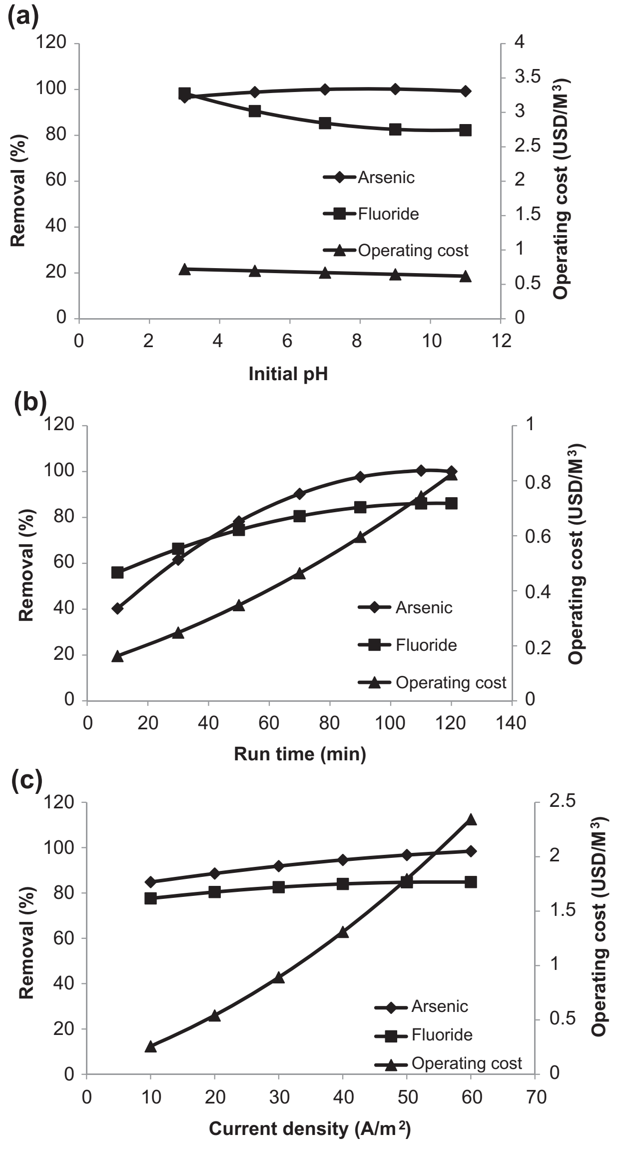

Fig. 2. Effect of process parameters on Y_1, Y_2 and Y_3 response on (a) initial pH, (b) run time, (c) current density.

charged species (Fig. 3(b)). Thus, within the pH range of 7–9 chemisorption of negatively charged As(III) species on positively charged aluminium oxides surface takes place, which results in the removal of As (III). Since the pH of the solution gradually increases with run time (Table 2 in supplementary data), adsorption takes place through different mechanisms. In context to experiment no. 7 (Table 2), solution pH increases from initial pH 3–5.9 in 10 min run time at which 49.52% arsenic removal is observed. This suggests that apart from bridge coagulation (adsorption), sweep coagulation (entrapment by lattice-like structure) and co-precipitation are also responsible for the removal of As(III) species. In electrocoagulation, polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$ are formed. This species are further transformed into amorphous $Al(OH)_{3(s)}$ accroding to complex precipitation kinetics [61]. Freshly formed amorphous $Al(OH)_3$ has minimum solubility and is finally polymerized in to $Al_n(OH)_{3n}$, which results into dense flocs formation. The dense floc has large surface area which provides entrapment of colloidal arsenic particles and thus, the arsenic removal occurs [49,86]. When initial pH value of 7 is used, the final pH value of the solution reaches within 8.8–9.6 under the experimental conditions. In this case, chemisorption is maximum as As(III) predominantly exists as negatively charged species and aluminium oxide exists as predominantly positively charged species, as a result, maximum removal of As (III) is obtained at initial pH value of 7.

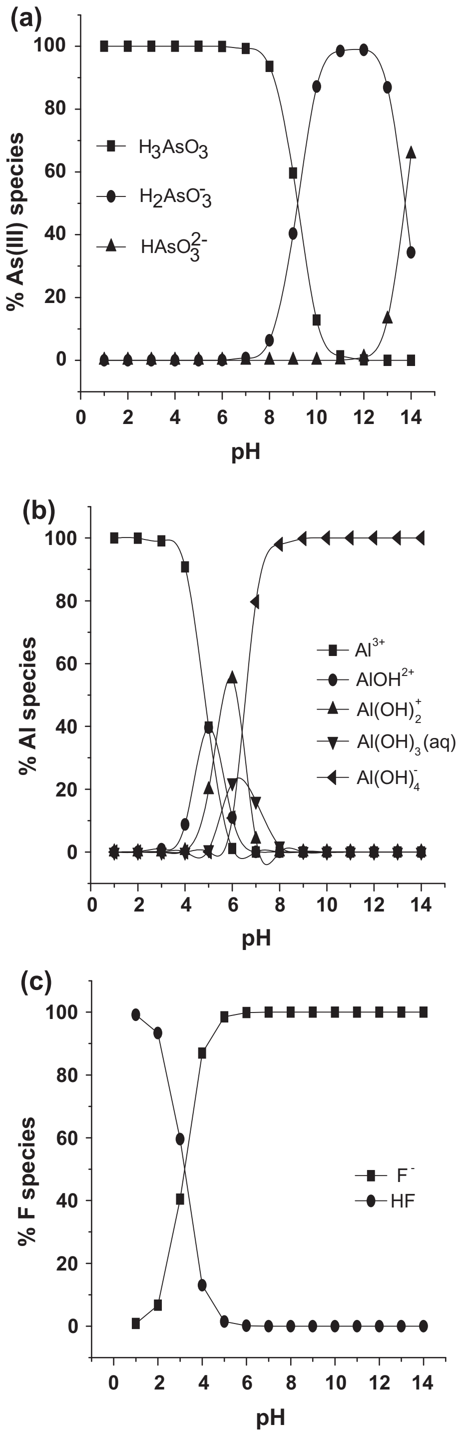

Fig. 3. Distribution of species as a function of pH, (a) arsenite, (b) aluminium, (c) fluoride, in solution simulated by Visual MINTEQ version 3.1 [89].

It is interesting to note that although the solution pH increases with increase in run time due to the generations of OH^- ions and H_2 [87,88] gas at the cathode as per Eq. (2) for lower initial pH value, the final pH becomes lower when initial pH is 11. At high pH, considering that aluminium hydroxides is typical amphoteric metal hydroxides, Eq. (14) could take place, leading to decline in pH [90].

$$Al(OH)_3(s) + (OH)^-(aq) \rightarrow Al(OH)_4^-(aq) \tag{14}$$

In the present case, it has been noted that under the experimental condition the final pH becomes within 9.5–9.8 when initial pH is 11. Due to this reason, removal of As(III) is higher even at initial pH of 11. Peak at the wavenumber of 617 cm^{-1} of FTIR spectra of sludge generated during electrocoagulation proves the presence of As(III) in the sludge [65].

From Fig 2(a) the percentage removal of fluoride is found maximum (~98%) at initial pH 3. At this pH, the amount of positive-charged aluminium species (Fig. 3(b)) and negative-charged F^- (Fig. 3(c)) are maximum; thus, the maximum fluoride removal attains due to charge neutralization. Fluoride removal decreases with the increase in initial pH as the positive-charged aluminium species drecreases. At the initial pH above 8, the negative-charged $Al(OH)_4^-$ species dominates in bulk solution, whereas the fluoride are also negatively charged as F^-, hence its removal decreases. Similar trend is also observed when real groundwater sample is used. The effect of initial pH on operating cost is negligable, as we have considered only electrode material loss and power used, which depends on applied voltage, current and time.

As depicted in Fig. 2(b), initially the fluoride removal is higher than the arsenic removal in the first 30 min and after that the arsenic removal increases rapidly as compared to fluoride removal. These results are also confirmed from Table 3, where run time and current density are found a significant factor for arsenic removal. Both arsenic and fluoride removal increases initially up to 90 min and then reaches near constant value. While, the operating cost increases with the run time of electrocaogulation process, as electrode mateial loss and electrical consumption both increase with run time during electrocoagulation.

It implies from Fig 2(c) that arsenic and fluoride removal as well as operating cost increase with increase in current density. According to Faradey law, loss in weight of material is proprtional to quantity of electricity passed in solution during electrocoagulation. However, due to super-faradic effect the actual loss in electrode weight is found greater than the loss calculated theoretically (according to Faraday law) [90]. Excess of dissolved aluminium (super-faradic) is primarily related to the chemical dissolution of aluminium [91]. Although the exact cause of super-faradaic disslouiton of electrocoagulant is unclear [90], it is suggested that the (hydr)oxide passivation layer undergoes localized attack in the presence of chloride ions causing super-faradaic aluminium electrocoagulant dissolution [92,93]. Hence, for conservative results on cost estimation, the experimental mass loss is considered, which is more than the theoretical mass loss (maximum upto 37%). As the current density increases, more metal hydroxides are produced in solution, which enhances both arsenic and fluoride removal. However, it simultaneously increases the operating cost also. For a better explanation of operating cost, a 3-D polt is depicted in Fig. 4. It is evident from Figs. 5(a)–(c) and 6(a)–(c) that aresnic and fluoride removals are sensitive to alteration of pH, current density and run time, respectively.

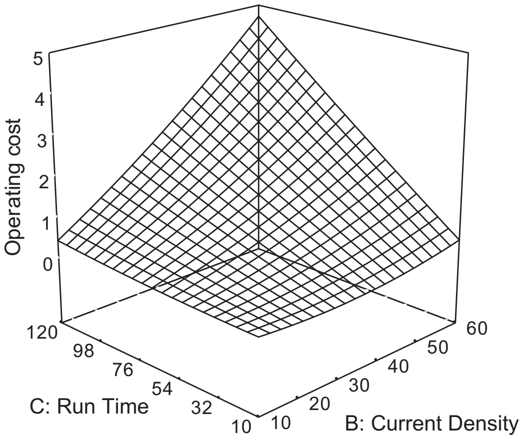

Fig. 4. 3-D surface plot of operating cost (USD/m^3) as a function of run time (min) and current density (A/m^2).

3.3. Process optimization

Optimization of the electrocoagulation process was performed to determine the optimum values of process variables such as initial pH, current density and run time for the removal of arsenic and fluoride alongwith operating cost using the models developed from the experimental data. For the optimization, point prediction option was carried out using Derringer's desired function methodology. In the present study, pH was defined as target 7.0 and operating cost was defined as minimum. The optimum conditions, according to BBD desgin are found as initial pH: 7, current density: 10A/m^2 and run time: 95 min. For the validation of model, the actual experiments were performed at these optimum conditions, determined by Design Expert software, and the predicted and experimental values of the responses are provided in Table 4, which elucidates that the arsenic and fluoride concentration in treated water reaches below WHO drinking water norms 10 μg/l and 1.5 mg/l, respectively [13]. It is noteworthy that arsenic and fluoride concentration in treated water may further be reduced if additional stirring time is provided to attain the equilibrium after switching off the DC power supply. As discussed above the model predicted values of the responses are in good agreement with experimental values, which proves that the models generated through RSM using Design Expert software are adequate for the prediction of arsenic and fluoride removal as well as operating cost for electrocoagulation process.

Further, the performance of electrocoagulation process is also evaluated for the removal of arsenic and fluoride from real groundwater sample collected from Kaudikasa Village, Rajnandgaon District, Chhattisgarh, India. The initial characteristic of groundwater was pH: 6.8, As: 512 μg/l, F: 6.3 mg/l, turbidity: 17 NTU, D.O.: 4 mg/l, total hardness: 105 mg/l, iron: 3.5 mg/l, nitrate: 42 mg/l, phosphate: 3 mg/l. Under optimum conditions, electrocoagulation process successfully reduced the arsenic and fluoride concentration to below maximum contaminant level as per WHO drinking water norms (% removal As: 98.41%, F: 96.69%) along with reduction of total hardness, iron, nitrate and phosphate to 73.33, 97.14, 30.95 and 82.12%, respectively.

Comparison of present process with some reported literature on the removal of arsenic and fluoride individually or simultaneously from water through electrocoagulation process are listed in Table 5. From Table 5, it is evident that initial concentration of arsenic and fluoride varies widely in these studies and thus it is difficult to precisely compare the performance of these processes. However, the concentration of both arsenic and fluoride considered in the present study are only similar to the prevailing concentration of these elements in real groundwater. Further, it is difficult to preciously compare the operating cost of different electrocoagulation process reported in Table 5, since the operating conditions, electrode material, etc. are not similar in these studies. Although the high % removal of arsenic (98.51%) and fluoride (88.33%) is obtained in the present research, further investigation is required, particularly in continuous reactor, to explore the possibility of the electrocoagulation process for treatment of arsenic and fluoride containing groundwater in large scale. Estimation of associated cost for continuous operation of such electrocoagulation unit is also required to compare the cost of the electrocoagulation process with other conventional processes used in large-scale treatment of water.

3.4. Characteristics of sludge

Sludge characterization was carried through SEM, EDX and FTIR analysis of produced sludge to put insight into its properties required to assess its further

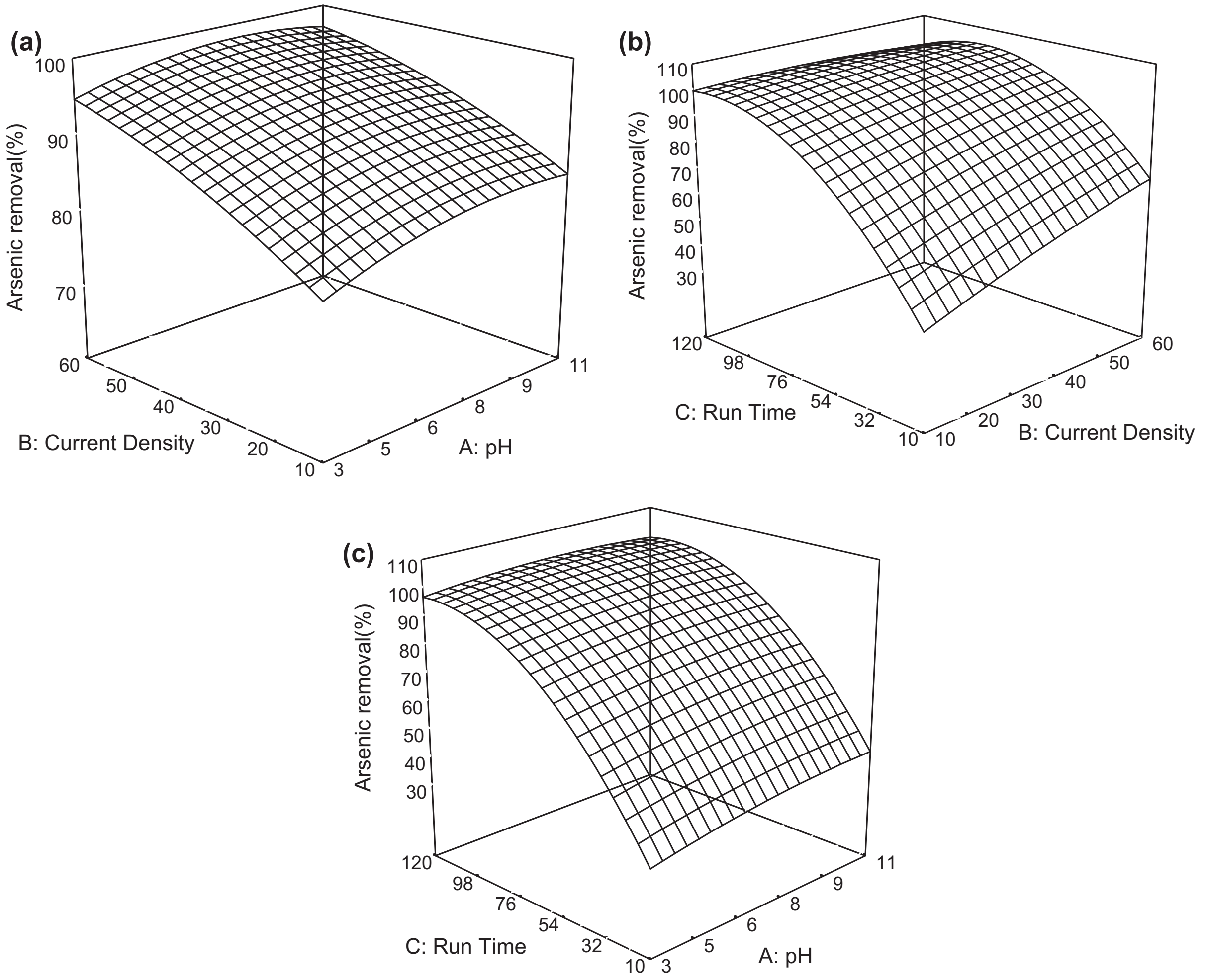

Fig. 5. 3-D surface plots of arsenic removal as a function of (a) current density (A/m^2) and pH, (b) run time (min) and current density (A/m^2), (c) run time (min) and pH.

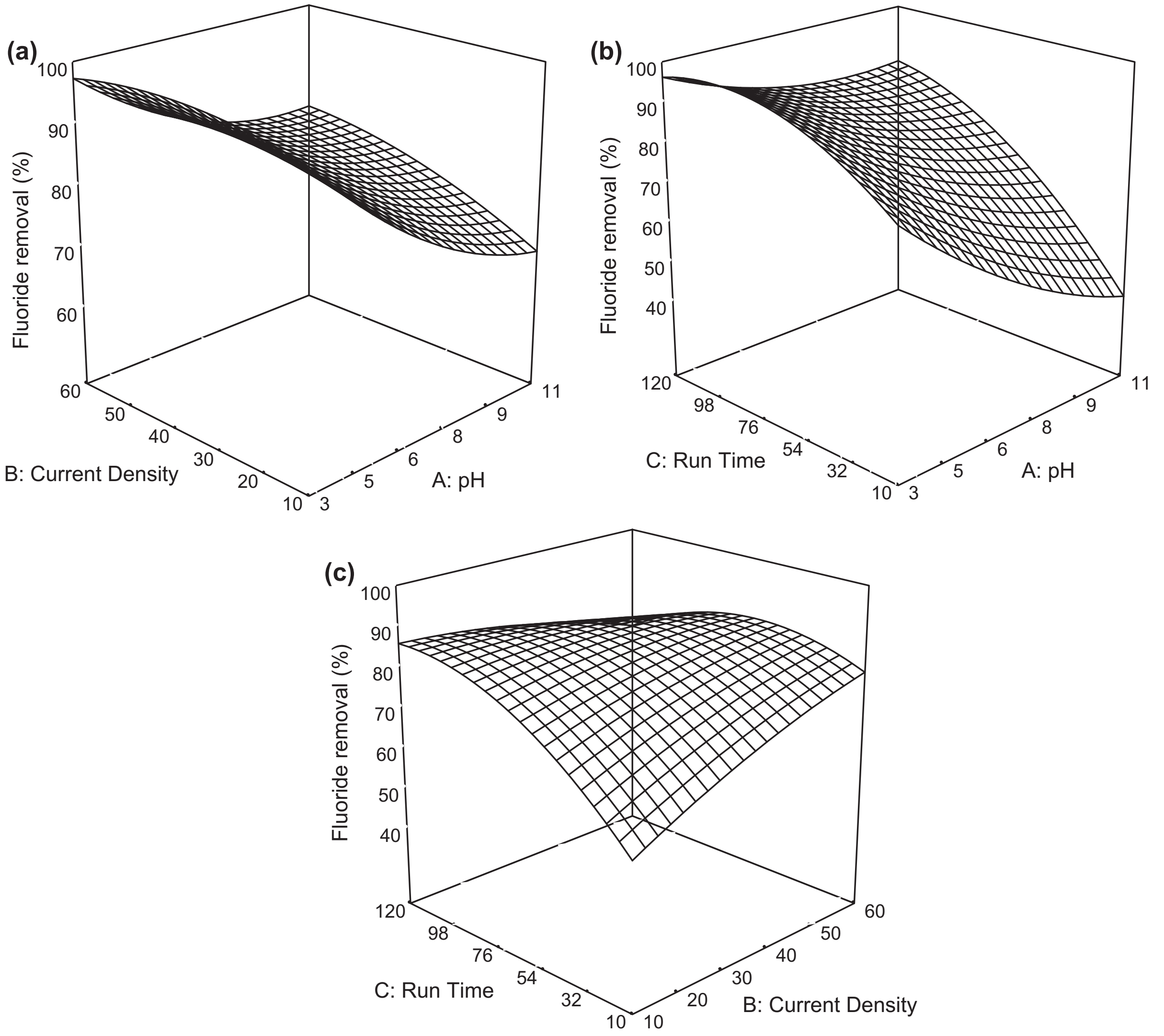

Fig. 6. 3-D plots of fluoride removal as a function of (a) current density (A/m^2) and pH, (b) run time (min) and pH, (c) run time (min) and current density (A/m^2).

Table 4
Comaprison of the predicted and experimental value at optimium conditions (initial pH 7, current density: 10A/m^2 and runtime: 95 min)

	Model predicted value	Experimental value
Y_1 (Arsenic removal %)	98.64	98.51
Y_2 (Fluoride removal %)	84.80	88.33
Y_3 (Operating cost USD/m^3)	0.354	0.343

utilization/management as well as to explore the mechanism for the removal of arsenic and fluoride through electrocoagulation. The surface morphology of sludge as depicted in Fig. 7 indicates the presence of its cake structure with cracks, which emerges due to drying. EDX analysis was used to find out the elements present in produced sludge. It is evident from Fig. 8 that arsenic, fluoride and aluminium are present in produced sludge with high amount (weight %) of aluminium as compared to arsenic and fluoride. EDX

Table 5
Comparison of the performance of some electrocoagulation processes along with operating cost for the individual and simultaneous removal of arsenic and fluoride

As and F concentration	Type of electrode	pH	Current density (A/m^2)	Run time (min)	% removal	Operating cost (USD/m^3)	Refs.
Simultaneous							
As(III)-550 µg/l F-12 mg/l	Al	7.0	10	95	As-98.5 F-88.3	0.343	This study
As(III)-1,000 µg/l F-4.5 mg/l	DSA[a] Fe Al	7.0	40	40	As-99 F-77.7	–	[63]
Individual							
As(III)-150 µg/l	Fe	6.5	2.5	12.5	93.5	0.022	[52]
As(III)-150 µg/l	Al	7.0	2.5	15	95.7	0.019	[52]
As(V)-500 µg/l	Al alloy	7.0	20	45	98.4	–	[94]
F-25 mg/l	Al	7.0	111	25	90	0.905	[61]
F-10 mg/l	Al	8.0	625	45	>90	For monopolar connection-0.38 For bipolar connection-0.62	[60]

[a] DSA—dimensionally stable electrode.

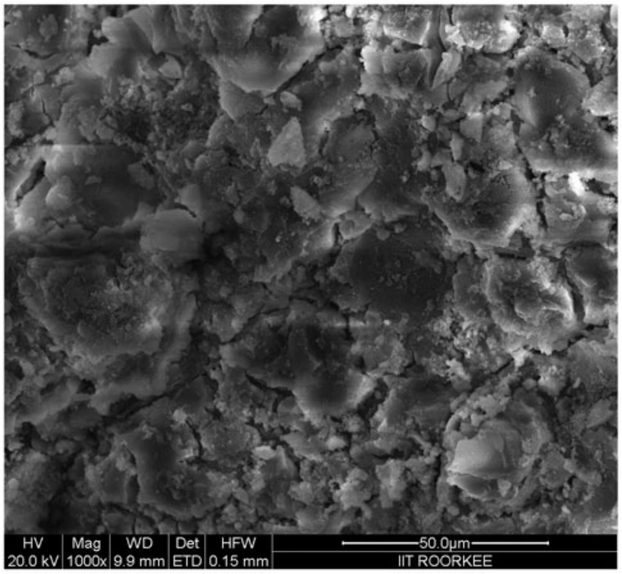

Fig. 7. SEM image of produced sludge.

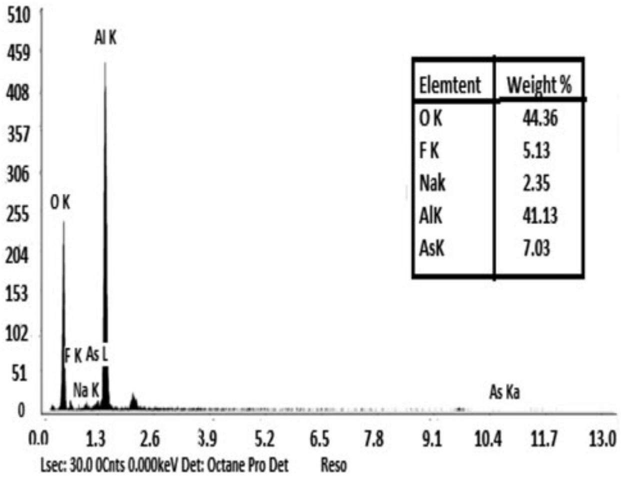

Fig. 8. EDX image of produced sludge.

analysis confirms that arsenic and fluoride are entrapped within the produced sludge and it can be explored for Al recovery. Cementation can also be a suitable option for the management of this sludge [95]. FTIR spectrum of the sludge as shown in Fig. 9 shows bands at 3,553, 3,458 and 3,431 cm^{-1}, which signify the presence of OH stretching for basic hydroxyl groups from aluminium hydroxide/oxyhydroxides [65,89]. The band at 1,640 and 1,388 cm^{-1} could be attributed to hydroxyl bending and Al–H stretching, respectively [96]. The band at 587 cm^{-1} can be assigned to strectching of Al–O [65,97]. The peak at 617 cm^{-1} is characteristic of As(III)–O, which confirms that some arsenic is removed as As(III) in electrocoagulation process [65].

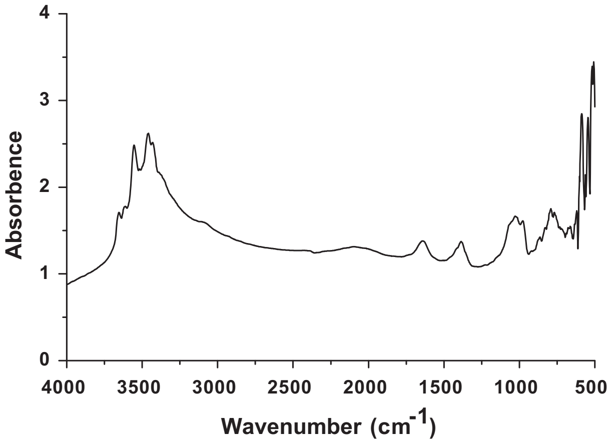

Fig. 9. FTIR spectra of produced sludge.

4. Conclusion

In the present study, simultaneous removal of arsenic and fluoride from synthetic water containing As(III) and fluoride at the concentration prevailing in real groundwater is studied through electrocoagulation process in batch mode. The BBD-based RSM was applied to fix the experimental matrix to study and optimize the process parameters such as initial pH, current density and run time for simultaneous removal of arsenic and fluoride along with its operating cost using Design Expert software. From the results, it is found that the process variables have significant effects on arsenic and fluoride removal (%) as well as operating cost. The quadratic model is found more significant than linear, two-factor interactions and cubic models for developing input–output models correlating the process variables with three responses separately (arsenic removal, fluoride removal and operating cost).The optimized parameters are found as initial pH: 7, current density: $10 A/m^2$ and run time: 95 min. Under these optimum conditions, the experimental values (arsenic removal: 98.51%, fluoride removal: 88.33% and operating cost: $0.343 USD/m^3$) are in close aggrement with the predicted values (arsenic removal: 98.64%, fluoride removal: 84.80% and operating cost: $0.354 USD/m^3$). Therefore, it has been proven that RSM is a powerful tool for evaluation and optimization of electrocoagulation process for simultaneous arsenic and fluoride removal and its operating costs from aqueous solutions. Analysing the characteristics of the sludge it seems that some amount of arsenic is removed as As(III) and the entrapment of As(III) in the aluminium oxides floc (sweep coagulation) is a possible mechanism for As (III) removal along with other phenomena like bridge coagulation (adsorption), co-precipitation. The produced sludge contains high amount of Al and can be explored for Al recovery. The present process also can reduce the arsenic and fluoride concentration below maximum contaminant level as per WHO drinking water norm from real groundwater sample collected from Kaudikasa Village, Rajnandgaon District, Chhattisgarh, India.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2016.1186564.

Abbreviations

FTIR	—	Fourier transform infrared spectrometer
FESEM	—	field emission scanning electron microscopy
WHO	—	World Health Organization
ICPMS	—	inductively coupled plasma mass spectrometer
EDX	—	energy-dispersive X-ray spectroscopy
RSM	—	response surface methodology
BBD	—	Box–Behnken design
TISAB	—	total ionic strength adjustment buffer

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