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Optimization of salicylic acid removal by electro Fenton process in a continuous stirred tank reactor using response surface methodology

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ABSTRACT

The aim of this work is to apply the response surface methodology (RSM) to optimize several operating conditions that significantly affect the removal of salicylic acid (SA) from aqueous solution by electro Fenton (EF) process. Optimization of the EF process for the removal of 100 mg/L of SA solution was carried out using a face centred central composite design in RSM to investigate the joint influence of four variables (catalyst concentration, pH, voltage and electrolysis time) at three different levels. 70.45% of SA was removed at the optimum catalyst concentration of 5.10 mg/L, pH of 2.42, voltage of 2.70 V and electrolysis time of 6 h. A validation experiment was performed under the operating conditions predicted by the models.

Keywords: Optimization; Response surface methodology; Electro Fenton; Salicylic acid

1. Introduction

Pharmaceutical industry produces a wide variety of products. Generally, most of these wastes are toxic to the biological life [1]. The existence of such compounds (e.g. pharmaceuticals and hormonally active substances) in the aquatic environment and their possible effects on living organisms are giving rise to growing concern [2]. Salicylic acid (SA) is a drug responsible for many cases of intoxication, since it is present in many medications and prescription drugs such as aspirin [3]. SA has several important metabolic effects that contribute to its toxicity. The net effects of salicylate as a metabolic poison are an increase in metabolic activity with the production of heat, generation of metabolic acidosis and ketoacidosis, and increased glucose utilization [4]. Many different approaches have been proposed to remove SA from aqueous solution such as membrane filtration [5], chemical coagulation/precipitation [6] and biological decomposition [7].

Recently, advanced oxidation processes (AOPs) have been proposed as an offering promise for wastewater treatment. Because, AOPs are able to oxidize a wide range of compounds that are otherwise difficult to degrade [8]. Among AOPs, oxidation using Fenton's reagent is an attractive treatment for the effective decolourization and degradation of pollutants, due to its low-cost, the lack of toxicity of the reagents (i.e. Fe^{2+} and H_2O_2), the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology [9].

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The Fenton system uses ferrous ion to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing ability to degrade organic pollutants as shown in Eqs. (1–4) [10,11].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \quad (1)$$

$$OH^{\cdot} + RH \rightarrow R^{\cdot} + H_2O \quad (2)$$

$$R^{\cdot} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \quad (3)$$

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{-} \quad (4)$$

Several studies demonstrated that one of the main drawbacks of Fenton treatment relies on the instability of H_2O_2 when it gets in touch with chemical species that are naturally in the environment [12,13]. These drawbacks can be eliminated by using electro Fenton (EF) process which offers significant advantages such as high mineralization efficiency, no sludge production and low operational cost [14–18]. EF process is a promising technology that combines electrochemical reactions and Fenton process [19]. EF is based on the production of continuous and large amount of hydrogen peroxide in the acidic solution by two-electron reduction of oxygen molecule (Eq. (1)) [20]. Combination of hydrogen peroxide with iron catalysts generates the oxidizing agent, $^{\cdot}OH$ from Fenton's reactions (Eq. (5)) [21].

$$O_{2(g)} + 2H^{+} + 2e^{-} \rightarrow H_2O_2 \quad (5)$$

The conventional practice of single factor optimization by maintaining other involving factors at unspecified constant level does not depict the combined effect of all factors involved and this method requires to carry out a number of experiments to determine the optimum levels, which will not give true values [22]. The drawbacks of single factor optimization process can be eliminated by optimizing all the affecting parameters together by statistical experimental design. Design of experiments using response surface methodology can be used as an effective tool to eliminate all these drawbacks [22]. Response surface methodology (RSM) is a collection of statistical and mathematical methods that are useful for design, empirical modelling and optimization of processes [23]. Response surface methodologies have been used to design and evaluate physical, chemical and biological experiments in which the outcomes are influenced by various input factors or process variables [24,25]. RSM comprises of the following three major components: (i) experimental design to determine the process factors' values based on which the experiments are conducted and data are collected; (ii) empirical modelling to approximate the relationship (i.e. the response surface) between responses and factors; and (iii) optimization to find the best response value based on the empirical model [26].

The goal of the experiment described in this paper was to improve the understanding of several response variables of interest and their behaviour in the electrolytic system. Continuous removal of SA from aqueous solution was carried out using continuous stirred tank reactor [27]. It was of interest to design an experiment that would allow the mathematical modelling of these response variables, such as catalyst concentration, pH, voltage and electrolysis time. Through mathematical modelling of these parameters a better understanding on the role of each parameter could be attained.

2. Materials and methods

2.1. Materials and instruments

99.8% pure SA ($C_7H_6O_3$) was obtained from Merck and used without further purification. Distilled water was used to make SA solutions of the desired concentration. Analytical grade ferrous sulphate was obtained from Merck. The solution pH was measured with a Orion EA940 Ion analyser (Thermo, USA). A Lambda 25 UV–visible spectrophotometer (Perkin Elmer, USA) was used to determine the concentration of SA in solution. Absorbance values of the solutions were measured at a wavelength of 298 nm, which correspond to the maximum absorbance of SA solution.

2.2. Experimental set-up and procedure

The electrolytic experiments were conducted in a 3 L rectangular reactor. The 100 mg/L SA solution was continuously introduced in the electrolytic cell throughout the experiment. The solution flow rate was kept constant by a flow control valve, which was consecutively placed between the storage tank and the electrolytic cell. This reactor was a single compartment cell containing three graphite plates (purchased from Anabond Sainergy Fuel Cell India Private Limited, Chennai, Tamil Nadu, India) as anode and three graphite plates as cathode. Air was continuously fed to the cathode with the help of fish aerators. The area of each electrode in contact with the electrolyte was maintained as 40 cm^2. The experiments were carried out at constant voltage provided by a DC power supply (0–5 A and 0–30 V). The concentration of SA was monitored with a UV–vis spectrometer at regular intervals.

2.3. Experimental design and optimization

The statistical analysis was performed using Design Expert Statistical Software package 8.0.7.1. The central composite design (CCD) of quadratic type is the most popular method in the response surface methodology. The CCD is ideal for sequential experimentation and allows a reasonable amount of information for testing lack-of-fit while not involving an unusually large number of design points [25]. In CCD, the central composite face centered (CCFC) experimental design was used in this study. From the preliminary experimental results, process variables and their ranges were determined. Catalyst concentration, pH, voltage and electrolysis time are the main parameters affecting the performance of an EF process. Initially several experiments were carried out to find the effect of these parameters on the EF performance. According to the procedure for the optimization by CCFC design, two other values at equal intervals from the optimal value should be taken. The optimal value was coded as 0 and other values as −1 and +1. The operating ranges and the levels of the considered variables are given as actual and coded values in Table 1.

This design consists of three types of points: cube points that come from factorial design, axial points and centre points, therefore total number of experiments (N) needed can be determined by $N = 2^k + 2k + C_0$, where k is the number of factors, 2^k is the cubic runs, $2k$ is the axial runs and C_0 is the centre point's runs [28]. Therefore, the central composite experimental design (CCD) consists of 30 experiments with 16 factorial points, 8 star points and 6 replicates at the centre points. A simple, general equation for a second-order response surface model describes a response y in terms of four variables A, B, C and D:

$$y = k_0 + k_1\mathrm{A} + k_2\mathrm{B} + k_3\mathrm{C} + k_4\mathrm{D} + k_{11}\mathrm{A}^2 + k_{22}\mathrm{B}^2 + k_{33}\mathrm{C}^2 + k_{44}\mathrm{D}^2 + k_{12}\mathrm{AB} + k_{13}\mathrm{AC} + k_{14}\mathrm{AD} + k_{23}\mathrm{BC} + k_{24}\mathrm{BD} + k_{34}\mathrm{CD} \quad (6)$$

Table 1
Actual and coded values of independent variables used for experimental design

Variable	Symbol	Real values of coded levels		
		−1	0	+1
Catalyst concentration (mg/L)	A	2.5	5	7.5
pH	B	2	2.5	3
Voltage (V)	C	1.5	2.5	3.5
Electrolysis time (h)	D	2	4	6

where y is the SA removal efficiency (%), k_0 is the intercept, k_i is the linear coefficient, $k_{ii}$is the squared coefficient and k_{ij} is the interaction coefficient (i and j are constants in between 1 and 4).

The response surface models were validated statistically for adequacy by the analysis of variance (ANOVA). The significant levels of model coefficients were estimated by the ANOVA test. A numerical optimization technique (desired function method) was employed for optimizing the various responses.

3. Results and discussion

3.1. Face centred central composite design (FCCCD) analysis

To establish an approximate range of different experimental parameters like catalyst concentration, pH, voltage and electrolysis time, a set of experiments were carried out in a CSTR reactor. These experimental results were used as the input data for central composite experimental design. The results of each experiment were performed as per the software, which are given in the Table 2. The following second-order empirical formula in terms of catalyst concentration, pH, voltage and electrolysis time was obtained after analysis.

$$\text{Removal efficiency\%} = 62.99 + 0.00\mathrm{A} - 2.72\mathrm{B} + 9.44\mathrm{C} + 3.94\mathrm{D} - 0.81\mathrm{AB} - 0.31\mathrm{AC} + 0.56\mathrm{AD} - 2.44\mathrm{BC} - 0.56\mathrm{BD} + 0.44\mathrm{CD} - 7.48\mathrm{A}^2 - 12.98\mathrm{B}^2 - 20.48\mathrm{C}^2 + 2.02\mathrm{D}^2 \quad (7)$$

where A, B, C and D indicate catalyst concentration (mg/L), pH, voltage (V) and electrolysis time (h), respectively.

3.2. Statistical analysis

Results of the quadratic response surface model fitting in the form of ANOVA are given in Table 3. The significance and adequacy of the model can be tested with the ANOVA data. The adequacy of model was tested through lack-of-fit F-tests.

$$F\ \text{value} = \frac{\text{Model mean square}}{\text{Appropriate error mean square}} \quad (8)$$

The obtained model F-value was 60.45, which indicates that the model is significant. Probability value (p), usually relating the risk of falsely rejected given

Table 2
Input data for FCCCD experimental design

Run	Factor 1 A: Catalyst concentration (mg/L)	Factor 2 B: pH	Factor 3 C: Voltage (V)	Factor 4 D: Electrolysis time (h)	Response 1: Removal efficiency (%)
1	7.5	2	3.5	6	46
2	5	2	2.5	4	48
3	5	2.5	2.5	4	65
4	5	2.5	2.5	4	65
5	7.5	3	1.5	2	13
6	7.5	3	3.5	2	21
7	5	2.5	2.5	6	70
8	2.5	2	1.5	6	20
9	5	2.5	2.5	2	56
10	5	2.5	2.5	4	65
11	7.5	2	3.5	2	34
12	5	2.5	2.5	4	65
13	2.5	3	3.5	6	32
14	5	2.5	3.5	4	56
15	2.5	2	1.5	2	12
16	2.5	2	3.5	2	34
17	2.5	3	3.5	2	27
18	2.5	2	3.5	6	40
19	5	2.5	1.5	4	25
20	2.5	3	1.5	6	17
21	5	2.5	2.5	4	65
22	5	3	2.5	4	48
23	2.5	3	1.5	2	12
24	7.5	2	1.5	2	13
25	5	2.5	2.5	4	65
26	2.5	2.5	2.5	4	54
27	7.5	2	1.5	6	20
28	7.5	3	3.5	6	30
29	7.5	2.5	2.5	4	53
30	7.5	3	1.5	6	18

hypothesis. Usually, a probability less than 0.05 is considered as significant. The obtained model probability value was less than 0.0001, which indicates that the model is significant. In this case B, C, D, BC, A^2, B^2 and C^2 were significant model terms, since its probability values are less than 0.05. Values greater than 0.1000 indicate that the model terms are insignificant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. But in this case more than half of the terms are significant, so that the present model is good enough.

Regression analysis is a method by which data is fitted to a mathematical model. The "Predicted R^2" of 0.9243 was in reasonable agreement with the "Adjusted R^2" of 0.9663. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 22.696 indicates an adequate signal. Therefore, this model can be used to navigate the design space.

R^2	0.982585	Predicted R^2	0.924278
Adjusted R^2	0.966332	Adequate Precision	22.69606

3.3. *Adequacy of the model*

Generally, the investigation of fitted response surface models may produce poor or misleading results, unless the model exhibits a good fit, which makes checking of the model adequacy essential [29]. The graph of actual vs. predicted values is given in Fig. 1, to evaluate the relationship and model satisfactoriness between experimental data and predicted data obtained from the developed model. Removal efficiencies obtained from experiments were taken as actual values and the values of the removal efficiencies predicted by the mathematical model under the same conditions were taken as predicted values. As can be seen from the figure that all points lay on a straight line and indicates

Table 3
Results of the quadratic response surface model fitting in the form of ANOVA

Source	Sum of squares	Degrees of freedom	Mean square	*F*-value	*p*-value Prob > *F*	
Model	11316.4	14	808.3145	60.45323	<0.0001	Significant
A—Catalyst conc.	−1.8E-12	1	−1.8E-12	−1.4E-13	1.0000	
B—pH	133.3889	1	133.3889	9.976054	0.0065	
C—Voltage	1605.556	1	1605.556	120.0783	<0.0001	
D—Electrolysis time	280.0556	1	280.0556	20.94514	0.0004	
AB	10.5625	1	10.5625	0.789961	0.3881	
AC	1.5625	1	1.5625	0.116858	0.7372	
AD	5.0625	1	5.0625	0.378621	0.5476	
BC	95.0625	1	95.0625	7.109653	0.0176	
BD	5.0625	1	5.0625	0.378621	0.5476	
CD	3.0625	1	3.0625	0.229042	0.6391	
A^2	145.0576	1	145.0576	10.84875	0.0049	
B^2	436.6826	1	436.6826	32.65916	<0.0001	
C^2	1086.967	1	1086.967	81.29342	<0.0001	
D^2	10.54625	1	10.54625	0.788746	0.3885	
Residual	200.5636	15	13.37091			
Lack-of-Fit	200.5636	10	20.05636			
Pure error	0	5	0			
Cor total	11516.97	29				

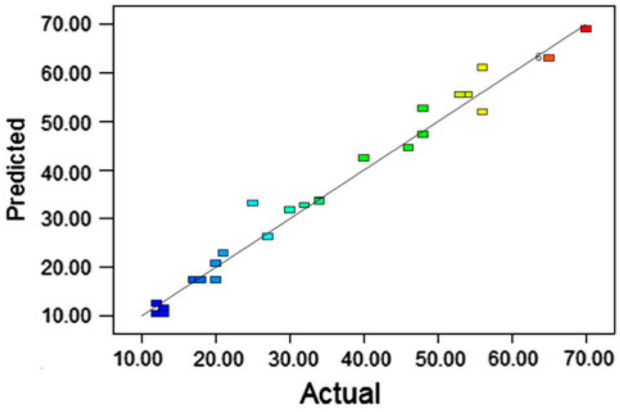

Fig. 1. The actual and predicted values of SA removal by EF process.

the good correlation between actual values and with the predicted values. Thereby, the models are considered adequate for the predictions and optimization of the process.

3.4. Contribution of operational parameters on the predicted responses

The contribution of each factor on the predicted response was calculated by the following formula:

$$\%\ \text{contribution} = \frac{\text{mean square of each factor}}{\text{sum of mean squares of all factors}} \tag{9}$$

It is obvious that the most important variable for EF system performance is voltage (C). Almost 42% of the total SA removal contribution was from the voltage factor. Electrolysis time (D) and pH (B) have significant role on SA removal efficiency as it contributes 7 and 4% to the predicted response. It was also noted that the catalyst concentration (A) has negligible effect on the performance of the system. This may be due to the very short variation of response within the selected range (2.5–7.5 mg/L). BC has a significant role on SA removal efficiency as it contributes 3% to the predicted response. CD, BD, AD, AB and AC have negligible effect on the performance of the system. Similarly, D^2 also has negligible effect on the performance of the system.

3.5. Interactions among the parameters

Fig. 2(a–f) shows the combined effect of different parameters on SA removal efficiency. The peak of the surface plot shows the maximum value of the percentage of SA removal for the relative effects of particular variables by keeping the other two variables at the midpoint values. Meanwhile, the shapes

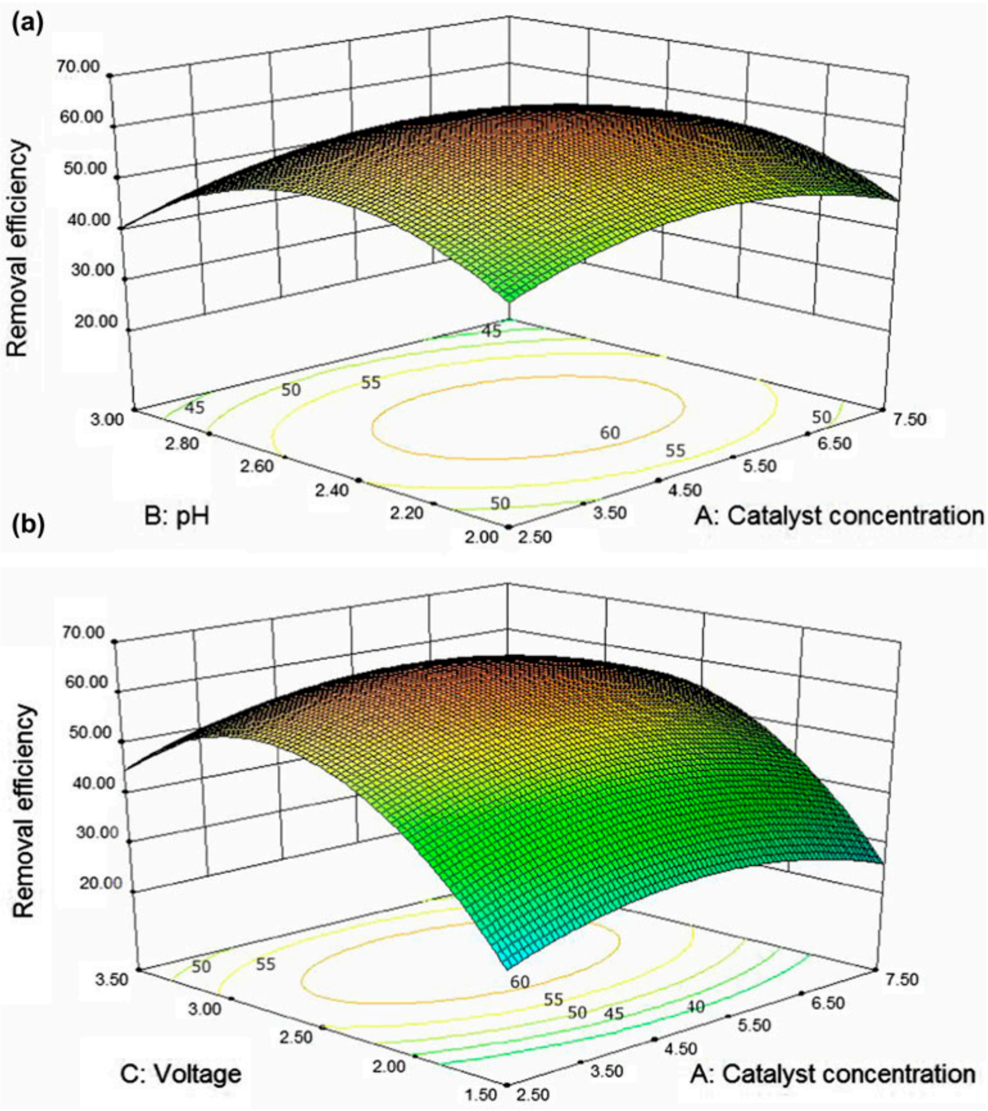

Fig. 2. Response surface and contour plots of SA removal. (a) pH and catalyst concentration, (b) voltage and catalyst concentration, (c) electrolysis time and catalyst concentration, (d) voltage and pH, (e) electrolysis time and pH and (f) electrolysis time and voltage.

of the contour plots indicate the nature and extent of the interactions. Prominent interactions are shown by the elliptical nature of the contour plots, while less prominent or negligible interactions would otherwise be shown by the circular nature of the contour plots.

It has been observed from Fig. 2(a) that the interaction effect between pH and catalyst concentration contributed a remarkable increase in SA removal efficiency. The SA removal efficiency was found maximum at approximately zero-coded level factor (0) and then decreased with further increase in pH and catalyst concentration. Fig. 2(a), (b) and (d) are followed at the same trend.

Fig. 2(a), (c) and (d) show the response surface plot related to the effect of interaction between catalyst concentration with pH, voltage and electrolysis time, respectively, on SA removal efficiency. As can be seen, initially the SA removal efficiency increased considerably with increasing catalyst concentration and then decreased with further increase in catalyst concentration. The increase in SA removal efficiency with increasing catalyst concentration is due to the enhancement of the rate of production of $OH^{\bullet}$ (Eq. (1)). At higher concentrations, Fe^{3+} ions could react with H_2O_2 to produce hydroperoxyl radicals ($HO_2^{\bullet}$) of less oxidation capability (Eqs. (10) and (11)) resulting in decrease in the rate of SA removal efficiency [30].

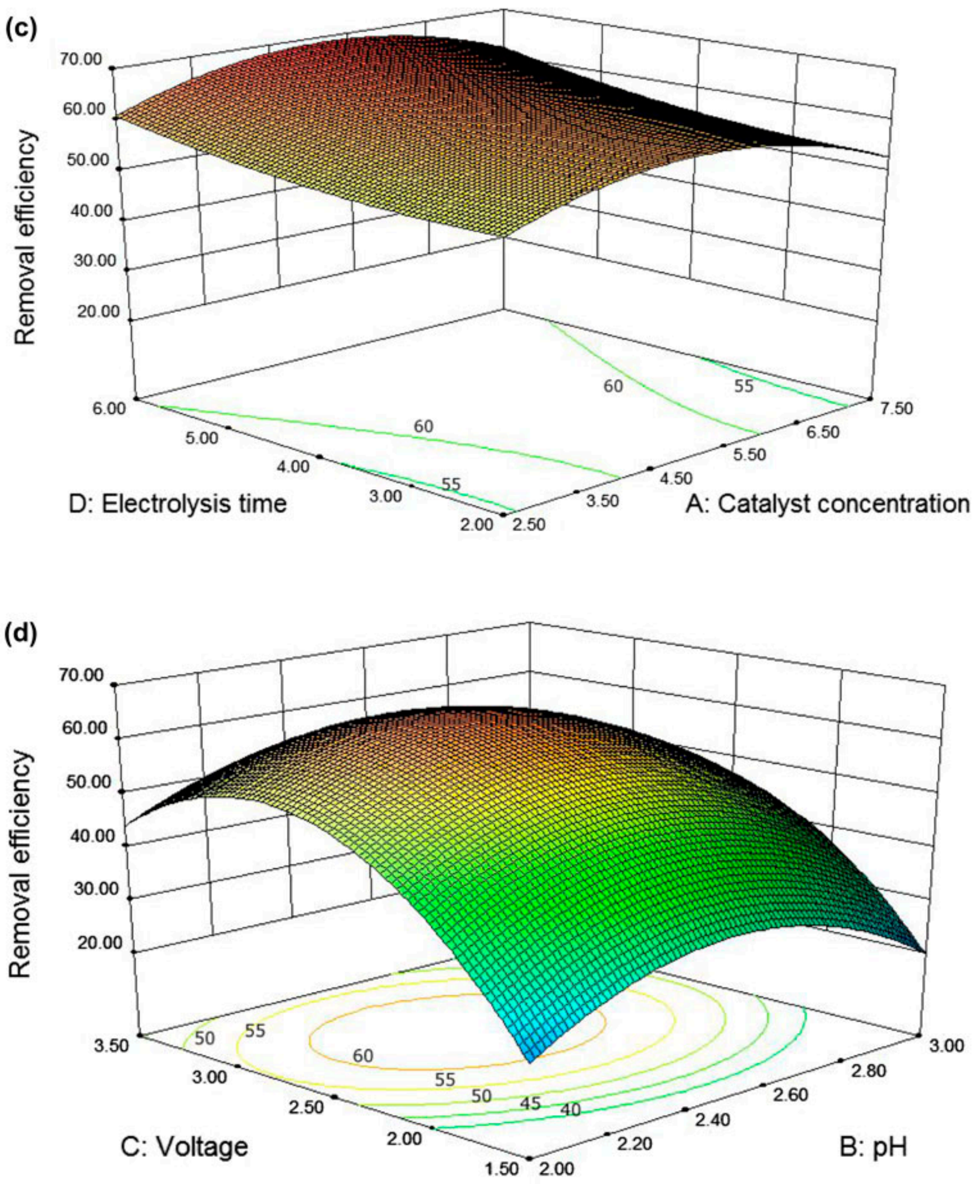

Fig. 2. (*Continued*).

$$Fe^{3+} + H_2O_2 \rightarrow Fe - OOH^{2+} + H^+ \quad (10)$$

$$Fe - OOH^{2+} \rightarrow Fe^{2+} + OH_2^{\cdot} \quad (11)$$

Fig. 2(c), (e) and (f) show the increase in SA removal efficiency with the increase in electrolysis time. The results demonstrated that the SA molecules were rapidly degraded by EF method. Major part of the SA removal occurred in the first 4 h of electrolysis. After 4 h, the increase in SA removal efficiency slowed down. This is mainly because of the formation of intermediate by-products during the electrolysis.

The combined effects of initial pH with catalyst concentration, voltage and electrolysis time on SA removal efficiency by EF method are given in Fig. 2(a), (d) and (e), respectively. As seen from the figures, initially the SA removal efficiency increased considerably with increasing pH and then decreased with further increase in pH. In solutions of low pH values, the reaction according to Eq. (2) could be slowed down during the reactions. Because, H_2O_2 can stay stable probably by solvating a proton to form peroxoniumions, $H_3O_2^+$ (Eq. (12)) [31].

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \quad (12)$$

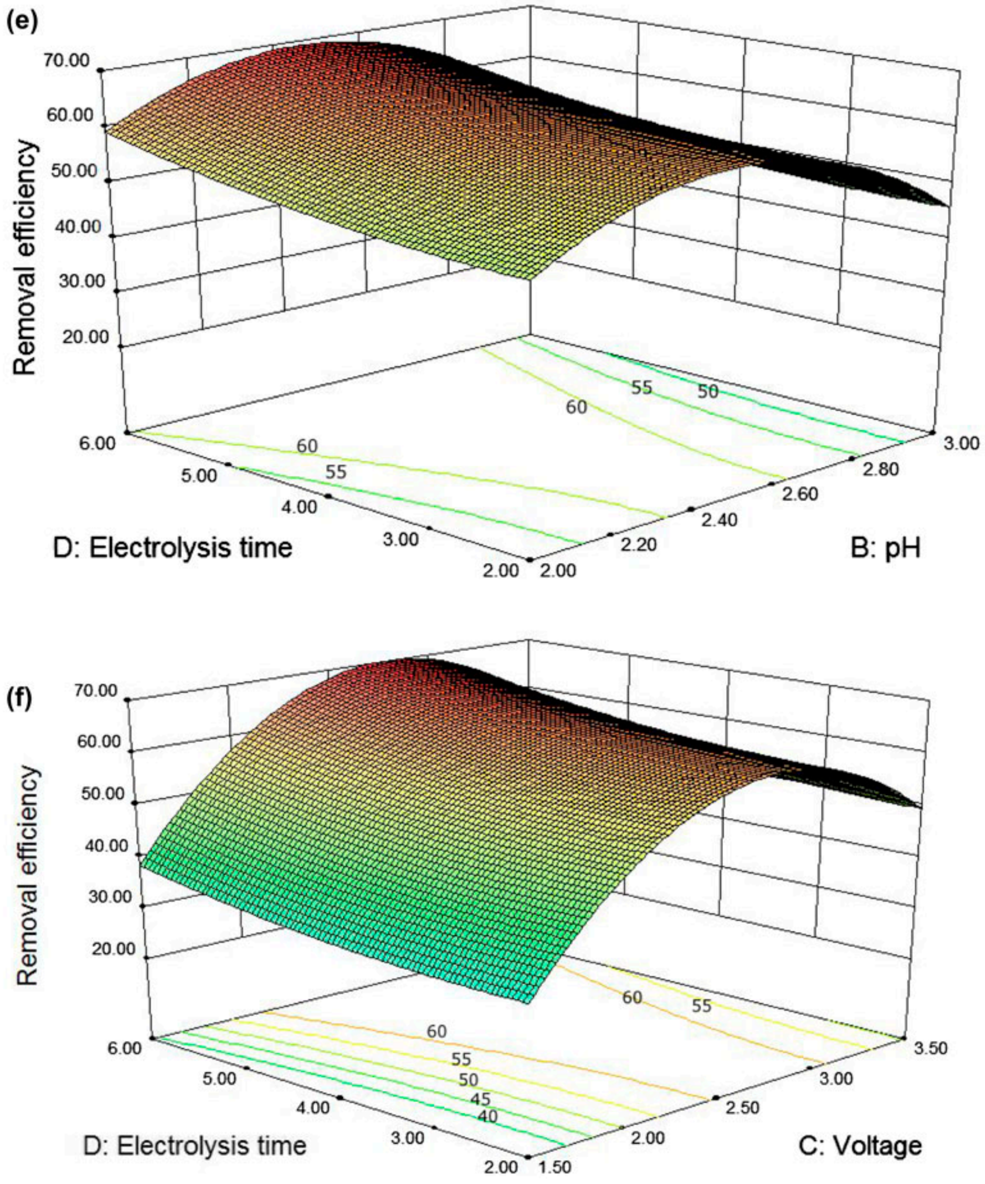

Fig. 2. (*Continued*).

At higher pH values, hydrolysis of Fe^{3+} ions and formation of $Fe(OH)_3(s)$ reduce the SA removal efficiency [32].

The combined effects of voltage with catalyst concentration, pH and electrolysis time on SA removal efficiency by EF method are given in Fig. 2(b), (d) and (f), respectively. As seen from the figures, initially the SA removal efficiency increased considerably with increasing voltage and then decreased with further increase in voltage. The enhancement of the SA removal efficiency with increase in voltage can be accounted for the production of greater amounts of $OH^{\cdot}$ from Fenton's reaction (1) due to the faster generation of H_2O_2 at the cathode (5) [33]. The decrease in removal efficiency with the further increase in voltage is due to the oxidation of $^{\cdot}OH$ to O_2 by reaction (Eq. (13)) and the demineralization of $^{\cdot}OH$ to H_2O_2 by reaction (Eq. (14)) [34].

$$2OH^{\cdot} \rightarrow O_2 + 2H^+ + 2e^- \tag{13}$$

$$2OH^{\cdot} \rightarrow H_2O_2 \tag{14}$$

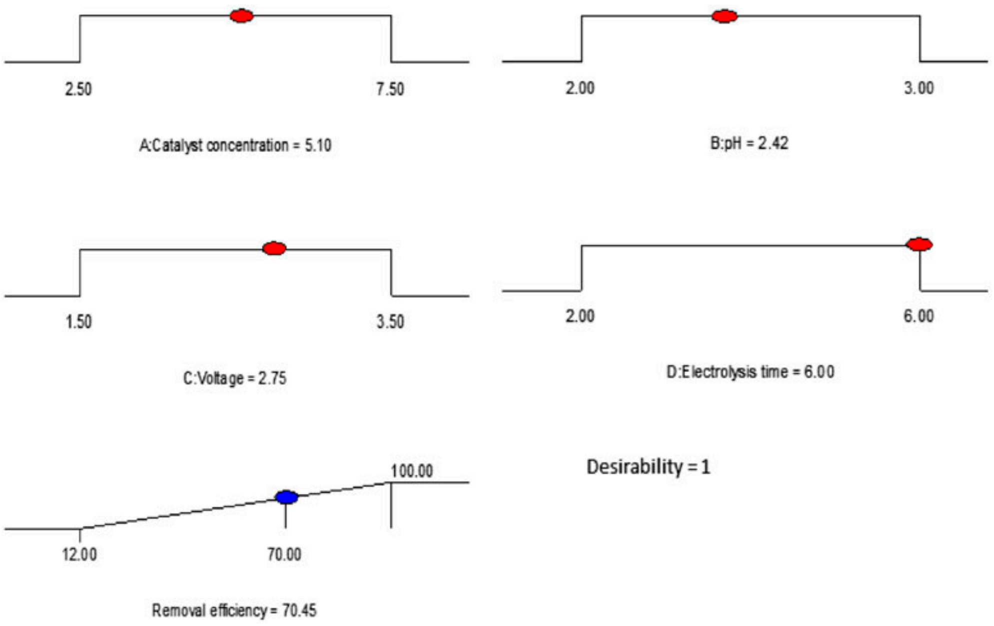

Fig. 3. Desirability ramp for numerical optimization.

3.6. Optimization

The response surface analysis was carried out after performing screening of factors and their interactions. Optimization was performed afterwards on the basis of desirability function in order to find the optimal conditions for the removal of SA. To find out the specific point that maximizes the desirability function, numerical optimization of the software was used. The desired goal was selected by adjusting the weight or importance that might alter the characteristics of a goal. The goal fields for response have five options: none, maximum, minimum, target and within range. From the ANOVA (Table 3), it has been observed that the effects of catalyst concentration, pH, voltage and electrolysis time were significant. Hence, the goal of these parameters was set as "within range". The goal for removal efficiency was set as "maximize" because our study preferred maximum SA removal. The lower limit and upper limit values of all responses are taken from the CCD design levels. Our main objective was to maximize the removal efficiency with recalculating all responsible factors by using desirability functions. By using all above-described settings and boundaries, the software optimized 70.45% removal efficiency with calculating the optimized model factors of catalyst concentration at 5.10 mg/L, pH at 2.42, voltage at 2.7 and electrolysis time at 6 h (Fig. 3).

3.7. Validation of experiment

The quadratic model obtained by the RSM can be used to optimize the operating conditions to obtain maximum SA removal efficiency. In order to confirm the reliability of the models established in this study, a validation experiment was performed under the operating conditions predicted by the models for maximum SA removal efficiency. Fig. 4 shows the

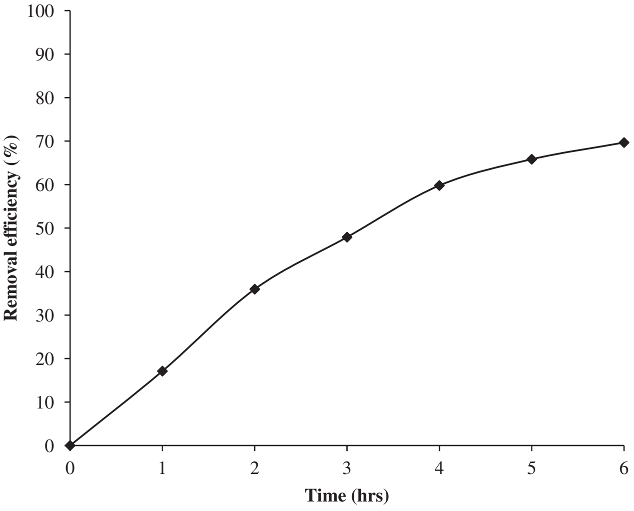

Fig. 4. Validation experiment result.

validation experimental results. The SA removal efficiency found out from the validation experiment was 69.66%. This result is in good agreement with the predicted result (70.45%). Hence, the optimum point determined by RSM was successfully validated and it was confirmed that RSM can be used to optimize the EF degradation process of SA.

4. Conclusions

From the quadratic models developed for SA removal and subsequent ANOVA test using Design Expert software version 8.0.7.1, the applied voltage was found to be the most influential factor, while all other factors were also significant. The high R^2, adjusted R^2 and predicted R^2 values indicated that the models fitted very well to the experimental data. The optimum values obtained after statistical analysis were found out as catalyst concentration of 5.10 mg/L, pH of 2.42, voltage of 2.70 V and electrolysis time of 6 h. Under the optimum condition, the SA removal efficiency was predicted to be 70.45% and the corresponding experimental values fitted well to the predicted values. The results obtained indicate that response surface methodology can be successfully used to analyze the effect of various operational parameters and develop an optimized condition thereby reducing the number of trials, time and cost of experiment.

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