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The investigation of chemical coagulation and electrocoagulation processes for tannery wastewater treatment using response surface methodology

Hanife Sari Erkan*, Senem Yazici Guvenc, Gamze Varank, Guleda Onkal Engin

Yildiz Technical University, Faculty of Civil Engineering, Department of Environmental Engineering, 34220 Davutpasa, Esenler, Istanbul, Turkey, Tel. +90 212 383 5383, Fax +90 212 383 5358, email: hsari@yildiz.edu.tr (H.S. Erkan), syazici@yildiz.edu.tr (S.Y. Guvenc), gvarank@yildiz.edu.tr (G. Varank), gengin@yildiz.edu.tr (G.O. Engin)

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ABSTRACT

This study deals with the comparison of chemical coagulation (CC) (using aluminum sulphate and iron chloride as coagulants) and electrocoagulation (EC) (using aluminium and iron electrodes) processes for TOC and total chromium removal from tannery industry wastewater. The parameters, namely, the coagulant dosage (for CC), current density (for EC), reaction time, and initial pH (for both processes) were optimized employing central composite design (CCD) of response surface methodology (RSM). Experimental data was analyzed by means of the analysis of variance (ANOVA) identifying the mechanism of interaction between the process variables and the dependent variables. High TOC removal efficiencies were obtained in the CC process (60.8% and 75.6% using aluminum sulphate and iron chloride, respectively) and the EC process (75.0% and 84.6% using aluminum and iron electrodes, respectively). No significant difference between CC and EC processes was found for the removal of total chromium in the optimum operation conditions (total chromium removal was over 98% for each process configuration). Even though an appreciable improvement in TOC and total chromium removal efficiencies were obtained in both processes, the CC process using iron chloride was found to be more effective to remove total chromium considering the operational costs.

Keywords: Tannery wastewater; Chemical coagulation; Electrocoagulation; Response surface methodology; Optimization

1. Introduction

As known, tannery wastewater composition is quite complex and the wastewater, itself, has high concentrations of various organic and inorganic pollutants such as, surfactants, biocides, organic acids, sulfonated oils, dyes, tannins, ammonium, chromium, sulfide salts and chloride, thereby increasing the chemical oxygen demand (COD) [1]. In particular, tannery wastewater contains high COD and total chromium concentration (up to 5000 mg/L) [2]. Discharging tannery effluents with high organic matter, organic nitrogen and total chromium content to receiving bodies causes considerable environmental problems. Treatment of tannery wastewater can be accomplished to remove COD, TOC and nitrogen by the application of several methods, namely, the coagulation/flocculation [3–5], biological treatment [6–10], adsorption [11,12], advanced oxidation processes [13–15], electrochemical processes [1,16,17], and membrane processes [18,19]. Although the common wastewater treatment processes is the biological treatment, the tannery wastewater can not be treated by means of biological treatment systems due to its low BOD_5/COD ratio and the toxic effect of chromium present [1]. Membrane processes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) are generally preferred for recovery or reuse purposes of tannery wastewater [18,20–22]. These processes have significant drawbacks, such as expensive equipment and monitoring system requirements and incomplete metal removal.

In chemical processes, the chemical coagulation (CC) is widely used for wastewater treatment. In CC process, coagulating agent is added to the wastewater and promoted by using aluminium and ferric salts [23]. In CC process; flocs form which adsorb the pollutants and the pollutants

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*Corresponding author.

are removed as the flocs are precipitated. The initial pH, the coagulant type, the wastewater characteristics and the coagulant dosage affect the removal efficiencies [3]. Synthetic polymers have also been experienced and have enhanced the coagulation process substantially. However, until today, no alternative coagulant is found to efficiently replace aluminium and ferric salts. Some investigations have shown that CC is a suitable method to treat tannery wastewater to remove the COD, suspended solids (SS) and chromium [3].

Electrocoagulation (EC) is also an efficient process and has been successfully used in treatment of various kinds of wastewater [24–36]. EC involves the supply of coagulant ions (Al^{3+}, Fe^{3+}) by the application of an electric current to a sacrificial metal anode placed in the reactor [37]. The electrical current causes the dissolution of metal into wastewater. The metal ions, at an appropriate pH value, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants [38,39]. In the case of aluminium, main reactions are as [39]:

$$\text{Anode: } Al \rightarrow Al^{3+} + 3e^{-} \tag{1}$$

$$\text{Cathode: } 3H_2O + 3e^{-} \rightarrow 3/2\,H_2 + 3OH^{-} \tag{2}$$

The generated Al^{3+} and OH^{-} react with each other to form $Al(OH)_3$.

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

While in the case of iron or mild steel electrodes, the mechanisms for the production of metal hydroxide are as [40–42]:

$$\text{Anode: } Fe \rightarrow Fe^{2+} + 2e^{-} \tag{4}$$

$$2Fe^{2+} + 5H_2O + 1/2O_2 \rightarrow 2Fe\left(OH\right)_3 + 4H^{+} \tag{5}$$

$$Fe^{2+} + 2OH^{-} \rightarrow Fe\left(OH\right)_2 \tag{6}$$

$$\text{Cathode: } 2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2 \tag{7}$$

$$2Fe + 5H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe\left(OH\right)_3 + 2H_2 \tag{8}$$

$$Fe + 2H_2O \rightarrow Fe\left(OH\right)_2 + H_2 \tag{9}$$

During electrocoagulation process, metal hydroxides formation occurs, these flocs have a large surface area, which are beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or flotation. Because of the characteristic of the tannery wastewater, molecular chlorine generates during electrolysis [39–43]:

$$2Cl \rightarrow Cl_2 + 2e^{-} \tag{10}$$

The generated molecular chlorine is hydrolyzed to form hypochlorous acid and hypochlorite ion.

$$Cl_2 + H_2O \rightarrow HOCl + H^{+} + Cl^{-} \tag{11}$$

EC can offer an alternative to CC in tannery wastewater treatment [44–46]. However, CC process causes a secondary source of pollution due to the chemical additives and has the drawback of high reagent costs. CC process also tends to generate large volumes of sludge with a high bound water content slowing down filtration and to increase the total dissolved solids content of the effluent [45]. On the other hand, the EC process generates relatively low sludge and the sludge tends to be readily settleable and easy to de-water, as it contains metallic oxides and hydroxides [47]. EC process is suitable for tannery wastewater treatment because of its high chloride concentrations [1,2,48]. The chloride leads to a decrease in energy consumption for the process owing to the increase in conductivity [38,44,49].

The present study investigates tannery wastewater treatment by both the CC and EC processes and is an attempt to: (1) to develop mathematical model and to optimize operating conditions on TOC and total chromium removal from tannery wastewater by the CC (using aluminum sulphate and iron chloride as coagulant) and the EC processes (using aluminum and iron electrodes), and (2) to evaluate the effects and interactions of process variables: coagulant dosage, reaction time, initial pH for the CC and current density, reaction time, initial pH for the EC.

2. Materials and methods

2.1. Tannery wastewater

The tannery wastewater used in the study was obtained from leather processing factory in Istanbul. During the experimental period, approximately 100 L of tannery wastewater was obtained from the factory and was stored at 4°C to prevent degradation. The characteristics of wastewater are shown in Table 1. Before the CC and EC applications, all the samples were preserved and analyzed according to the Standard Methods [50].

2.2. Experimental set-up and analysis

$FeCl_3{\cdot}6H_2O$ and $Al_2(SO_4)_3{\cdot}18H_2O$ salts were dissolved in water in order to prepare a stock solution of 10 g/L for the CC process. 500 mL of wastewater was used for each experimental test. In the first step of CC process, the pH of tannery wastewater was adjusted to desired value by the addition of sulphuric acid (6N) and sodium hydroxide (6N). The necessary amount of coagulant was supplemented. After that, rapid mixing is achieved through a Jar test equipment at 200 rpm for 5 min. In each experimental run, the effluent sample was then gently stirred at 20 rpm for a desired reaction time. To prevent interferences in analytical

Table 1
Characterization of tannery wastewater

Parameter	Value
pH	3.32 ± 0.1
Electrical conductivity, (mS/cm)	85.6 ± 2
COD (mg/L)	2,500 ± 35
TOC (mg/L)	1,890 ± 15
TSS	915 ± 20
Total Chromium (mg/L)	400 ± 20
Chloride, (mg/L)	28,120 ± 60

measurements, the pH was adjusted to around 7.0 by adding an NaOH solution and after the pH adjustment, the sample was settled for 60 min. 200 mL of the supernatant was taken for further analysis (Fig. 1a).

A laboratory-scale EC reactor made of plexiglas having 9 cm diameter and 13 cm height was used. The aluminum and iron electrodes (consisting of two anodes and two cathodes) comprised of four monopolar parallel plates in sizes of 6 cm width, 11.5 cm height and 0.1 cm thickness with an effective area of 46.2 cm^2 for each one, were situated 1.5 cm apart. A digital DC power supply was used during the EF study (Good Will GPC-3060D). The volume of the wastewater sample was kept at 500 mL for each run. The electrolyte solution was not used, as wastewater samples contained high chloride and conductivity values. Prior to each experimental run, the surfaces of electrodes were cleaned with acetone and then kept in a cleaning solution (35% 100 cm^3 hydrochloric acid and 2.8% 200 cm^3 hexamethylenetetramine) for at least 5 min, and after that rinsed with tap water. The EC experiments were initiated by using tannery wastewater for the desired reaction time with a current density of 22–110 mA/cm^2. At the end of each experimental run, the floated and precipitated materials were withdrawn and the clarified effluent sample was pipetted out from the reactor, and then allowed to settle for 60 min in a polyethylene flask (Fig.1b).

The TOC and total chromium analysis were performed by using TOC-TN analyzer and ICP-OES, respectively. All other analyses were performed in accordance with the Standard Methods [50]. All the chemicals used were of analytical-reagent grade.

2.3. Design of experiments and data analysis

In this study, the full-factorial Central Composite Design (CCD) based on response surface methodology (RSM) was used to design the set of experiments for the CC and EC processes. RSM is fundamentally a particular set of mathematical and statistical methods for designing experiment, buildings models, determining the effect of variables, and investigating optimum conditions of operating [51]. Statgraphics Centurion XVI.I software programme was used for the statistical design of experiments and data analysis. The three operational parameters: coagulant dosage (X_1), operating time (X_2), and initial wastewater pH (X_3) were optimized for the CC process, whereas current density (X_1), electrocoagulation time (X_2), and initial wastewater pH (X_3), were optimized for the EC process in tannery wastewater treatment. Each independent factor was coded at three levels in the range of –1 and +1 determined by preliminary experiments. The coded and actual values of variables of the experimental design matrix for EC and CC processes are given in Table 2.

RSM makes it possible to represent independent process parameters in quantitative form as:

$$Y = f\left(X_1, X_2, X_3, \ldots, X_n\right) \pm \varepsilon \quad (12)$$

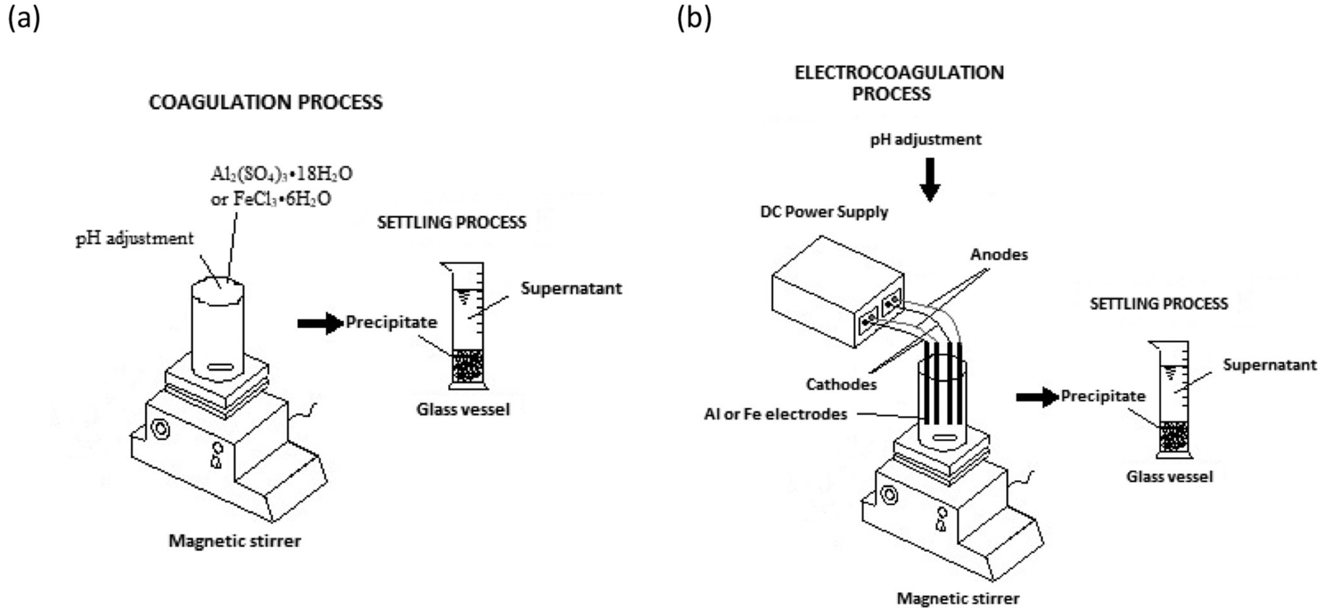

Fig. 1. Schematic presentations of (a) coagulation and (b) electrocoagulation processes.

Table 2
The coded and actual values of variables of the experimental design matrix for EC and CC processes

	Variables	Symbol	–1	0	1
CC	Coagulant dosage (mg/L)	X_1	500	1000	1500
	Reaction time (min)	X_2	15	30	45
	Initial pH	X_3	5	7	9
EC	Current density (mA/cm^2)	X_1	5	25	45
	Electrolysis time (min)	X_2	10	20	30
	Initial pH	X_3	5	7	9

where Y is the response (dependent parameter), f is the response function, ε is the experimental error and X_1, X_2, X_3,…., X_n are independent variables. In the optimization process, the responses can be related to independent factors by linear or quadratic models. A quadratic model which includes the linear model is given in Eq. (13).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \tag{13}$$

where β is set of regression coefficients: the intercept (β_0), linear (β_1, β_2, β_3), interaction (β_{12}, β_{13}, β_{23}) and quadratic coefficients (β_{11}, β_{22}, β_{33}).

Analysis of variance (ANOVA) was used to analyze the data and to obtain the interaction between the independent variables and the responses. The quality of the fit polynomial model was evaluated by R^2, and its statistical significance was checked by the Fisher *F*-test. Model terms were evaluated by *p*-value and *F*-value.

3. Results and discussion

3.1. Pollutant removal mechanisms and effect of variables

Chromium occurs in the environment in different forms under various chemical, physical, and morphological conditions. Only Cr(III) and Cr(VI) are stable in chromium forms. Chromium takes place as Cr(III) cation only in a strongly acidic and reducing medium, while Cr(VI) occurs in a strongly basic and oxidizing medium asanion. The predominant species below pH 2 is $Cr^{3+}$and between pH 6.5 and 10 the predominant species is $Cr(OH)_3$. At pH 4, the $Cr^{3+}$and $Cr(OH)^{2+}$ species are present in an approximate distribution of 40 and 60%, respectively. At pH 5, the $Cr(OH)^{2+}$species dominates accounting for nearly 70% of the chromium present with the other major form as $Cr_3(OH)_4^{5+}$ accounting for around 20%. At pH 6 the complexes $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$ and $Cr_3(OH)_4^{5+}$ represent approximately 40, 35, 25% of the aqueous chromium, respectively [52]. In tannery wastewater Chromium ion occurs in two forms; trivalent Cr^{3+} and hexavalent Cr^{6+}.

The removal of chromium is effected by the formation of oxyhydroxyl species in aqueous solutions related to the time and current density in EC process [53–55]. The hydroxyl species thus formed have a pronounced tendency to undergo polymerization due to interaction between hydroxyl groups of adjacent molecules. The polymerized complex molecules act as coagulants which help in the removal of chromium [45]. After dissolution of $FeCl_3{\cdot}6H_2O$ and $Al_2(SO_4)_3{\cdot}18H_2O$ salts Al^{3+}, Fe^{2+}, and Cr^{3+} ions form complexes with OH^- species at the appropriate pH, Ionic metal hydroxides are soluble, whereas the solubility of neutral $Fe(OH)_3$, $Al(OH)_3$, and $Cr(OH)_3$ is very low and they can be considered as solids [31,56]. For Cr(VI) removal, hexavalent chromium is reduced to Cr(III). In EC process reduction of Cr(IV) by using Al and Fe electrodes are given below [31]:

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{+3} + H_2O \tag{14}$$

or

$$Cr_4^{2-} + 4H_2O + 3e^- \rightarrow Cr\left(OH\right)_3 + 5OH^- \tag{15}$$

$$Cr_4^{2-} + 8H^+ + 3Fe^{2+} \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O \tag{16}$$

Metal cations were produced from dissolution of electrodes in EC process and from aluminium and iron salts in CC process. They form polymeric metal hydroxide species negatively charged particles and the particles bind together to form aggregates of flocs, resulting in pollutant removal by adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or flotation. Significant COD and TOC removal efficiencies were obtained by these mechanisms [17,57,58].

The effect of inorganic coagulants dose can be explained by using the "coagulation zone" concept. In zone I; not enough coagulant is present for the destabilization of the colloids. In zone II; coagulant is sufficient, and in weakly acidic or nearly neutral condition, the dissolved positively charged ions are adsorbed onto the colloidal particles thus destabilizing the suspension (via decreasing the negative surface charge of the colloidal particles). In zone III; coagulant has excess concentration causing charge reversal and re-stabilization of particles. In zone IV; in neutral or basic environment, the high concentration of coagulant cause over saturation with metal hydroxide precipitations which entrap the colloidal particle and produces very effective sweep coagulation [59,60]. Depending on this concept, removal efficiency of TOC and total Chromium increased as the coagulant dose increased representing the first two zones, than remained constant.

pH of the reaction solution changes during the electrocoagulation process and the final pH of the effluent actually affects the overall treatment performance [39,61]. When the initial pH value is less than 4 (acidic), the effluent pH increases, while it tends to decrease when the initial pH value is higher than 8 (basic), and the pH of the effluent changes only slightly when the initial pH value is in the neutral range (around 6–8) [62]. Since the initial pH value of the tannery wastewater was determined to be 3.32, pH of the processed wastewater tended to increase during the preliminary experimental study. This pH increase can be attributed to hydrogen evolution at cathodes [63], CO_2 release from wastewater owing to H_2 bubble disturbance [38] or continuous OH^- formation at the cathode as a result of chemical dissolution of metals [55].

The current supplied to the electrochemical reactor is usually expressed in terms of current density and the current density is defined as the ratio of current input to the electrolytic cell to the surface area of the electrode [45]. The removal efficiency increases with the increasing cell current for a given time interval. The amount of metal oxidized increases, resulting in a greater amount of hydroxide flocs, the bubble density increases and the buble size decreases at higher cell current values resulting in a faster removal of pollutants [35,64–67].

Increasing reaction time shows same trend with current density and coagulant doses. Higher reaction time led to increase in TOC and chromium removal efficiencies by increasing the amount of metal species formed by dissolution of the anode in EC process and by allowing effective interaction of flocs and pollutants in CC process due to the oxidation and reduction reactions [45]. Similar results regarding the effect of treatment time were also reported by Kobya et al. [68], Gupta and Babu [69], Babu et al. [45], Daneshvar et al. [39] and Nourouzi et al. [70].

Results of the study were found to be consistent the ones reported by several researchers in literature [3,17,55,71–74].

3.2. Model development, regression analysis and optimization

The response (Y) of TOC and total chromium removal from tannery wastewater by CC and EC experiments and corresponding predicted values of TOC and total chomium removal are given in Table 2. The experimental data were fitted to linear and quadratic models to obtain the regression equations. The quadratic equation obtained in terms of coded factors is given in Eqs. (17)–(24):

$$\begin{aligned}&\textit{TOC removal by CC} - \textit{Al}, \% =\\&\quad -16,24 + 0,023X_1 + 0,79X_2 + 14,61X_3\\&\quad -0,000014X_1X_1 + 0,000034X_1X_2 + 0,00031X_1X_3\\&\quad -0,0132X_2X_2 - 0,0042X_2X_3 - 0,9931X_3X_3\end{aligned} \tag{17}$$

$$\begin{aligned}&\textit{Total chromium removal by CC} - \textit{Al}, \% =\\&\quad 117,91 + 0,0052X_1 + 0,173X_2 - 11,33X_3\\&\quad -0,0000032X_1X_1 + 0,000032X_1X_2 - 0,000034X_1X_3\\&\quad -0,0025X_2X_2 - 0,0074X_2X_3 + 0,9996X_3X_3\end{aligned} \tag{18}$$

$$\begin{aligned}&\textit{TOC removal by CC} - \textit{Fe}, \% =\\&\quad 113,6 - 0,0095X_1 - 0,43X_2 - 14,61X_3\\&\quad +0,000006X_1X_1 + 0,000071X_1X_2 - 0,000011X_1X_3\\&\quad +0,0027X_2X_2 + 0,012X_2X_3 + 1,21X_3X_3\end{aligned} \tag{19}$$

$$\begin{aligned}&\textit{Total chromium removal by CC} - \textit{Fe}, \% =\\&\quad 109,47 - 0,0017X_1 - 0,0067X_2 - 6,84X_3\\&\quad -0,0000023X_1X_1 + 0,000047X_1X_2 - 0,00055X_1X_3\\&\quad -0,0003X_2X_2 - 0,0099X_2X_3 + 0,71X_3X_3\end{aligned} \tag{20}$$

$$\begin{aligned}&\textit{TOC removal by EC} - \textit{Al}, \% =\\&\quad 19,72 - 0,496X_1 + 0,205X_2 + 12,22X_3\\&\quad +0,0205X_1X_1 - 0,022X_1X_2 + 0,01X_1X_3\\&\quad -0,0072X_2X_2 + 0,081X_2X_3 - 0,997X_3X_3\end{aligned} \tag{21}$$

$$\begin{aligned}&\textit{Total chromium removal by EC} - \textit{Al}, \% =\\&\quad 47,196 + 0,405X_1 + 0,92X_2 + 8,86X_3\\&\quad -0,0043X_1X_1 - 0,00017X_1X_2 - 0,0194X_1X_3\\&\quad -0,01X_2X_2 - 0,054X_2X_3 - 0,41X_3X_3\end{aligned} \tag{22}$$

$$\begin{aligned}&\textit{TOC removal by EC} - \textit{Fe}, \% =\\&\quad 72,01 + 0,59X_1 - 0,85X_2 - 5,38X_3\\&\quad +0,0144X_1X_1 - 0,0134X_1X_2 - 0,127X_1X_3\\&\quad +0,0685X_2 - 0,186X_2X_3 + 0,926X_3X_3\end{aligned} \tag{23}$$

$$\begin{aligned}&\textit{Total chromium removal by EC} - \textit{Fe}, \% =\\&\quad 45,77 + 0,76X_1 + 0,935X_2 + 8,24X_3\\&\quad -0,0024X_1X_1 - 0,0060X_1X_2 - 0,0608X_1X_3\\&\quad -0,0026X_2X_2 - 0,078X_2X_3 - 0,30X_3X_3\end{aligned} \tag{24}$$

The coefficients with one factor (X_1, X_2 or X_3) represent the effects of the linear main factor, the coefficients with two factors (X_1X_2, X_1X_3, or X_2X_3) and the second order terms (X_{12}, X_{22} or X_{32}) represent the interaction between the two factors and the quadratic effects, respectively. The positive sign in front of the coefficients indicates a synergistic effect, whereas the negative sign indicates an antagonistic effect [47,75]. Comparison between the actual and predicted values of Y for TOC and total chromium removal (Tables 3 and 4) showed a good correlation between the experimental and the predicted values with a coefficient of determination (R-squared) value over 95%.

The ANOVA results for the second-order equation fitted are given in Table 5. The ANOVA of TOC removal by the CC using $Al_2(SO_4)_3{\cdot}18H_2O$ and $FeCl_3{\cdot}6H_2O$ as coagulants and by the EC process using Al and Fe electrodes showed F-value of 13.28, 35.42, 12.92, and 50.18 respectively. The ANOVA of total chromium removal by the CC using $Al_2(SO_4)_3{\cdot}18H_2O$ and $FeCl_3{\cdot}6H_2O$ as coagulants and by the EC process using Al and Fe electrodes showed F-value of 20.48, 38.46, 40.99, and 21.64 respectively. High F values obtained for the quadratic model imply that the model is significant. A "Prob > F" lower than 0.0001 for the second-order polynomial fitting indicates that the model is statistically highly significant, and that the model terms are significant at 95% probability level. Values of "Prob. > F" less than 0.05 indicate that the model terms are significant.

ANOVA results for the response surface quadratic model for TOC and total chromium removal by the CC process using $Al_2(SO_4)_3{\cdot}18H_2O$ and $FeCl_3{\cdot}6H_2O$ as coagulants and by the EC process using Al and Fe electrodes are given in Tables 6 and 7, respectively. According to ANOVA results it can be concluded that only the terms of X_3, X_1X_1, X_2X_2, and X_3X_3 were found to be significant on TOC removal by the CC using $Al_2(SO_4)_3{\cdot}18H_2O$ as coagulant (Table 6), whereas

Table 3
Comparison of the experimental and the predicted values of the TOC and total chromium removal by CC

Run	X_1	X_2	X_3	$FeCl_3·6H_2O$				$Al_2(SO_4)_3·18H_2O$			
				TOC		Total chromium		TOC		Total chromium	
				Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
1	–1	–1	0	60.0	60.1	89.9	90.1	55.8	55.3	90.9	90.7
2	1	–1	0	70.1	70.8	99.9	100.0	53.3	54.0	89.6	89.7
3	–1	1	0	65.5	64.8	92.1	91.7	55.4	54.7	90.5	90.4
4	1	1	0	75.5	75.5	99.9	99.7	53.9	54.4	90.1	90.3
5	–1	0	–1	62.5	63.5	90.1	90.7	52.4	52.5	90.0	90.3
6	1	0	–1	73.1	73.5	99.9	100.0	52.2	51.1	89.9	89.8
7	–1	0	1	59.9	59.5	90.3	89.9	54.4	55.5	99.9	99.9
8	1	0	1	72.0	71.0	98.9	98.3	55.4	55.3	99.7	99.4
9	0	–1	–1	64.4	63.4	94.2	93.4	51.7	52.2	90.1	90.0
10	0	1	–1	67.3	67.0	93.3	93.1	51.7	52.3	90.7	90.6
11	0	–1	1	58.8	59.1	91.0	91.3	56.6	56.0	99.9	100.0
12	0	1	1	63.7	64.8	91.6	92.4	56.1	55.6	99.7	99.8
13	0	0	0	61.1	61.4	92.0	92.0	61.6	61.0	93.4	91.7
14	0	0	0	61.4	61.4	92.1	92.0	60.3	61.0	91.7	91.7
15	0	0	0	61.7	61.4	92.1	92.0	61.0	61.0	89.8	91.7

Table 4
Comparison of the experimental and the predicted values of the TOC and total chromium removal by EC

Run	X_1	X_2	X_3	Fe electrode				Al electrode			
				TOC		Total chromium		TOC		Total chromium	
				Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
1	–1	–1	0	57.8	58.9	90.3	91.1	61.2	60.7	94.4	94.7
2	1	–1	0	72.2	71.7	99.9	100.0	74.4	75.8	96.7	96.7
3	–1	1	0	74.5	74.9	99.9	99.8	69.5	68.1	97.4	97.4
4	1	1	0	68.5	67.4	99.8	99.0	64.9	65.4	99.7	99.3
5	–1	0	–1	62.3	61.7	93.5	93.2	59.1	61.3	91.4	91.6
6	1	0	–1	70.9	71.8	99.9	100.0	66.3	66.6	94.5	95.1
7	–1	0	1	75.2	74.2	99.6	99.1	61.4	61.0	99.8	99.3
8	1	0	1	68.9	69.4	99.8	100.0	70.2	68.0	99.9	99.7
9	0	–1	–1	63.7	63.2	94.5	93.9	59.1	57.4	92.2	91.6
10	0	1	–1	74.4	74.5	99.8	100.0	53.5	52.7	96.6	96.4
11	0	–1	1	73.7	73.6	99.4	99.0	53.8	54.7	99.8	100.0
12	0	1	1	73.7	74.2	99.9	100.0	54.8	56.5	99.9	100.0
13	0	0	0	59.7	58.8	99.9	99.6	60.1	60.0	99.6	99.8
14	0	0	0	58.1	58.8	99.1	99.6	59.4	60.0	99.9	99.8
15	0	0	0	58.5	58.8	99.9	99.6	60.6	60.0	99.8	99.8

X_1, X_2, X_3 in linear coefficients, X_1X_1 and X_3X_3 in quadratic coefficients have significant effect on TOC removal by the CC using $FeCl_3·6H_2O$ (Table 6) as coagulant. As can be seen from Table 7 that X_1 in linear coefficients, X_1X_1 in quadratic coefficients, X_1X_2 in interaction terms have significant effect on TOC removal by the EC using Al electrode, whereas all coefficients have significant effect on TOC removal by the EC using Fe electrode.

Table 5
ANOVA results of the predicted response surface quadratic model

Process	Coagulant/ Electrode	Model	R^2	Adj. R^2	Sum of squares	Mean square	*F*-value	Prob. > *F*
CC	$Al_2(SO_4)_3$	TOC	0.959	0.887	144.01	16.00	13.285	0.0054318
		Total Chromium	0.973	0.926	252.28	28.03	20.480	0.001975
	$FeCl_3$	TOC	0.984	0.956	388.46	43.16	35.416	0.000531
		Total Chromium	0.985	0.960	201.35	22.37	38.457	0.000435
EC	Al	TOC	0.958	0.884	502.71	55.86	12.9185	0.005793
		Total Chromium	0.986	0.962	126.84	14.09	40.995	0.000372
	Fe	TOC	0.989	0.969	627.63	69.74	50.185	0.000227
		Total Chromium	0.975	0.929	125.59	13.95	21.637	0.001734

Table 6
ANOVA results for the response surface quadratic model for TOC and total chromium removal by CC process using $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3 \cdot 6H_2O$ as coagulants

	Source	Sum of squares	*Df*	Mean square	*F*-ratio	*P*-value	Remark
TOC removal by CC- $Al_2(SO_4)_3 \cdot 18H_2O$	X1	1.34808	1	1.34808	1.12	0.3385	Not significant
	X2	0.0126326	1	0.0126326	0.01	0.9224	Not significant
	X3	25.5638	1	25.5638	21.23	0.0058	Significant
	X1X1	42.7639	1	42.7639	35.51	0.0019	Significant
	X1X2	0.266721	1	0.266721	0.22	0.6577	Not significant
	X1X3	0.38732	1	0.38732	0.32	0.5952	Not significant
	X2X2	32.778	1	32.778	27.21	0.0034	Significant
	X2X3	0.0633026	1	0.0633026	0.05	0.8278	Not significant
	X3X3	58.2701	1	58.2701	48.38	0.0009	Significant
	Total error	6.02206	5	1.20441			
	Total (corr.)	150.032	14				
Total Chromium by CC- $Al_2(SO_4)_3 \cdot 18H_2O$	X1	0.541958	1	0.541958	0.40	0.5568	Not significant
	X2	0.0331724	1	0.0331724	0.02	0.8824	Not significant
	X3	185.349	1	185.349	135.42	0.0001	Highly significant
	X1X1	2.38266	1	2.38266	1.74	0.2442	Not significant
	X1X2	0.234014	1	0.234014	0.17	0.6964	Not significant
	X1X3	0.00453771	1	0.00453771	0.00	0.9563	Not significant
	X2X2	1.15543	1	1.15543	0.84	0.4004	Not significant
	X2X3	0.196848	1	0.196848	0.14	0.7201	Not significant
	X3X3	59.0261	1	59.0261	43.13	0.0012	Significant
	Total error	6.8435	5	1.3687			
	Total (corr.)	259.129	14				
TOC removal by CC- $FeCl_3 \cdot 6H_2O$	X1	43.9472	1	43.9472	36.06	0.0018	Significant
	X2	21.003	1	21.003	17.23	0.0089	Significant

Table 6 (Continued)

	Source	Sum of squares	*Df*	Mean square	*F*-ratio	*P*-value	Remark
	X3	230.511	1	230.511	189.14	0.0001	Highly significant
	X1X1	8.45213	1	8.45213	6.94	0.0463	Significant
	X1X2	1.12891	1	1.12891	0.93	0.3800	Not significant
	X1X3	0.000529	1	0.000529	0.00	0.9842	Not significant
	X2X2	1.37248	1	1.37248	1.13	0.3371	Not significant
	X2X3	0.55577	1	0.55577	0.46	0.5294	Not significant
	X3X3	86.3885	1	86.3885	70.89	0.0004	Significant
	Total error	6.09354	5	1.21871			
	Total (corr.)	394.554	14				
Total Chromium by CC- $FeCl_3{\cdot}6H_2O$	X1	0.401498	1	0.401498	0.69	0.4440	Not significant
	X2	3.95606	1	3.95606	6.80	0.0478	Significant
	X3	164.226	1	164.226	282.29	0.0001	Highly significant
	X1X1	1.19977	1	1.19977	2.06	0.2105	Not significant
	X1X2	0.502327	1	0.502327	0.86	0.3954	Not significant
	X1X3	1.22136	1	1.22136	2.10	0.2070	Not significant
	X2X2	0.0169438	1	0.0169438	0.03	0.8712	Not significant
	X2X3	0.352955	1	0.352955	0.61	0.4713	Not significant
	X3X3	29.8743	1	29.8743	51.35	0.0008	Significant
	Total error	2.90882	5	0.581765			
	Total (corr.)	204.264	14				

Table 7
ANOVA results for the response surface quadratic model for TOC and total chromium removal by EC-Al and EC-Fe electrode

	Source	Sum of squares	*Df*	Mean square	*F*-ratio	*P*-value	Remark
TOC removal by EC-Al electrode	X1	76.2761	1	76.2761	17.64	0.0085	Significant
	X2	4.2137	1	4.2137	0.97	0.3689	Not significant
	X3	0.582552	1	0.582552	0.13	0.7286	Not significant
	X1X1	248.183	1	248.183	57.40	0.0006	Significant
	X1X2	79.1228	1	79.1228	18.30	0.0079	Significant
	X1X3	0.642242	1	0.642242	0.15	0.7158	Not significant
	X2X2	1.93057	1	1.93057	0.45	0.5336	Not significant
	X2X3	10.5248	1	10.5248	2.43	0.1795	Not significant
	X3X3	58.7434	1	58.7434	13.59	0.0142	Significant
	Total error	21.6192	5	4.32384			
	Total (corr.)	524.335	14				
Total Chromium removal by EC-Al electrode	X1	7.55506	1	7.55506	21.98	0.0054	Significant

Table 7 (Continued)

	Source	Sum of squares	*Df*	Mean square	*F*-ratio	*P*-value	Remark
	X2	13.638	1	13.638	39.67	0.0015	Significant
	X3	76.7897	1	76.7897	223.36	0.0001	Highly significant
	X1X1	11.0792	1	11.0792	32.23	0.0024	Significant
	X1X2	0.00460702	1	0.00460702	0.01	0.9123	Not significant
	X1X3	2.41787	1	2.41787	7.03	0.0453	Significant
	X2X2	3.74901	1	3.74901	10.90	0.0214	Significant
	X2X3	4.7284	1	4.7284	13.75	0.0139	Significant
	X3X3	9.93475	1	9.93475	28.90	0.0030	Significant
	Total error	1.71897	5	0.343794			
	Total (corr.)	128.563	14				
TOC removal by EC-Fe electrode	X1	69.4578	1	69.4578	49.98	0.0009	Significant
	X2	50.8647	1	50.8647	36.60	0.0018	Significant
	X3	14.1818	1	14.1818	10.21	0.0241	Significant
	X1X1	122.959	1	122.959	88.49	0.0002	Significant
	X1X2	28.831	1	28.831	20.75	0.0061	Significant
	X1X3	104.12	1	104.12	74.93	0.0003	Significant
	X2X2	173.114	1	173.114	124.58	0.0001	Highly significant
	X2X3	55.6165	1	55.6165	40.02	0.0015	Significant
	X3X3	50.632	1	50.632	36.44	0.0018	Significant
	Total error	6.94798	5	1.3896			
	Total (corr.)	634.582	14				
Total Chromium removal by EC-Fe electrode	X1	30.2252	1	30.2252	46.87	0.0010	Significant
	X2	15.038	1	15.038	23.32	0.0048	Significant
	X3	33.2012	1	33.2012	51.48	0.0008	Significant
	X1X1	3.41259	1	3.41259	5.29	0.0697	Not significant
	X1X2	5.66256	1	5.66256	8.78	0.0314	Significant
	X1X3	23.6889	1	23.6889	36.73	0.0018	Significant
	X2X2	0.242937	1	0.242937	0.38	0.5662	Not significant
	X2X3	9.74368	1	9.74368	15.11	0.0116	Significant
	X3X3	5.17969	1	5.17969	8.03	0.0365	Significant
	Total error	3.22466	5	0.644932			
	Total (corr.)	128.817	14				

In linear coefficients X_3 have high significant effect and in quadratic coefficients X_3X_3 have significant effect on total chromium removal by the CC using $Al_2(SO_4)_3{\cdot}18H_2O$ as a coagulant. In linear coefficients X_2 have significant effect, X_3 have high significant effect and in quadratic coefficients X_3X_3 has significant effect on total chromium removal by the CC using $FeCl_3{\cdot}6H_2O$ as a coagulant (Table 6). ANOVA study showed that all independent factors and their interaction and quadratic effects have significant effect, except X_1X_2 on total chromium removal by the EC using Al electrode (Table 7). It can be concluded from Table 7 that linear coefficients, the interacting coefficients and the quadratic parameters, except the X_1X_1 and X_2X_2, have significant effect on total chromium removal by the EC process using Fe electrode.

The effect of operating parameters for the CC and EC processes on TOC and total chromium removal are shown in the response surface graphs in Figs. 2a–f, 3a–f, 4a–f, and 5a–f. All the plots indicating optimum operating conditions have clear peaks, meaning that the optimum conditions for the maximum values of the responses are attributed to all the variables in the design space. As can be seen from Figs. 2–5, one variable was kept at the central level and the other two variables varied within the experimental ranges. Fig. 2 shows the results regarding TOC and total chromium removal including (a) surface plot for X_1 and X_3; (b) surface plot for X_1 and X_2; and surface plot for X_2 and X_3 on TOC removal by the CC process using $Al_2(SO_4)_3{\cdot}18H_2O$ as a coagulant, whereas Figs. 2d, e and f show relationship between two operating parameters on total chromium removal by the CC process using $Al_2(SO_4)_3{\cdot}18H_2O$. On the other hand, Fig. 3 shows response surface graphs for TOC and total chromium removal by the CC process using $FeCl_3{\cdot}6H_2O$ as a coagulant. Figs. 4 and 5 show response graphs for TOC and total chromium removal by the EC process using Al and Fe electrodes, respectively. As can be seen in Figs. 2–5, the total chromium removal efficiencies were much higher than the TOC removal efficiencies for both processes.

The optimum operating conditions are shown in Table 8. The obtained results revealed that the maximum TOC removal efficiencies (61.2% for the CC using $Al_2(SO_4)_3{\cdot}18H_2O$, 76.8% for the CC using $FeCl_3{\cdot}6H_2O$, 75.8% for EC using Fe electrodes and 85.2% for the EC using Al electrodes) were achieved. The highest TOC removal was obtained by the EC process using Fe electrodes. It can also be concluded that there is no significant difference between the total chromium removal efficiencies obtained by the CC and EC processes and all the optimum chromium removal efficiencies were found to be over 98.2%. As can be seen in Table 8, the experimental values were found to be consistent with the predicted ones.

3.3. Cost evaluation

Operational cost analysis plays an important role in the treatment of industrial wastewaters, as treatment process should be cost effective. The amount of energy consumption, the amount of electrode material and the amount of chemicals are the most important parameters in the CC and EC processes for the estimation of operational costs. The operating cost was calculated by the equation as follows [24]:

$$\text{Operating cost}\left(\frac{\text{cost}}{m^3}\right) = aENC + bELC + cCHC \quad (25)$$

where ENC is energy consumption (kWh/m^3), ELC is electrode consumption (kg/m^3), and CHC is the chemical consumption (kg/m^3).

The ELC was calculated using the following equation:

$$ENC = \frac{U \times I \times t}{V} \quad (26)$$

where U is the applied voltage (V), I is the current intensity (A), t is the reaction time (h), and V is the volume of treated wastewater (m^3).

The ENC was calculated by the following equation:

$$ELC = \frac{I \times t \times M}{Z \times F \times V} \quad (27)$$

where t is the reaction time, M is the molecular mass of the electrode (g/mol), and Z is the number of electrons transferred ($Z_{Al} = 3$, $Z_{Fe} = 3$), F is the Faraday constant (96, 487 C/mol).

The CHC was calculated using the following equation:

$$CHC = \frac{\text{Chemicals used}(\text{kg})}{V} \quad (28)$$

In this study, the ENC and ELC costs were taken into consideration, as the cost items for the EC process, whereas only the CHC cost was taken into consideration as the major cost component for the CC process. For total chromium removal, operational cost of the CC process using $Al_2(SO_4)_3{\cdot}18H_2O$ and $FeCl_3{\cdot}6H_2O$ as coagulants performed at optimum conditions was determined to be 0.17 and 0.20 €/m^3, respectively and the operational cost of the EC process using Al and Fe electrodes was found to be 2.05 and 4.84 €/m^3, respectively. For TOC removal, operational cost of the CC process using $Al_2(SO_4)_3{\cdot}18H_2O$ and $FeCl_3{\cdot}6H_2O$ and the EC process using Al and Fe electrodes was determined to be 0.18, 0.61, 1.55, and 4.85 €/m^3, respectively. It can be concluded that the CC process is far more feasible for tannery wastewater treatment.

4. Conclusion

In this study, CCD was adopted to model and to optimize the performance of the CC and EC processes and to determine the optimal experimental conditions in TOC and total chromium removal from tannery wastewater treatment. The influence of variables; initial pH, current density, and operation time for EC and initial pH, coagulant dosage and operation time for CC on the TOC and total chromium removal was investigated. The quadratic model developed in this study showed the presence of a high correlation between the experimental and predicted values. ANOVA showed high determination of the coefficient values thus, ensuring a satisfactory adjustment of the second-order regression model with the experimental data. The results indicated that RSM was a powerful technique for optimizing the operational conditions. The results also showed that the CC and EC processes can be both recommended as effective processes for tannery wastewater treatment. According to the results obtained, total chromium discharge limits for tannery wastewaters (direct discharge to a receiving water body) have been met based on the standards in Water Pollution Control Regulation of Turkey (<3 mg/L for 2 h composite sample) by means of both the CC (using $FeCl_3{\cdot}6H_2O$) and the EC (using Fe electrode) [76]. CC process was found to be more cost effective whereas EC process has the advantages of less coagulant requirement and thereby less sludge formation.

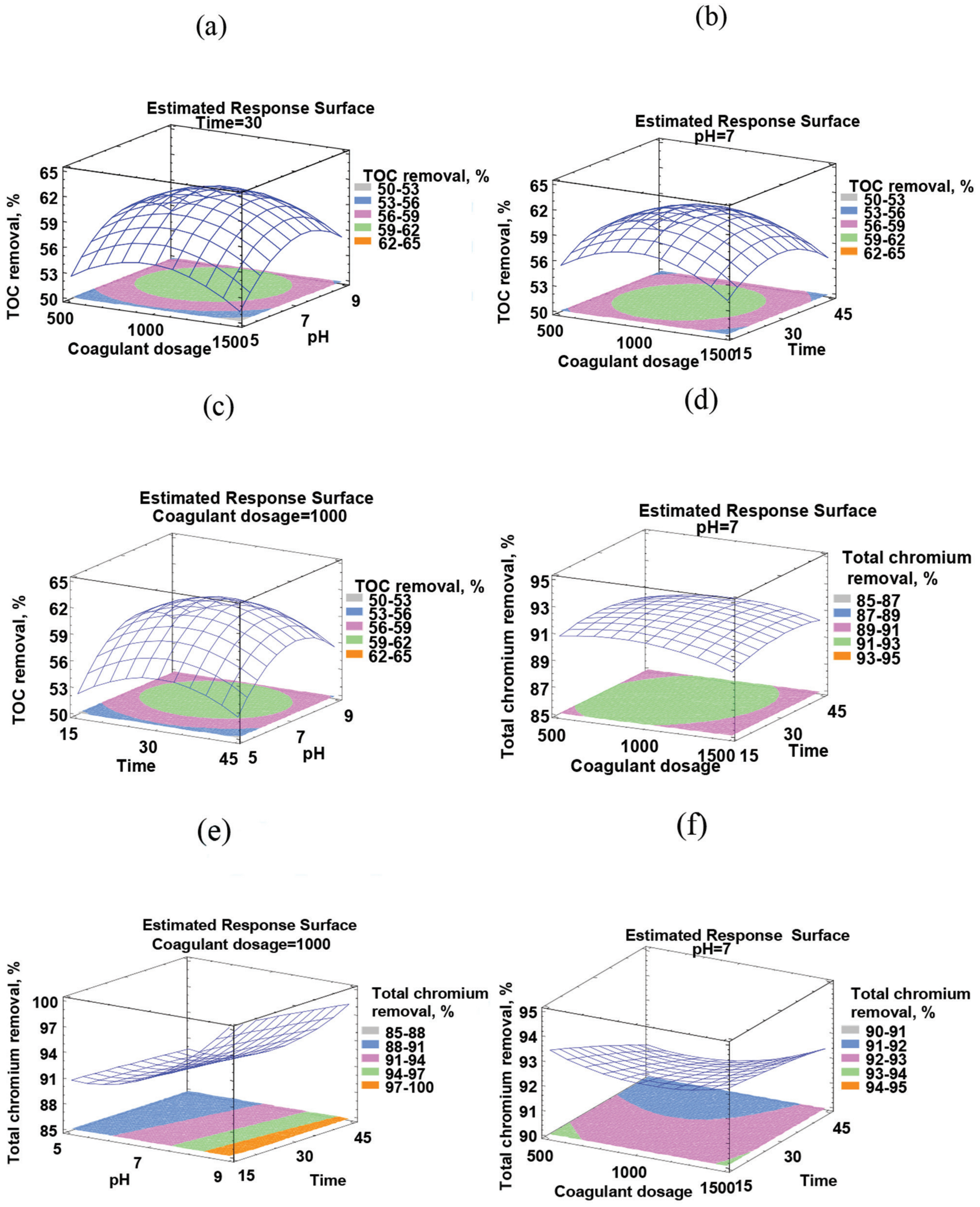

Fig. 2. Response surface graphs for the CC process using $Al_2(SO_4)_3·18H_2O$ (a) pH vs. dosage for TOC removal, (b) pH vs. time for TOC removal, (c) dosage vs. time for TOC removal, (d) pH vs. dosage for total chromium removal, (e) pH vs. time for total chromium removal, (f) dosage vs. time for total chromium removal.

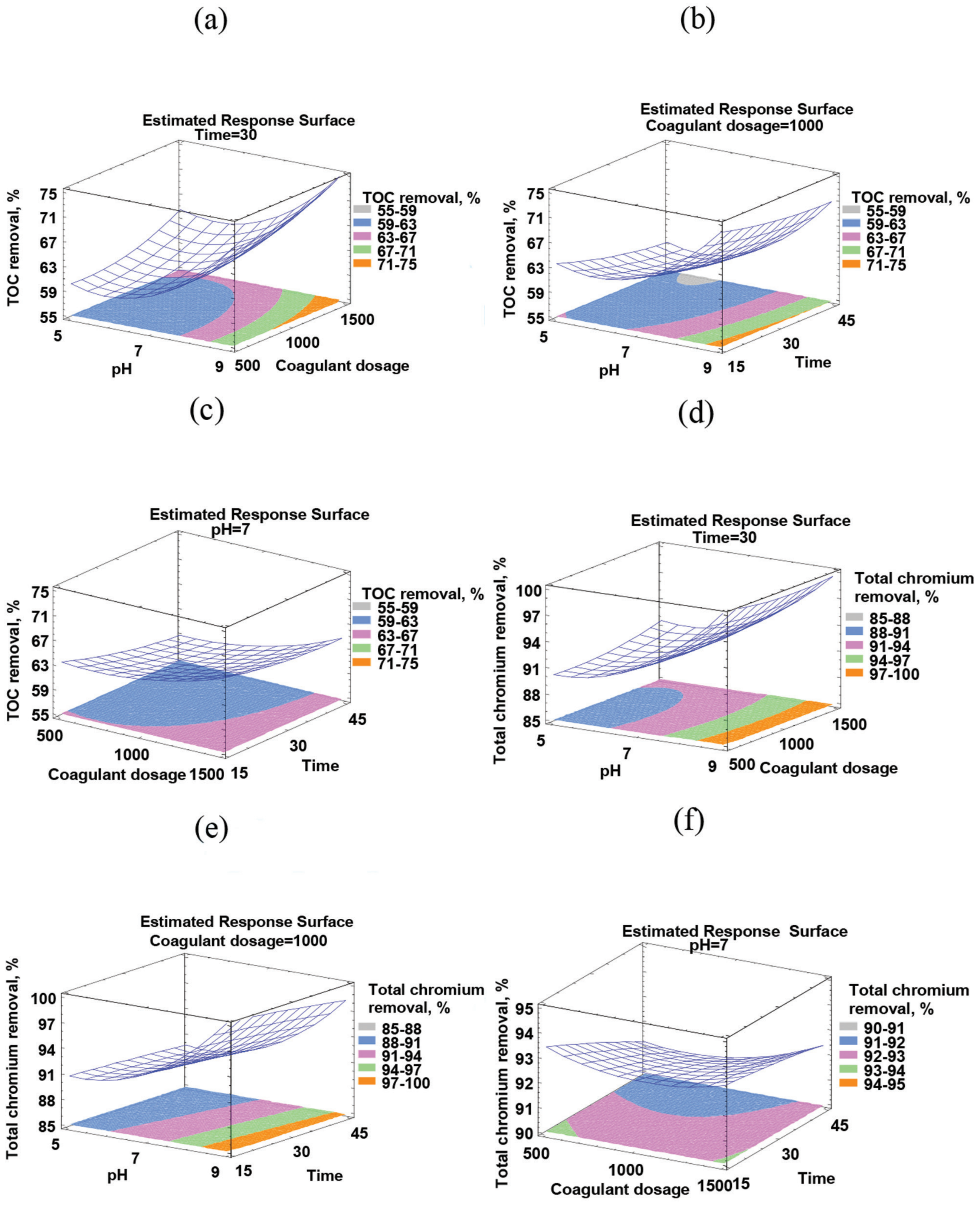

Fig. 3. Response surface graphs for the CC process using $FeCl_3·6H_2O$ (a) pH vs. dosage for TOC removal, (b) pH vs. time for TOC removal, (c) dosage vs. time for TOC removal, (d) pH vs. dosage for total chromium removal, (e) pH vs. time for total chromium removal, (f) dosage vs. time for total chromium removal.

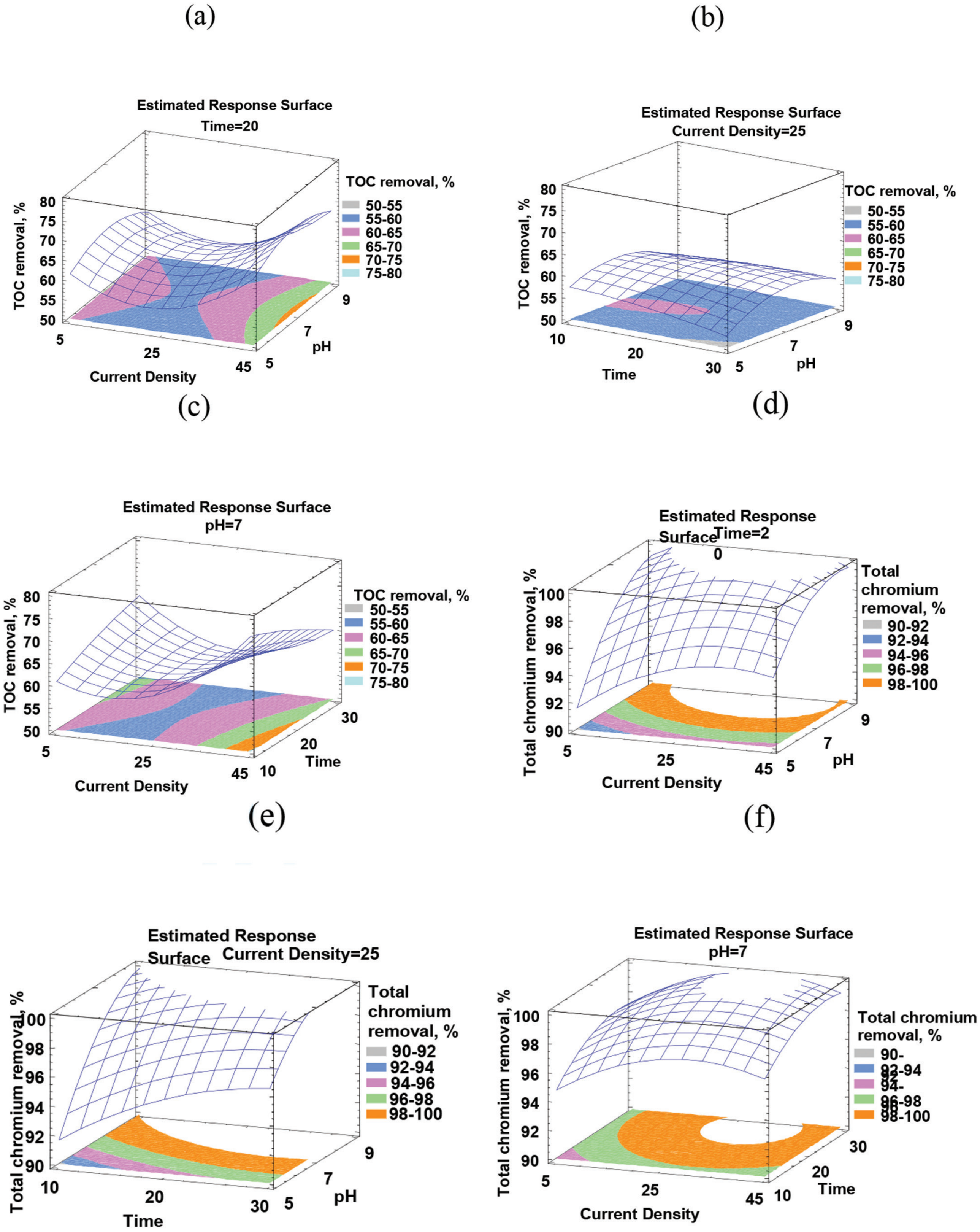

Fig. 4. Response surface graphs for EC process using Al electrode (a) pH vs. current density for TOC removal, (b) pH vs. time for TOC removal, (c) current density vs. time for TOC removal, (d) pH vs. current density for total chromium removal, (e) pH vs. time for total chromium removal, (f) current density vs. time for total chromium removal.

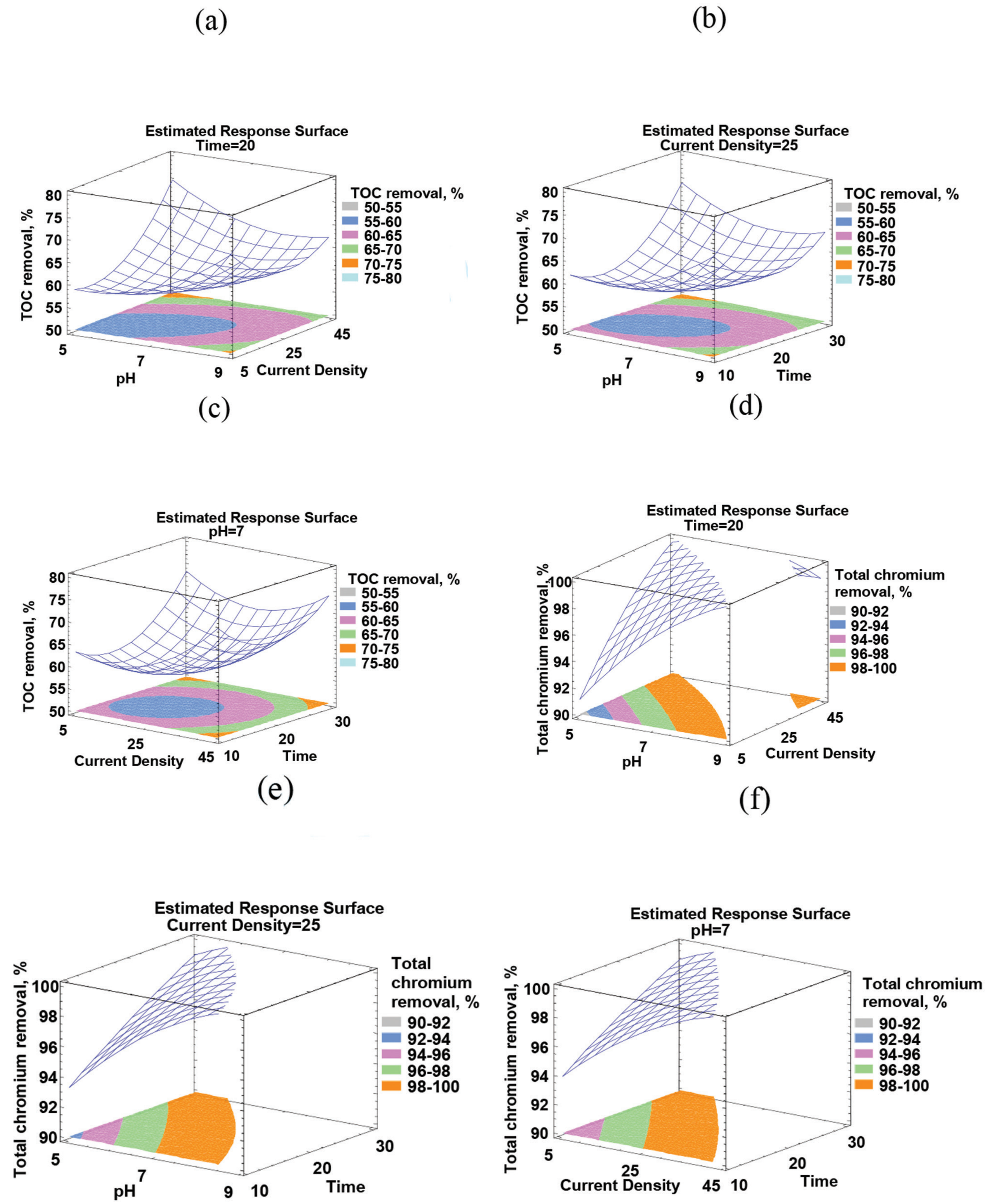

Fig. 5. Response surface graphs for EC process using Fe electrode (a) pH vs. current density for TOC removal, (b) pH vs. time for TOC removal, (c) current density vs. time for TOC removal, (d) pH vs. current density for total chromium removal, (e) pH vs. time for total chromium removal, (f) current density vs. time for total chromium removal.

Table 8
Optimum operating conditions and confirmation experiment at optimum conditions

Process		$Al_2(SO_4)_3\cdot 18H_2O$		$FeCl_3\cdot 6H_2O$	
	Factor	TOC	Total chromium	TOC	Total chromium
CC	Coagulant dosage (mg/L)	975	895	1500	500
	Reaction time (min)	29.80	27.18	15	15
	Initial pH	7.45	9.00	9.0	8.98
	Model prediction results (%)	61.2	98.5	76.8	99.5
	Experimental results (%)	60.8	98.2	75.6	99.4
		Al-electrode		Fe-electrode	
EC	Current density (mA/cm^2)	45	26.70	45	45
	Reaction time (min)	10	21.80	30	30
	Initial pH	6.76	8.73	5.025	5.38
	Model prediction results (%)	75.8	99.3	85.2	99.4
	Experimental results (%)	75.0	99.1	84.6	99.3

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