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Statistical optimization of process parameters for tannery wastewater treatment by electrocoagulation and electro-Fenton techniques

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ABSTRACT

In this paper, the response surface methodology (RSM) approach using central composite design (CCD) was applied to develop mathematical model and to optimize process parameters for COD and TSS removal from tannery wastewater by electrocoagulation and electro-Fenton processes using iron electrodes. Analysis of variance (ANOVA) was used to analyze the data and to obtain the interaction between the process variables and the responses. ANOVA showed the relative significance of process parameters in the removal process. The second-order regression model was developed to predict the removal efficiency using Statgraphics Centurion XVI.I software program. The optimal conditions were determined as reaction time 5.0 min, pH 3.31, current density 53.72 mA/cm^2, and H_2O_2 dose 0.14 g/L for electro-Fenton process, and reaction time 40.4 min, pH 7.0, and current density 50.9 mA/cm^2 for electrocoagulation process. At optimum conditions 54.8 and 87.3% COD removal efficiencies, 86 and 88% TSS removal efficiencies were achieved in electrocoagulation and electro-Fenton processes, respectively. The operating costs for elecrocoagulation and electro-Fenton processes at optimized conditions were calculated to be 6.4 and 6.8 €/m^3. Electro-Fenton process was found to be more effective for tannery wastewater treatment.

Keywords: Tannery wastewater; Electrocoagulation; Electro-Fenton; RSM; Cost analysis

1. Introduction

Tannery wastewaters cause serious environmental problems because of large number of low biodegradable chemicals used in leather tanning processes. The large volume of effluent produced in this industry can be characterized by high concentrations of COD, chromium, total suspended, total dissolved solids, and chloride [1,2]. Various wastewater treatment methods such as coagulation–flocculation [3,4], advanced oxidation processes [5–7], biological treatment [8–10], ozonation [11,12] and adsorption [13,14] have been applied for tannery wastewater treatment.

As known, chemical methods are widely used in tannery wastewater treatment. However, these processes tend to generate large volumes of sludge with a high bound water content slowing down filtration and increasing the total dissolved solids content of the effluent producing turbidity in treated wastewater [15]. Conventional biological methods are often inadequate to remove pollutants completely because of low biodegradability of the influent. Membrane

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applications are also used to recover tannery wastewater, but these processes have considerable disadvantages of expensive equipment and monitoring systems requirement. High influent suspended solids concentration constitutes a great problem of applying ion-exchange method as the suspended solids may clog the resin causing inefficient operation. Ion exchangers also require costly regenerants and produce troublesome waste streams [16].

Innovative and inexpensive techniques for the treatment and reuse of industrial wastewater have become an absolute necessity with the objective of protecting the environment. In recent years, there has been increasing interest in the use of electrochemical methods in the purification of various industrial wastewaters [17–22]. Although electrochemical methods are available for more than a century, it now appears to be one of the most effective approaches having the features of low operational cost and high treatment efficiency.

Electrocoagulation process provides a direct current source between metal electrodes immersed in wastewater. The electrical current causes the dissolution of metal electrodes, and the dissolved metal ions form coagulated species and metal hydroxides, at an appropriate pH. Metal hydroxides, which destabilize and aggregate the suspended particles, precipitate by adsorbing dissolved contaminants. Main processes that occur during electrocoagulation can be given as follows: (i) migration to an oppositely charged electrode and aggregation due to charge neutralization; (ii) formation of cation or hydroxyl ion (OH^-) precipitate with pollutant; (iii) interaction of metallic cation with OH^- to form a hydroxide, which has high adsorption properties thus bonding to the pollutant; (iv) formation of larger lattice-like structured hydroxides which sweep through the water; (v) oxidation of pollutants to less toxic species; (vi) removal by electroflotation or sedimentation and adhesion to bubbles [19,23,24].

In electrocoagulation process, where iron electrodes are used in electrolytic system, iron hydroxide complexes ($Fe(OH)n$ where $n = 2$ or 3) are produced [25,26] as given in Eqs. (1)–(5):

$$Fe \longrightarrow Fe^{2+} + 2e^- \text{ (anode)} \quad (1)$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \text{ (cathode)} \quad (2)$$

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \text{ (in bulk solution)} \quad (3)$$

$$2Fe^{2+} + 5H_2O + 1/2O_2 \longrightarrow 2Fe(OH)_3 + 4H^+ \text{ (in bulk solution)} \quad (4)$$

$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3 \text{ (in bulk solution)} \quad (5)$$

When Fe electrodes are used, ferric ions generated by the electrocoagulation process may form monomeric and polymeric hydroxyl complexes (i.e. hydrolysis products) as $FeOH^{2+}$; $Fe(OH)_2^+$; $Fe(OH)_2^{4+}$; $Fe(OH)^-$; Fe $(H_2O)^{3+}$; $Fe(H_2O)_6^{3+}$; $Fe(H_2O)_5OH^{2+}$ $Fe(H_2O)_4(OH)^{2+}$; $Fe(H_2O)_8(OH)^{4+}$; $Fe_2(H_2O)_6(OH)_4^{2+}$, etc. depending on pH of the aqueous medium. The complexes have a pronounced tendency to polymerize at pH 3.5–7.0 [27].

In electro-Fenton process, the electrocoagulation and Fenton processes are combined together to increase pollutant removal rate [28]. In conventional Fenton process, both H_2O_2 and Fe^{2+} are externally applied, whereas in the EF process, H_2O_2 is added to the system but Fe^{2+} is provided from sacrificial cast iron anodes [29]. This technology is based on simultaneous production of H_2O_2 and Fe^{2+} in an aqueous medium by the reduction of molecular oxygen and ferric ions. Hydroxyl radicals are powerful oxidants and attack organic matter present at the or near electrode surface [30]. The related reactions can be found in Eqs. (6)–(9):

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \text{ (in bulk solution)} \quad (6)$$

$$Fe^{2+} + {}^{\cdot}OH \longrightarrow Fe^{3+} + OH^- \text{ (in bulk solution)} \quad (7)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HO_2^{\cdot} \text{ (in bulk solution)} \quad (8)$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \text{ (cathode)} \quad (9)$$

Conventionally, multifactor processes are optimized by varying a single factor while keeping all other factors fixed at a specific set of conditions (one at a time method). This method is not only time-consuming by numerous experimental runs, but also incapable of obtaining competent optimization because of ignoring the interaction effects among the variables [31,32]. The mentioned limitations can be eliminated by the application of experimental design methodologies, such as response surface methodology (RSM). This methodology utilizes mathematical and statistical techniques for: (i) developing second-order polynominal model, (ii) understanding the effects of different variables (factors) and their interactions on response, (iii) determining comparative significance of several effective factors, and (iv) optimizing the process [33].

The aim of the present study was to investigate pollutant removal from tannery wastewater by electrocoagulation and electro-Fenton processes using iron electrodes in a batch mode operation. The effects of operating parameters for electrocoagulation and electro-Fenton processes on the removal efficiencies of COD and TSS were studied to determine the optimum operating conditions. The RSM approach using CCD was used to develop the mathematical model and to study the interactive effect of process parameters. Operating cost analysis was also performed.

2. Material methods

2.1. Tannery wastewater

The samples used in the study were obtained from an equalization tank of leather processing factory wastewater. Samples were collected and stored in containers which were kept at 4˚C. The characterization of tannery wastewater is given in Table 1. Before the electrocoagulation and electro-Fenton treatments, all tannery effluent samples were preserved and analyzed according to the Standard Methods recommended by the American Public Health Association [34].

2.2. Experimental setup and procedure

The experimental setup used for the electrocoagulation studies is shown in Fig. 1. A laboratory-scale plexiglass EC reactor with 9 cm diameter and 13 cm height was constructed. Electrode sets (two anode and two cathode electrodes) comprised four monopolar (MP) parallel iron plates (6 cm width × 11.5 cm height and 0.1 cm thickness), each having an effective area of 46.2 cm^2. The electrodes were placed 1.5 cm apart from each other. A valve was installed at the bottom of the reactor to withdraw the precipitated material through a sludge chamber. For each test, 600 mL wastewater sample was used. Electrolyte solution was not used because of high salinity of the wastewater

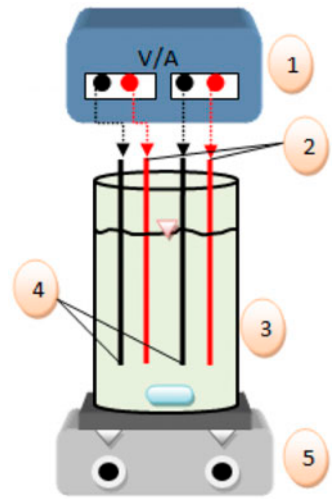

Fig. 1. Experimental setup.
Notes: (1) DC power supply, (2) anode electrodes, (3) reactor, (4) cathode electrodes, and (5) magnetic stirrer.

samples. Before each run, electrodes were washed with acetone, and the impurities on the iron electrode surfaces were removed by dipping in a solution freshly prepared by mixing 100 cm^3 of HCl solution (35%) and 200 cm^3 of hexamethylenetetramine aqueous solution (2.80%) for 5 min [27].

All the chemicals used were of analytical-reagent grade. The solution's pH was adjusted to 3 prior to the experiments and agitated with a magnetic stirrer at 200 rpm in the EF process. A desired amount of H_2O_2 was added to the electrolytic reactor before the electrical current was turned on. The electrocoagulation experiments were initiated by using tannery effluent for 45 min with a current density of 25–65 mA/cm^2, which was imposed by means of a DC power supply. At the end of each 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 a few hours in a polyethylene flask. Finally, the clarified supernatant liquid was collected and preserved according to the standard methods [34] and stored for characterization.

Table 1
Characterization of tannery wastewater

Parameter	Range	Mean value
pH	3.21–3.26	3.24
Conductivity (mS/cm)	41.2–42.7	41.8
COD (mg/L)	2,832–2,861	2,850
TSS (mg/L)	1,076–1,093	1,085
Turbidity (NTU)	223–226	225
Chloride (mg/L)	24,355–25,240	24,989

2.3. Analytical procedures

All analyses were carried out in accordance with the Standard Methods of the APHA [34]. COD was measured by open reflux titrimetric method because of high chloride concentration of the tannery wastewater. The analysis of H_2O_2 was carried out by the permanganometric method. Residual H_2O_2 was also measured in the supernatant to evaluate possible interference with COD. In electro-Fenton process, the study was carried out at lower pH values, because pH plays a more important role in this process, as compared with the electrocoagulation process. pH controls the production of hydroxyl radicals and the concentration of ferrous ions in the solution [35]. Highest electro-Fenton activity was attained at pH values lower than 4. When pH increases, the iron ions, especially the Fe^{3+} ions precipitate, inhibiting the regeneration of ferrous ions. Additionally, the amount of hydroxyl radicals generated decrease, as pH increases. It can be noted that hydrogen peroxide is unstable under alkaline conditions and rapidly decomposes to water and oxygen as pH increases above 5. It was reported that stable hydroxyl radicals, that have high oxidizing potential, are produced at pH values of 2–4 [35–37]. On the other hand, H_2O_2 cannot be decomposed to $OH^{\cdot}$ by Fe^{2+} at pH values lower than 2, converting to H_3O^{2+}. As the rate of reaction between H_2O_2 and Fe^{2+} decrease, removal efficiencies decrease. Similarly, current density plays a more important role in electro-Fenton. At high values of current density, competitive electrode reactions form inhibiting main reactions. Because of this fact, high current density values are not preferred.

2.4. Experimental design and statistical analysis

Experimental design of the electrocoagulation and electro-Fenton processes for COD and TSS removal from tannery wastewater was carried out by using the RSM. RSM uses mathematical and statistical techniques for the modeling, analyzing, and optimizing the conditions of variables that influence the response to predict targeted responses. RSM not only explains the mechanism of the system or process; but also provides evaluation of relations existing between a group of controlled experimental factors and the observed results [38]. In this study, the central composite design (CCD), a widely used form of RSM, was used for the optimization of electrocoagulation and electro-Fenton processes for COD and TSS removal from tannery wastewater. The CCD is an ideal design tool for sequential experimentation and allows testing the lack of fit when an adequate number of experimental values are available. In the present study, a three-factorial and a five-level central composite experimental design, with three replicas at the center point leading to a total number of 20 experiments was employed for electrocoagulation process and a four-factorial and a five-level central composite experimental design, with three replicas at the center point leading to a total number of 30 experiments for electro-Fenton process for response surface modeling. Statgraphics Centurion XVI.I software program was used for design, mathematical modeling, and optimization. The variables (independent factors) used in the electrocoagulation study were pH (X_1), current density (mA/cm^2) (X_2), and reaction time (min) (X_3), whereas variables used in electro-Fenton study were pH (X_1), current density (mA/cm^2) (X_2), reaction time (min) (X_3), and H_2O_2 concentration (g/L) (X_4). COD and TSS removal efficiencies (%) (Y_1 and Y_2, respectively) were considered to be dependent factors (responses).

The actual values of process variables and their ranges were determined by preliminary experiments and coded as shown in Table 2. Performance of the process was evaluated by analyzing the COD and TSS removal efficiencies.

For statistical calculations, the selected independent variables were converted into dimensionless codified values according to the equation given as follows:

$$x = \frac{X_i - X_0}{\Delta X} \quad i = 1, 2, \ldots.., k \tag{10}$$

where X_i is the dimensionless coded value of the ith independent variable, X_0 is the value of X_i at the center point, and ΔX is the step change value.

For the evaluation of experimental data, the response variable was fitted by a second-order model in the form of quadratic polynomial equation given below:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=1} \beta_{ij} X_i X_{ij} + \varepsilon \tag{11}$$

where Y is the predicted response; X_i and X_j are the variables (independent factors), and β_0 is the constant coefficient, β_i, β_{ii}, and β_{ij} are the coefficients for the linear, quadratic, and interaction effect, k signifies the number of independent variables and ε is the random error.

Analysis of variance (ANOVA) was used to analyze the data and to obtain the interaction between the process variables and the responses. Three-dimensional plots and their respective contour plots were developed. The quality of the fit polynomial model was expressed by the coefficient of determination R^2, and its statistical significance was checked by Fisher F-test. Model terms were evaluated by p-value and F-value.

Table 2
Coded and actual values of variables of the design of experiments for overall electrocogulation and electro-Fenton optimization

	Symbol	Factor	Coded variables				
			−2	−1	0	1	2
Electrocoagulation	X_1	pH	3	4	5	6	7
	X_2	Current density (mA/cm^2)	25	35	45	55	65
	X_3	Reaction time (min)	5	15	25	35	45
Electro-Fenton	X_1	pH	2	2.5	3	3.5	4
	X_2	Current density (mA/cm^2)	25	35	45	55	65
	X_3	Reaction time (min)	5	15	25	35	45
	X_4	H_2O_2 dosage (g/L)	0.06	0.08	1.0	1.2	1.4

Table 3
The actual design of experiments and responses for COD and TSS removal by electrocoagulation optimization

	Factors			Response 1		Response 2	
				COD removal (%)		TSS removal (%)	
Run	pH	Current density	Reaction time	Actual	Predicted	Actual	Predicted
1	−1	−1	−1	8.0	5.107	99.26	99.5427
2	1	−1	−1	24.3	21.25	96.0	96.35
3	−1	+1	−1	21.2	18.13	91.0	91.72
4	1	+1	−1	27.2	30.11	88.94	89.43
5	−1	−1	+1	31.7	26.78	90.0	90.31
6	1	−1	+1	37.5	38.57	90.2	90.27
7	−1	+1	+1	34.9	35.99	99.0	99.45
8	1	+1	+1	42.7	43.62	99.8	100.31
9	−2	0	0	12.9	16.81	95.5	95.02
10	+2	0	0	42.5	40.58	93.0	92.68
11	0	−2	0	14.1	17.99	93.2	93.09
12	0	+2	0	37.9	36.06	96.0	95.31
13	0	0	−2	3.51	5.552	96.1	95.57
14	0	0	+2	40.8	40.74	97.5	97.22
15	0	0	0	31.0	30.91	94.4	94.23
16	0	0	0	30.8	30.91	94.4	94.23
17	0	0	0	30.3	30.91	94.2	94.23
18	0	0	0	30.5	30.91	94.4	94.23
19	0	0	0	30.0	30.91	94.0	94.23
20	0	0	0	30.9	30.91	94.8	94.23

3. Results and discussion

3.1. Model development, regression analysis and optimization

A second-order (quadratic) polynomial response surface model was applied to fit the experimental results obtained by CCD. Based on the experimental design results, the regression equations with coded variables obtained in electrocoagulation and electro-Fenton processes can be presented as follows:

$$\begin{aligned}\text{COD removal by electrocoagulation, \%} &= -134.5 + 18.88\,X_1 + 2.084\,X_2 + 2.824\,X_3 \\ &\quad - 0.554\,X_1^2 - 0.103\,X_1\,X_2 - 0.109\,X_1\,X_3 \\ &\quad - 0.009\,X_2^2 - 0.009\,X_2\,X_3 - 0.019\,X_3^2 \end{aligned} \tag{12}$$

$$\begin{aligned}\text{TSS removal by electrocoagulation, \%} &= 157.1 - 2.615\,X_1 - 1.109\,X_2 - 2.53277\,X_3 \\ &\quad - 0.095\,X_1^2 + 0.022\,X_1\,X_2 + 0.079\,X_1\,X_3 \\ &\quad - 0.00008\,X_2^2 + 0.042\,X_2\,X_3 + 0.005\,X_3^2 \end{aligned} \tag{13}$$

Table 4
The actual design of experiments and responses for COD and TSS removal by electro-Fenton optimization

	Factors				Response 1		Response 2	
					COD removal (%)		TSS removal (%)	
Run	pH	Current density	Reaction time	H_2O_2 dosage	Actual	Predicted	Actual	Predicted
1	+1	+1	+1	+1	69.9	70.92	98.7	98.57
2	+1	+1	+1	−1	71.9	71.42	98.8	98.28
3	+1	+1	−1	+1	81.5	79.68	96.8	96.68
4	+1	+1	−1	−1	67.2	67.97	92.0	92.86
5	+1	−1	+1	+1	61.0	57.18	94.4	94.17
6	+1	−1	+1	−1	68.2	68.30	96.0	96.37
7	+1	−1	−1	+1	74.8	76.26	97.7	96.67
8	+1	−1	−1	−1	79.1	75.19	95.7	95.39
9	−1	+1	+1	+1	65.4	66.74	98.8	98.70
10	−1	+1	+1	−1	65.6	61.86	99.0	100.51
11	−1	+1	−1	+1	78.0	75.64	97.0	97.11
12	−1	+1	−1	−1	57.3	58.56	95.6	95.45
13	−1	−1	+1	+1	59.0	55.96	93.4	93.06
14	−1	−1	+1	−1	62.5	61.71	97.7	97.41
15	−1	−1	−1	+1	77.3	75.18	95.7	95.86
16	−1	−1	−1	−1	72.0	68.73	96.1	96.73
17	+2	0	0	0	66.3	67.17	95.3	95.92
18	−2	0	0	0	52.6	56.54	98.1	97.41
19	0	+2	0	0	66.3	65.84	97.9	97.20
20	0	−2	0	0	57.0	62.27	93.5	94.08
21	0	0	+2	0	66.5	68.76	99.4	99.38
22	0	0	−2	0	82.0	84.55	96.8	96.78
23	0	0	0	+2	71.0	73.23	94.4	95.29
24	0	0	0	−2	64.7	67.28	96.8	95.83
25	0	0	0	0	65.6	66.93	96.0	96.23
26	0	0	0	0	67.6	66.93	96.1	96.23
27	0	0	0	0	67.6	66.93	96.6	96.23
28	0	0	0	0	67.0	66.93	96.3	96.23
29	0	0	0	0	66.2	66.93	96.4	96.23
30	0	0	0	0	67.6	66.93	96.0	96.23

$$\begin{aligned}\text{COD removal by electro-Fenton, \%} &= 56.18 + 42.33\,X_1 - 1.68\,X_2 - 1.26\,X_3 - 156.24\,X_4 \\ &\quad - 5.067\,X_1^2 + 0.147\,X_1X_2 + 0.006\,X_1X_3 \\ &\quad - 134.25\,X_1X_4 - 0.007\,X_2^2 + 0.025\,X_2X_3 \\ &\quad + 13.28\,X_2X_4 + 0.024\,X_3^2 - 15.24\,X_3X_4 \\ &\quad + 2082.81\,X_4^2\end{aligned} \tag{14}$$

$$\begin{aligned}\text{TSS removal by electro-Fenton, \%} &= 118.25 - 6.29\,X_1 - 0.194\,X_2 - 0.269\,X_3 \\ &\quad - 118.69\,X_4 + 0.432\,X_1^2 - 0.062\,X_1X_2 \\ &\quad + 0.015\,X_1X_3 + 53.81\,X_1X_4 - 0.001\,X_2^2 \\ &\quad + 0.011\,X_2X_3 + 3.171\,X_2X_4 + 0.005\,X_3^2 \\ &\quad - 4.34\,X_3X_4 - 417.44\,X_4^2\end{aligned} \tag{15}$$

The removal efficiencies of COD and TSS from tannery wastewater by electrocoagulation and electro-Fenton processes predicted by Eqs. (12)–(15) are given in Tables 3 and 4 with the experimental results. The statistical significance of the model was further evident from the fact that the values calculated with the predictive equations were determined to be very close to the experimental values (Fig. 2). This illustrated that the prediction of experimental data is quite satisfactory.

The significance and adequacy of the model was evaluated by ANOVA. ANOVA of regression parameters of the predicted response surface quadratic model for COD and TSS removal efficiencies by electrocoagulation and electro-Fenton processes using the results of the experiments performed is given in Table 5. The larger the F-value, the more significant is the

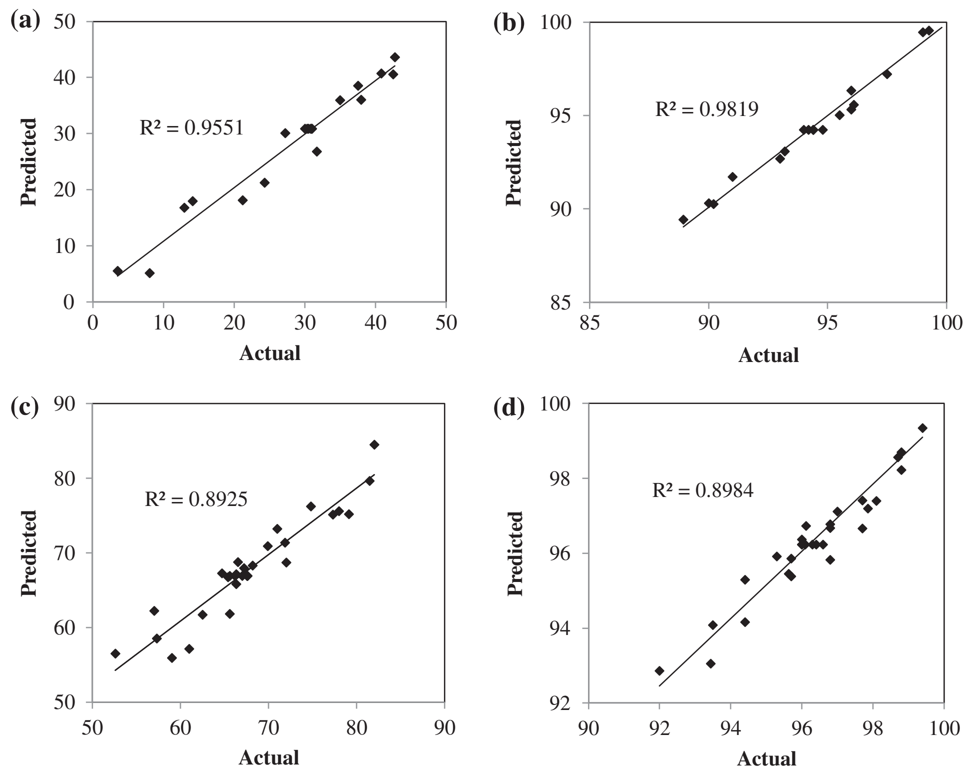

Fig. 2. Comparisons of predicted and experimental values of COD and TSS for electrocoagulation (a, b) and for electro-Fenton (c, d).

Table 5
ANOVA results of the predicted response surface quadratic model

Process	Model	R^2	Adjusted R^2	Sum of squares	Mean square	F-value	Prob. > F
Electrocoagulation	COD	0.9551	0.9147	2258.652	250.961	23.6431	0.0000136
	TSS	0.9819	0.9657	171.070	19.0078	60.4150	0.000000156
Electro-Fenton	COD	0.8924	0.7921	1295.706	92.550	8.89270	0.0000686
	TSS	0.8983	0.8035	80.6632	5.7616	9.47177	0.0000465

corresponding term. Furthermore, the p-value related to the F-value could be used to show whether the F-value is large enough or not [33,39]. The values of Prob. > F less than 0.05 imply that the model terms are significant, whereas the values greater than 0.1 indicate that the model terms are insignificant [40–43]. According to the results (Table 5) in both processes, F-values of regressions, defined as the ratio of mean square of the regression due to the residual error, were found to be high enough. As it can be seen from Table 5, Prob. > F-values of the models were determined to be less than 0.0001 for the second-order polynomial fitting indicating that the model is highly significant statistically.

Model F-value is determined to be 23.64 with corresponding p-value of 0.0000136 and high SS value (Table 6) implying that the model is highly significant and can appropriately explain the relationship between response and independent variables for COD removal in electrocoagulation process. It can be concluded that linear coefficients were found to be more significant than quadratic and interacting coefficients. As can be seen from Table 7 that the ANOVA of the TSS removal by electrocoagulation process showed F-value of 60.42 and for the quadratic model implying that the model is highly significant. The ANOVA table obtained from the response surface quadratic model shows that linear coefficients were found to be

Table 6
ANOVA results for the response surface quadratic model for COD removal by electrocoagulation

Source	Sum of squares	Df	Mean square	F-Ratio	p-value	Remark
Model	2,258.652	9	250.9614	23.64	0.0000136	Highly significant
X_1	565.132	1	565.132	53.24	<0.0001	Highly significant
X_2	326.615	1	326.615	30.77	0.0002	Significant
X_3	1,238.51	1	1238.51	116.7	<0.0001	Highly significant
X_1X_1	7.72878	1	7.72878	0.73	0.4135	Not significant
X_1X_2	8.63201	1	8.63201	0.81	0.3884	Not significant
X_1X_3	9.48301	1	9.48301	0.89	0.3668	Not significant
X_2X_2	23.7512	1	23.7512	2.24	0.1656	Not significant
X_2X_3	7.27711	1	7.27711	0.69	0.4270	Not significant
X_3X_3	94.8162	1	94.8162	8.93	0.0136	Significant
Total error	106.145	10	10.6145			
Total (corr.)	2,364.8	19				

Note: R^2 = 95.51%.

Table 7
ANOVA results for the response surface quadratic model for TSS removal by electrocoagulation

Source	Sum of squares	Df	Mean square	F-ratio	p-value	Remark
Model	171.071	9	19.0078	60.4150	0.000000156	Highly significant
X_1	5.4289	1	5.4289	17.26	0.0020	Significant
X_2	4.9284	1	4.9284	15.66	0.0027	Significant
X_3	2.7225	1	2.7225	8.65	0.0147	Significant
X_1X_1	0.229091	1	0.2290	0.73	0.4135	Not significant
X_1X_2	0.405	1	0.405	1.29	0.2830	Not significant
X_1X_3	4.9928	1	4.9928	15.87	0.0026	Significant
X_2X_2	0.00159	1	0.001590	0.01	0.9447	Not significant
X_2X_3	143.821	1	143.821	457.12	<0.0001	Highly significant
X_3X_3	7.38731	1	7.38731	23.48	0.0007	Significant
Total error	3.14621	10	0.31462			
Total (corr.)	174.217	19				

Note: R^2 = 98.19%.

significant, whereas X_1X_3 and X_2X_3 in interacting coefficients and X_3X_3 in quadratic coefficients have significant effect on TSS removal (Table 7).

As can be seen from Tables 8 and 9, the ANOVA of the COD and TSS removal by electro-Fenton process showed F-values of 8.89 and 9.47, respectively. Corresponding p-values were determined to be 0.0000686 and 0.0000465, respectively, implying that the model is highly significant. The pH values and H_2O_2 dosage have significant effect on COD removal, whereas reaction time has highly significant effect. ANOVA study showed that X_2X_3, X_3X_4, and X_2X_4 have significant effect whereas the interaction effect on COD removal between pH and other parameters is insignificant. The only parameter which has significant effect in quadratic parameters was the H_2O_2 dosage. The ANOVA study of TSS removal by electro-Fenton process showed similar results with that of COD removal. It can be concluded from Table 9 that linear coefficients, except the H_2O_2 dosage, among the interacting coefficients X_2X_3, X_3X_4, and X_2X_4 has significant effect on TSS removal. The only parameter which has significant effect in quadratic parameters was the reaction time.

The statistical significance of the model was also confirmed by the determination of the model coefficients. In electrocoagulation process, R^2 values of the models obtained for COD and TSS removal were determined to be 0.955 and 0.982, respectively. This showed that only 4.5% (COD removal) and 1.8% (TSS removal) of the variability in the response were not explained by the models. In electro-Fenton process, R^2 values of the models obtained for COD and TSS removal were found to be 0.892 and 0.898,

Table 8
ANOVA results for the response surface quadratic model for COD removal by electro-Fenton process

Source	Sum of squares	Df	Mean square	F-ratio	p-value	Remark
Model	1,295.706	14	92.5504	8.89270	0.0000686	Highly significant
X_1	169.708	1	169.708	16.31	0.0011	Significant
X_2	19.1174	1	19.1174	1.84	0.1954	Not significant
X_3	373.513	1	373.513	35.89	<0.0001	Highly significant
X_4	53.1633	1	53.1633	5.11	0.0391	Significant
X_1X_1	44.0221	1	44.0221	4.23	0.0575	Not significant
X_1X_2	8.73202	1	8.73202	0.84	0.3742	Not significant
X_1X_3	0.0169	1	0.0169	0.00	0.9684	Not significant
X_1X_4	28.8369	1	28.8369	2.77	0.1167	Not significant
X_2X_2	14.0958	1	14.0958	1.35	0.2627	Not significant
X_2X_3	106.709	1	106.709	10.25	0.0059	Significant
X_2X_4	112.997	1	112.997	10.86	0.0049	Significant
X_3X_3	162.38	1	162.38	15.60	0.0013	Significant
X_3X_4	148.718	1	148.718	14.29	0.0018	Significant
X_4X_4	19.0381	1	19.0381	1.83	0.1963	Not significant
Total error	156.112	15	10.4075			
Total (corr.)	1,451.82	29				

Note: R^2 = 89.24%.

Table 9
ANOVA results for the response surface quadratic model for TSS removal by electro-Fenton process

Source	Sum of squares	Df	Mean square	F-ratio	p-value	Remark
Model	80.6632	14	5.76166	9.47177	0.0000465	Highly significant
X_1	3.293	1	3.293	5.41	0.0344	Significant
X_2	14.5548	1	14.5548	23.93	0.0002	Significant
X_3	9.86884	1	9.86884	16.22	0.0011	Significant
X_4	0.429337	1	0.429337	0.71	0.4140	Not significant
X_1X_1	0.32005	1	0.32005	0.53	0.4794	Not significant
X_1X_2	1.54381	1	1.54381	2.54	0.1320	Not significant
X_1X_3	0.091506	1	0.091506	0.15	0.7036	Not significant
X_1X_4	4.63326	1	4.63326	7.62	0.0146	Significant
X_2X_2	0.592536	1	0.592536	0.97	0.3393	Not significant
X_2X_3	19.2502	1	19.2502	31.65	<0.0001	Highly Significant
X_2X_4	6.43891	1	6.43891	10.59	0.0053	Significant
X_3X_3	5.75405	1	5.75405	9.46	0.0077	Significant
X_3X_4	12.093	1	12.093	19.88	0.0005	Significant
X_4X_4	0.764765	1	0.764765	1.26	0.2798	Not significant
Total error	9.12447	15	0.608298			
Total (corr.)	89.7877	29				

Note: R^2 = 89.84%.

respectively. It can be concluded that R^2 values determined for both processes are desirable, because for a good fit of a model, it is suggested that the rate of R^2 should be at least 80%.

The response surface plots were developed based on the RSM equations providing a three-dimensional view of the COD and TSS removal surface with different combinations of independent variables. The corresponding response surface plots are illustrated in Figs. 3(a)–(c), 4(a)–(c), 5(a)–(d), and 6(a)–(d). All response surface plots indicating optimum operating conditions have clear peaks, meaning that the optimum conditions for maximum values of the responses are attributed to all variables in the design space. As can be seen in Figs. 3–6, the TSS removal efficiencies were much higher than the COD removal efficiencies

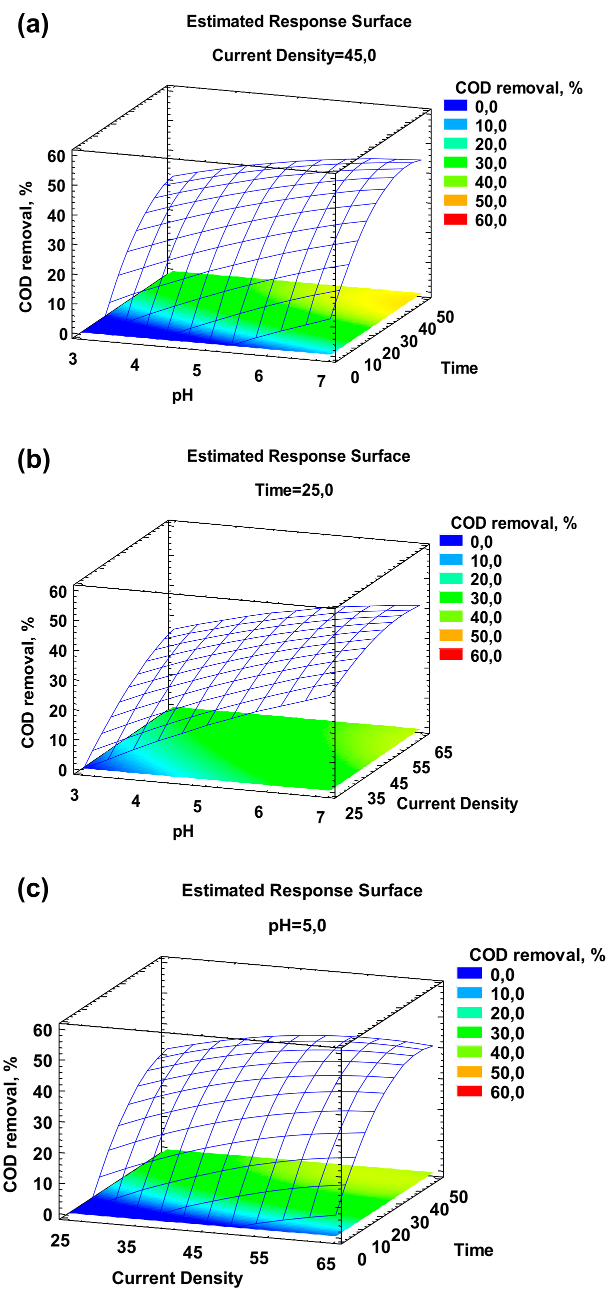

Fig. 3. Three-dimensional response surface graphs for the electrocoagulation treatment of tannery wastewater using Fe electrodes (a) COD removal vs. pH and contact time, (b) COD removal vs. pH and current density, and (c) COD removal vs. current density and time.

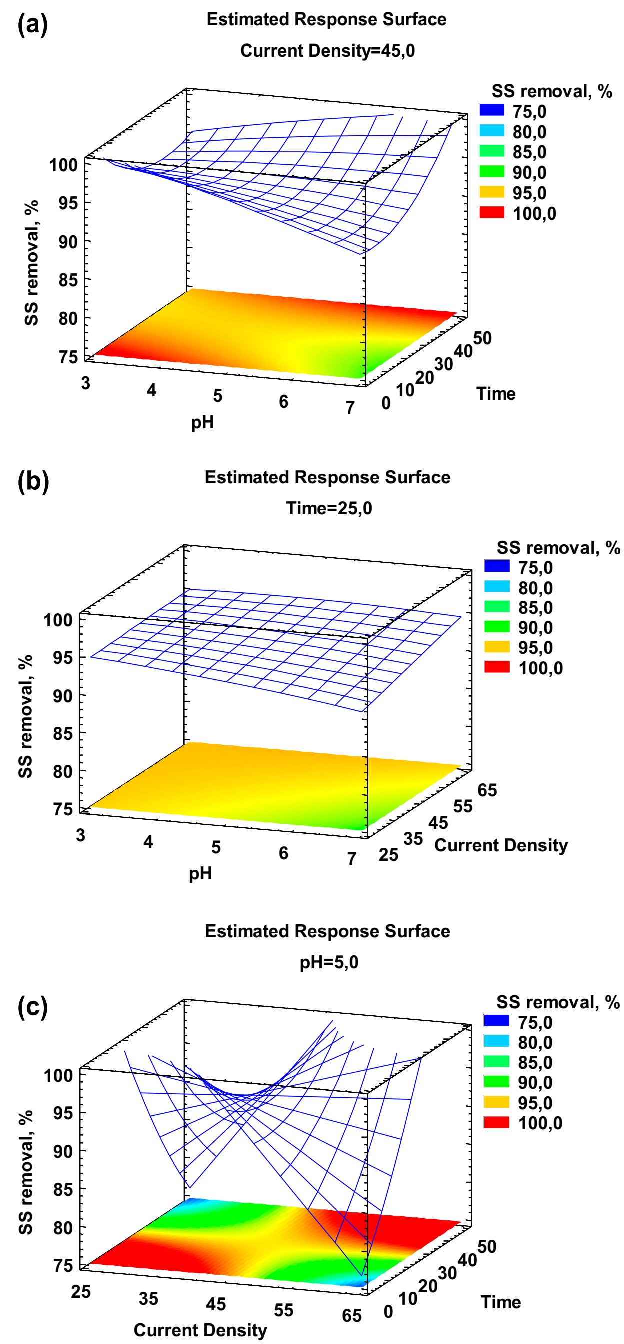

Fig. 4. Three-dimensional response surface graphs for the electrocoagulation treatment of tannery wastewater using Fe electrodes (a) TSS removal vs. pH and contact time, (b) TSS removal vs. pH and current density, and (c) TSS removal vs. current density and time.

during the electrocoagulation and electro-Fenton processes. It can also be concluded that there is no significant difference between the TSS removal efficiencies obtained by the electrocoagulation and electro-Fenton processes, but the COD removal efficiencies obtained by the electro-Fenton process was determined to be much higher than that obtained by the electrocoagulation.

Numerical optimization based on response surface and desirability functions was used to determine the optimum process parameters for maximum COD and

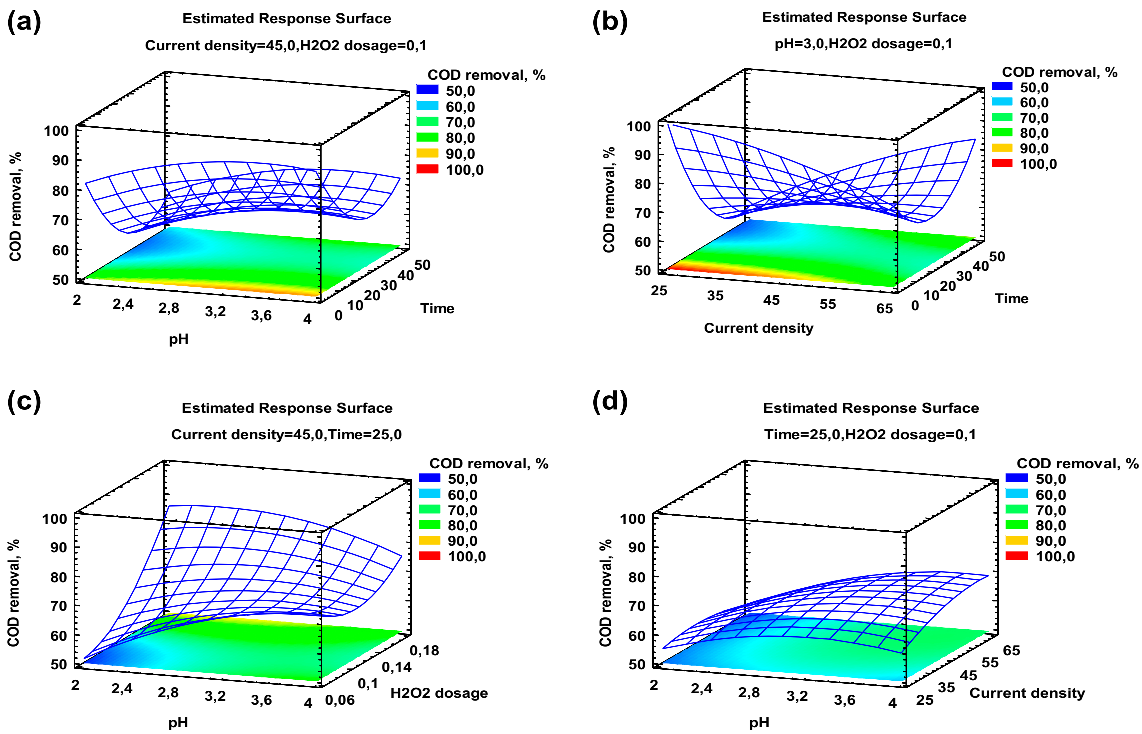

Fig. 5. Three-dimensional response surface graphs for the electro-Fenton treatment of tannery wastewater using Fe electrodes (a) COD removal vs. pH and H_2O_2 dosage, (b) COD removal vs. pH and current density, (c) COD removal vs. current density and time, and (d) COD removal vs. pH and contact time.

TSS removal by the electrocoagulation and elecro-Fenton processes. The optimized conditions are given in Table 10 in order to confirm the accuracy of the predicted models and the reliability of the optimum combination. As can be seen, the experimental values were found to be consistent with the predicted ones. The experimental results under the optimum conditions and predicted values from the proposed models are presented in Table 10.

3.2. Cost evaluation

The amount of energy consumption and the amount of electrode material are the two important parameters in the electrocoagulation and electro-Fenton processes in the estimation of operational costs. The operational cost of the processes applied at optimum conditions was calculated by the equation given as follows:

$$\mathrm{OC} = \mathrm{aENC} + \mathrm{bELC} \tag{16}$$

where ENC evaluates the electrical energy consumed and bELC estimates the material cost.

The electrical energy consumption was calculated using the following equation [27]:

$$C_{\text{energy}} = \frac{U \times i \times t_{\text{EC}}}{v} \tag{17}$$

where C_{energy} is the energy consumption (kWh/m^3), U is the applied voltage (V), I is the current intensity (A), t is the electrocoagulation time (s), and V is the volume of the treated wastewater (m^3).

The amount of electrode dissolved was calculated theoretically by using the Faraday's law:

$$C_{\text{electrode}} = \frac{i \times t_{\text{EC}} \times M_{\text{W}}}{Z \times F \times v} \tag{18}$$

where $C_{\text{electrode}}$ (kg/m^3) is the iron or aluminum electrode consumption in the electrolytic cell, I is the current intensity (A), t is the electrocoagulation time (s), M_{w} is the molecular mass of the electrode (g/mol), Z is the number of electrons transferred ($Z_{\text{Fe}} = 3$), F is the Faraday constant (96,487 C/mol), and V is the volume of the treated wastewater (m^3). It should be noted that the cost for chemical consumption in both processes was ignored.

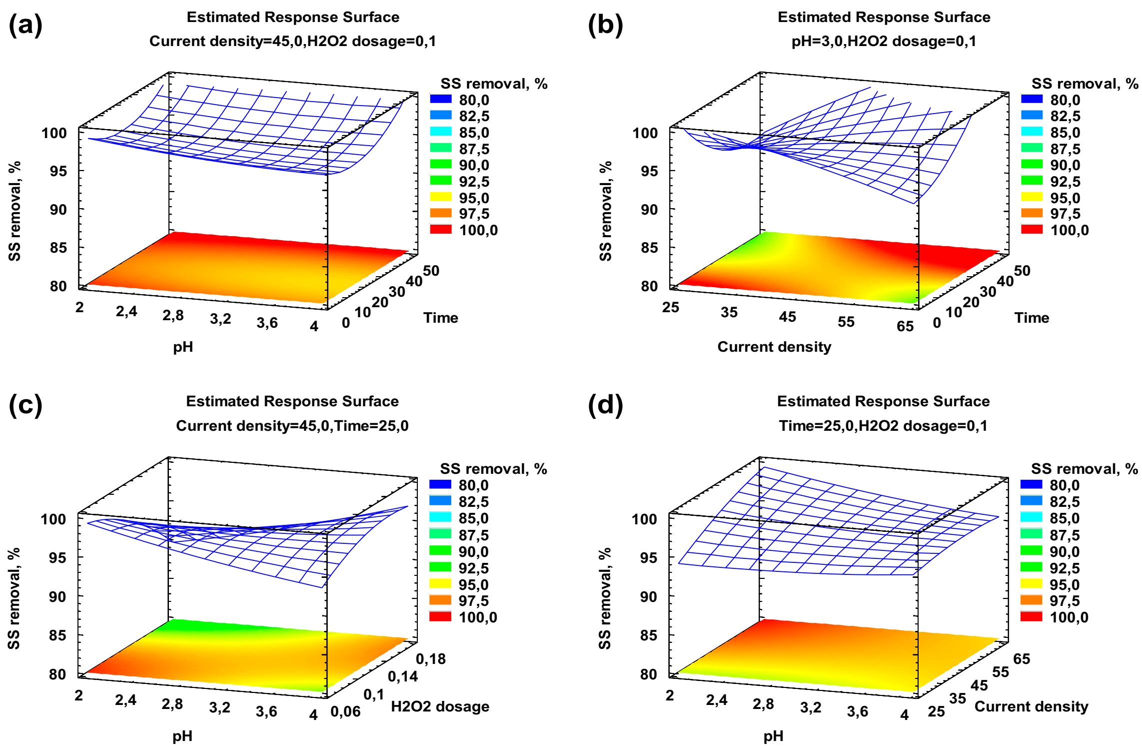

Fig. 6. Three-dimensional response surface graphs for the electro-Fenton treatment of tannery wastewater using Fe electrodes (a) TSS removal vs. pH and H_2O_2 dosage, (b) TSS removal vs. pH and current density, (c) TSS removal vs. current density and time, and (d) TSS removal vs. pH and contact time.

Table 10
Optimum operating conditions of the process variables

	Electrocoagulation		Electro-Fenton	
Factor	COD	TSS	COD	TSS
pH	7.0	5.48	3.31	2.0
Current density (mA/cm^2)	50.92	65.0	53.72	65.0
Time (min)	40.39	45.0	5.0	45.0
H_2O_2 dosage (g/l)	–	–	0.14	0.06

Operational cost of the electrocoagulation and electro-Fenton processes applied to tannery wastewater for COD removal at optimum conditions was determined to be 6.4 and 6.8 €/m^3, respectively. In comparison with the operational cost of electrocoagulation and electro-Fenton methods, there is no significant difference between the two processes.

4. Conclusions

In this study, the efficiency of electrocoagulation and electro-Fenton processes on tannery wastewater treatment was investigated. CCD and RSM were adopted to model and optimize the performance of the processes and to determine the optimal experimental conditions. The quadratic model developed in the study showed the presence of a high correlation between experimental and predicted values. Analysis of variance showed high determination coefficients ($R^2 > 0.80$), thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. In electrocoagulation process under optimal values of process parameters (current density: 50.92 mA/cm^2, initial pH: 7, electrolysis time: 40.39 min), 54.8% COD removal was obtained, whereas in electro-Fenton process under optimum conditions (current density: 53.72 A/m^2, initial pH: 3.31, electrolysis time:5 min, H_2O_2 dosage: 0.14 g/L), 87.3% COD removal was obtained. The results show that electrocoagulation and electro-Fenton processes are recommended as powerful techniques for tannery wastewater treatment, but electro-Fenton treatment achieves more effective removal of COD and TSS. Additionally, the results confirm that RSM is a powerful tool for optimizing the operational conditions of electrocoagulation and electro-Fenton processes for COD and TSS removals from tannery wastewater.

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