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Removal of ecotoxicological matters from tannery wastewater using electrocoagulation reactor: modelling and optimization

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ABSTRACT

This study investigated the possibilities of electrocoagulation reactor to reduce the colour, oil and grease and chemical oxygen demand (COD) from tannery industry wastewater using stainless steel electrodes. Effects of pH, electrolysis time, current density and NaCl dose were investigated using four factors three-level Box–Behnken response surface design coupled with response surface methodology. From the experimental results, second-order polynomial mathematical models were developed to describe the treatment process statistically. Analysis of variance was used to evaluate the adequacy of developed mathematical models. Three-dimensional (3D) response surface plots were constructed to study the interactive effects of process variables on the treatment efficiency. Optimum operating conditions such as pH of 9, electrolysis time of 40 min, current density 20 $mAcm^{-2}$ and sodium chloride (NaCl) dose of 1,016 mg l^{-1} show 92, 95 and 80% of colour, oil and grease, and COD removal, respectively. The electrical energy consumption of the present treatment process in optimum condition was found to be 6 $KWhm^{-3}$. The obtained results indicate that EC reactor is the best option to treat tannery industry wastewater in terms of removal efficiency and operating cost.

Keywords: Tannery wastewater; Electrocoagulation reactor; Stainless steel electrodes; Box–Behnken design; Optimization

1. Introduction

Tannery industry wastewater is a powerful pollutant that can cause severe environmental problems related to its high chemical oxygen demand (COD), oil and grease together with deep colour content. Tanning is a process where the addition of a tanning agent (chromium salts, aluminium, zirconium, vegetable extracts of mimosa, etc.) stabilizes the skin structure by forming transverse bonds among its fibres [1]. This process consists of three sequential processes namely beamhouse, tanyard and finishing. Through these methods, the leather is turned into a durable material. The tanning process and the effluents generated from various stages have been shown in Fig. 1. In India, more than 25,000 ton $year^{-1}$ of leather are produced which generate more than 5.68×10^7 m^3 of wastewater $year^{-1}$ [2]. Wastewater discharged from this industry is highly complex, concentrated and toxic. Tannery wastewater can cause significant pollution to the ecological system unless treated prior to discharge. Many conventional treatment processes were carried out to

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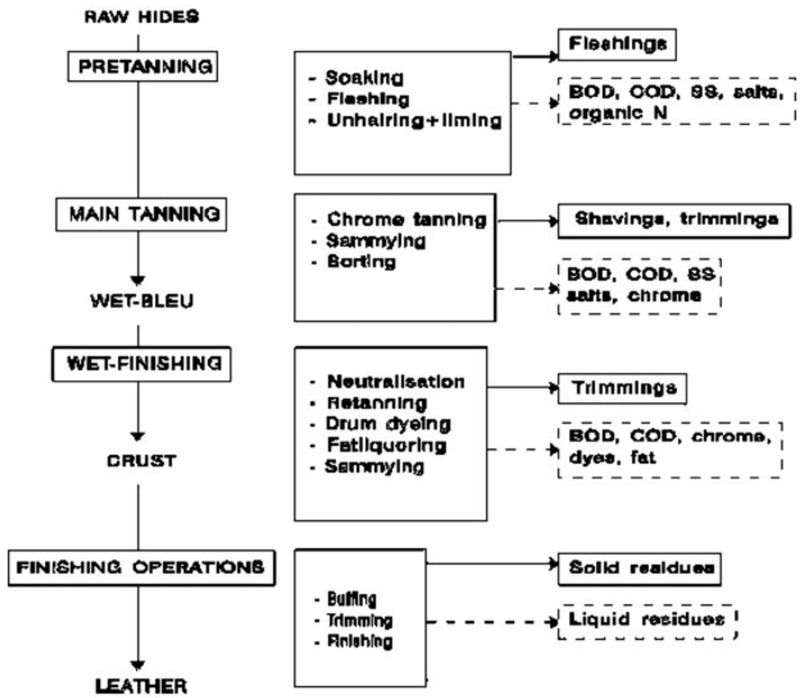

Fig. 1. Production of wastewater at various stages of tannery industry processing.

treat wastewater from tannery industry such as physical treatment, biological treatment, chemical treatment processes including coagulation–flocculation, ion exchange, adsorption, electrochemical and combined chemical/biological processes. But, these treatment methods show several disadvantages including lower treatment efficiency, higher sludge yield and high capital [3]. Therefore, there is a critical need to develop a technically and economically viable technique to treat tannery industry wastewater.

Over the past decades, research on devising appropriate treatment technologies for tannery wastewaters has gone through different phases of development. The method of electrochemical oxidation for treatment of organic contaminants contained in wastewater has become a hot focus because of its better effects than traditional chemical, physical and biological methods. Electrocoagulation (EC) consists of metal sheets called electrodes that are arranged in pairs of anode and cathode. Using the principles of electrochemistry, the cathode is oxidized, while the water is reduced, thereby making the wastewater better treated. When the cathode electrode makes the contact with wastewater, the metal is produced into the EC reactor [4]. During this reaction, the particulates are neutralized by the formation of hydroxide complexes thus forming agglomerates. These agglomerates settles at the bottom of the tank thus removing toxic matters. Compared to other methods in treating wastewater, EC possesses few advantages. Energy consumption could be decreased for the better conductivity, due to the masses of salt, and the reaction conditions could be easily controlled by changing the electro cell voltage. The fine bubbles and poly-nuclear hydroxy complexes produced by the EC float on wastewater which affects treatment efficiency and hence need to be removed [5]. Also, process parameters such as pH, electrolysis time, current density and NaCl dose significantly influence the treatment efficiency and its optimization will help in reducing the operating cost with maximum removal efficiency.

In conventional multifactor experiments for the wastewater treatment, optimization is usually carried out by varying a single factor while keeping all other factors fixed at a constant level. It is not only time-consuming, but also usually incapable of reaching the true optimum due to ignoring the interactions among variables [6]. Thus, it is enviable to enlarge an adequate process in shortest possible time using minimum number of experiments, hours and raw materials with reduced operating cost. In addition, the technique of the statistical experimental design is an efficient method to indicate the virtual significance of a number of process parameters and their interactions [7]. Response surface methodology (RSM) coupled with Box–Behnken response surface design (BBD) is a statistical technique for designing experiments, building models, evaluating the effects of several factors and searching optimum conditions for desirable responses. Recently, this method has been used to determine optimum parameters in different wastewater treatment processes. However, to our best knowledge, no research reports are available on the treatment of tannery industry wastewater using EC via RSM. Hence, the primary objective of the present study was made to investigate and optimize the individual and the interactive effect of process variables such as pH, electrolysis time, current density and NaCl dose on the EC treatment of tannery industry wastewater using BBD coupled with Derringer's desired function methodology. Treatment efficiency was calculated using reduction in colour, oil and grease, and COD. Finally, electrical energy consumption (EEC) is also calculated in order to examine the economic viability EC treatment in tannery industry wastewater treatment plants.

2. Materials and methods

2.1. Materials

Tannery industry wastewater was collected from the local industry near Erode, Tamil Nadu, India and was stored at 4˚C prior to the experiments. The characteristics of tannery industry wastewater are determined using APHA standard methods and are shown in Table 1. Sodium chloride (NaCl) was purchased from local suppliers, Erode, India. All the chemicals used in this study were of analytical grade and were purchased from Sigma chemicals, Mumbai.

2.2. Experimental set-up

The EC cell was constructed with Plexiglas having a dimension of 0.15 × 0.25 × 0.2 m (Fig. 2). The total volume of wastewater in each experiment was approximately 0.005 m^3. Stainless steel (SS) plate with total surface area of 0.0250 m^2 was used as the sacrificial electrodes. The composition of SS electrodes is as follows; Fe, <0.08% C, 17.5–20% Cr, 8–11% Ni, <2% Mn, <1% Si, <0.045% P, <0.03% S. These SS electrodes also reduce the thermal expansion for better dimensional stability with lowest price. The homogeneity of wastewater was maintained using a magnetic stirrer with 250 rpm and the distance between plates was fixed at approximately 0.05 m. To achieve good mass transfer in the system, a desired amount of electrolyte was added in the reactor using a digital balance. pH of the wastewater was adjusted by using 0.1 N HCl or H_2SO_4. A regulated DC power supply was employed to supply the external electricity. During the treatment, the properties of wastewater were analysed at a preferred time interval with settling time of 30 min. All the experiments were conducted in triplicate and the average value is determined.

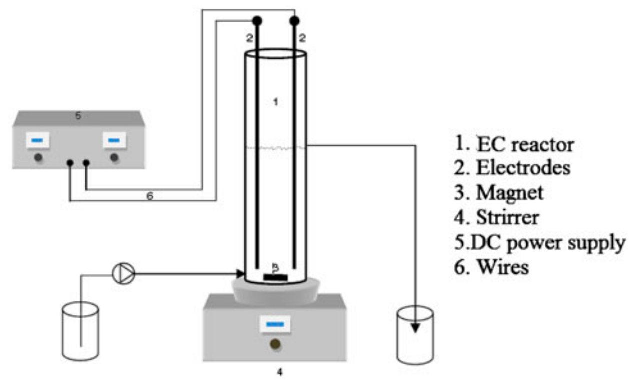

Fig. 2. Schematic diagram of EC reactor.

Table 1
Characteristics of tannery industry wastewater

Characteristics	Values
Colour, NTU	458
Oil and grease, mg l^{-1}	1,574
COD, mg l^{-1}	2,185
pH	6.9
Conductivity, ms cm^{-1}	0.658
Total dissolved solids, mg l^{-1}	4,876

2.3. Analytical methods

American public health association standard methods were used to determine the wastewater characteristics such as initial pH, colour, oil and grease, COD and conductivity. The removal efficiency (R) was calculated using the following equation [8]:

$$R = \frac{Y_0 - Y}{Y_0} \times 100 \qquad (1)$$

where R is the removal efficiency (%), Y_0 and Y were initial and final values of colour, oil and grease, and COD, respectively. EEC of the present treatment is calculated as follows [9]:

$$\text{EEC}\ (\text{KWh/m}^3) = \text{volts (V) amperes (A)} \times \text{electrolysis time (h)/volume of effluent (m}^3) \qquad (2)$$

2.4. Experimental design

The most popular class of second-order designs called BBD was used for the RSM in the experimental design. The BBD was first introduced by Box and Wilson in 1951, and is well suited for fitting a quadratic surface, which usually works well for the process optimization [10]. For EC process, four important operating parameters such as pH (X_1), electrolysis time (X_2), current density (X_3) and NaCl dose (X_4) were considered as the independent variables, while responses are colour removal (Y_1), oil and grease removal (Y_2), COD removal (Y_3) and EEC (Y_4). The low, middle and high levels of each variable were designated as −1, 0 and +1, respectively. The coded and actual values of the four independent variables together with their ranges are shown in Table 2. After selection of process (independent) variables and their ranges, experiments were established based on a BBD and the complete design consists of 29 experiments with five centre points. An empirical second-order polynomial equation was fitted to correlate the relationship between independent variables and responses. The general mathematical form of second-order polynomial equation is given below [11]:

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} X_i X_j + e_i \quad (3)$$

where Y is the response; X_i and X_j are the variables (i and j range from 1 to k); β_0 is the model intercept coefficient; β_j, β_{jj} and β_{ij} are the interaction coefficients of linear, quadratic and the second-order terms, respectively; k is the number of independent parameters ($k = 4$ in this study); and e_i is the error. Adequacy of the proposed model is then examined using the diagnostic checking tests and ANOVA. The quality of the fit polynomial model was expressed by the coefficient of determination R^2. These analyses are done by means of Fisher's F test and p-value (probability). Model terms were evaluated by the p-value with 95% confidence level. Finally, the optimal values of the critical parameters were obtained by analysing the surface and counter plots and by Derringer's desired function methodology [12]. All the statistical analyses were done with the help of Stat ease Design Expert 8.0.7.1 statistical software package (Stat-Ease Inc., Minneapolis, USA).

Table 2
Ranges of independent variables and their levels

Variable (unit)	Factors X	Level −1	Level 0	Level 1
Initial pH	A	3	6	9
Electrolysis time (min)	B	30	45	60
Current density (mA cm^{-2})	C	10	20	30
NaCl dose (mg l^{-1})	D	250	750	1,250

3. Results and discussion

The removal of colour, oil and grease, and COD with EEC from tannery industry water was investigated by EC method using SS plate as an electrode. The effects of process variables such as pH (A), electrolysis time (B), current density (C), NaCl dose and (D) on the treatment efficiency were investigated using RSM. BBD experimental design with results is shown in Table 3. Different response functions such as linear, interactive, quadratic and cubic models were used to correlate the experimental data and to obtain the best fit regression equation.

3.1. Model development

To decide about the adequacy of the models to represent EC process, sequential model sum of squares was carried out in the present study and the results are presented in Table 4. Cubic model was not recommended for this system due to insufficient points to estimate the coefficients for this type of the model. Sequential model sum of squares indicated that the quadratic model provided the best fit to experimental data with the higher F-value and the lowest p-value [13]. Therefore, the quadratic model is chosen for further analysis. Experimental data were used for determining of the response function (Eqs. (4–7)) coefficients for each independent variable. The response function with the determined coefficients is presented as follows:

$$\begin{aligned} Y_1 = {} & 84.50 + 6.21A - 3.91B + 11.45\,C + 7.81D - 7.30AB \\ & - 2.77AC - 0.80AD - 3.43\,BC - 5.57\,BD - 4.70CD \\ & - 0.85A^2 - 19.46B^2 - 6.33C^2 - 11.50\,D^2 \end{aligned} \quad (4)$$

$$\begin{aligned} Y_2 = {} & 95.28 + 5.15A - 3.01B + 11.83C + 10.92D - 8.00AB \\ & - 0.52AC + 1.87AD - 3.74BC - 4.73BD - 5.93CD \\ & - 7.99A^2 - 27.61B^2 - 13.47C^2 - 17.31D^2 \end{aligned} \quad (5)$$

$$\begin{aligned} Y_3 = {} & 72.14 + 6.21A - 3.91B + 11.45C + 7.81D - 7.30AB \\ & - 2.77AC - 0.80AD - 3.43BC - 5.56BD - 4.70CD \\ & - 0.85A^2 - 19.46B^2 - 6.33C^2 - 11.50\,D^2 \end{aligned} \quad (6)$$

Table 3
Box–Behnken experimental design and observed responses

Run. no	A	B	C	D	Y_1	Y_2	Y_3	Y_4
1	6	30	30	750	78.24	73.54	65.88	12.96
2	3	30	20	750	55.35	50.38	42.99	7.695
3	6	45	20	750	84.5	95.28	72.14	7.29
4	3	45	10	750	57.25	58.62	44.89	3.51
5	6	30	20	250	45.54	38.28	33.18	9.72
6	6	60	20	1,250	50.22	53.64	37.86	7.29
7	6	45	20	750	84.5	95.28	72.14	7.695
8	6	30	10	750	48.34	42.52	35.98	3.51
9	6	45	30	250	73.06	73.88	60.7	14.58
10	9	60	20	750	59.32	53.26	46.96	9.315
11	6	60	20	250	48.68	40.28	36.32	10.53
12	3	45	30	750	84.34	79.64	71.98	10.8
13	6	30	20	1,250	69.34	70.54	56.98	5.67
14	9	45	20	1,250	84.68	90.28	72.32	6.075
15	6	45	10	250	39.54	34.56	27.18	2.7
16	6	45	20	750	84.5	95.28	72.14	7.695
17	6	45	10	1,250	70.54	67.28	58.18	3.24
18	6	45	20	750	84.5	95.28	72.14	6.48
19	9	30	20	750	79.58	71.28	67.22	7.695
20	3	60	20	750	64.28	64.38	51.92	8.505
21	9	45	30	750	91.67	88.65	79.31	11.88
22	3	45	20	1,250	71.54	70.56	59.18	6.885
23	3	45	20	250	57.36	52.48	45	10.125
24	6	60	30	750	61.54	57.46	49.18	12.42
25	6	60	10	750	45.38	41.38	33.02	2.43
26	6	45	20	750	84.5	95.28	72.14	6.48
27	6	45	30	1,250	85.27	82.89	72.91	7.5
28	9	45	10	750	75.65	69.7	63.29	2.16
29	9	45	20	250	73.68	64.7	61.32	9.72

$$Y_4 = 7.13 - 0.056A + 0.27B + 4.38C - 1.73D + 0.20AB + 0.61AC - 0.10AD + 0.13BC + 0.20BD - 1.90CD + 0.44A^2 + 0.87B^2 - 0.39C^2 + 0.40D^2 \quad (7)$$

where Y_1, Y_2, Y_3 and Y_4 are colour, oil and grease, COD removal and EEC, respectively.

3.2. Adequacy of mathematical models

The statistical significance of the response functions (Y_1–Y_4) is checked by F-test, and the ANOVA results for response surface quadratic models and model terms are summarized in Table 5. The model F-value and very low probability value (0.0001) indicated that the model is statistically significant and model equation can adequately be used to describe the EC process under a wide range of operating conditions [14]. Moreover, F-values and p-values of individual and interactive terms show the suitability of the developed models. The goodness of fit of the models were evaluated by coefficient of variance (CV%) and adequate precision (AP). The lower CV% values revealed that the developed models are capable to predict the experimental data. The AP values of the models compare the predicted data at the design points with the average prediction error. In the present study, AP values were obtained as >4, indicating an appropriate signal, and suggested that the regression models could be used to navigate the design space. The value of AP values is in reasonable agreement with experimental data. The adequacy of developed mathematical models is also evaluated by constructing diagnostic plots such as predicted vs. actual plots (Fig. 3). The data points on this plot lie very close to the diagonal line, which indicates the good adequate agreement between experimental data and the data predicted by the developed models [15]. The high value of R^2 (>0.9) for the all the developed models indicated a high dependence and correlation between the observed and the predicted values of response. The ANOVA analysis showed that the form of the model chosen to explain the relationship between the factors and the response is correct.

3.3. Influence of process variables on the EC treatment efficiency

Three dimensional (3D) response surface plots were constructed from the developed models in order to study the individual and interactive effect of the process variables on the responses and also used to locate the optimal condition of each factor to find out the maximum removal efficiencies with reduced operating cost.

3.3.1. Effect of pH

pH plays an important role in the EC process. Charge on hydrolysis products and precipitation of metal hydroxides are both controlled by pH variations. To examine its effect on the treatment efficiency, the pH was varied in the range of 3–9 and the results are shown in Fig. 4((a)–(d)). From the figures, it is found that the percentage of colour, oil and grease, and COD removals was increased by increasing the pH throughout the wide range studied. Charge neutralization is considered to be a prerequisite condition for most EC processes to occur. As the functional groups of wastewater are anionic, hydrolysis products of the SS electrodes (substantially metal hydroxides) can neutralize the negative charges. Therefore, the most likely mechanism dealing with EC process seems

Table 4
Sequential model sum of squares for responses

Source	Sum of squares	Df	Mean square	F-value	Prob. > F	Remarks
Sequential model sum of squares for colour removal						
Mean	136,952.09	1.00	136,952.09			
Linear	2,951.67	4.00	737.92	4.92	0.0048	
2FI	505.52	6.00	84.25	0.49	0.8069	
Quadratic	3,009.04	4.00	752.26	129.17	<0.0001	Suggested
Cubic	79.03	8.00	9.88	23.72	0.0005	Aliased
Residual	2.50	6.00	0.42			
Total	143,499.85	29.00	4,948.27			
Sequential model sum of squares for oil and grease removal						
Mean	133,359.89	1.00	133,359.89			
Linear	3,537.85	4.00	884.46	3.09	0.0349	
2FI	557.10	6.00	92.85	0.26	0.9465	
Quadratic	6,204.09	4.00	1,551.02	182.40	<0.0001	Suggested
Cubic	116.20	8.00	14.53	30.62	0.0003	Aliased
Residual	2.85	6.00	0.47			
Total	143,777.98	29.00	4,957.86			
Sequential model sum of squares for COD removal						
Mean	1,707.96	1.00	1,707.96			
Linear	267.15	4.00	66.79	50.49	<0.0001	
2FI	16.43	6.00	2.74	3.22	0.0251	
Quadratic	8.40	4.00	2.10	4.25	0.0185	Suggested
Cubic	4.78	8.00	0.60	1.68	0.2724	Aliased
Residual	2.14	6.00	0.36			
Total	2,006.85	29.00	69.20			
Sequential model sum of squares for EEC						
Mean	1,707.96	1.00	1,707.96			
Linear	267.15	4.00	66.79	50.49	<0.0001	
2FI	16.43	6.00	2.74	3.22	0.0251	
Quadratic	8.40	4.00	2.10	4.25	0.0185	Suggested
Cubic	4.78	8.00	0.60	1.68	0.2724	Aliased
Residual	2.14	6.00	0.36			
Total	2,006.85	29.00	69.20			

to be charge neutralization [16]. However, the EEC value is not much affected by wide range of pH. Similar kind of trend is obtained for the treatment of paper industry wastewater using EC process.

3.3.2. Effect of electrolysis time

Electrolysis time is one of the important parameter which affects the EC process significantly. In order to investigate the effect of electrolysis time on treatment efficiency, the experiments were carried out by varying the electrolysis time from 30 to 60 min and the results are shown in Fig. 4((a)–(d)). From the observation, it is found that the percentage of colour, oil and grease, and COD removals were increased with increasing electrolysis time up to 50 min. This can be attributed due to the formation of higher amount of monomeric species in the EC reactor as following electrochemical reactions [17]:

$$\text{At the anode: } M_{(s)} \rightarrow M^{3+}{}_{(aq)} + 3e^{-} \quad (8)$$

$$\text{At the cathode: } 3H_2O_{(l)} + 3e^{-} \rightarrow 3/2\ H_2 + 3OH^{-} \quad (9)$$

$$\text{In wastewater: } M^{3+}{}_{(aq)} + 3H_2O \rightarrow M(OH)_{3(s)} + 3H^{+}{}_{(aq)} \quad (10)$$

M^{3+} (aq) and OH^- ions generated by the electrode reactions (8) and (9) react, respectively, to form various monomeric species, depending on pH range, which change finally into $M(OH)_3$ according to complex precipitation kinetics. This amorphous $M(OH)_3$ flocs with large surface areas are favourable for a rapid adsorption of organic compounds and colloidal particles. Consequently, these flocs can be removed by sedimentation or by flotation using H_2 bubbles produced at the cathode [18]. Whereas, EEC is linearly

Table 5
ANOVA table for responses

Responses	Colour removal		Oil and grease removal		COD removal		EEC	
	F-value	*p*-value	*F*-value	*p*-value	*F*-value	*p*-value	*F*-value	*p*-value
Model	79.31	<0.0001	86.51	<0.0001	42.21	<0.0001	42.21	<0.0001
X1	79.33	<0.0001	37.44	<0.0001	0.08	0.7857	0.08	0.7857
X2	31.57	<0.0001	12.80	0.0030	1.77	0.2046	1.77	0.2046
X3	270.22	<0.0001	197.61	<0.0001	466.47	<0.0001	466.47	<0.0001
X4	125.71	<0.0001	168.20	<0.0001	72.38	<0.0001	72.38	<0.0001
X1X2	36.58	<0.0001	30.14	<0.0001	0.33	0.5736	0.33	0.5736
X1X3	5.26	0.0378	0.13	0.7279	2.99	0.1059	2.99	0.1059
X1X4	0.43	0.5207	1.65	0.2193	0.08	0.7775	0.08	0.7775
X2X3	8.10	0.0129	6.56	0.0226	0.15	0.7067	0.15	0.7067
X2X4	21.27	0.0004	10.50	0.0059	0.33	0.5736	0.33	0.5736
X3X4	15.16	0.0016	16.53	0.0012	29.38	<0.0001	29.38	<0.0001
$X1^2$	0.80	0.3874	48.69	<0.0001	2.58	0.1304	2.58	0.1304
$X2^2$	421.64	<0.0001	581.63	<0.0001	9.83	0.0073	9.83	0.0073
$X3^2$	44.63	<0.0001	138.32	<0.0001	2.01	0.1786	2.01	0.1786
$X4^2$	147.34	<0.0001	228.55	<0.0001	2.12	0.1670	2.12	0.1670
Std. Dev	2.41		2.92		0.70		0.70	
CV	3.51		4.30		9.16		9.16	

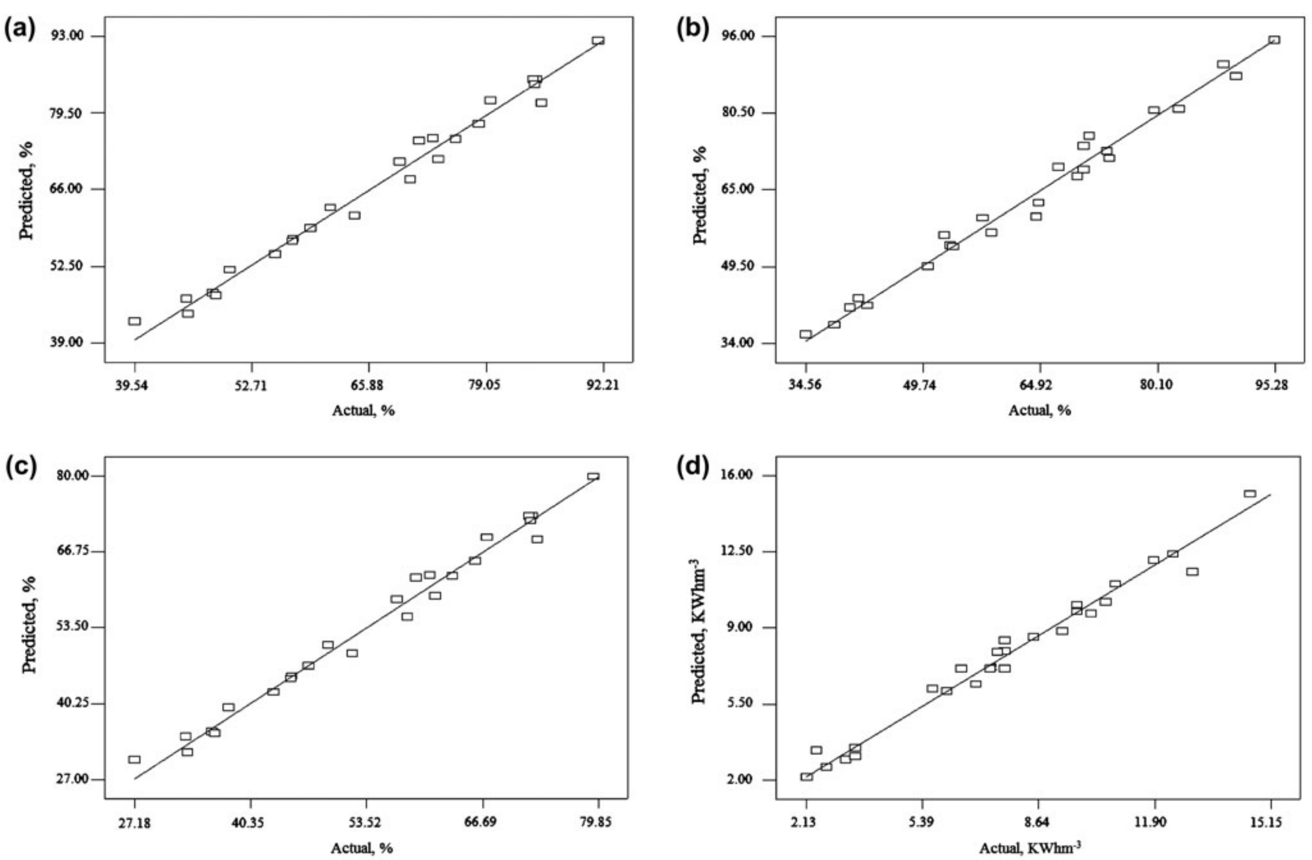

Fig. 3. Actual vs. predicted plot for responses (a) colour removal, (b) oil and grease removal, (c) COD removal and (d) EEC.

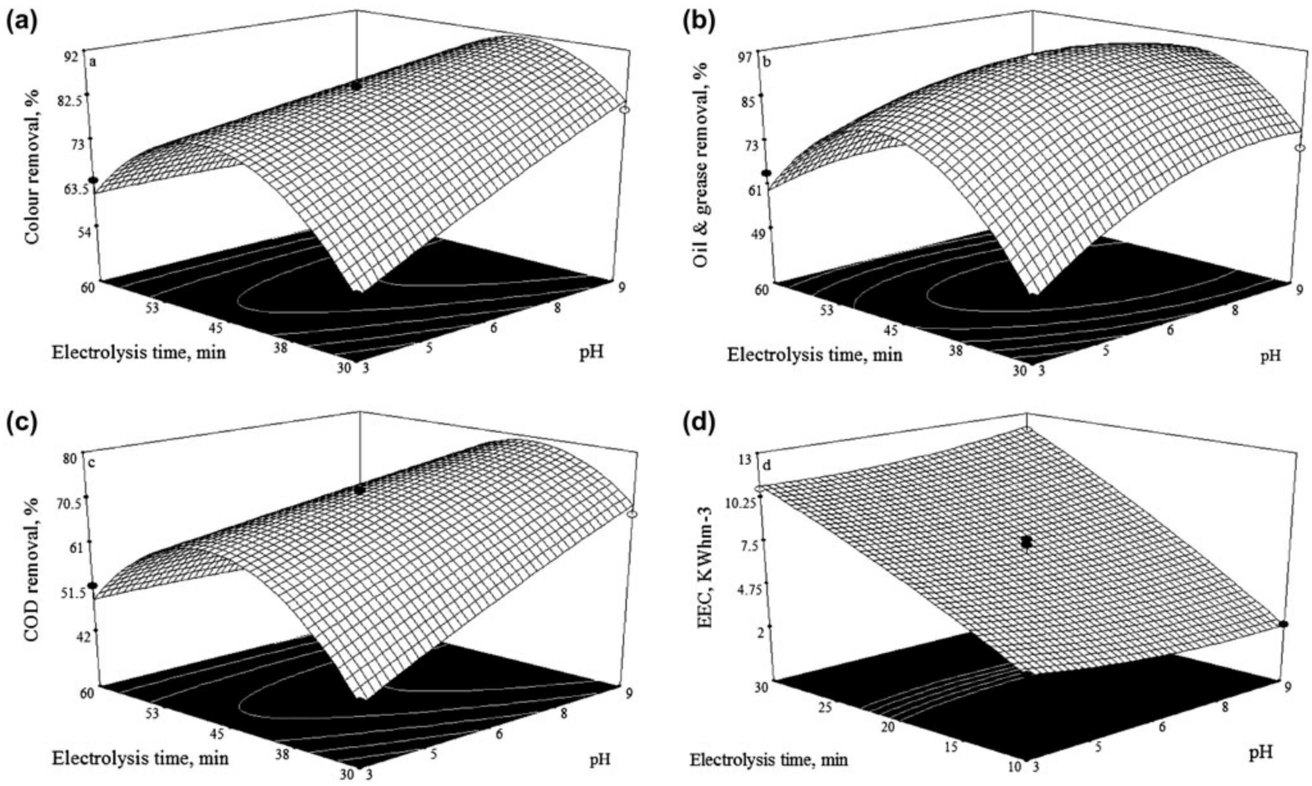

Fig. 4. Effect of NaCL dose and current density on EC treatment efficiency. (a) Colour removal, (b) oil and grease removal, (c) COD removal and (d) EEC.

increased with increasing electrolysis time throughout the experiments. These findings are consistent with the results of previous studies on the treatment of egg industry wastewater using a EC process.

3.4. Effect of current density

Current density is one of the most important parameters which shows the significant effect on the treatment efficiency of EC process to treat tannery industry wastewater. In order to study the effect of current density on the maximum removal efficiency of colour, oil and grease, and COD, experiments were carried out in various current densities (10–30 $mAcm^{-2}$) and results are depicted in Fig. 5((a)–(d)). From the results, it is found that the removal efficiency of colour, oil and grease, and COD was increased with increasing current density up to 25 $mAcm^{-2}$. This is because when high current was supplied to the EC cell, a large amount of monomeric and polymeric species were produced according to Faraday's law, leading to the decrease of pollutants in the wastewater to be treated. Faraday's law can be explained as follows [19]:

$$\mathrm{ELC} = \frac{i t_{\mathrm{EC}} M_w}{z \mathrm{Fv}} \tag{11}$$

where t_{EC}(s) is the operating time, z is the number of electrons involved in oxidation/reduction reaction, M_w is the atomic weight of anode material, F is Faraday's constant (96,485 C/mol) and v is the volume (m^3) of the wastewater in the EC reactor. However, it is noticed that increasing current density increases the EEC throughout the experiment due to the consumption of higher voltage during the EC process.

3.5. Effect of NaCl dose

NaCl dose is one of the crucial parameter in EC process to treat tannery industry wastewater. In order to investigate the effect of NaCl dose on the treatment efficiency, various NaCl doses were investigated and results are shown in Fig. 5((a)–(d)). It can be seen from results that the percentage of removal efficiencies increases with an increase in the NaCl dose up to 1,000 mg l^{-1}. This can be explained that

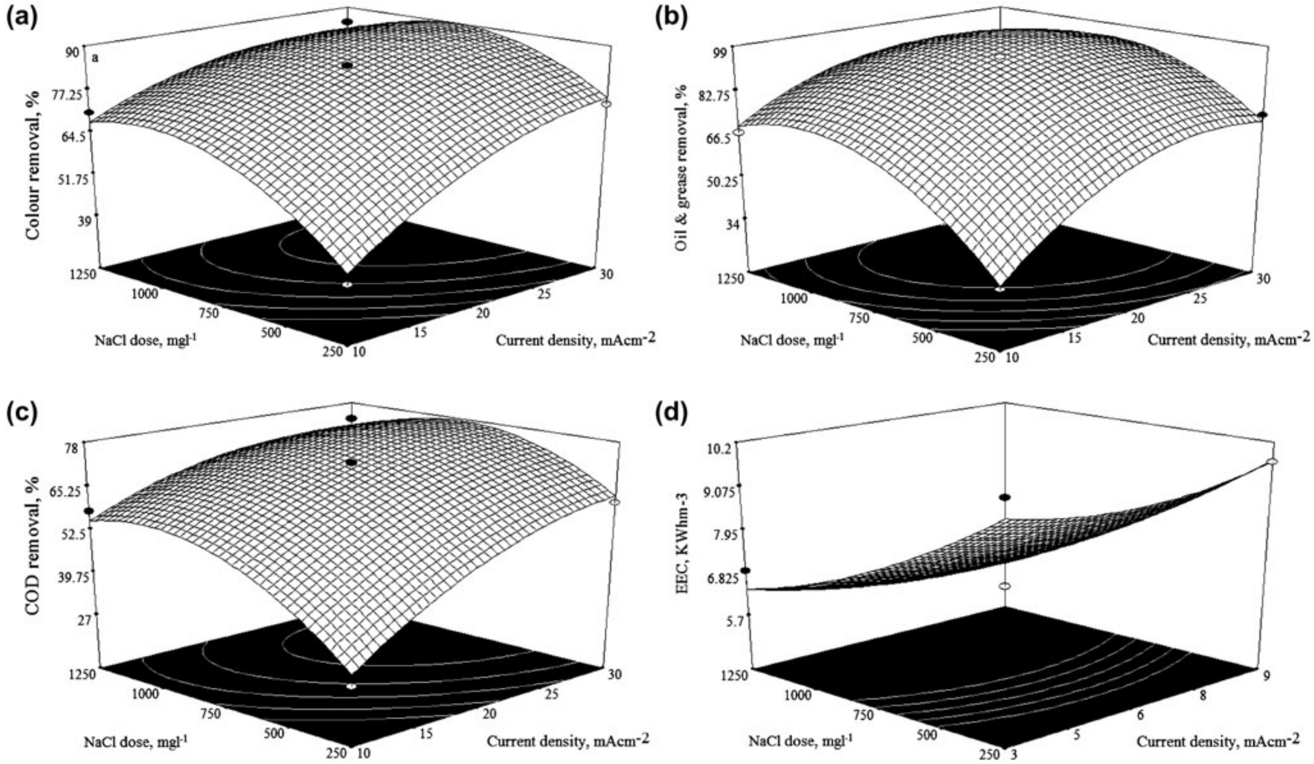

Fig. 5. Effect of pH and electrolysis time on EC treatment efficiency. (a) Colour removal, (b) oil and grease removal, (c) COD removal and (d) EEC.

addition of NaCl to the wastewater creates the following reactions [20]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{12}$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \tag{13}$$

$$HOCl \rightarrow OCl^- + H^+ \tag{14}$$

As shown in above reactions, the electrochemically generated Cl_2 served as a strong oxidant which could oxidize some organic compounds remaining in the tannery wastewater. Beyond that, NaCl dose shows the negligible effect on the EC process. However, it is found that NaCl dose resulted in the reduction of cell voltages which caused a decrease in EEC from 250 to 1,250 mg l^{-1}.

3.6. Optimization

In order to find out the optimum operating conditions to treat tannery industry wastewater using EC treatment method, simultaneous optimization of the multiple responses was carried out using Derringer's desired function methodology [21,22]. Here, process parameters (A, B, C and D) were selected as within range and responses (Y_1, Y_2 and Y_3) fixed as a maximize and Y_4 fixed as a minimize. Optimal operating conditions as follows: such as pH of 9, electrolysis time of 40 min, current density 20 mAcm^{-2} and sodium chloride (NaCl) dose of 1,016 mg l^{-1}. Under these conditions, 92, 95 and 80% of colour, oil and grease, COD removal, respectively were achieved. The EEC of the present treatment process in optimum condition was found to be 6 KWhm^{-3}. This is validated by conducting additional experiments under the optimal conditions.

4. Conclusions

In this study, BBD was employed to study and optimize the process variables such as pH, electrolysis time, current density and NaCl dose in EC reactor to reduce the colour, oil and grease, and COD from tannery industry wastewater using iron electrodes. Four factors three-level BBD was used to develop the second-order polynomial mathematical models and it was used to construct the 3D response surface plots. Optimum operating conditions were found to be: pH of 9, electrolysis time of 40 min, current density of 20 $mAcm^{-2}$ and NaCl dose of 1,016 $mg\,l^{-1}$. Under these conditions, colour (92%), oil and grease (95%), COD removals (80%) were achieved with EEC of 6 $KWhm^{-3}$. These results indicate that treatment of tannery industry wastewater using EC reactor is an effective pretreatment in terms of removal efficiency and operating cost reduction.

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