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Electrocoagulation Treatment of Petroleum Refinery Wastewater: Optimization through RSM

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ABSTRACT

The optimization of the electrocoagulation process used to accomplish the treatment of a turbid petroleum refinery wastewater has been carried out in this work.The turbidity removal and the operating cost of the process were chosen as the response (dependent) variables whilethe current density, the initial wastewater conductivity, the initial pH and the electrolysis time were selected as the input (independent) variables. A set of 30 experimental runs were designed using Central Composite Design of Response Surface Methodology. The designed experiments were run in the experimental setup of the process from where the data used for model development were obtained. The developed models were, thereafter, analyzed and optimized to obtain the optimum values of the electrocoagulation system. The results obtained revealed that the turbidity removal and the operating cost were largely affected by the current density and the electrolysis time. Also, the analyses of variance (ANOVA) of the models showed that the developed models for the turbidity removal and the operating cost were significant with p-values of 0.0003 and less than 0.0001, respectively. In addition, the estimated optimum conditions of the treatment system were 9.9 mA/cm^2, 5 mS/cm, 9 and 18 min for the current density, the conductivity, the pH and the electrolysis time, respectively. Using the estimated optimum values to run the experimental system, 96.94% of turbidity and 78.77% of chemical oxygen demand (COD) removals were achieved at the operating cost of 0.654 US$/m^3.

Keywords: Electrocoagulation, Petroleum refinery wastewater, Optimization, Response Surface Methodology (RSM), Central Composite Design, ANOVA.

1. INTRODUCTION

Petroleum refinery generates significant volume of wastewater that are in the range of 0.4-1.6 times the amount of the crude oil processed (Coelho et al., 2006). Petroleum refinery wastewater is characterized by high concentrations of aliphatic and aromatic hydrocarbons, which usually have detrimental and harmful effects on plant, aquatic life as well as surface and ground water sources (El-Naas et al., 2009). Prior to biological treatments, petroleum refinery wastewater is usually treated using physicochemical and mechanical methods. Physicochemical process, such as coagulation, generates large amount of sludge. The sludge treatment cost can increase the total cost of the wastewater treatment. Biological method, on the other hand, cannot efficiently treat wastewater containing non-biodegradable pollutants. Also, mechanical method may require additional maintenance and operation costs.

Electrocoagulation is a wastewater treatment method that is based on electrolytic generation of coagulant in aqueous medium. The commonly used electrodes for the process are usually made up of aluminum and iron. The use of titanium (Chen and Deng, 2012) and stainless steel (Olmez, 2009) electrodes have also been reported. The main three steps involved in this process are: (1) electrolytic oxidation of anode electrode - on passage of electric current, metallic anode dissolves to form metallic ions (e.g., Al^{3+}) with simultaneous production of hydroxyl ion (OH^-) at the cathode; (2) formation of coagulant (e.g., aluminum hydroxide) from reaction between metallic ion and hydroxyl ion; (3) destabilization of pollutants which occurs through the adsorption of the pollutants on the surface of coagulant or by oxidation.

The advantage of this method include high treatment efficiency, requirement of simple equipment and ease of operation. Moreover, it can be carried out without addition of any chemical. Thus, the amount of sludge generated by this process is usually lower than that generated by chemical coagulation.

This method has been used to treat a wide variety of wastewaters including paper mill wastewater (Katal and Pahlavanzadeh, 2011), synthetic diary effluents (Tchamango et al., 2010), black liquor from paper industry (Zaied and Bellakhal, 2009). However, the efficiency of electrocoagulation process depends on factors such as current density, electrolysis time, initial pH of the wastewater, conductivity of the solution or supporting electrolyte concentration, pollutant initial concentration and temperature.

Conventionally, the efficiency of a multi variable dependent process is studied by varying one factor at a time while other factors are kept constant. This method normally ignores the interactions occurring among the factors. Thus, it may not actually give the best conditions that givethe optimum efficiency of the process under investigation. Consequently, Response Surface Methodology (RSM) has been discovered as an effective statistical method of optimizing a process using designs such as Central Composite Design (CCD), Box-Behnken design and D-optimal design. Response Surface Methodology, apart from revealing the true optimum conditions with minimal number of experiments compared to the conventional method, gives the mathematical model(s) defining the relationships between the response(s) and the factors.

Therefore, in this work, using Central Composite Design, Response Surface Methodology has been applied to optimize the electrocoagulation process used to treat a petroleum refinery wastewater. In order to achieve the aim of this work, the turbidity removal efficiency and the operating cost of the treatment were taken as the responses of the system while the four chosen independent variables were the current density, the conductivity, the pH and the electrolysis time.

2. MATERIALS AND METHOD

The electrocoagulation experiments of this work were carried out in batch mode using four aluminum electrodes contained in a plexi glass made reactor having a capacity of 1.5 L, as shown in Figure 1. The 45mm x 60mm x 3mm plates having total effective area of 96 cm^2 were placed vertically in the reactor at a distance of 1.5 cm apart. Before and after each experimental run, the electrodes were thoroughly rinsed with distilled water to remove clingy impurities from their surfaces. To ensure uniform concentration of the solution in the reactor, the solution was gently stirred using a laboratory stirrer (MTOPS, MS-3020). Conductivity and pH of the solution were measured using conductivity and pH meter (Mettler Toledo M200 easy), respectively. The pH and the conductivity adjustments were also done respectively by adding H_2SO_4/NaOH (0.5 M) and NaCl. During the treatment,the temperature of the wastewater was controlled by circulating cold water round the reactor using a refrigerated and heated circulation bath (Hoefer RCB20-PLUS). Thus, all the experiments were carried out at room temperature.

For each experimental run 1 L of petroleum refinery wastewater was used. The measured characteristics of the wastewater are given in Table 1. The experimental conditions for each run are also given in the design matrix contained in Table 3. The turbidity of the wastewater was measured using a water analysis system (Orbeco-Hellige, Model 975-MP) and its chemical oxygen demand (COD) was analyzed using open reflux method (standard method 5220 B).

Shown in Equation (1) is the expression used to estimatethe turbidity and the COD removal efficiencies of the treatment.The treatment operating cost (OC, US $/m^3$) for each experimental run was also calculated using Equation (2).

$$Y(\%) = \frac{(C_o - C_t)}{C_o} \times 100 \qquad (1)$$

$$OC = aC_{energy} + bC_{electrode} \qquad (2)$$

In Equation (1) above, Y, C_o and C_t are the pollutant removal efficiency, the initial concentration and the concentration at a specific time t. Also, in Equation (2), C_{energy} (kWh/m^3) and $C_{electrode}$ (kg Al/m^3) are the quantities of energy and the electrodes consumed respectively for the treatment. The energy consumption was calculated using Equation (3) and the quantity of Al used was determined by deducting the final weights of the electrodes from their initial weights. Coefficients a

and *b* are the industrial energy and the wholesale electrode prices which were obtainedrespectively to be 0.098064 US$/kWh and 3.9852 US $/kgAl.

$$C_{energy} = \frac{IVt}{v} \qquad (3)$$

In Equation (3) I, V, t and v are the applied current (A), the voltage (V), the time (h) and the volume of the treated wastewater (m^3), respectively.

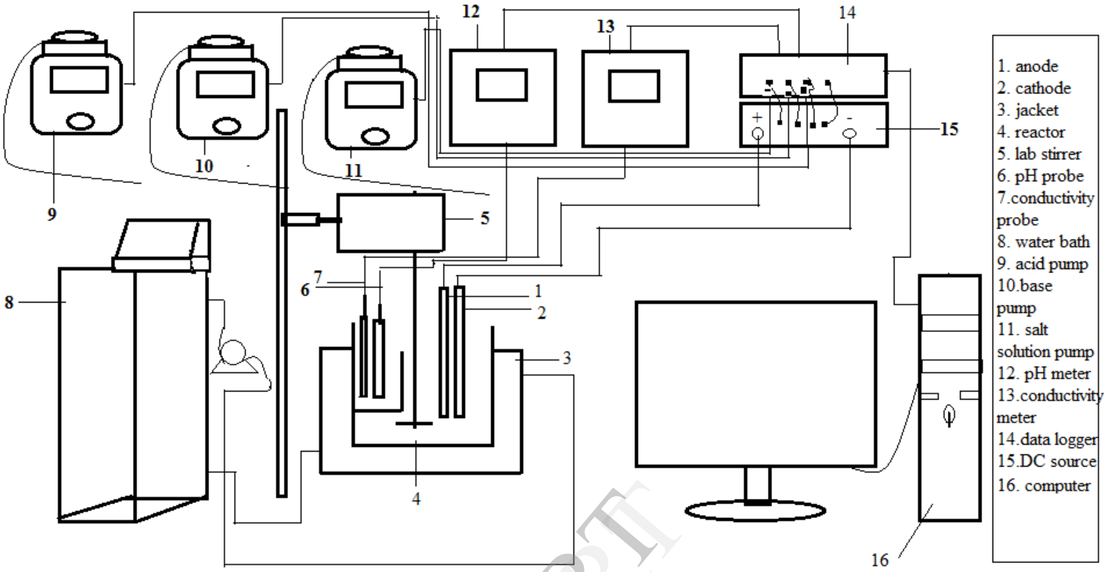


Figure 1. The schematic diagram of the experimental set up

In order to optimize the turbidity removal efficiency of the electrocoagulation system and its operating cost, 30 experimental runs were designed based on Central Composite Design. The experimental matrix comprised16 factorial runs, 6 center point runs and 8 axial runs (see Table 3). The details of the design matrix including the levels used are given in Table 2.

The experimental data were analyzed using a reduced quadratic polynomial model and the regression coefficients were obtained. The optimization was done using numerical approach. The goal of the optimization was set to finding the operating conditions that would give the maximum turbidity removal efficiency at the minimum operating cost. The experimental design, the statistical analysis and the optimization were accomplished with the aid of Design-Expert 7.0.0.

Table 1. The measured characteristics of the petroleum refinery wastewater

Pollutant parameters	Quantity
Turbidity (FTU)	44.5
COD (mg/L)	130
conductivity (mS/cm)	1.96
pH	7.48

Table 2. The levels of the factor in the design matrix

Actual variable, unit	Factor	levels				
		-α	-1	0	1	+ α
Current density, mA/cm^2	X_1	4.17	7.29	10.42	13.54	16.67
Conductivity, mS/cm	X_2	2	3	4	5	6
pH	X_4	6	7	8	9	10
Electrolysis time, min	X_3	10	15	20	25	30

3. RESULTS AND DISCUSSIONS

3.1 Experimental Findings

The results of the electrocoagulation experiments obtained are given in Table 3. The turbidity removal efficiency and operating cost were found to be affected by the variation of the current density, the conductivity, the pH and the electrolysis time. The center point experiments (conditions: 10.42 mA/cm^2, 4 mS/cm, 9 (pH) and 18 min) gave average turbidity removal of 92.6% with operating cost approximately equal to 1US$/m^3. In the axial experiments, increasing the current density and the electrolysis time caused increase in the turbidity removal efficiency and the operating cost. Increasing the current density by 6.25 mA/cm^2 led to turbidity removal and operating cost of 94.22% and 1.3259 US$/m^3, decreasing by the same amount resulted in turbidity removal and operating cost of 30.11% and 0.4481 US$/m^3, respectively. Also, as seen in Table 3, at the negative and the positive electrolysis time axial experiments, the turbidity removal were 82.83% and 94.54% with operating costs of 0.4886 US$/m^3 and 1.7485 US$/m^3, respectively. Though, axial variation of pH and conductivity had little significant on the responses.

Looking at Table 3, in the factorial experiments, the single effect of all the factors were not very significant but they were found to affect the two responses considered in this work in interactive forms. For instance, at 3 mS/cm, 9 pH and 25 min, when the current density was increased from 7.29 mA/cm^2 to 13.54 mA/cm^2, the turbidity removal decreased from 98.36% to 79.21%. However, at this conditions, the operating cost increased from 0.9135 US$/m^3 to 1.4859 US$/m^3. Also, when the current density and the electrolysis time were simultaneously varied in such a way that at the maximum current density, the electrolysis time was minimum, the significant effects of these factors were noted on the turbidity removal efficiency and the operating cost. This can be seen clearly in Table 3 by comparing run numbers 16 and 23. Also, the variations of the current density and the pH, and the current density and the conductivity in the same manner led to increase in the turbidity removal and the operating cost. According to the results obtained, one of the factorial experimentscarried out led to maximum turbidity removal efficiency of 98.36% with operating cost of 0.9135 US $/m^3.

Table 3. Experimental design matrix and the petroleum refinery wastewater treatment results

	Factors				Responses	
Run	X_1, mA/cm^2	X_2, mS/cm	X_3	X_4, min	T, %	OC, US $/m^3
1	10.42	4	8	20	92.61	0.7780
2	13.54	3	9	25	79.21	1.4859
3	7.29	5	9	25	89.53	1.9019
4	7.29	5	9	15	92.11	0.5908
5	10.42	4	10	20	92.54	0.9394
6	13.54	3	9	15	86.70	0.8144
7	10.42	6	8	20	94.83	0.9250
8	7.29	3	9	15	90.16	0.9693
9	7.29	3	7	25	91.35	0.8434
10	10.42	4	6	20	92.00	1.1698
11	16.67	4	8	20	94.22	1.3259
12	10.42	4	8	20	92.58	1.1514
13	10.42	4	8	10	82.83	0.4886
14	13.54	3	7	25	79.46	2.3947
15	13.54	5	7	25	79.19	1.8683
16	13.54	5	7	15	87.12	1.8534
17	10.42	4	8	20	92.63	1.1606

18	4.17	4	8	20	30.11	0.4881
19	7.29	3	9	25	98.36	0.9135
20	10.42	4	8	30	94.54	1.7485
21	13.54	5	9	25	91.46	1.8527
22	10.42	4	8	20	92.67	0.9657
23	7.29	5	7	25	73.93	1.06402
24	7.29	5	7	15	40.45	0.56288
25	10.42	4	8	20	92.52	0.97767
26	10.42	2	8	20	91.30	1.39421
27	13.54	5	9	15	96.58	0.98259
28	10.42	4	8	20	92.70	1.11715
29	7.29	3	7	15	64.83	0.95358
30	13.54	3	7	15	95.71	1.38424

3.2 Statistical Studies Findings

As seen in the previous section,where the results of the experiments carried with the design of Central Composite Design were presented, it was found that Central Composite Designnormally combines factors in such a way that they are easily understood by the experimenter. Thus, it enhances easy study of both the single and the interactive effects of the factors on the chosen response(s) after the experiments by merely looking at the table containing the design matrix and the results, even before any statistical analysis. This seems to be one of thesignificant advantages ofthis experimental design methodology (Central Composite Design).

The reduced quadratic model obtained for the turbidity removal and the operating cost are given in Equations (1) and (2), respectively. Results of the analysis of variance (ANOVA) showed that these models were significant with p-values of 0.0003 (see Table4) and less than 0.0001 (see Table 5), respectively. The high R-square values of the models confirm their agreements with the experimental data.

For the turbidity removal, the significant model terms were found to be X_1, X_3, X_1X_3, X_1X_4 and X_1^2. This revealed thatthe turbidity removal data predicted by the models were affected by single variation of current density, pH, interactively affected by combination of current density and pH, current density and electrolysis time as well as by the quadratic term of the current density. The contour plots given in Figures 2(b) and 3(b) revealed that simultaneous increase in current density and pH or electrolysis time led to increase in turbidity removal. As seen in the 3D surface graphs of the results, the maximum turbidity removal efficiency was achieved within the design points by varying the current density and the pH (Figure 2(a)) and the current density and the electrolysis time (Figure 3(a)).

Similarly, the significant model terms for the operating cost model were obtained to be X_1, X_4 and X_1X_3. This impliedthat the operating cost was singly affected by the current density and the electrolysis time, and interactively influenced by the current density and the pH. It was also discovered from the contour plot shown in Figure 4(b) that the pH of the wastewater affected the operating cost almost in parabolic manner with increase in the current density. It was then noted that the effect to current density over weighted that of the pH because the graph moved rightward more. The 3D surface plot of the results of the operating cost model also revealed that the minimum operating cost was within the design points.

$$\begin{aligned} T = {} & -99.82521 + 35.75256X_1 - 48.75449X_2 + 6.38474X_3 + 4.35887X_4 \\ & + 1.2391X_1X_2 - 1.74247X_1X_3 - 0.40962X_1X_4 + 4.11938X_2X_3 \\ & + 0.085674X_2X_4 - 0.77473X_1^2 \end{aligned} \qquad (1)$$

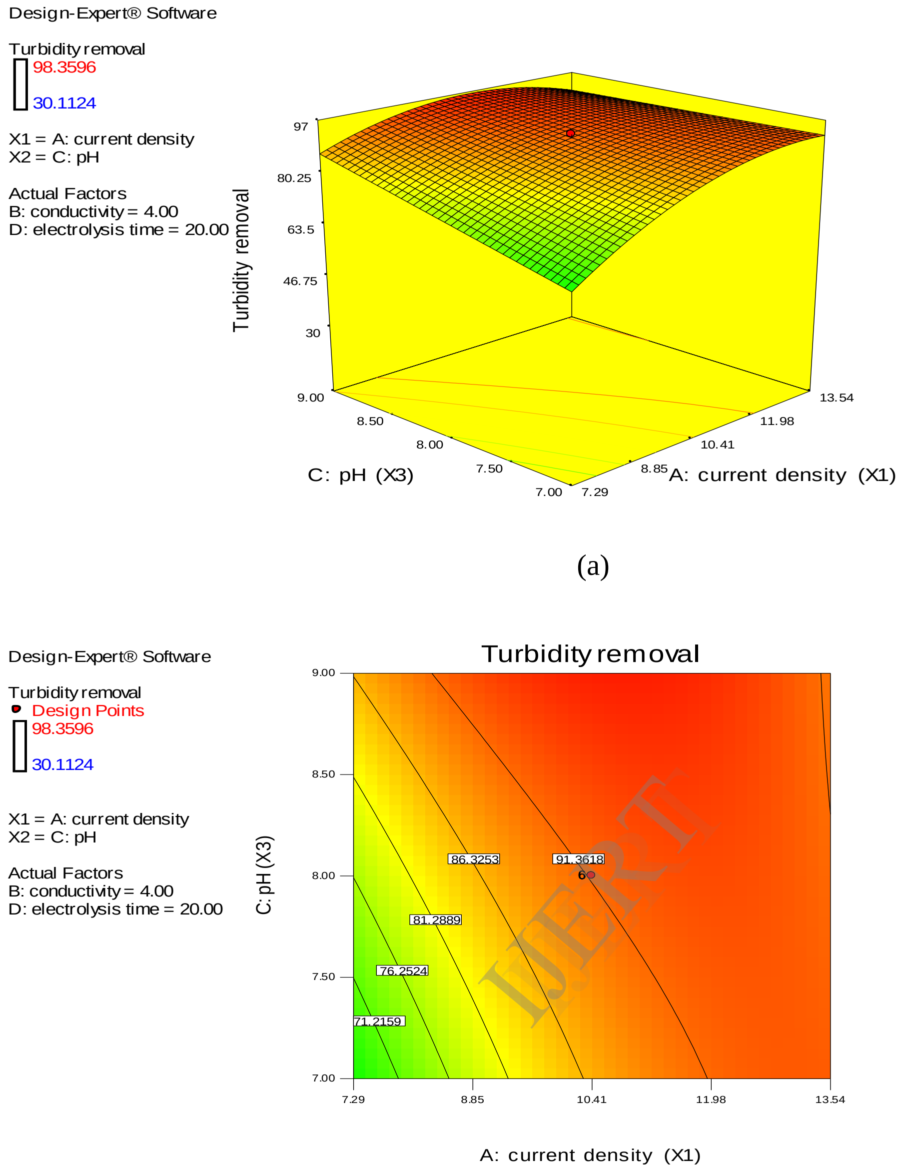
$$C_2 = -3.14056 + 0.64422X_1 - 0.68707X_2 + 0.26964X_3 + 0.056109X_4 - 0.066331X_1X_3 + 0.085776X_2X_3 - 0.0012837X_1^2 \quad (2)$$

Table 4. Results of analysis of variance (ANOVA) for turbidity removal model

Source	Sum of squares	Degree of freedom	Mean square	f-value	P-value
Model	5367.81	10	536.78	6.24	0.0003
X_1	1394.52	1	1394.52	16.2	0.0007
X_2	33.46	1	33.46	0.39	0.5404
X_3	533.42	1	533.42	6.2	0.0222
X_4	113.74	1	113.74	1.32	0.2646
X_1X_2	239.9	1	239.9	2.79	0.1114
X_1X_3	474.41	1	474.41	5.51	0.0299
X_1X_4	655.42	1	655.42	7.61	0.0125
X_2X_3	271.51	1	271.51	3.15	0.0918
X_2X_4	2.94	1	2.94	0.034	0.8554
X_1^2	1648.51	1	1648.51	19.15	0.0003
Residual	1635.7	19	86.09		
Lack of fit	1635.67	14	116.83	27874.73	< 0.0001
Pure error	0.021	5	0.00419		
Total cor.	7003.51	29			
R-squared= 0.7664 Adj R-squared = 0.6435					

Table 5. Results of analysis of variance (ANOVA) for operating cost model

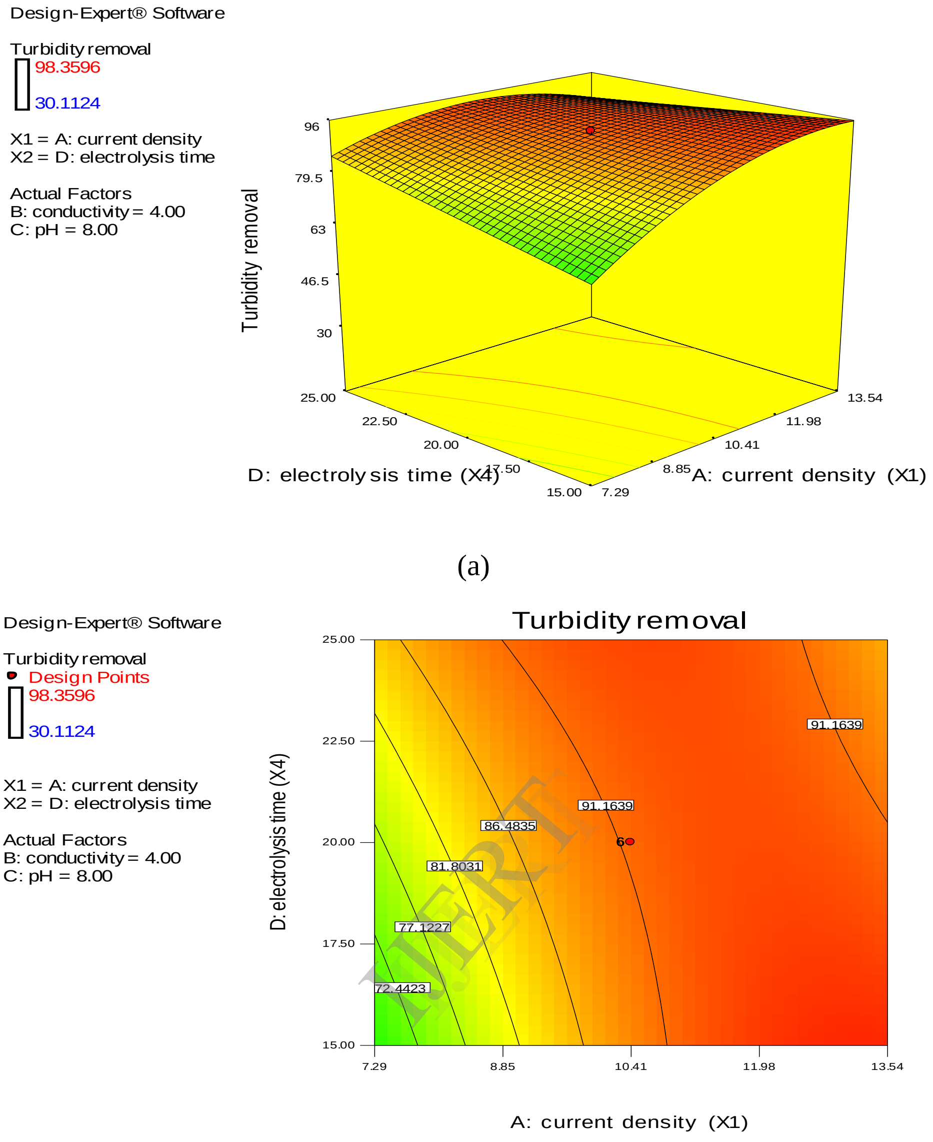
Source	Sum of squares	Degree of freedom	Mean square	F- value	p-value
Model	4.61	7	0.66	7.99	< 0.0001
X_1	1.77	1	1.77	21.44	0.0001
X_2	1.79E-05	1	1.79E-05	2.18E-04	0.9884
X_3	0.15	1	0.15	1.78	0.1963
X_4	1.89	1	1.89	22.91	< 0.0001
X_1X_3	0.69	1	0.69	8.34	0.0085
X_2X_3	0.12	1	0.12	1.43	0.2448
X_1^2	4.53E-03	1	4.53E-03	0.055	0.8169
residual	1.81	22	0.082		
Lack of fit	1.7	17	0.1	4.57	0.0504
Pure error	0.11	5	0.022		
Totalcor.	6.43	29			
R-squared = 0.7178 Adj R-squared = 0.6280					



(a)

(b)

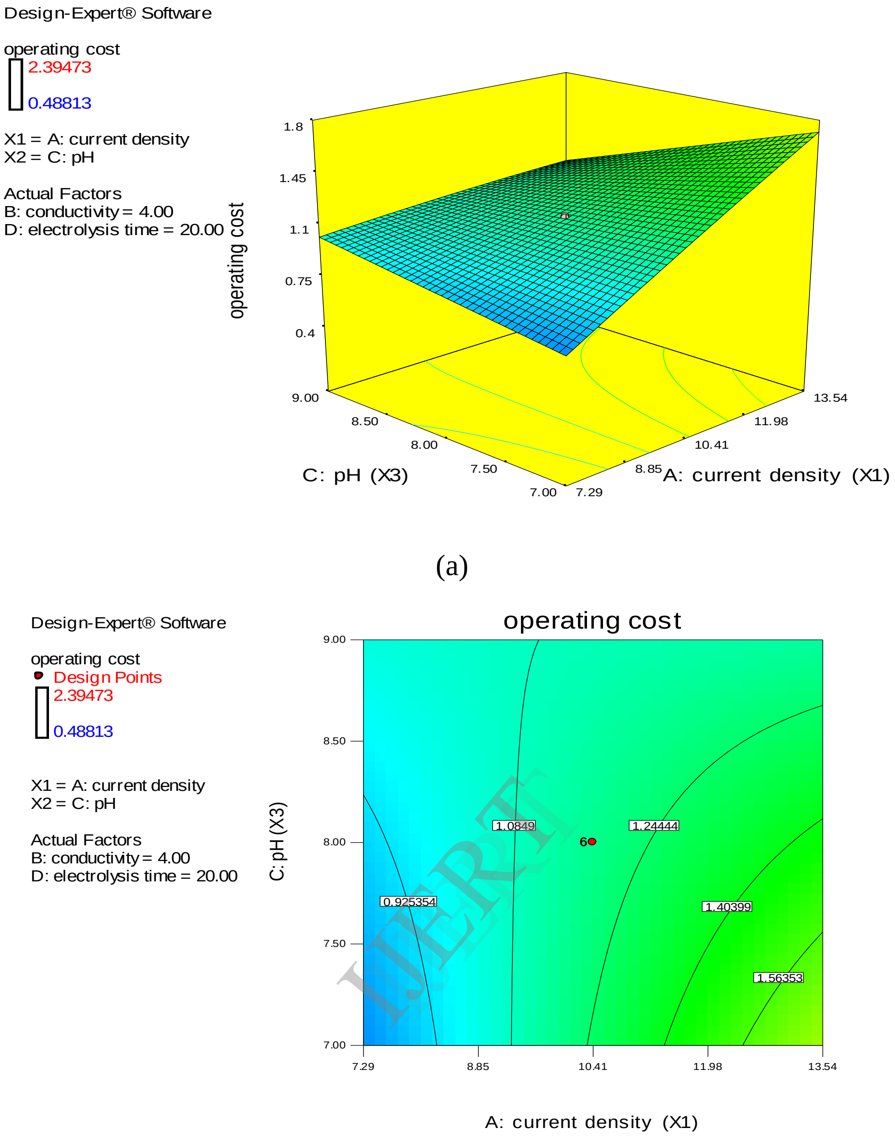
Figure 2. The 3D surface graph (a) and contour plot (b) for interactive effect of current density and pH on turbidity removal



(a)

(b)

Figure 3. The 3D surface graph (a) and contour plot (b) for interactive effect of current density and electrolysis time on turbidity removal



(a)

(b)

Figure 4. The 3D surface graph (a) and contour plot (b) for interactive effect of current density and pH on operating cost

From the numerical optimization that was carried out, 9.9 mA/ cm^2, 5 mS/cm, 9 (pH) and 18 min were estimated as the optimum conditions. Under these conditions, the predicted maximum turbidity removal was found to be 96.50% and the minimum operating cost to achieve this was also calculated to be 1.0627 US\$/m^3. The optimization resultsobtained were validated experimentally by using the obtained optimum input parameters to run the experimental setup and it was discovered from the validation experiment carried out that the optimum conditions of 96.94% turbidity and 78.77% COD removals were achieved at the operating cost of 0.654 US\$/m^3.

4. CONCLUSIONS

From the results obtained in this work,it has been discovered that Central Composite Design of Response Surface Methodology has been successfully applied to the electrocoagulation process used for the treatment of a petroleum refinery wastewater. The turbidity removal and the operating cost were found to be largely affected by the current density and the electrolysis time. Also, the initial pH of the wastewater was found to influence the system responses (the turbidity removal and the operating cost) significantly. The results of the ANOVA carried out showed that the turbidity removal and the operating cost models were significant with p-values of 0.0003 and less than 0.0001, respectively. In addition, good correlation coefficients of 0.76 and 0.72 were obtained respectively for the turbidity removal and the operating cost models. The optimum conditions of the treatment were obtained to be 9.9 mA/cm^2, 5 mS/cm, 9 and 18 min for the current density, the conductivity, the pH and the electrolysis time, respectively. Under these conditions, 96.94% of turbidity and 78.77% of chemical oxygen demand (COD) removals were achieved experimentally at the operating cost of 0.654 US\$/m^3.

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