Optimization of Turbidity Removal from Petrochemical Wastewater by Electrocoagulation Using Response Surface Methodology

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ABSTRACT

Electrocoagulation is a variant of conventional chemical coagulation which its high efficiency can be achieved if appropriate operating conditions are chosen. Thus, RSM becomes a very useful statistical tool through which the optimum performance of such system can be achieved. The aim of this study was to optimize the turbidity removal efficiency of an electrocoagulation process and its operating cost using response surface methodology (RSM). To achieve this, 20 experimental runs were developed according to central composite design and analyzed with the aid of a software package (Design Expert 7.0.0). The results of the experiments showed that the treatment process and its operating cost were dependent on current density, electrolyte concentration and electrolysis time. Analysis of variance (ANOVA) showed squared correlation coefficients (R^2) of 0.9638 and 0.9958 for turbidity removal efficiency and operating cost respectively. This implies that the experimental data correlated very well with the quadratic model chosen for the analysis. At the obtained optimum conditions of 18.17 mA/cm^2, 1.25 g/l and 27.50min, the maximum turbidity removal efficiency of the process was found to be 96.8% and the operating cost of the treatment under the same conditions was 2.6 US$/m^3.

Key words: Response surface methodology; electrocoagulation; petrochemical wastewater treatment.

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INTRODUCTION

Petrochemical industry can be considered as one of the most important industries which were exposed to a great development due to increasing demand for petrochemical products during the last years (Mirbagheri et al., 2010). However, extensive use of these products leads to pollution of almost all environmental resources (Shokrollahzadeh et al., 2008). Wastewater of some petrochemical plants contains groups of organic compounds which are listed as priority pollutants due to their potential harm to both humans and the environment as a whole. Some of these compounds are carcinogenic in nature (Sponza and Oztekin 2010; Verma et al., 2010). Besides, Petrochemical wastewater has characteristics of large water volume and poor biodegradability (Zhang et al., 2011). Treating such wastewater for reuse purpose by using efficient technology can minimize environmental pollution and industrial demand for fresh water. Biological method is one of the means widely used for the treatment of industrial wastewater. But, the process cannot effectively treat petrochemical wastewater containing non-biodegradable pollutants. Chemical method, on the other hand, produces large amount of sludge.

Electrocoagulation (EC) is a simple, efficient and promising method in which the flocculating agent is generated in situ from electro-oxidation of sacrificial anode electrodes, usually made up of iron or aluminum (Gomes et al., 2007, Holt et al., 2005). Anodic

dissolution occurs simultaneously with hydrolysis of water. Metallic ions react with hydroxyl ions in water through series of intermediates to form active metallic oxide which destabilize pollutants present in the water. The destabilized particles then aggregate to form flocs. Hydrogen bubbles produced from the reduction of hydrogen ions at the cathode can float some portion of the flocculated pollutants to the surface. But, this depends on the operating conditions of the reactor and the pollutant (Holt et al., 2005). Recently, electrocoagulation (EC) has received considerable attention for treatment of wastewater from various industrial processes. A removal efficiency as high as 99% through EC has been reported for treatments of arsenic (Wan et al., 2011), iron containing water (Ghosh et al., 2008) and manganese solution (Shafaei et al., 2010). Also, Tchamango et al. (2010) reported complete turbidity removal from diary wastewater using the same process. Another importance of electrocoagulation is that the small amount of sludge produced (Sayiner et al., 2008) by the process is readily settleable and the supernatant contains less total dissolved solids compared to chemical coagulation (Golder et al., 2007). However, the efficiency of this process depends on factors such as current density, initial pH, temperature, conductivity, pollutant concentration and electrolysis time. Therefore, optimization of the process is very necessary.

Conventionally, multifactor processes are optimized by varying a single factor while keeping all other factors fixed at a specific set of conditions. This method is not only time consuming but also incapable of reaching the true optimum because it ignores the interactions among the variables (Tir and Moulai-Mostefa, 2008).These limitations can be eliminated by using a statistical optimization approach. One of these approaches is "response surface methodology (RSM)". RSM is a collection of effective statistical technologies used to optimize a multifactor dependent system by making use of statistically designed experiments. It also gives the mathematical relationship between the specified dependent variables (responses) and independent variables (factors), and evaluates their relative significance and interactions (Behbahani et al., 2011).

In this work, optimization of turbidity removal from petrochemical wastewater by electrocoagulation is presented. A three factorial central composite design was employed to generate the experimental runs used to model and optimize the process. The responses of the system were turbidity removal efficiency and operating cost, and the three dependent variables were current density, supporting electrolyte (NaCl) and electrocoagulation time. These factors were chosen to evaluate the efficiency of the electrocoagulation due to their more significant influences (compared to other factors) on the process (El-Naas, 2009).

MATERIALS AND METHODS

The experiments were carried out in a batch reactor with three aluminum electrodes connected in monopolar mode to a D.C power source. The 45 mm x 53 mm x 3 mm plates having total effective area of 56.7 cm^2 were placed vertically in the reactor at a distance of 1.5 cm apart. Prior to each experimental run, the electrodes were thoroughly cleaned and then rinsed with distilled water to remove impurities from their surfaces. During the experiment, the solution was stirred using a magnetic stirrer (Chiltern Hotplate Magnetic Stirrer HS31). Temperature and conductivity were measured using a conductivity sensor (Mettler Toledo M200 easy). Turbidity was measured using water analysis system (Orbeco-Hellige Model 975-MP). The set-up for the experiment is given in Figure 1. For each experiment, 1 liter of wastewater was used. The characteristics of the real petrochemical wastewater are given in Table 1. The experiments were carried out according to the operating conditions given in the design matrix (Table 3). The pH of the wastewater was not adjusted. Turbidity removal efficiency was calculated using Equation (1) below:

$$T(\%) = \frac{(C_o - C_t)}{C_o} \times 100 \quad (1)$$

Table1. Characteristics of the wastewater

Turbidity, FTU	pH	Conductivity, mS/cm	Temperature (^oC)
208	10.92	6.21	19

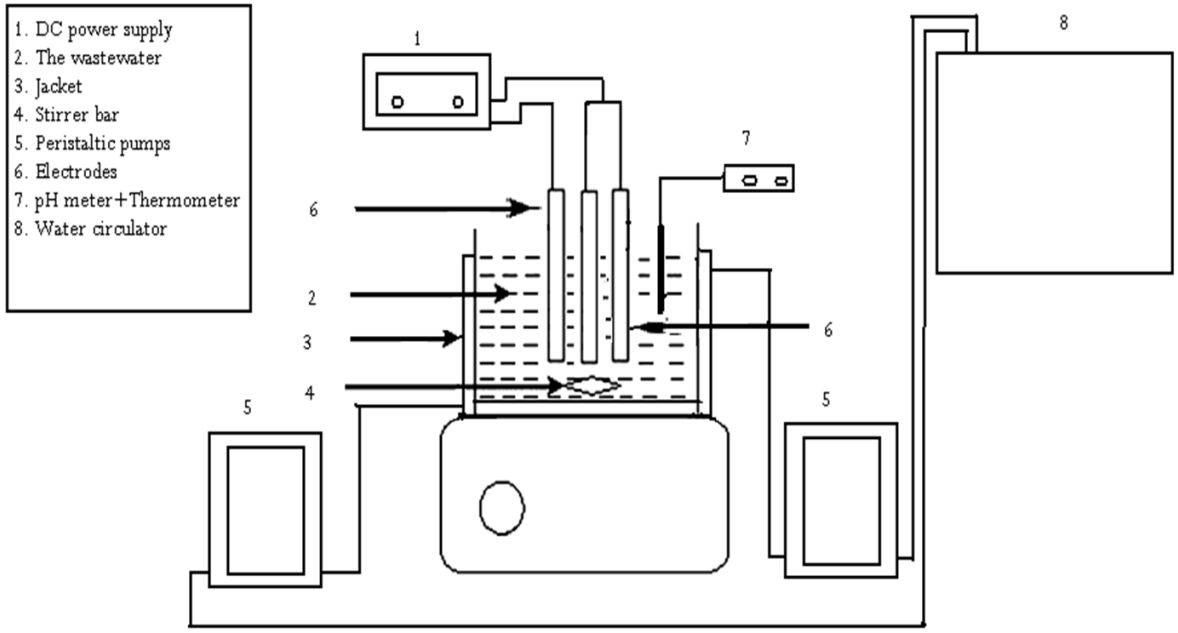


Figure 1. The experimental setup for the batch electrocoagulation process

The operating cost (US \$/m^3) for each experimental run was calculated using Equation (2).

$$Operating\ cost = aC_{energy} + bC_{electrode} \quad (2)$$

whereC_{energy} (kWh/m^3) and $C_{electrode}$ (kg Al/m^3) are the quantities of energy and electrodes consumed for the treatment respectively. Energy consumption was calculated using Equation (3) and the quantity of Al used was determined by deducting the final weight of the electrodes from the initial weight of the electrodes. Coefficients *a* and *b* are the industrial energy and wholesale electrode prices which were found to be 0.09355 US\$/kWh 0.875 US\$/kgAl respectively.

$$C_{energy} = current \times voltage \times time \quad (3)$$

A total of 20 experimental runs were carried out according to a 2^3 full factorial central composite design. These consisted of 8 factorial experiments, 6 axial experiments and 6 center point experiments. The design and analysis of the experimental data were done using Design-Expert 7.0.0. The real values of the coded factors in the design matrix are given in Table 2. The experimental results were fitted to a quadratic polynomial model given in Equation (4) and the regression coefficients were obtained with the aid of Design-Expert 7.0.0.

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i x_i \sum_{i,j=1}^{3} \beta_{ij} x_{ij} + \sum_{i=1}^{3} \beta_{ii} x_i^2 \quad (4)$$

where β_o , β_i, β_{ii} and β_{ij} are the regression coefficients for intercept, linear, squared and interaction terms respectively. Y is the response and x is the dependent variable.

Table 2. The real values of coded factors in the design matrix

Actual factor, unit	**Real values of factors**				
	-1.8618	-1	0	1	1.8618
Current density (x_1), mA/cm^2	6.005	10.935	18.166	25.397	30.327
NaCl concentration (x_2), g/l	0.5	0.8	1.25	1.7	2
Electrolysis time (x_3), min	10	17.09	27.5	37.9	45

The statistical significances of the models were evaluated using the results of analysis of variance. In case of optimization, a numerical approach in which targets were chosen for the output variables was used. The goal of optimizing the turbidity removal efficiency was to find the condition at which its value would be maximal. Also, the operating cost was optimized to find the cost in the lower and upper limit corresponding to the targeted factors. The targets for current density, NaCl concentration and electrolysis time were 18.17 m A/cm^2, 1.25 g/l and 27.50 min respectively.

RESULTS AND DISCUSSIONS

The experimental design matrix, the values of turbidity removal efficiency and operating cost obtained from each experiment and their values predicted by the models are given in Table 3. The second order model obtained for turbidity removal (Y_1) and operating cost (Y_2) are given in equations (5) and (6). Results of ANOVA showed that the models were highly significant with low p-value of 0.0001 and high f-value of 53. 02 and 238.35 for turbidity removal efficiency and operating cost respectively. Since the p-values were less than 0.05, it was discovered that the developed models were statistically significant. Base on this, the significant model terms for turbidity removal were x_1, x_2, x_3, x_1x_3, x_1^2, x_2^2 and x_3^2 (Table 5) and that of operating cost were x_1, x_2, x_3 and x_1x_3 (Table 6). Also, for the models, the squared of the correlation coefficient (R^2) values were very close to 1 and R^2_{adj} was in reasonable agreement with and R^2_{pred} (see Table 4). The high correlations of the models were also evident in the prediction of the responses in which case that the experimental results and the model (predicted) results were in good agreement (Table 3).

$$Y_1 = -66.0902 + 5.6765x_1 + 49.4551x_2 + 3.9112x_3 - 0.3531x_1x_2 + \cdots \\ \cdots - 0.03557x_1x_3 + 0.1053x_2x_3 - 0.09050x_1^2 - 14.9056x_2^2 - 0.04534x_3^2 \quad (5)$$

$$Y_2 = -1.624 + 0.01649x_1 1.7666x_2 - 5.0368E-004x_3 - 0.03508x_1x_2 + \cdots \\ + 7.8230E-003x_1x_3 - 0.02018x_2x_3 + 4.6074E-004x_1^2 + \cdots \\ \cdots - 0.3446x_2^2 - 3.6363E-004x_3^2 \quad (6)$$

Table 3. The experimental design matrix for turbidity removal efficiency and operating cost

Run No.	Current density (x_1)	NaCl concentration (x_2)	Electrolysis time (x_3)	Turbidity removal (%)		Operating cost, US$/m^3	
				Actual	Predicted	Actual	Predicted
1	0	0	0	94.21	96.60	2.60	2.60
2	-1	1	1	96.16	94.53	1.22	1.33
3	1	-1	-1	80.00	82.01	2.62	2.54
4	0	0	0	97.79	96.60	2.67	2.60
5	-1	-1	1	83.65	83.54	1.58	1.55
6	0	0	0	98.19	96.60	2.69	2.60
7	-1	-1	-1	63.00	60.37	0.32	0.54
8	1	1	-1	86.00	86.49	2.18	2.25
9	0	0	0	97.76	96.60	2.59	2.60
10	1	-1	1	95.50	94.48	5.90	5.91
11	1	1	1	97.90	100.91	5.41	5.24
12	-1	1	-1	68.00	69.41	0.66	0.69
13	0	0	1.8618	99.00	99.03	4.19	4.25
14	-1.8618	0	0	70.00	71.94	0.44	0.26
15	0	0	0	96.31	97.14	2.62	2.68
16	0	-1.8618	0	81.00	82.22	2.75	2.70
17	0	1.8618	0	97.00	95.23	2.27	2.27
18	0	0	-1.8618	68.00	67.42	1.00	0.88
19	0	0	0	96.32	97.14	2.56	2.68
20	1.8618	0	0	98.00	95.51	5.11	5.23

Table 4. Analysis of variance for turbidity removal and efficiency and operating cost

Response	Source	Sum ofsquares	Degree of freedom	Mean squares	f-value	p-value
Y_1	Model	2825	9	313.95	53.05	<0.0001
	Residual	53.25	9	5.92		
	Lack of fit	42.86	2	8.57	3.3	0.1335
	Pure error	10.4	4	2.6		
	Total	2878.83	19			
	R^2=0.9815					
	Adj. R^2=0.9638					
	Pred. R^2=0.8338					
Y_2	Model	46.88	9	5.21	238.35	<0.0001
	Residual	0.20	9	0.022		
	Lack of fit	0.19	5	0.038	17.62	0.0079
	Pure error	8.541E-003	4	2.135E-003		

	Total	47.11	19			
	R^2=0.9958					
	Adj. R^2=0.9916					
	Pred. R^2=0.9609					

Table 5. ANOVA results for turbidity removal efficiency model terms

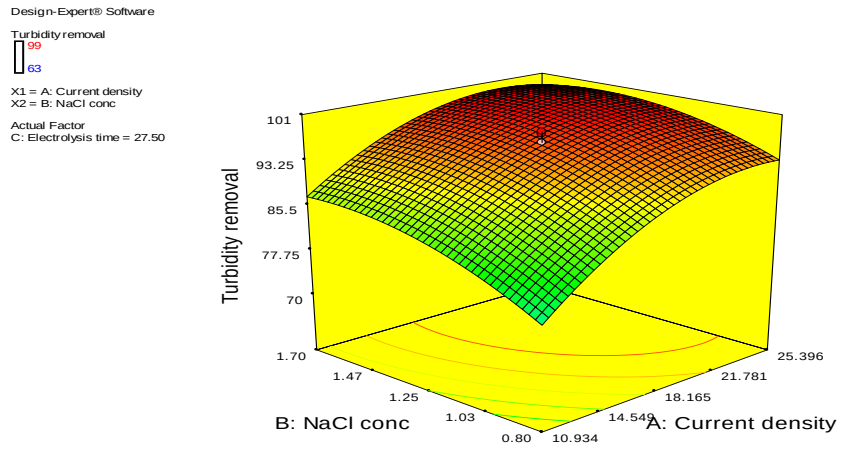
Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	2825.56	9	313.95	53.05	< 0.0001
x_1-Current density	670.34	1	670.34	113.27	< 0.0001
x_2-NaCl concentration	204.28	1	204.28	34.52	0.0002
x_3-Electrolysis time	1206.18	1	1206.18	203.81	< 0.0001
x_1x_2	10.37	1	10.37	1.75	0.2181
x_1x_3	57.30	1	57.30	9.68	0.0125
x_2x_3	1.91	1	1.91	0.32	0.5838
x_1^2	323.63	1	323.63	54.68	< 0.0001
x_2^2	127.27	1	127.27	21.51	0.0012
x_3^2	348.22	1	348.22	58.84	< 0.0001

Table 6. ANOVA results for operating cost model terms

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	46.8800	9	5.2100	238.35	< 0.0001
x_1-Current density	29.8700	1	29.8700	1366.78	< 0.0001
x_2-NaCl concentration	0.2200	1	0.2200	10.25	0.0108
x_3-Electrolysis time	13.7400	1	13.7400	628.7	< 0.0001
x_1x_2	0.1000	1	0.1000	4.68	0.0586
x_1x_3	2.7700	1	2.7700	126.84	< 0.0001
x_2x_3	0.0700	1	0.0700	3.21	0.1068
x_1^2	0.0074	1	0.0074	0.34	0.574
x_2^2	0.0700	1	0.0700	3.22	0.1063
x_3^2	0.0240	1	0.0240	1.09	0.323

Numerical optimization results revealed that 18.166 mA/cm^2, 1.25 g/l and 27.5 min were the optimum conditions for the removal of turbidity from the petrochemical wastewater. Under these conditions, the turbidity removal efficiency and operating cost were 96.8% and 2.6 US$/m^3 respectively. Figures 2, 3, 4 show the 3D surface graphs and contour plots for turbidity removal efficiency while Figures 5, 6 and 7 show the 3D surface graphs and contour plots for operating cost. Looking at Figures 2, 3 and 4, it can been seen that the turbidity removal efficiency obtained at the optimum conditions was very close to the maximum removal efficiency obtained at 18.17 mA/cm^2, 1.25 g/l and 45 min. Moreover, as illustrated in Figures 3a and 3b, turbidity removal efficiency increased with increase in current density and electrolysis time, though it was also affected by NaCl concentration but its effect was not very significant compared to that of current density and electrolysis time (Figures 2 and 4).

Operating cost was also affected by operating conditions in a similar manner (Figures 5-7). The minimum operating cost of 0.32 US$/$m^3$ was obtained at 10.94 mA/cm^2 current density, 0.8 g/lNaCl concentration and 17.09 min electrolysis time. At this point, the turbidity removal was 63 %. The optimum operating cost was discovered to be far less than the maximum operating cost obtained at 25.397 mA/cm^2, 0.8 g/l and 37.9 min.



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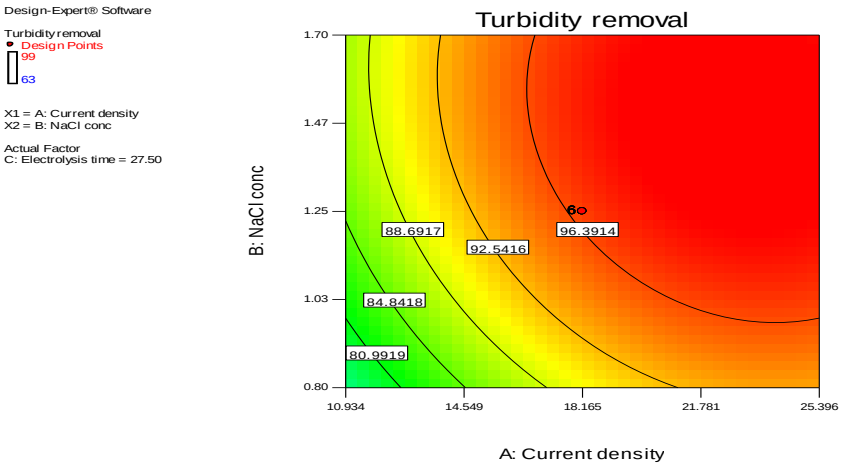
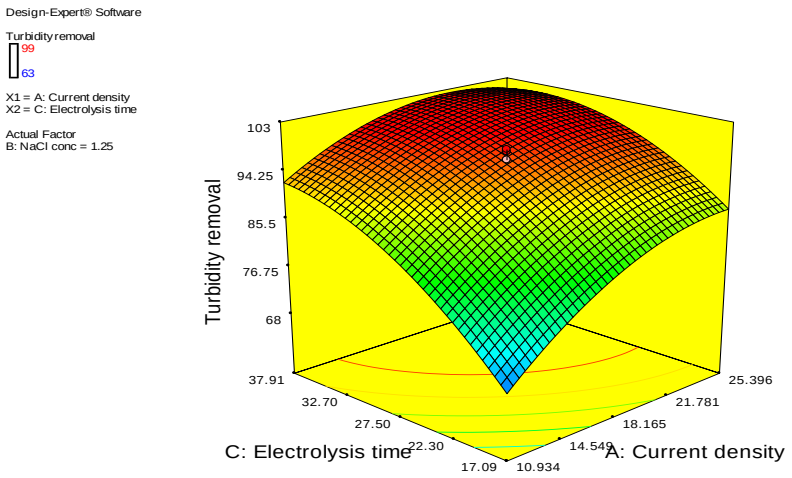


(b)

Figure 2. The 3D surface (a) and contour plot (b) for turbidity removal as a function of current density and NaCl concentration.



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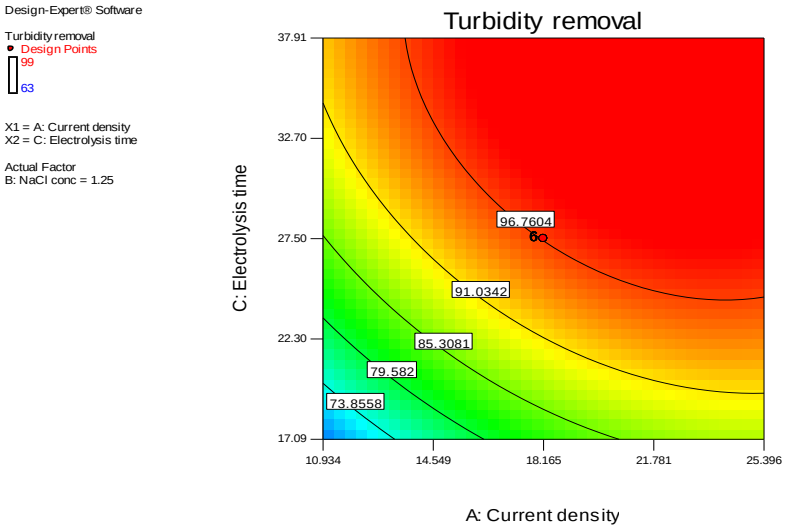
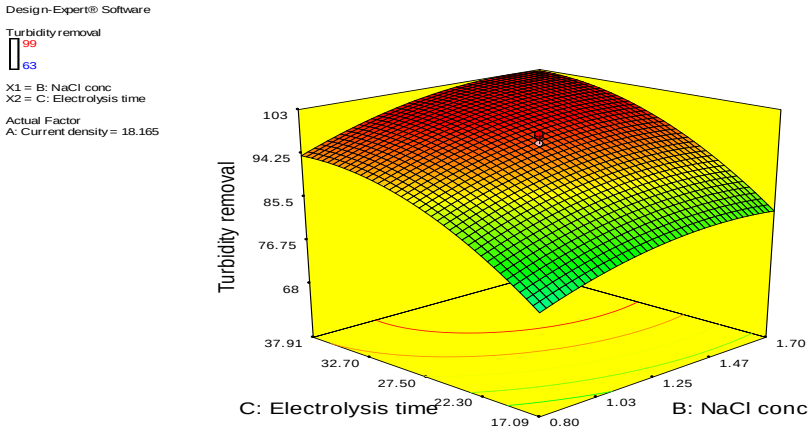


(b)

Figure 3. The 3D surface (a) and contour plot (b) for turbidity removal as a function of current density and electrolysis time.



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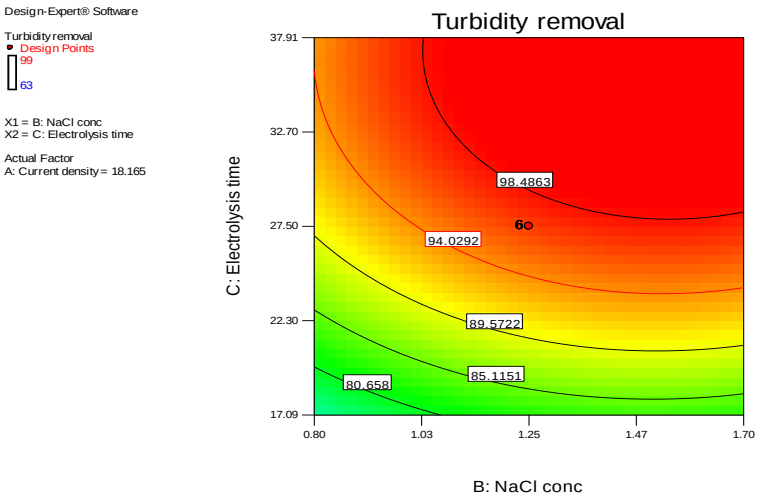
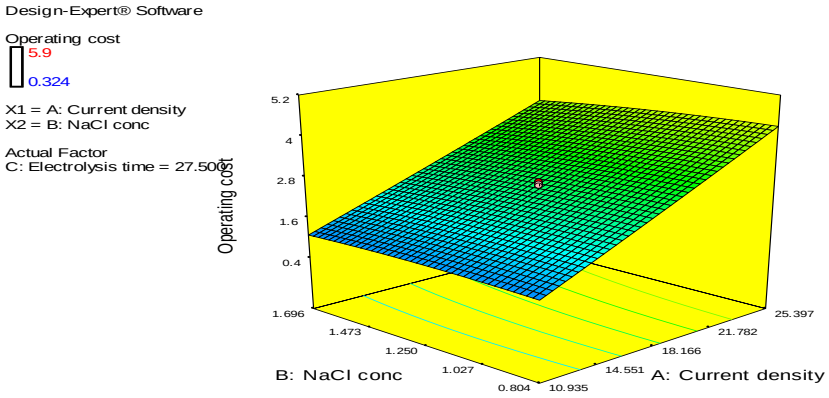


(b)

Figure 4**.** The 3D surface (a) and contour plot (b) for turbidity removal as a function of NaCl concentration and electrolysis time



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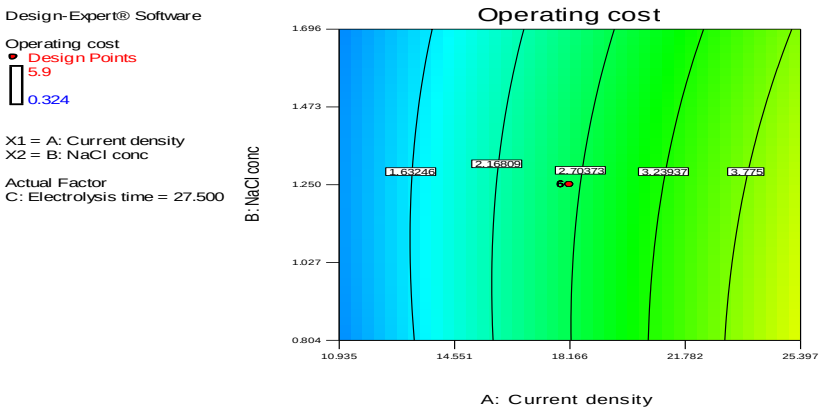

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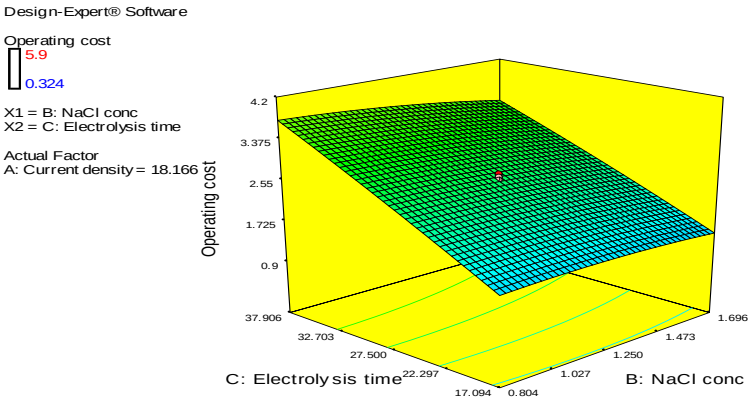
Figure 5. The 3D surface (a) and contour plot (b) for operating cost as a function of current density and NaCl concentration.



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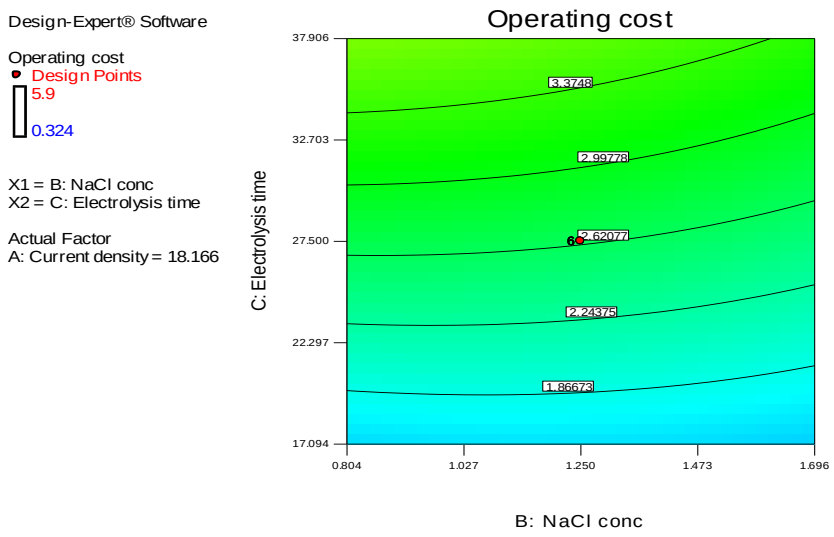
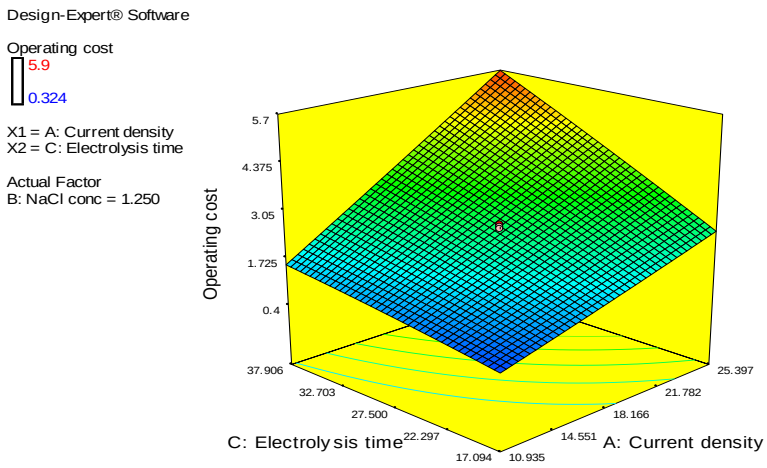


(b)

Figure 6. The 3D surface (a) and contour plot (b) for operating cost as a function of NaCl concentration and electrolysis time.



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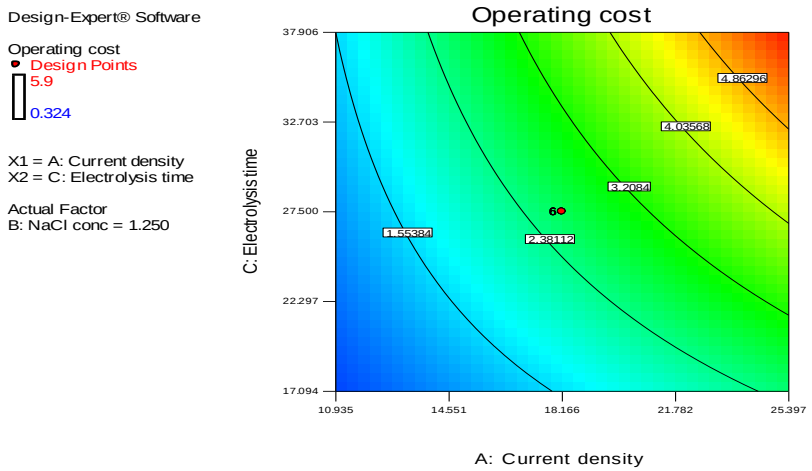

(b)

Figure 7. The 3D surface (a) and contour plot (b) for operating cost as a function of current density and electrolysis time.

Although good results were obtained from the electrocoagulation experiments, these were supposed to be obtained in shorter time to reduce operating cost. The results obtained here was found to be contrary to the ones reported by Merzouk et al., (2009) where the maximum turbidity removal from heavy metal containing synthetic wastewater was found to be 89.54% at the optimum conditions of 11.55mA/cm^2 current density, 7.6 initial pH and 10 min electrocoagulation time. High pH of the real industrial wastewater used for the experiments must have contributed to these results. This means that pH affects rate of electrocoagulation.

CONCLUSIONS

In this work, response surface methodology (RSM) has been successfully applied to an electrocoagulation system used for the treatment of petrochemical wastewater. Turbidity removal efficiency of the process and the operating cost were found to be dependent on current density, electrolyte concentration and electrolysis time. The quadratic models developed for the responses were found to be significant with p-value less than 0.0001. High squared correlation coefficients (R^2) of 0.9815 and 0.9958 were obtained for turbidity removal efficiency and operating cost respectively, thus ensuring a satisfactory agreement of the second-order regression model with the experimental results. At the optimum conditions of 18.17 mA/cm^2, 1.25 g/l and 27.5 min, 96.8% turbidity removal was achieved and the operating cost used to achieve this was found to be 2.6 US$/m^3.

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