Electrochemical Treatment of Plating Effluent: Kinetics and Statistical Modeling

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Abstract

In the present study it is attempted to treat plating effluent using electrocoagulation. Experiments were carried out in a batch electrochemical reactor using mild steel anode and stainless steel cathode covering wide range in operating conditions. A Box–Behnken experimental design has been adopted to evaluate the individual and interactive effects of current density, electrolyte pH, supporting electrolyte concentration and electrolysis time on percentage COD/colour removal. Analysis of variance showed a high coefficient of determination value R^2 for the percentage COD/colour removal.

1. Introduction

Plating industries are rated as one of the major water polluting industries with respect to effluent discharge. The effluent from plating industries contains high organic matter, dissolved solids, strong color and high chemical oxygen demand (COD) concentration [1-3]. The effluent color is attributed due to the presence of compounds such as biocides, corrosion inhibitors, and surfactants etc. Numerous treatment techniques have been practiced for treating plating effluents: chemical coagulation, precipitation, co-precipitation, air flotation, flocculation, adsorption, ion exchange processes, membrane processes, biological processes, phytoextraction and extraction [4-7]. However these treatments methods are cost intensive and do not reduce the pollutants level to the satisfactory levels of pollution control board norms. For example, in chemical coagulation, coagulants such as alum, ferric chloride, lime is added for the treatment, generates large amount of sludge which itself needs further treatment. The low biodegradability index (less than 0.4) of electroplating effluent clearly shows that this effluent cannot be treated effectively through biochemical methods. This necessitated the industries to look for an alternative treatment method for better treatment of plating effluent. In recent years, there has been increasing interest in the use of electrochemical techniques such as electrocoagulation for plating effluent treatment.

Electrocoagulation is a complex and interdependent process where the generation of coagulants takes place in situ by dissolving sacrificial anode. Aluminum or mild steel is mostly used as sacrificial electrode [8]. In electrocoagulation (EC), the coagulating agent is generated in situ by electrooxidation of sacrificial anode and the process is carried out without addition of any chemicals. The generation of coagulants (flocks) can be controlled by the applied charge, thus the amount of sludge generation is very much minimized resulting in a lucrative technology for water/wastewater treatment. electrocoagulation process has been tried to treat various industrial effluents such as electroplating wastewater, pharmaceutical wastewater, petrochemical wastewater, municipal wastewater, paper and pulp wastewater, brackish water, portable water, oil mill wastewater, nitrite effluent, textile dyes, agro industries wastewater, laundry wastewater etc. [9-11]. EC proves to be an ideal technique for effluent treatment because of its versatility, energy efficiency, amenability, cost effectiveness and environmental compatibility. Though electrocoagulation has been successfully demonstrated for treatment of various organic effluents, the application EC on plating effluent treatment is very scarce. The objective of the present work is to treat plating effluent using electrocoagulation.

Response Surface Method (RSM) is a statistical and mathematical tool often used for modeling and optimization where the response

of interest is influenced by several variables. It defines the effect of the operating parameter on the process efficiency either individually or collectively. The RSM generates empirical model which can describe the process and analyze the influence of independent variables on a specific dependent variable (response). The independent variables denoted by x_1, x_2, …, x_k are presumed to be continuous and can be controlled with negligible error. The response (y) is postulated to be a random variable. The individual variables (x_1, x_2, …, x_k) and the response (y) can be related as follows [12,13]

$$y = f(x_1, x_2, x_3......x_k) + \varepsilon \qquad (1)$$

where y the response of the system, f the unknown function of response, x_1, x_2, x_3 ……x_k the independent variables, k the number of independent variables, and ε the statistical error.

RSM postulates the functional relationship between the response (y) and the independent variables. A first order RSM can be expressed as follows:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \varepsilon \qquad (2)$$

For maximization problem, experiments are conducted along the path of steepest ascent until no further increase in the response is observed. The set of values of independent variables where no further increase in response is observed is known as optimal region. In most of the cases a second order response surface model is used which can be given as

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1}\sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon$$

$$(3)$$

where x_i, x_j - coded independent variables. $\beta_0, \beta_i, \beta_{ii}, \beta_{ij}(i=1,2....k), \beta_{ij}(i=1,2,....k; j=1,2,....k)$ regression coefficients for intercept, linear, quadratic and interaction terms respectively. ε statistical error.

In the present study, the RSM has been used to determine the relation between COD removal with operating parameters such as pH, initial effluent concentration, supporting electrolyte concentration and applied charge density. The

uncoded variables are converted to coded variables using the following equation

$$x = \frac{X - [X_{max} + X_{min}]/2}{[X_{max} - X_{min}]/2} \qquad (4)$$

where, X = natural variable and x = coded variable.

The dimensional coded variables x_1, x_2, x_3, x_4 vary between -1 and +1, while the variables are designated as -1, 0 and $+1$. The mathematical representation of the response Y and the variables is given as [14]

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2{}^2 +$$
$$\beta_{44} x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4$$

$$(5)$$

and

$$\beta_{i,j} = 0,1,2,3,4....k \qquad (6)$$

where β and k are regression coefficients and variables. In the present work, the Box–Behnken experimental design has been chosen to find the relationship between the response functions and variables.

2. Materials and Methods

Experiments were carried out in a batch electrochemical reactor of 1000 ml capacity. Mild steel and stainless steel were used as anode and cathode respectively. Six pair of electrodes (10cm×3cm each) were used in the present study. The electrodes were cleaned manually by abrasion followed by washing with 15% hydrochloric acid and distilled water prior to every run. Uniform electrolyte concentration was maintained during the process. DC supply was given using regulated power supply (HIL model 3161). The anode was weighed before and after the experiment for each run to estimate the electrode consumption. All the experiments were carried out under potentiostatic conditions at ambient temperature (28°C). The electrolyte pH was adjusted with HCl/or NaOH. The samples were collected at regular intervals of time and analyzed for pollutant degradation using standard procedure. The Table 1 gives the characteristics of plating effluent.

Table 1. Characteristics of plating effluent

Characteristics	pH	Colour	COD (mgl^{-1})	BOD (mgl^{-1})	SS (mgl^{-1})	DS (mgl^{-1})	TS (mgl^{-1})
Value	2	Dark green	11,000	2100	1200	2800	4000

3. Results and Discussions

The parameters and their ranges covered in the present investigation are listed in Table 2. The electrolyte pH, electrolysis time, supporting electrolyte dosage and applied charge density are referred by uncoded variables as A, B, C and D respectively. The variables are designated as −1, 0 and +1. Experiments were carried out according to the experimental conditions designed by RSM and the responses are summarised in Table 3.

Table 2. The level and range of independent variables chosen for electrocoagulation

Factor	Variables	Range of actual and coded variables		
		-1	0	+1
A	pH	6	7	8
B	Time (min)	20	40	60
C	NaCl (ppm)	100	200	300
D	CD (Adm^{-2})	2	3	4

Table 3. Actual design of experiments and response for % COD/Color removal

Run	Variable factors				% removal			
	pH	t (min)	NaCl (ppm)	CD (A dm^{-2})	$y_{COD,exp}$	$y_{COD,pred}$	$y_{colour,exp}$	$y_{colour,pred}$
1	6	40	200	4	81.10	80.12	86.00	83.00
2	8	40	200	4	78.23	77.75	83.00	82.20
3	7	40	100	2	65.89	63.30	71.10	68.50
4	7	60	300	3	93.51	91.51	99.00	96.00
5	8	60	200	3	79.92	79.26	86.00	83.78
6	6	60	200	3	85.83	84.50	91.00	90.00
7	7	60	100	3	75.06	76.37	81.76	82.00
8	8	40	300	3	71.10	74.09	77.82	78.00
9	8	20	200	3	38.21	37.16	43.10	42.30
10	8	40	200	2	62.80	61.82	68.00	66.80
11	7	40	300	4	90.23	90.40	95.10	94.64
12	6	40	100	3	65.00	65.26	70.67	71.10
13	6	40	300	3	74.00	77.35	77.81	76.58
14	7	40	100	4	71.71	71.71	76.00	76.00
15	7	40	300	2	74.91	72.00	80.14	76.00
16	7	40	200	3	78.00	78.00	83.00	83.00
17	7	40	200	3	78.00	78.00	83.00	83.00
18	7	20	100	3	35.24	35.37	40.52	40.40
19	7	60	200	2	81.46	84.35	86.18	88.46
20	7	20	200	2	30.00	33.35	36.79	38.68
21	7	40	200	3	78.00	78.00	83.12	83.00
22	6	20	200	3	42.00	41.50	47.14	46.50
23	7	20	300	3	51.00	47.50	55.48	52.11
24	6	40	200	2	71.00	69.20	75.59	75.40

The results are presented in both surface and contour plots. The mathematical relationship between the independent variables and their responses can be given as

%COD removal = 78.00 - 2.43A + 21.25B + 6.85C + 6.71D - 0.25AB - 0.80AC + 1.25AD + 0.75BC - 3.75BD + 2.50CD - 5.62A^2 - 11.78B^2 - 3.50C^2 - 0.15D^2 (7)

%Color removal = 83.00 - 2.60A + 21.25B + 6.35C + 6.60D - 0.50AB + 1.05AC + 1.75AD + 0.50BC - 3.25BD + 2.50CD - 5.54A^2 - 11.82B^2 - 3.67C^2 - 0.69D^2 (8)

The predictions of percentage COD/color removal using the Eqs. (7) and (8) are compared with the experimental observations in Fig. 1. It can be ascertained that the predictions using

above equations satisfactorily match with the experimental observations within the acceptable error percentage.

Figure 1. Comparison of model prediction on (a) percentage COD removal, (b) percentage color removal with experimental observations.
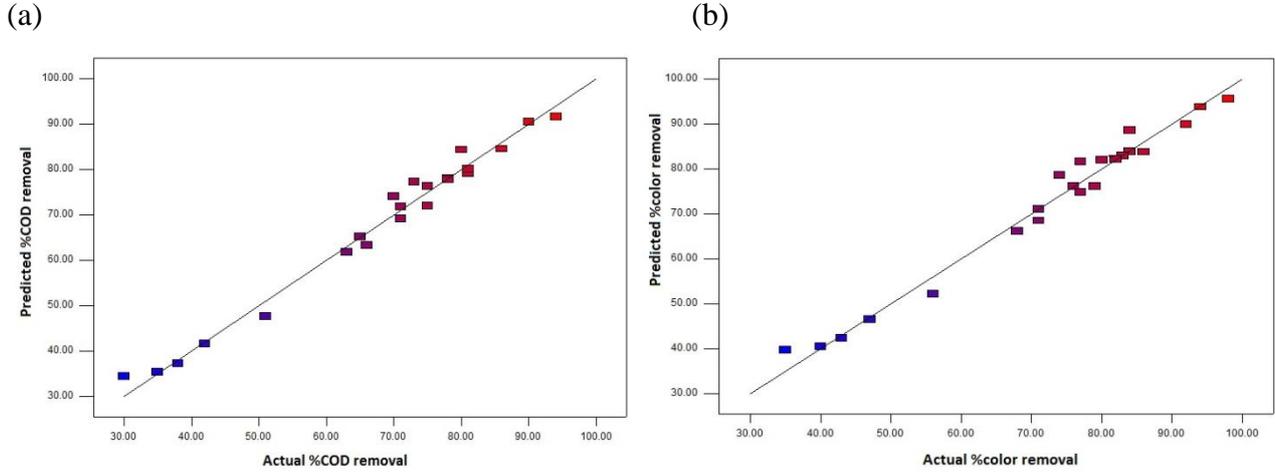
(a)

(b)

Figure 2 shows the combined effect of applied current density and supporting electrolytic concentration on percentage COD removal. It can be ascertained from the figure that the percentage COD removal increased with both current density and supporting electrolyte concentration. The rate of generation

of coagulant increases with an increase in current density and in turn improves the percentage COD removal. Similar observation has been recorded for color removal (Fig. 2b). These observations are in qualitatively agreed with our earlier findings [15].

Figure 2. Combined effects of current density and supporting electrolyte dosage on (a) percentage COD removal, (b) percentage color removal.

(a)

(b)
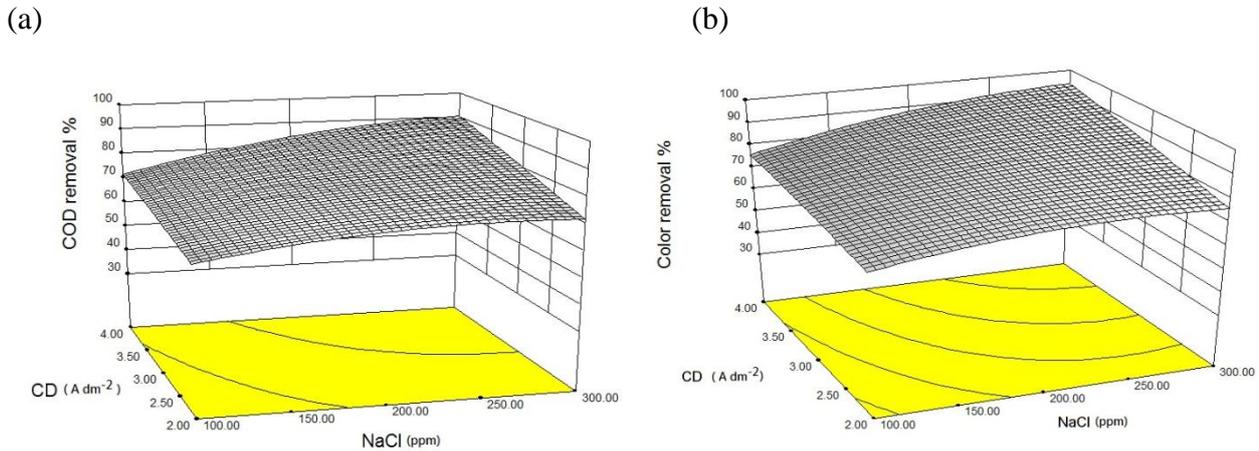
3.1. Effect of pH and Current Density

It has been well established that electrolyte pH is an important parameter and has significant influence on electrocoagulation process. The combined effect of electrolyte pH and *current density* on percentage COD/color removal is given in Fig. 3. It can be ascertained from Fig. 3a that the percentage COD removal increases with increase in the electrolyte pH from acidic condition to neutral for a given electrolysis time.

Further increase in the electrolyte pH did not show any significant improvement in the percentage COD removal, which is due to the fact that the activities of oxidants are good at neutral pH. Increasing electrolyte pH beyond 7 enhances the solubility of $Fe(OH)_3$ resulting formation of soluble $Fe(OH)_4^-$ which does not contribute to percentage COD removal. Similar observation has been recorded for color removal (Fig. 3b).

Figure 3. Combined effects of current density and pH on (a) percentage COD removal, (b) Percentage color removal.

(a)
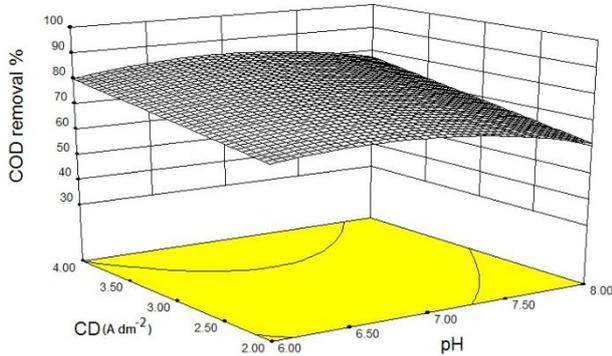
(b)
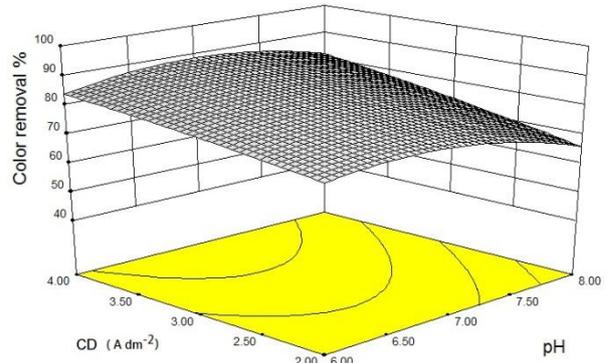
3.2. Effect of Electrolysis Time and Current Density

The Fig. 4 shows the surface response of combined effect of applied current density and electrolysis time on the percentage COD/color removal. It can be noticed that the percentage

COD removal increased with both current density and the electrolysis time. As stated earlier, the amount of flocks generated increased with current density or time and in turn the percentage COD removal. Similarly observation has been recorded for color removal.

Figure 4. Combined effects of electrolysis time and current density on (a) percentage COD removal, (b) percentage color removal.

(a)
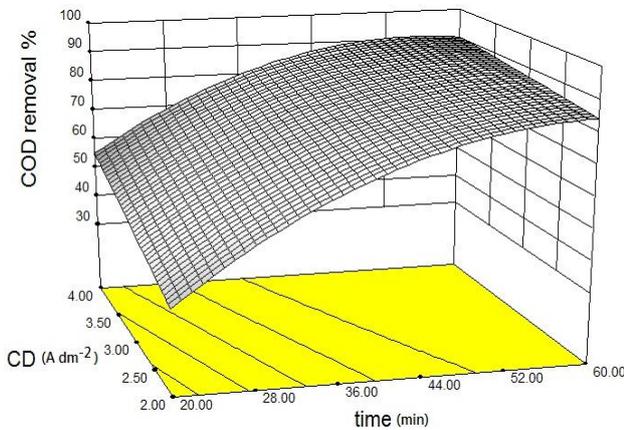
(b)
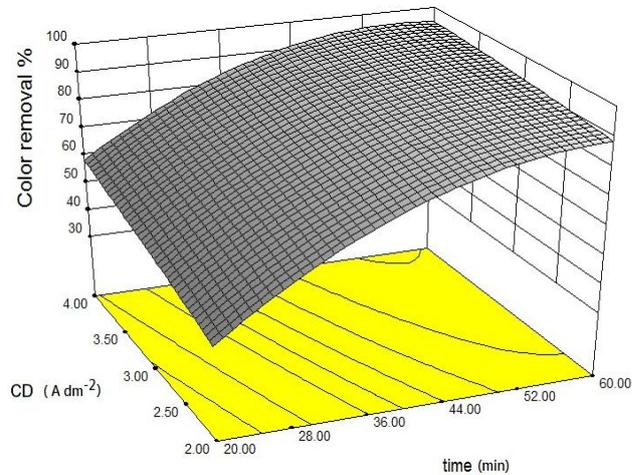
3.3. Analysis of Variance (ANOVA)

Analysis of variance (ANOVA), was carried out to determine the significant effects of process variable on percentage removal for COD (Table 4). It can be noticed from Table 4 that the F-statistics values for the regressions are higher. The large F-values for percentage COD removal indicate that the response fits more favourable for the regression model. The associated p-value is used to estimate whether the F-statistics are large enough to indicate statistical significance. P-values lower than 0.05 indicates that the model is statistically significant for percentage COD removal. The residual error term in the ANOVA table, which shows the amount of variation in the response data left unexplained by the model. Similarly ANOVA for percentage colour removal has been summarised in Table 5.

Table 4. ANOVA of the second order polynomial equation for the percentage COD removal

Source	Coefficient estimate	Sum of squared	DF	Mean square	F-value	p-value prob > F
Model intercept	78.00	6812.46	14	486.60	35.75	<0.0001
A	-2.43	58.57	1	58.57	4.30	0.0679
B	21.25	3612.50	1	3612.50	265.40	<0.0001
C	6.85	463.87	1	463.87	34.08	0.0002
D	6.71	398.62	1	398.62	29.29	0.0004
AB	-0.25	0.25	1	0.25	0.018	0.8952
AC	-0.80	1.57	1	1.57	0.12	0.7418
AD	1.25	6.25	1	6.25	0.46	0.5151
BC	0.75	2.25	1	2.25	0.17	0.6938
BD	-3.75	22.50	1	22.50	1.65	0.2306
CD	2.50	25.00	1	25.00	1.84	0.2084
A^2	-5.62	144.64	1	144.64	10.63	0.0098
B^2	-11.78	609.16	1	609.16	44.75	<0.0001
C^2	-3.50	56.00	1	56.00	4.11	0.0731
D^2	-0.15	0.10	1	0.10	0.0074	0.9332
Residual		122.50	9	13.61		
Lack of fit		122.50	7	17.50		
Pure error		0.0000	2	0.000		
Cor total		6934.96	23			

Table 5. ANOVA of the second-order polynomial equation for the percentage colour removal

Source	Coefficient estimate	Sum of squared	DF	Mean square	F-value	p-value prob > F
Model intercept	83.00	6627.96	14	473.43	29.59	<0.0001
A-pH	-2.60	66.87	1	66.87	4.18	0.00713
B-time	21.25	3612.50	1	3612.50	225.78	<0.0001
C-NaCl	6.35	398.63	1	398.68	24.91	0.0007
D-CD	6.60	350.68	1	350.38	21.92	0.0011
AB	-0.50	1.00	1	350.68	0.062	0.8082
AC	1.05	2.70	1	1.00	0.17	0.6907
AD	1.75	12.25	1	2.70	0.77	0.4043
BC	0.50	1.00	1	12.25	0.062	0.8082
BD	-3.25	16.90	1	1.00	1.06	0.3309
CD	2.50	25.00	1	16.90	1.56	0.2428
A^2	-5.54	140.39	1	25.00	8.77	0.0159
B^2	-11.82	613.48	1	140.39	38.34	0.0002
C^2	-3.67	61.46	1	613.48	3.84	0.0817
D^2	-0.69	2.11	1	61.46	0.13	0.7248
Residual		144.00	9	2.11		
Lack of fit		144.00	7	16.00		
Pure error		0.000	2	20.57		
Cor total		6771.96	23	0.0000		

3.4. Adequacy of the Models for the Removal Percentage

In the present investigation, linear, interactive, quadratic and cubic models were fitted to the experimental data to obtain the

regression equations. The adequacy of models to represent removal percentage was tested by various models and the results are given in Table 6. The model adequacies were checked with R^2 and adj-R^2. It can be noticed from Table that the cubic model shows good response. A higher value of coefficient of determination R^2 for percentage COD removal shows that the model follows the response successfully. The Table 7 presents similarly analysis for percentage color removal. The normality for both COD reduction and color removal is given Fig. 5.

Table 6. Adequacy of the models tested for the percentage COD removal (sequential model sum of squares)

Source	Sum of squares	DF	Mean square	F-Value	Prob > F	Remark
Mean	113300	1	113300			
Linear	5902.05	4	1475.51	27.14	<0.0001	Suggested
2FI	57.98	6	9.66	0.13	0.9903	
Quadratic	852.43	4	213.11	15.66	0.0004	Suggested
Cubic	122.44	6	20.41	979.52	<0.0001	Aliased
Residual	0.063	3	0.021			
Total	120233	24	5009.79			
Model summary statistics						
Source	SD	R^2	Adj-R^2	Pred-R^2	PRESS	Remark
Linear	7.37	0.8511	0.7197	0.7692	1600.93	Suggested
2FI	8.66	0.8594	0.6513	0.4969	3489.29	
Quadratic	3.69	0.9823	0.8549	0.7045	2049.07	Suggested
Cubic	0.14	1.0000	0.9999			Aliased

Table 7. Adequacy of the models tested for percentage color removal (sequential model sum of squares)

| Source	Sum of squares	DF	Mean square	F-Value	Prob > F	Remark
Mean	129500	1	129500			
Linear	5744.42	4	1436.10	26.55	< 0.0001	Suggested
2FI	59.65	6	9.94	0.13	0.9894	
Quadratic	823.89	4	205.97	12.87	0.0009	Suggested
Cubic	143.44	6	23.91	127.50	0.0011	Aliased
Residual	0.56	3	0.19			
Total	136300	24	5678.29			
Model summary statistics						
Source	SD	R^2	Adj-R^2	Pred-R^2	PRESS	Remark
Linear	7.35	0.8483	0.7163	0.7663	1582.32	Suggested
2FI	8.63	0.8571	0.6471	0.4877	3469.50	
Quadratic	4.00	0.9887	0.8457	0.6467	2392.43	Suggested
Cubic	0.43	0.9999	0.9994			Aliased

4. Conclusions

Experiments were carried to percentage COD and color removal by electrocoagulation from plating effluent covering wide range in operating conditions. The percentage of COD and color removal shows significant influence by operating conduction such as current density, electrolyte pH, electrolysis time and supporting electrolyte dosage. The experimental data were analyzed using response surface methodology. Three-level four factorial Box–Behnken experimental design was applied in the present investigation. Regression equations have been developed for percentage COD and color removal.

Figure 5. Normal % probability versus residual error on (a) percentage COD removal, (b) percentage color removal.

(a)
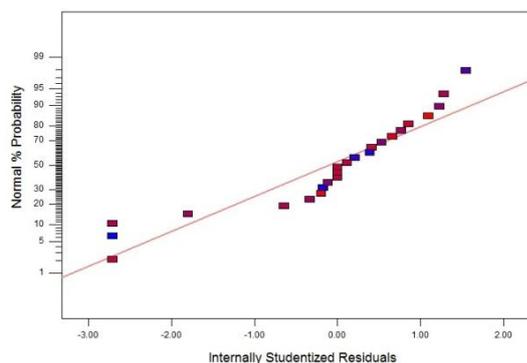
(b)
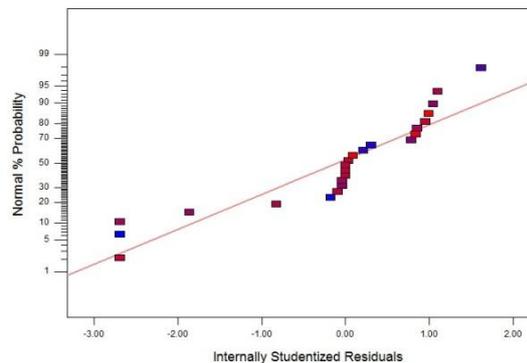
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