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Modeling and Optimization of Electrocoagulation Process for the Removal of Yellow145 dye Based on Central Composite Design

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Abstract

In this study, Central Composite Design (CCD) approach of Response Surface Methodology (RSM) was applied to develop a mathematical model and to optimize the parameters of electrocoagulation process (EC) for the removal of Yellow145 (Y145) dye. The EC process was studied by using coupled electrodes of Fe-Fe and Al-Al, separately. The operational parameters of the process such as dye concentration, pH, electrolysis time and amount of NaCl were studied to obtain their desired levels for getting the high value of the removal of the dye. The values of correlation coefficient (R^2) of the model were found to be 81.71%, 56.93% for Fe-Fe and Al-Al, respectively. Analysis of variance (ANOVA) helped in finding the significant variables of the process. The response surface plots were plotted to observe the interaction between the levels of the factors on the response of the process.

Keywords: Electrocoagulation process, Response surface methodology, Central composite design, Yellow145, FTIR, Cost analysis.

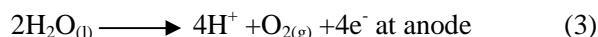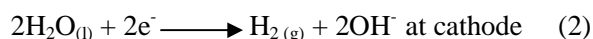
Introduction

The textile industrial sector consumes large volume of water during dyeing and finishing operations. This sector also discharges large portion of effluent into the natural resources of water. The textile effluent contains many dyes which cause environmental and health problems. Azo dyes are used in the textile, paint, ink and plastic industries. These dyes show stability against bio-degradation [1-4]. Electrochemical-based systems are controlled and rapid process. They need only electrons to treat wastewater. They do not require chemicals and micro-organisms [5, 6]. Among the electrochemical techniques, (EC) process has a wide applications for the treatment of industrial effluents.

The theory of EC and chemical coagulation is almost similar. In EC, the coagulant of Al^{3+}, Fe^{3+} ions are supplied by applying an electric current to the metal anodes kept in a EC reactor [7, 8]. Firstly, the metal anode is oxidized as follows:

$$M_{(S)} \longrightarrow M_{(aq)}^{n+} + ne^- \qquad (1)$$
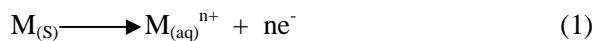
Additionally, the electrolysis of water takes place at the cathode and anode as follows:

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2\,(g)} + 2OH^- \text{ at cathode} \qquad (2)$$

$$2H_2O_{(l)} \longrightarrow 4H^+ + O_{2(g)} + 4e^- \text{ at anode} \qquad (3)$$

The formed chemical species of dissolved metal cations destabilize the contaminants, particulate suspension, and also break emulsions. The generation of hydrogen gas is also promote the

floatation process to remove the flocculated particles out of the water.

Furthermore, the hydroxide ions formed at the cathode increase the pH of the EC system and induce the formation of precipitates of metal ions with the hydroxides as follows:

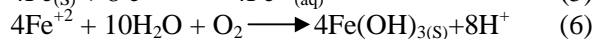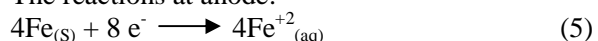$$M_{(aq)}^{n+} + nOH^- \longrightarrow M(OH)_{n(s)} \qquad (4)$$

Eventually, the destabilized particles in the EC system undergo aggregation to form flocs [9].

In case of using iron electrodes, the following two mechanisms have been proposed for the formation of the metal hydroxide [10]:
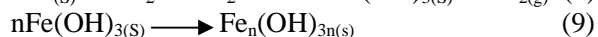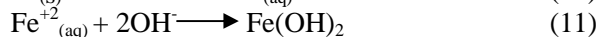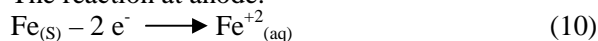
Mechanism-1

The reactions at anode:
$$4Fe_{(S)} + 8\ e^- \longrightarrow 4Fe^{+2}_{(aq)} \qquad (5)$$
$$4Fe^{+2} + 10H_2O + O_2 \longrightarrow 4Fe(OH)_{3(S)} + 8H^+ \qquad (6)$$

The reactions at cathode:
$$8H^+ + 8e^- \longrightarrow 4H_{2(g)} \qquad (7)$$

Overall reactions:
$$4Fe_{(S)} + 10H_2O + O_2 \longrightarrow 4Fe(OH)_{3(S)} + 4H_{2(g)} \quad (8)$$
$$nFe(OH)_{3(S)} \longrightarrow Fe_n(OH)_{3n(s)} \qquad (9)$$

Mechanism-2

The reaction at anode:
$$Fe_{(S)} - 2\ e^- \longrightarrow Fe^{+2}_{(aq)} \qquad (10)$$
$$Fe^{+2}_{(aq)} + 2OH^- \longrightarrow Fe(OH)_2 \qquad (11)$$

The reaction at cathode:
$$2H_2O + 2\ e^- \longrightarrow 2OH^- + 4H_{2(g)} \qquad (12)$$

Overall reactions:
$$Fe_{(S)} + 2H_2O \longrightarrow Fe(OH)_2 + H_{2(g)} \qquad (13)$$
$$nFe(OH)_{2(S)} \longrightarrow Fe_n(OH)_{2n(s)} \qquad (14)$$
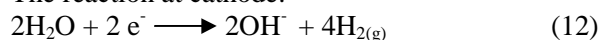
The way of removing dye from wastewater.

Precipitation:
$$Dye + [Monomeric\ Fe] \longrightarrow [Dye\text{-}Monomeric\ Fe] \quad (15)$$
$$Dye + Polymeric\text{-}Fe \longrightarrow [Dye\text{-}Polymeric\ Fe] \quad (16)$$

Adsorption:
$$Dye + Fe_n(OH)_n \longrightarrow Sludge(s) \qquad (17)$$
$$[Dye\text{-}Polymeric\ Fe] + Fe_n(OH)_n \longrightarrow Sludge(s) \quad (18)$$
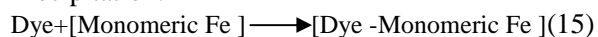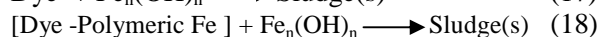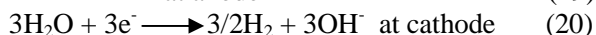
The main reactions at the electrodes in case of Al-Al electrodes combination are:

$$Al \longrightarrow Al^{+3}\ \text{at anode} \qquad (19)$$
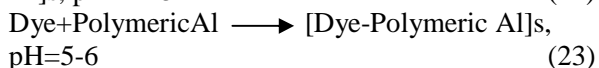$$3H_2O + 3e^- \longrightarrow 3/2H_2 + 3OH^-\ \text{at cathode} \qquad (20)$$

At high pH, the formation of hydrogen gas at the cathode generates OH^- ions [11].

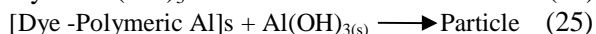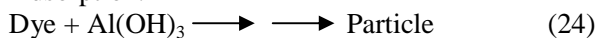$$2Al + 6H_2O + 2OH^- \longrightarrow 2Al(OH)_4^- + 3H_2 \qquad (21)$$
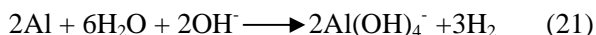
The formed aluminium and hydroxide ions react to form various monomeric species which are finally changed into $Al(OH)_3$ according to complex precipitation kinetics. The following interaction mechanisms are possible between the molecules of a dye and hydrolysis by-products [12, 13].
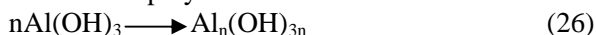
Precipitation:
$$Dye + [Monomeric\ Al] \longrightarrow [Dye\text{-}Monomeric\ Al]s,\ pH = 4\text{-}5 \qquad (22)$$
$$Dye + PolymericAl \longrightarrow [Dye\text{-}Polymeric\ Al]s,\ pH = 5\text{-}6 \qquad (23)$$

Adsorption:
$$Dye + Al(OH)_3 \longrightarrow \longrightarrow Particle \qquad (24)$$
$$[Dye\text{-}Polymeric\ Al]s + Al(OH)_{3(s)} \longrightarrow Particle \quad (25)$$
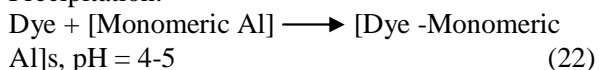
These flocs polymerise as :
$$nAl(OH)_3 \longrightarrow Al_n(OH)_{3n} \qquad (26)$$

In EC process the excessive amount of coagulants is not added owing to their direct generation by electro-oxidation of a sacrificial anode. EC equipment is simple and easy to operate and also require short reaction time and low sludge production [14].

The EC process is optimized to determine the best levels of the factors to get maximum efficiency of the process in the treatment of aqueous discharges. Recently, the experiments based on statistical design are used to determine interactions among the factors to optimize the operating parameters in multivariable analysis. They are also used to obtain statistically significant models by performing the minimum number of experiments. RSM is used for modeling and optimizing a response of a process. It is also analyzed the ways in which several variables influence a response of interest [15]. The CCD, the

design under RSM, is an efficient method. It provides more detailed information regarding the data obtained from a treatment process in fewer number of experiments. This article present the results of the laboratory scale studies on the removal of Y145 dye from simulated wastewater using coupled iron-iron (Fe-Fe) and aluminium-aluminium (Al-Al) electrodes by EC process. The study will provide guidance in operating and designing reactors for the treatment of large volume of wastewater.

Materials and Methods
Experimental Setup and Procedure

A laboratory-scale glass EC setup was used. For each test, a 1000 mL of Y145 dye sample was used. Before each run, acetone was used to wash the electrodes and the impurities were removed by dipping in a solution of HCl solution [16]. All the chemicals used to be of analytical-reagent grade. The EC experiments were conducted by applying a voltage of 15V by means of a DC power supply (Yaxun 1502DD; 15V, 2A). At the end of each run, the sample was collected and filtered to remove floated and precipitated materials. After that, the filtrate was analyzed with T80 UV/VIS spectrophotometer. The dye and the obtained sludge were characterized by FTIR model NICOLET 6700 [17].
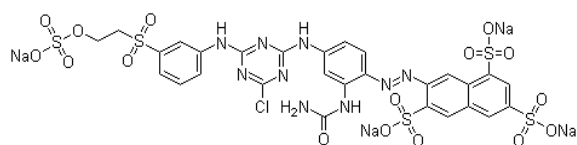

Figure 1. The structure of Y145 dye

Experimental Design and Model Development

The optimum levels of the factors of EC process were found in three analytical steps; adequacy of various model tests (sequential model sum of squares and model summary statistics), ANOVA, and the response surface plotting for the removal of Y145 from simulated wastewater. The data were analyzed with the Minitab Software 17. A total of 31 experiments were conducted in this study. The levels of the variables are given in Table 1. Table 2 is representing the treatments and corresponding the removal of Y145 by using two separate electrodes systems. The linear, quadratic, and combined effects of the operational parameters on the removal of the dye were described by a second-order polynomial as given below:

$$Y = \beta_o + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \sum_{j=1}^{4} \beta_{ij} x_i x_j + \sum_{i=1}^{4} \beta_{ii} x_i^2 \quad (27)$$

Table 1. The levels of the factors of EC process.

Independent Variables	-œ	-1	0	+1	+ œ
[A] [dye] (mg/L)	100	150	200	250	300
[B] NaCl (g/L)	1	1.25	1.5	1.75	2
[C] pH	3	5	7	9	11
[D] Electrolysis Time (min)	10	15	20	25	30

Table 2. The full-factorial design used for the removal of Y145 dye using EC.

[dye] (mg/L)	NaCl (g/L)	pH	Electrolysis Time (min)	Fe-Fe	Al-Al
250	1.25	9	15	100	83
250	1.75	5	25	100	92
150	1.25	9	25	100	87
250	1.25	9	25	100	82
100	1.5	7	20	96	87
250	1.75	9	25	100	90
150	1.75	5	25	96	87
200	1.5	7	10	100	99
200	1.5	7	20	99	80
300	1.5	7	20	100	52
250	1.25	5	15	96	87
150	1.25	5	15	100	92
250	1.25	5	25	96	87
250	1.75	5	15	100	95
200	1.5	7	20	100	96
200	2	7	20	93	75
150	1.75	9	15	89	94
150	1.25	9	15	97	78
200	1.5	7	30	100	81
200	1.5	7	20	99	87
150	1.25	5	25	100	92
200	1.5	11	20	100	89
150	1.75	9	25	94	83
200	1.5	7	20	96	86
250	1.75	9	15	99	76
200	1.5	7	20	96	86
200	1.5	3	20	95	99
200	1.5	7	20	100	76
200	1.5	7	20	96	86
200	1	7	20	100	81
150	1.75	5	15	94	93

Where *Y* is the predicted response and considered as a dependent variable. The X_i and X_j show the independent variables. While, β_0 is the constant coefficient, and β_i, β_{ij} and β_{ii} are the coefficients of linear, interaction and quadratic terms, respectively [18].

Results and Discussion
Statistical Analysis and Optimization
EC process using Fe-Fe and Al-Al electrodes

The experimental results obtained by CCD were fitted to the second-order (quadratic) polynomial response surface model. The following regression equations with the coded variables were obtained using Fe-Fe and Al-Al electrodes for the removal of Y145 dye:

Fe-Fe=134.1- 0.2260A- 8.3 B+ 0.28C - 0.823 D- 0.000029 AA- 7.17BB - 0.0495 CC+0.0171 DD+ 0.1550 AB+ 0.01062AC - 0.00225AD – 1.625 BC+ 0.250BD+ 0.0437 CD   (28)

Al-Al = 112 + 0.341 A + 57.6 B - 14.00 C –

4.09D - 0.001279 AA - 17.1 BB + 0.732 CC+ 0.0771 DD+ 0.030AB - 0.0050 AC + 0.00450AD + 0.50 BC - 0.70BD + 0.125 CD   (29)

The synergistic effect of the factors is shown by the positive sign of the coefficients in equation (28, 29), whereas the negative sign suggests antagonistic effect [18].

Statistical testing of the model was evaluated by the ANOVA. The data are tabulated in Table 3. It can be noted that the regression model was significant for Fe-Fe electrodes, while insignificant for Al-Al electrodes. The significance of the parameters is given in Table 4. It was also encountered that the concentration of the dye (A), and amount of electrolyte (B) were showing linearly and combined effects on the removal of the dye in Fe-Fe electrodes system. In the second electrode system, the concentration of the dye (A) has a linear and quadratic effect on the removal of the dye. The significance of the model can be analyzed in Table 5 [19-24].

Table 3. **ANOVA for the removal of Y145 dye using Fe-Fe and Al-Al electrode combinations.**

Source	DF	Adj SS	AdjMS	F-Value	P-Value	DF	Adj SS	AdjMS	F-Value	P-Value
			Fe-Fe						**Al-Al**	
Model	14	194.003	13.8573	5.11	0.001	14	1383.34	98.81	1.51	0.213
Linear	4	82.167	20.5417	7.57	0.001	4	562.33	140.5	2.15	0.122
A	1	35.042	35.0417	12.91	0.002	1	294.00	294.0	4.49	0.050
B	1	40.042	40.0417	14.76	0.001	1	4.17	4.167	0.06	0.804
C	1	2.042	2.0417	0.75	0.399	1	216.00	216.0	3.30	0.088
D	1	5.042	5.0417	1.86	0.192	1	48.17	48.16	0.74	0.404
Square	4	13.461	3.3653	1.24	0.334	4	756.26	189.0	2.89	0.056
AA	1	0.152	0.1520	0.06	0.816	1	292.17	292.2	4.47	0.051
BB	1	5.737	5.7371	2.11	0.165	1	32.83	32.82	0.50	0.489
CC	1	1.120	1.1201	0.41	0.530	1	245.25	245.2	3.75	0.071
DD	1	5.216	5.2159	1.92	0.185	1	106.36	106.3	1.63	0.220
2-Way Interaction	6	98.375	16.3958	6.04	0.002	6	64.75	10.79	0.16	0.983
AB	1	60.062	60.0625	22.13	0.000	1	2.25	2.250	0.03	0.855
AC	1	18.063	18.0625	6.66	0.020	1	4.00	4.000	0.06	0.808
AD	1	5.062	5.0625	1.87	0.191	1	20.25	20.25	0.31	0.586
BC	1	10.563	10.5625	3.89	0.066	1	1.00	1.000	0.02	0.903
BD	1	1.562	1.5625	0.58	0.459	1	12.25	12.250	0.19	0.671
CD	1	3.062	3.0625	1.13	0.304	1	25.00	25.000	0.38	0.545
Error	16	43.417	2.7135	*	*	16	1046	65.41	*	*
Lack-of-Fit	10	21.417	2.1417	0.58	0.784	10	813.17	81.32	2.09	0.190
Pure Error	6	22.000	3.6667	*	*	6	233.43	38.905	*	*
Total	30	237.419	*	*	*	30	2429.94	*	*	*

Table 4. **Student t and p-values for the removal of Y145 dye using Fe-Fe and Al-Al electrode combinations.**
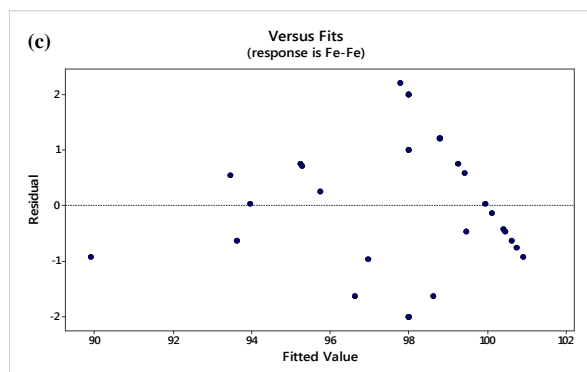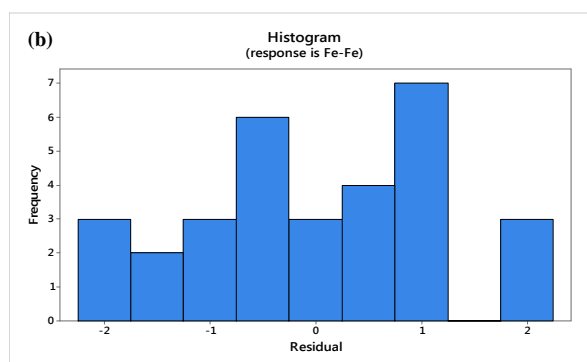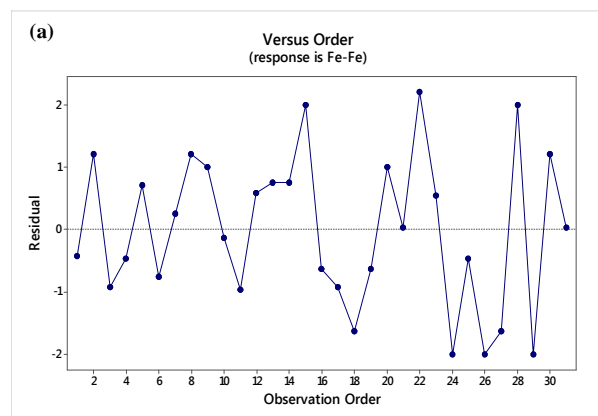
| Term | Fe-Fe | | | | | | Al-Al | | | | | |
	Effect	Coef	SECoef	T-Value	P-Value	VIF	Effect	Coef	SECoef	T-Value	P-Value	VIF
Constant		98.00	0.623	157.40	0.000			85.29	3.06	27.90	0.000	
A	2.417	1.208	0.336	3.590	0.002	1.00	-7.00	-3.50	1.65	-2.12	0.050	1.00
B	-2.583	-1.292	0.336	-3.840	0.001	1.00	0.83	0.42	1.65	0.25	0.804	1.00
C	0.583	0.292	0.336	0.870	0.399	1.00	-6.00	-3.00	1.65	-1.82	0.088	1.00
D	0.917	0.458	0.336	1.360	0.192	1.00	-2.83	-1.42	1.65	-0.86	0.404	1.00
AA	-0.146	-0.073	0.308	-0.240	0.816	1.03	-6.39	-3.20	1.51	-2.11	0.051	1.03
BB	-0.896	-0.448	0.308	-1.450	0.165	1.03	-2.14	-1.07	1.51	-0.71	0.489	1.03
CC	-0.396	-0.198	0.308	-0.640	0.530	1.03	5.86	2.93	1.51	1.94	0.071	1.03
DD	0.854	0.427	0.308	1.390	0.185	1.03	3.86	1.93	1.51	1.28	0.220	1.03
AB	3.875	1.937	0.412	4.700	0.000	1.00	0.75	0.37	2.02	0.19	0.855	1.00
AC	2.125	1.062	0.412	2.580	0.020	1.00	-1.00	-0.50	2.02	-0.25	0.808	1.00
AD	-1.125	-0.562	0.412	-1.370	0.191	1.00	2.25	1.12	2.02	0.56	0.586	1.00
BC	-1.625	-0.812	0.412	-1.970	0.066	1 .00	0.50	0.25	2.02	0.12	0.903	1.00
BD	0.625	0.313	0.412	0.760	0.459	1.00	-1.75	-0.87	2.02	-0.43	0.671	1.00
CD	0.875	0.437	0.412	1.060	0.304	1.00	2.50	1.25	2.02	0.62	0.545	1.00

Table 5. **Model summary of EC process for the removal of Y145 dye.**

Statistical parameters	Fe-Fe	Al-Al
$S_{(square mean of error)}$	1.647	8.088
R^2	81.71%	56.93%
$R^2(adj)$	65.71%	19.24%
$R^2(pred)$	35.43%	0.000%

Residual plots

In the normal probability plots the data were around the normal line it mean the second order polynomial model was well fitted to the data. The residuals were lying between 1 to -1 in Fe-Fe electrode system while in Al-Al electrode system the residuals were between 10 to -10. The residual plots are shown in Fig. 2-3.
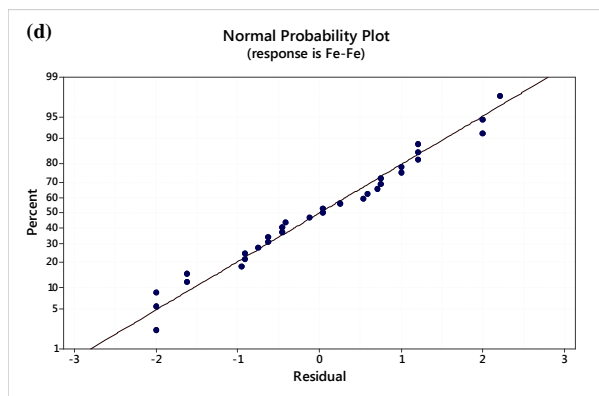

(b) Histogram (response is Fe-Fe)

(a) Versus Order (response is Fe-Fe)

(c) Versus Fits (response is Fe-Fe)

(d)

Normal Probability Plot
(response is Fe-Fe)

Figure 2. **Residual plots for the removal of Y145 dye using Fe-Fe electrodes**

(a)

Versus Order
(response is Al-Al)

(b)

Histogram
(response is Al-Al)

(c)

Versus Fits
(response is Al-Al)

(d)

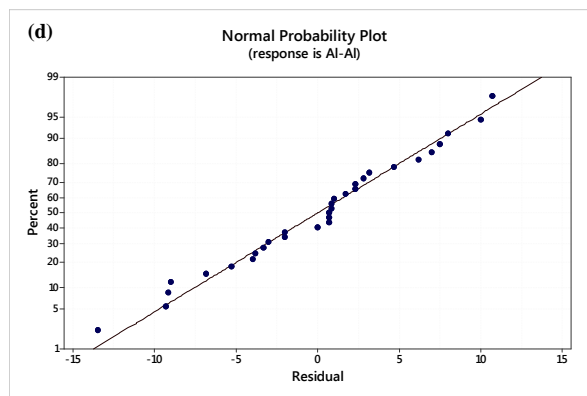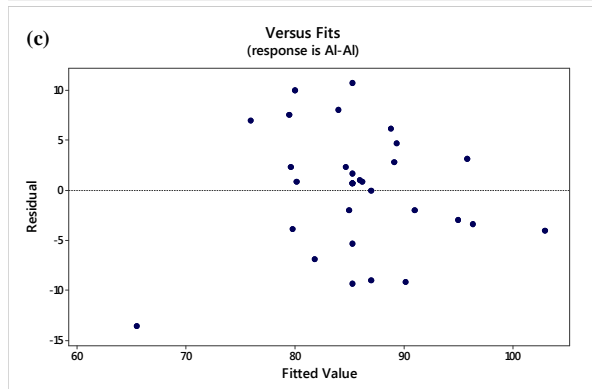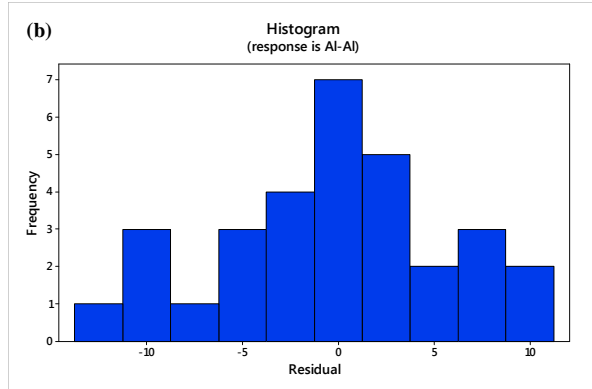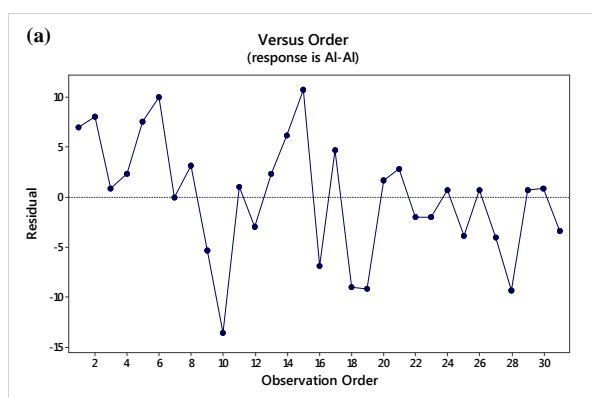Normal Probability Plot
(response is Al-Al)

Figure 3. **Residual plots for the removal of Y145 dye using Al-Al electrodes**
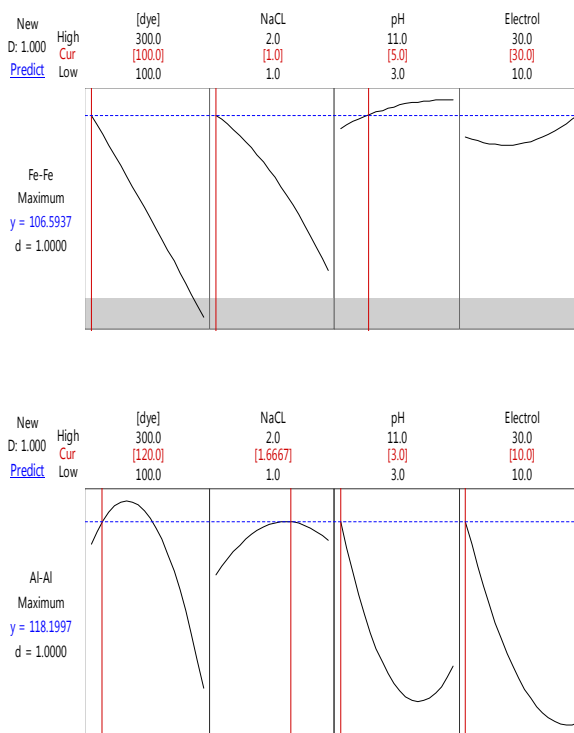
The desired levels of the variables of the process are given in Fig. 4.

Figure 4. **Optimum operating conditions of the process**

Main interaction plots

The main interaction plots were showed that as the levels of the factors were changing the removal of Y145 dye was also changing. It was more prominent in Fe-Fe electrode system as compared to Al-Al electrode system as shown in Fig 5a-b.

(a)

(b)
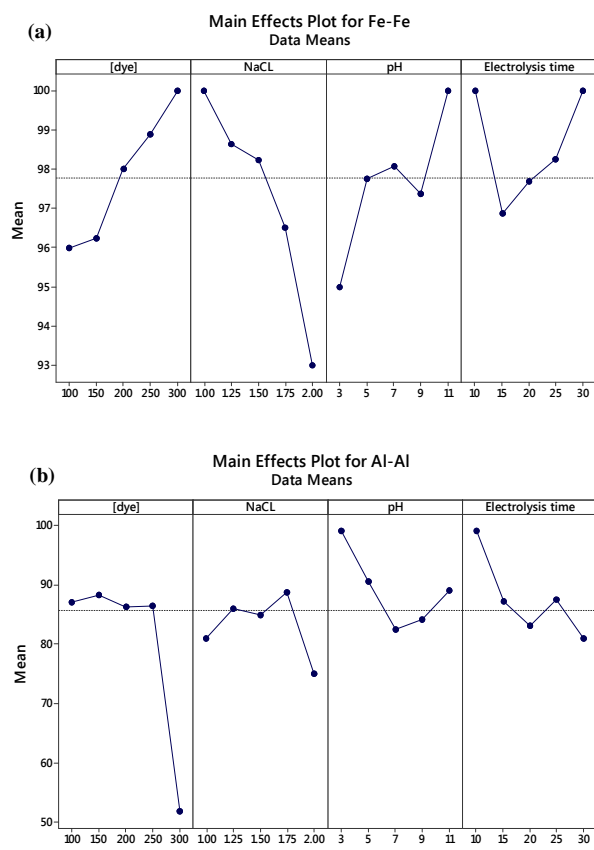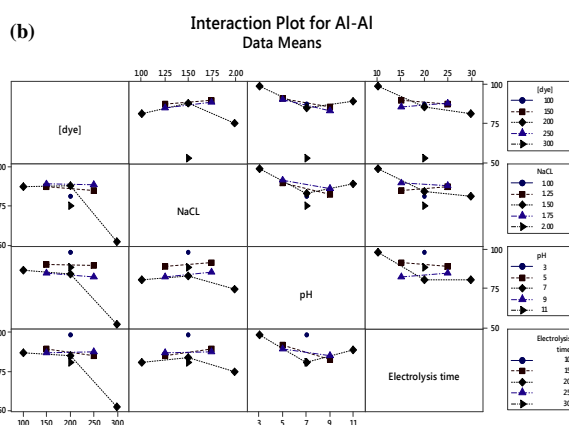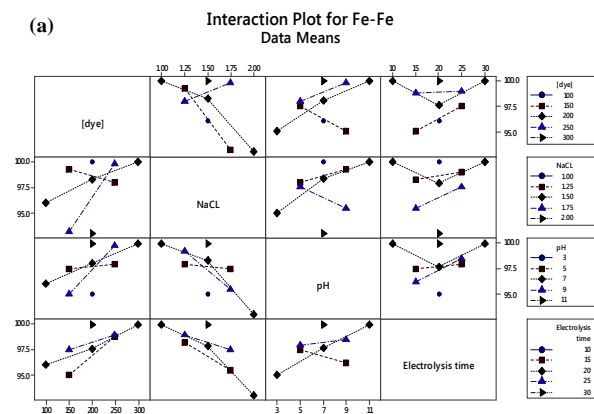

Figure 5. Main effect plots

(b)

Figure 6. **Interaction Plots**

The effect of factors on the percent removal of Y145 dye using Fe-Fe and Al-Al electrode combinations.

The effect of dye concentration

To observe the effect of initial dye concentration on the removal of the dye using two electrode systems by EC, the experiments were carried out for five different dye concentrations (100,150, 200, 250 and 300 mg/L). The higher removals of the dye were obtained using Fe-Fe electrodes as compared to Al-Al electrodes. Furthermore, at the low concentration of the dye the removal was greater as compared to presence of the high concentration of the dye. Because, the high concentration requires the high quantity of coagulant for coagulation in a fixed period of time [25]. The effect of concentration of the dye combined with other factors on the removal efficiency of the dye is shown in Fig. 7, and Fig. 8.

The effect of NaCl

The effect of amount of supporting electrolyte (NaCl) on the removal of Y145 dye is given in Fig. 7 and 8. It can be ascertained from Fig. 7a-d that the dye removal efficiency was not increasing with an increase in the supporting electrolyte concentration in Fe-Fe electrode system while it was increasing using Al-Al electrode system as shown in Fig. 8a-d. The formation of chlorine gas and OCl$^-$ owing to the oxidation of chloride ions at the anode, additionally, provides support for the removal of contaminants in the EC system. Thus, the supporting electrolyte not only

Full interaction plots

The lines in the full interaction plots were not parallel to both X-axis and Y-axis. This indicated that the levels of the factors were varying the removal of Y145 dye during the EC process using Fe-Fe and Al-Al electrodes systems as shown in Fig. 6a-b.

(a)

increases the conductivity but also contributes as a strong oxidizing agent [26].

The effect of pH

The pH of the EC system significantly affects the efficiency of EC process. The pH determines the type of hydroxide of metal cations in the EC system and also determines the interaction between the formed coagulants and the molecules of dye in the solution. Consequently, It influences the mechanism of the removal of dye from the aqueous system. In order to investigate the effect of the pH of the solution on the removal of the dye, the experiments were performed by adjusting the initial pH such as 3, 5, 7, 9 and 11. Fig. 7 and Fig. 8 are showing that the removal of

the dye was higher in the acidic condition as compared to the basic environment of the EC system. Because, the acidic condition increases the rate of formation of Fe^{+3} cations in the system [27]. The effect of pH of the dye solution combined with other factors on the removal efficiency of the dye is shown in Fig. 7 and 8.

The effect of electrolysis time

The removal efficiency of the dye was increasing with the increase of electrolysis time for both the electrode combinations. It was also in agreement with the reported data [28, 29]. The effect of electrolysis time combined with other factors on the removal efficiency of the dye is shown in Fig. 7 – 8.
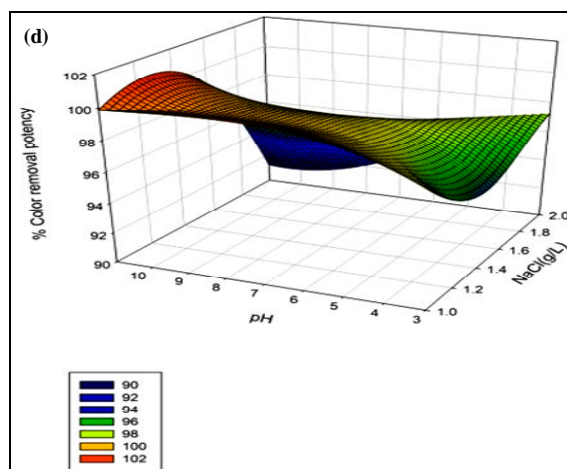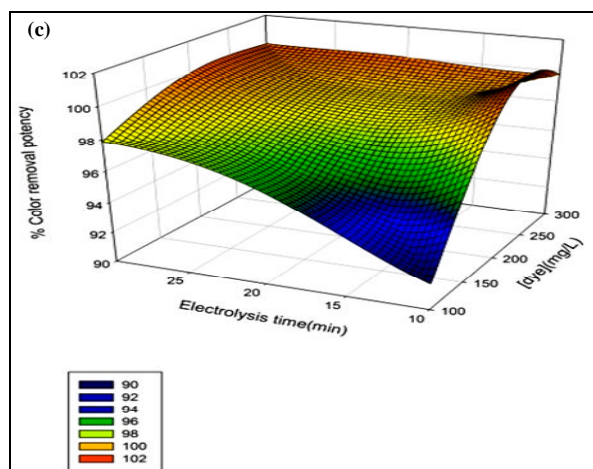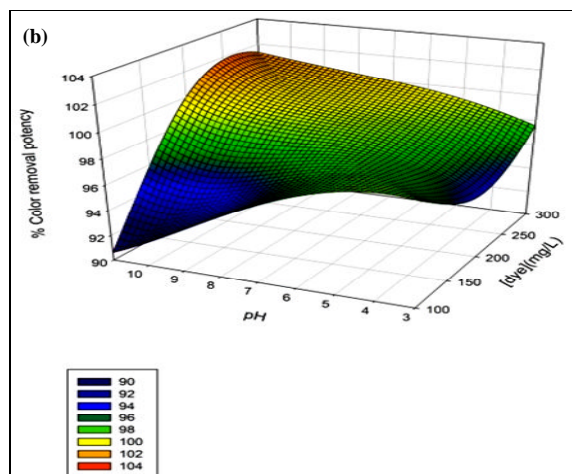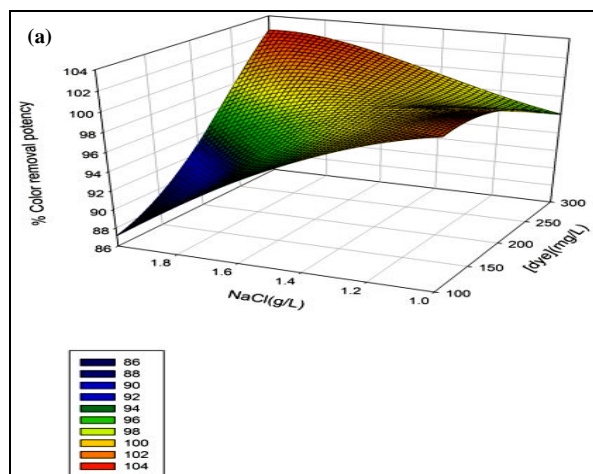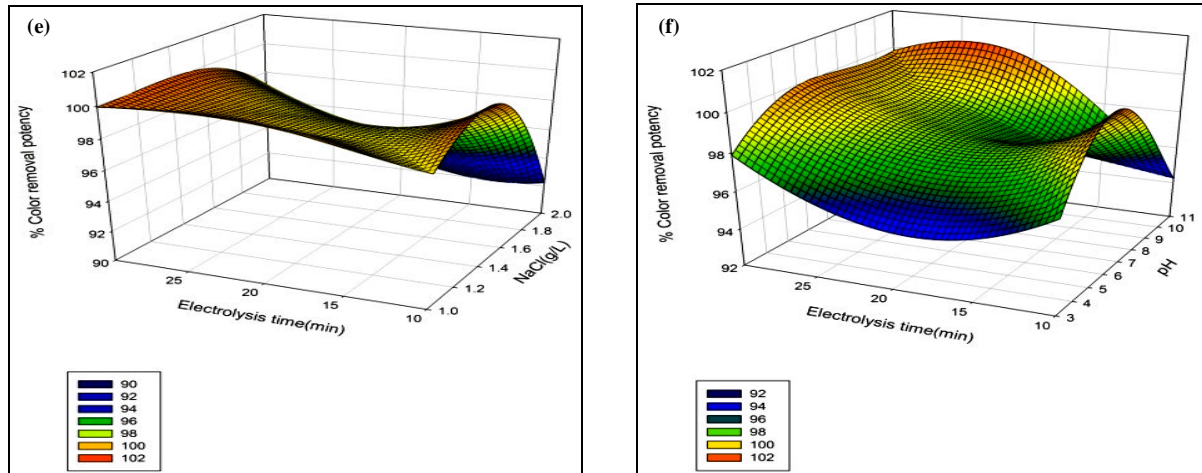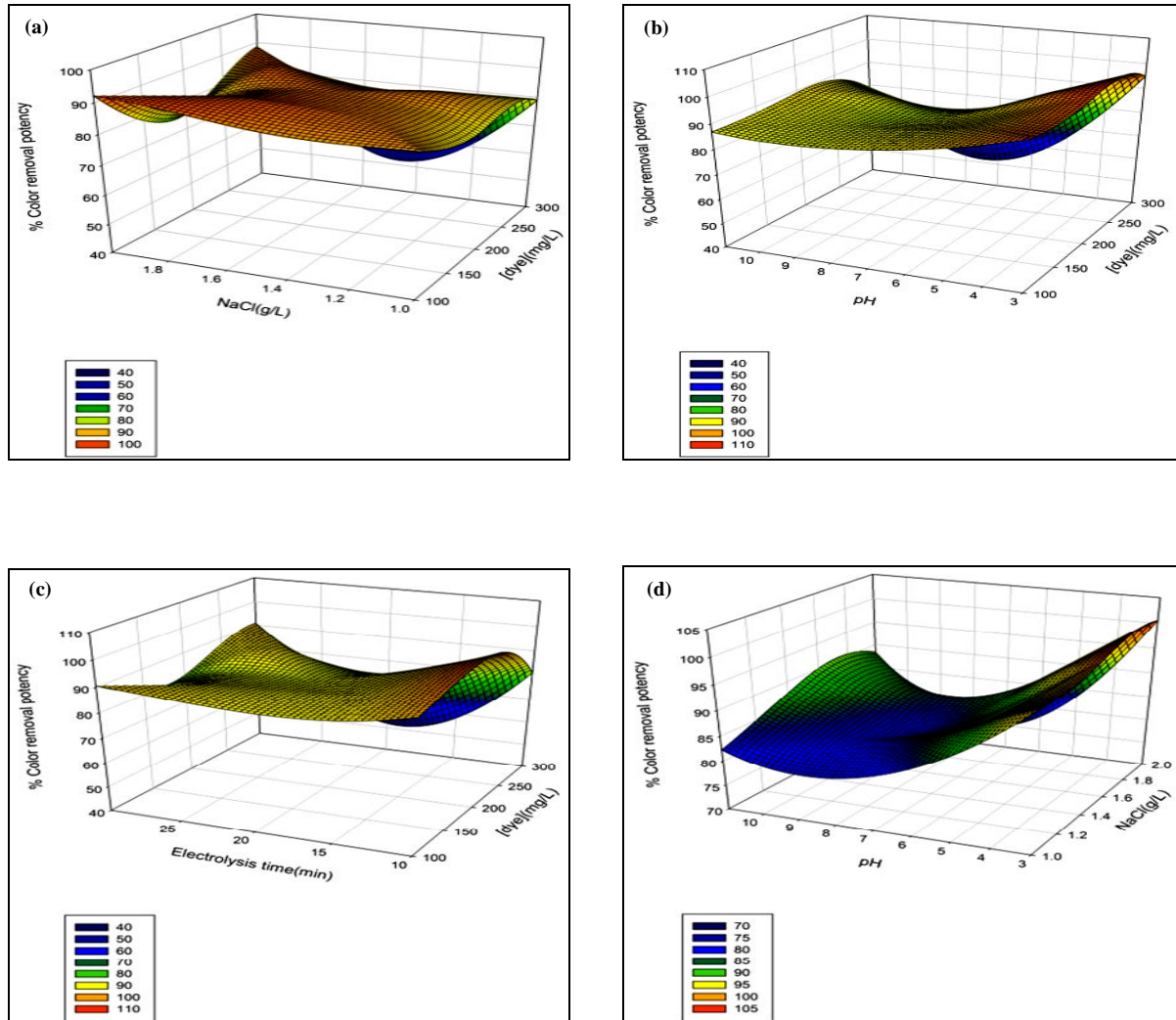
Figure 7. **Response surface plots for the removal of Y145 dye using Fe-Fe electrodes**
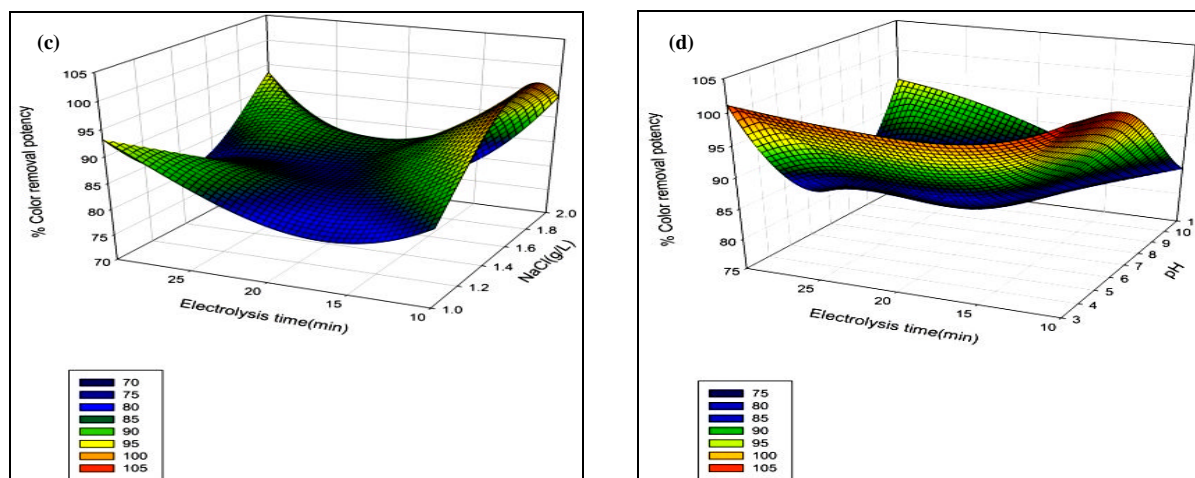
Figure 8. **Response surface plots for the removal of Y145 dye using Al-Al electrodes**

The effect of nature of electrode system

In EC process, the electrodes of Al and Fe were used. They are easily available, low cost, and undergo better dissolution [30]. The published data of some authors pointed out to the benefits of Fe electrodes, while others pointed out to the advantages of using Al anodes. It is also pointed out that Fe is relatively cheaper [31]. Fe forms more denser flocks of coagulated contaminants as compared to Al because it is heavy in mass [32]. Furthermore, Fe has better complex formation nature with inorganic/organic pollutants than Al [33]. However, it is also reported that Al/Al electrode combinations effectively utilized for the removal of dyes and Fe/Fe electrode worked better for COD and phenol removal, while Al/Fe and Fe/Al electrode combinations were successfully applied for the treatment of paper mill wastewater [34]. It is found that around 9 carbon atoms are complexed by one Fe atom, whereas 3 carbon atoms are allowed for complexation by an Al atom. It is also determined that ''coordination'' numbers of Fe or Al largely depend on the wastewater to be treated. Therefore, the efficiency of the type of electrode is depend upon the type of effluent [35]. In this work Fe-Fe electrode system provided the data of higher removal of Y145 dye as compared to Al-Al electrode system. Therefore, Fe-Fe electrode system will be proved more effective for the removal of the dye in the real effluent.

FT-IR analysis

Fig. 9 shows the FT-IR spectrum of Y145 dye. The IR absorption bands of Y145 dye are given in Table 6.

Table 6. **The IR absorption bands for the given functional groups in the dye.**

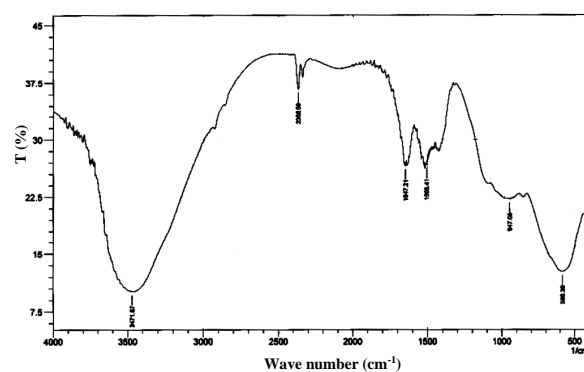| Functional groups	Wave number (cm^{-1})
NH	3450
CH, Arom	3096
C=C-	1481
N=N	1435
-C=N-	1587
C-N	1221
Sulfonates	1365–1340/1200–1100
Disulfides (CS stretch)	705–570
Sulfate ion	1130–1080/680–610

Figure 9. **FT-IR spectrum of Y145 dye**

Conclusion

In the present study, CCD was successfully applied to optimize the parameters of the EC process for the removal of Y154 dye from the simulated wastewater using Fe-Fe and Al-Al electrodes. The optimum operating parameters for the Fe-Fe electrode system were 100 mgL^{-1} of dye concentration, 1.0 gL^{-1} of NaCl, pH of 5.0 and 30 min of electrolysis time. The maximum removal of the dye was found to be 99.21%. On the other hand, the optimum operating parameters for the Al-Al electrode system were 120 mgL^{-1} of dye concentration, 1.66 gL^{-1} of NaCl, pH of 3.0 and 10 min of electrolysis time. The percent removal of the dye was found to be 98.24%. Furthermore, It was also encountered that the concentration of the dye (A), amount of electrolyte (B) were showing linearly and combined effect on the removal of the dye in Fe-Fe electrodes system. In the second electrode system, the concentration of the dye (A) has a linear and quadratic effect on the removal of the dye. It is concluded that the process can be effectively applied for the removal of Y145 dye from wastewater at large scale.

Acknowledgment

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