

# Electrochemical treatment of simulated textile wastewater with industrial components and Levafix Blue CA reactive dye: Optimization through response surface methodology

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## Abstract

The electrochemical oxidation of simulated textile wastewater was studied on iron electrodes in the presence of NaCl electrolyte in a batch electrochemical reactor. The simulated textile wastewater was prepared from industrial components based on the real mercerized and non-mercerized cotton and viscon process, being first in literature. The highest COD, color and turbidity removals were achieved as 93.9%, 99.5%, and 82.9%, respectively, at 40% pollution load, 8 V applied potential, 37.5 g/L electrolyte concentration and 30 °C reaction temperature. The electrochemical treatment of industrial textile wastewater was optimized using response surface methodology (RSM), where applied potential and electrolyte concentration were to be minimized while COD, color and turbidity removal percents were maximized at 100% pollution load. In a specific batch run under the optimum conditions of 30 °C reaction temperature, 25 g/L electrolyte concentration and 8 V applied potential applied with 35.5 mA/cm<sup>2</sup> current density at 100% pollution load, COD, color and turbidity removals were realized as 61.6%, 99.6% and 66.4%, respectively. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Electrochemical treatment; Textile wastewater; Statistical experiment design; Optimization; Response surface methodology (RSM)

## 1. Introduction

Textile manufacturing is one of the largest industrial producers of wastewater; approximately 125–150 L of water are used for 1 kg of textile product. It is also a chemically intensive one, the wastewater from textile processing contains processing bath residues from preparation, dyeing, finishing, slashing and other operations. These residues can cause pollution if not properly treated before discharge to the environment [1–3]. Dyes and auxiliary chemicals used in textile mills are improved to be resistant to environmental influences for better performance. As a result they are hardly removed from wastewater generated during the dyeing processes [1]. In this content, the textile industry is concerned with some pollutants, which might not be suitable to treat with existing treatment technologies [2]. These pollutants generally include color residues, heavy metal ions, and electrolytes

in dyeing wastewater, and toxic air emissions from discharged wastewater.

Textile wastewater is well known with its high chemical oxygen demand, strong color, large amount of suspended solids, variable pH, salt content and high temperature. Therefore, the treatment systems combined with physical, biological and chemical methods become inefficient for the effective treatment of industrial textile wastewater due to the variation of wastewater characteristics and heavy COD load [4–9]. On the other hand, electrochemical oxidation is becoming an alternative wastewater treatment method because many industrial processes produce toxic wastewaters, which are not easily biodegradable and requiring costly physical or physicochemical pretreatments [10].

The electrochemical treatment of textile wastewater has been previously studied in the literature [4–9,11–18]. In recent studies, Shen et al. [11] investigated the effect of operational parameters of electrolyte concentration, temperature, stirring and voltage in the degradation effect of electrochemical treatment of dye wastewater using nanophase TiO<sub>2</sub> catalyst and

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Co–Bi–PbO<sub>2</sub>/Ti anodes with Na<sub>2</sub>SO<sub>4</sub> electrolyte at 8 V applied potential and 25 °C temperature, except testing their influence [11]. Daneshvar et al. [12] used electrocoagulation for the removal of color from C.I. Basic Red 46 (BR46) and C.I. Basic Blue 3 (BB3) containing solutions with NaCl electrolyte [12]. Awad and Galwa [13] studied the electrocatalytic degradation of Acid Blue and Basic Brown dyes from simulated wastewater on lead dioxide anode in H<sub>2</sub>SO<sub>4</sub>, NaOH and NaCl electrolytes within a current density range of 0–45 mA/cm<sup>2</sup> [13]. Carneiro et al. [14] investigated the electrochemical oxidation of Reactive Blue 4 using glassy carbon electrode, reticulated vitreous carbon electrode, dimensionally stable anodes of Ti/SnO<sub>2</sub>/SbO<sub>x</sub>/RuO<sub>2</sub> [14]. Sakalis et al. [15] studied the electrolytic degradation of Reactive Orange 91, Reactive Red 184, Reactive Blue 182 and Reactive Black 5 azodyes using both synthetic and real wastewater samples using carbon fleece as cathode and the anode was made of titanium substrate coated with platinum film with NaCl or Na<sub>2</sub>SO<sub>4</sub> electrolytes [15]. Alinsafi et al. [16] investigated the electrocoagulation and response surface optimization of Drimarene K2LR CDG Blue using rectangular flat aluminum electrodes [16]. Fernandes et al. [17] studied the electrochemical oxidation of C.I. Acid Orange 7 (AO7) on boron doped diamond anode and copper foil cathode using KCl and Na<sub>2</sub>SO<sub>4</sub> electrolytes at 25 °C, with a current density of 1.25–10 mA/cm<sup>2</sup> [17]. Cerón-Rivera et al. [18] studied the electrochemical treatment of Basic Yellow 28 (SLY) and Reactive Black 5 (CBWB) methine and sulfoazo textile dyes using diamond-, aluminium-, copper- and iron–zinc alloy electrodes [18].

In this study, the electrochemical treatment of a simulated industrial textile wastewater was investigated using iron electrodes in the presence of NaCl and the treatment performance was optimized using response surface methodology (RSM). RSM is essentially a particular set of mathematical and statistical methods used by researchers in order to aid in the solution of certain types of problems, which are pertinent to scientific or engineering processes. Response surface procedures are not primarily used for the purpose of allowing the researcher in order to understand the mechanism of the system or process; rather its purpose is to determine the optimum operating conditions or to determine a region for the factors at a certain operating specifications are met [19,20]. Its greatest applications have been in industrial research, particularly in situations where a large number of variables influencing the system feature. This feature termed as the response and normally measured on a continuous scale, which represents the most important function of the systems [19,20].

In the study, the optimization of electrochemical treatment of industrial textile wastewater was aimed through batch runs using RSM by Design Expert 6.0 (trial version). The runs were designed in accordance with the central composite design (CCD) and carried out batch-wise. Five factors; pollution load percent, applied potential, electrolyte concentration, reaction temperature and reaction time were selected as effective process (independent) variables while COD, color and turbidity removal percents as the response (dependent variable). The real industrial mercerized and non-mercerized cotton and viscon process wastewater with Levafix CA reactive dye was synthetically

prepared from industrial components for the standardization of textile wastewater throughout the study. In the study, Levafix CA reactive dye was chosen mainly because of increasing regional use for its high fastness profile and meeting most requirements set by textile manufacturers for fastness to light, perspiration, chlorine and repeated washing. In the runs, pH adjustment, coagulant addition and other physicochemical processes were not employed in order to assess the electrochemical treatment performance clearly.

## 2. Materials and methods

### 2.1. Chemicals and materials

Levafix Blue CA gran. reactive dye (DyStar), Cottoclarin F (Cognis), Belsoft 200 (Cognis), dextrin (Sigma), sucrose (Merck), hydrogen peroxide (Merck), sodium hydroxide (Merck), sodium silicate (Merck), acetic acid (Merck), sodium carbonate (Merck) and sodium chloride (Merck) were obtained in extra pure grade and double distilled water was used for the preparation of simulated industrial textile wastewater. All chemicals used for the analysis were obtained in highest degree of purity from various sources. The chemical structures of commercial Levafix CA reactive dyes are not disclosed.

### 2.2. Simulated industrial textile wastewater

In order to standardize the textile wastewater in the runs, the industrial textile wastewater was synthetically prepared based on real process information of pretreatment and dyeing stages of non-mercerized and mercerized cotton and viscon process, where the model process was composed of sizing, desizing, singeing, scouring, bleaching, mercerization and dyeing.

The composition and the characteristics of simulated industrial textile wastewater are presented in Tables 1 and 2, respectively. Some of the common components also used in the literature were dextrin as 444 mg/L [21], 1000 mg/L [22]; sucrose as 400 mg/L [22]; hydrogen peroxide as 10 mL/L [23]; sodium hydroxide as 400 mg/L [23]; softening agent as 1000 mg/L [24]; dye as 60 mg/L [11], 20–100 mg/L [12],

Table 1  
The composition of simulated industrial textile wastewater

Pollutant	Concentration
Cottoclarin F (mg/L)	500
Dextrin (mg/L)	1600
Sucrose (mg/L)	640
Hydrogen peroxide (35–40%, <i>d</i> = 1.133) (mL/L)	4
Sodium hydroxide (mg/L)	1200
Sodium silicate (mg/L)	2.5
Belsoft 200 (mg/L)	400
Acetic acid (mg/L)	165
Levafix reactive dye (mg/L)	1200
Sodium carbonate (mg/L)	700
Sodium chloride (mg/L)	5000
Ethylene dinitrilo tetra acetic acid (EDTA) (mg/L)	300
Detergent (mg/L)	300
Silicone oil (mg/L)	20

Table 2  
The characteristics of simulated industrial textile wastewater

Parameter	Value
Chemical oxygen demand (mg/L)	3505
Turbidity, NTU	11.4–19.1
pH	11.52
Dissolved oxygen (mg/L)	5.07
Total solids (mg/L)	12,380
Total suspended solids (mg/L)	120
Total volatile solids (mg/L)	4990
Non-volatile solids, mg/L	7390
Chloride (mg/L)	3761
Conductivity (mS)	14(=15.78 mS/cm)
Density (g/mL)	0.992

10–200 mg/L [13], 50 mg/L [16], 20–360 mg/L [17], 100 mg/L [18], 373 mg/L [21], 20 mg/L [22], 100 mg/L [24]; sodium carbonate as 40 mg/L [22]; sodium chloride as 7410 mg/L [21], 1000 mg/L [22], 8500 mg/L [24]; detergent as 55 mg/L [21], 60 mg/L [22], 1000 mg/L [24].

The characteristics of textile wastewater used in literature studies were, COD as 460–1500 mg/L [4], 1081–2130 mg/L [25], 1520–3325 mg/L [9], 1425 mg/L [21], 2154 mg/L [24], 420–1400 mg/L [26], 250–1800 mg/L [27]; pH as 9–10 [4], 6–9 [5], 11 [28], 10–11.82 [9], 10.3 [26], 5.1–9.2 [27]; turbidity as 9.3 NTU [7], 50–210 NTU [27]; conductivity as 2.1–2.9 mS [4], >2 mS/cm [5], 4.85 mS/cm [7], 0.134 mS/cm [21], 4.2–14 mS/cm [26]; total suspended solids as 91–250 mg/L [4], <200 mg/L [5], 26.4 mg/L [7], 82–110 mg/L [25], 34 mg/L [8], 18–34 mg/L [9], 1–150 mg/L [26], 45–320 mg/L [27].

The literature data showed that the simulated industrial textile wastewater used in this study was successfully prepared to simulate the real case. In the runs for concentration effect, the wastewater was accordingly diluted regarding the composition in Table 1 as 100%.

### 2.3. Experimental set-up and procedure

The electrochemical reactor designed in our laboratory [29] was used batch-wise in the experiments designed in accordance with CCD (central composite design). The reactor was made of Pyrex® glass having a volume of 600 mL with a heating and cooling coil around. The three pairs of iron electrodes (o.d. = 12 mm) were used as anode and cathode and placed 1.5 cm apart on a Plexiglas® reactor cover. The total anode area was 75.35 cm<sup>2</sup> and the net wastewater volume was 400 mL. A glass stirrer with a single 4 cm diameter paddle was driven with a Heidolph-RZR 1 model mixer for homogenization at 575 rpm. The reaction temperature was controlled with circulating water recycled from a temperature controlled water bath (New Brunswick, G-86) and monitored with a glass thermometer immersed. The current was applied by a constant voltage/current controlled dc power source, NETES NPS-1810D.

Simulated industrial textile wastewater was loaded into the batch electrochemical reactor and the Plexiglas® reactor cover was placed tightly. A sample of 5 mL was taken from the reactor with an injector to determine the initial chemical oxygen demand

(COD), color, turbidity and pH prior to the reaction. The reaction started with the application of specified voltage, and the recycling water for temperature control was pumped through the reactor jacket. At appropriate time intervals, samples of 5 mL were taken from the reactor and analyzed to determine the COD, color, turbidity and pH during electrochemical treatment.

After each run, the corroded part of the anodes and electroreduced substances on the cathodes were removed with a revolving metal brush. Then the surface of the electrodes was replenished with a water sandpaper prior to a new experiment. The maximum use of Fe electrodes was experienced between 50 and 80 h of operation depending on toughness of reaction conditions [30].

### 2.4. Experimental design and optimization

The most popular class of second-order designs, the central composite design (CCD), was used for RSM in the experimental design and presented in Table 3. The central composite design with five factors at five levels was applied using Design-Expert 6.0 with the bounds of the factors (independent variables). Each independent variable was coded at five levels between –2 and +2 at the ranges determined by the preliminary experiments, where the independent variables were pollution load, 20–100%; applied potential, 2–10 V; electrolyte concentration, 0–50 g/L; reaction temperature, 25–45 °C and reaction time, 0–240 min.

The total number of experiments with five factors was 50 ( $=2^k + 2k + 8$ ), where  $k$  is the number of factors. Forty-two experiments were augmented with eight replications at the design center to evaluate the pure error and were carried in randomized order as required in many design procedures. First six columns of Table 3 show run number and experimental conditions of the runs arranged by the CCD. Performance of the process was evaluated by analyzing the responses; COD, color and turbidity removal percents.

In the optimization process, the responses can be simply related to chosen factors by linear or quadratic models. A quadratic model, which also includes the linear model, is given as:

$$\eta = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i < j=2}^k \sum_i \beta_{ij} x_i x_j + e_i \quad (1)$$

where  $\eta$  is the response,  $x_i$  and  $x_j$  are variables ( $i=1-5$ ),  $\beta_0$  is the constant coefficient,  $\beta_j$ ,  $\beta_{jj}$  and  $\beta_{ij}$  ( $i$  and  $j=1-5$ ) are interaction coefficients of linear, quadratic and the second-order terms, respectively, and  $e_i$  is the error. COD, color and turbidity removal percent data were processed for Eq. (1) using Design-Expert 6.0 program including ANOVA to obtain the interaction between the process variables and the response. The quality of the fit of polynomial model was expressed by the coefficient of determination  $R^2$  and  $R^2_{\text{adj}}$ , and statistical significance was checked by the  $F$ -test in the program. For optimization, a module in Design-Expert software searched for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. The desired goals were selected as maximum COD, color and turbidity removal percent at minimum reaction time within temperature range.

Table 3  
Central composite design (CCD) and experimental results

Run No.	$x_1$ (%)	$x_2$ (V)	$x_3$ (g/L)	$x_4$ (°C)	$x_5$ (min)	COD removal (%)	Color removal (%)	Turbidity removal (%)
1	40	4	37.5	30	180	50.04	98.15	89.05
2	40	8	37.5	40	180	93.72	97.97	36.03
3	80	4	37.5	40	60	45.34	97.73	59.26
4	100	6	25.0	35	120	54.57	99.64	23.67
5	40	8	37.5	30	180	93.93	99.51	82.89
6	60	6	25.0	35	120	33.66	99.39	81.37
7	60	6	25.0	25	120	45.48	99.44	93.81
8	80	8	37.5	30	180	55.57	99.81	86.20
9	40	8	12.5	40	60	42.75	99.37	82.17
10	80	4	12.5	40	180	53.57	98.52	19.95
11	20	6	25.0	35	120	94.98	94.96	64.82
12	80	8	37.5	30	60	39.72	97.08	87.72
13	60	6	25.0	35	0	0	0	0
14	60	6	25.0	35	120	33.66	99.39	81.37
15	60	6	25.0	35	240	64.44	99.81	76.55
16	60	6	25.0	45	120	50.41	99.67	71.09
17	60	6	25.0	35	120	33.66	99.39	81.37
18	40	4	37.5	30	60	32.87	60.18	83.09
19	40	4	37.5	40	180	67.29	98.94	74.06
20	80	8	12.5	30	180	53.16	99.24	84.07
21	40	4	12.5	40	60	47.88	97.30	0.00
22	60	6	25.0	35	120	57.50	99.66	71.91
23	80	4	37.5	30	180	35.68	99.65	89.80
24	80	8	37.5	40	180	67.39	99.83	87.11
25	60	6	25.0	35	120	57.50	99.66	71.91
26	80	4	12.5	30	60	26.51	63.20	24.93
27	80	4	37.5	30	60	24.08	99.27	74.88
28	60	6	25.0	35	120	57.50	99.66	71.91
29	80	4	12.5	30	180	45.40	93.32	66.81
30	60	6	50.0	35	120	61.03	99.47	81.73
31	60	6	25.0	35	120	56.29	99.25	86.64
32	40	8	37.5	30	60	60.95	99.08	59.82
33	40	4	12.5	30	180	32.64	96.90	78.88
34	40	8	37.5	40	60	93.62	96.53	24.36
35	80	4	37.5	40	180	55.49	99.79	56.30
36	40	4	12.5	40	180	49.93	99.14	62.25
37	80	8	12.5	30	60	32.52	84.99	0.00
38	80	8	12.5	40	180	65.03	99.42	69.01
39	40	8	12.5	40	180	60.70	99.50	87.77
40	60	10	25.0	35	120	65.17	99.56	83.45
41	60	2	25.0	35	120	41.84	98.87	95.36
42	80	8	37.5	40	60	58.99	98.77	90.51
43	80	8	12.5	40	60	56.67	98.92	71.56
44	60	6	0.0	35	120	18.38	73.72	0
45	60	6	25.0	35	120	56.29	99.25	86.64
46	40	8	12.5	30	60	36.88	90.01	33.63
47	40	4	12.5	30	60	23.86	67.69	70.63
48	40	4	37.5	40	60	56.69	99.52	88.19
49	40	8	12.5	30	180	53.03	99.03	43.05
50	80	4	12.5	40	60	32.41	78.39	0

Corresponding importances of goals were selected as 1 for all of the dependent and independent variables. These individual goals were combined into an overall desirability function by Design-Expert software for maximization to find the best local maximum.

### 2.5. Analysis

During the reaction 5 mL samples were taken from the electrochemical reactor at appropriate time intervals and pH was

measured with a NEL pH30 model pH meter, then centrifuged at 5000 rpm for 10 min to have supernatant for analysis and measurements. The color of the reaction medium was monitored by a Hitachi 150–20 model spectrophotometer at 610 nm and the turbidity was measured by a Hach 2100 AN IS model turbidimeter at 860 nm. COD analysis was performed with Palintest PL464 test kit after color and turbidity analysis. In order to prevent the precipitation of  $\text{Ag}^+$  ions in COD test kits with  $\text{Cl}^-$  ions present in the sample, the samples were pre-treated with appropriate amounts of 2 mol/L  $\text{AgNO}_3$  prior to COD analysis.  $\text{AgCl}$

precipitated due to the addition of  $\text{AgNO}_3$  and the sample was centrifuged again at 5000 rpm for 10 min. The supernatant was removed and the precipitate was washed with 0.5 mL pure sulphuric acid for desorption of the adsorbed waste and centrifuged at 5000 rpm for 10 min. This procedure was repeated twice. All of the collected supernatants were mixed and 1 mL of the sample mixture was added to the COD kit for digestion. For COD analysis, Grant QBT2 model block heater was turned on and the temperature was set to  $150^\circ\text{C}$ . Sample and blank tubes were digested for 2 h. Then, the tubes were allowed to cool down to room temperature and the absorbance of the samples was read at 605 nm at Hitachi 150–20 model spectrophotometer. The COD of the samples was calculated using a calibration curve prepared previously.

### 3. Results and discussion

The nature of the anode is the most important parameter in electrochemical wastewater treatment [10]. Therefore, carbon, iron and SS304 anodes, all commercially used electrode materials, and the spacing between the electrodes were tested at 100% pollution load, 25 g/L NaCl, 15.5 mA/cm<sup>2</sup> current density (6 V applied potential) and 240 min reaction time. Under specified conditions, COD, color and turbidity removals were realized as 13.0%, 88.1%, 0% for carbon; 61.6%, 99.6%, 55.8% for iron and 80.4%, 99.7%, 66.8% for SS304 electrodes, respectively. Carbon electrodes proved to be inefficient for COD and turbidity removal, thus were not considered. SS304 electrodes, iron-based alloys of Fe/Ni/Cr, rapidly eroded in the reactor leaving large amount of precipitate including  $\text{Fe}_2\text{O}_3$ , FeO,  $\text{Fe}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{FeCr}_2\text{O}_4$ . Although the best treatment performance of COD, color and turbidity removals were obtained with SS304 electrode, iron electrodes were chosen in the study due to being more corrosion resistant under extreme conditions. Iron electrodes have also been previously studied in the literature for electrochemical treatment of textile wastewater [4,5,12,31–33].

The spacing of 1.5 and 8.0 cm was studied with selected iron electrodes under the same conditions of electrode material testing. COD, color and turbidity removals were realized as 61.6%, 99.6%, 55.8% for 1.5 cm and 29.3%, 78.3% and 43.8% for 8 cm, respectively. The narrow electrode spacing minimizes ohmic losses permitting relatively high current densities, in return high reaction rate, to be attained. The electrode reaction occurs in the region where by the influence of the electrode charge an electric field is formed, characterized by the distribution of the electric potential as a function of the distance from the electrode surface [34]. This electric field affects the concentrations of the reacting substances and also the activation energy of the electrode reaction. In the electrode reaction the reacting particles approach the electrode to the smallest possible distance they can reach without adsorption [34].

Therefore the batch runs were conducted using iron electrodes at 1.5 cm electrode spacing in 50 CCD designed experiments to visualize the effects of independent factors on responses and the results along with the experimental conditions were presented in Table 3. In this study, being different

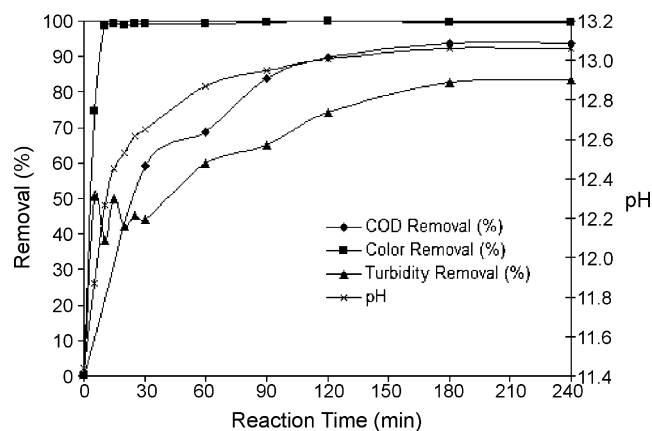


Fig. 1. COD, color and turbidity removal profiles for run 5 (pollution load: 40%; applied potential: 8 V (32.8 mA/cm<sup>2</sup> current density); electrolyte concentration: 37.5 g/L; reaction temperature: 30 °C).

from the literature studies [11–18], the main source of the COD was not only the textile dye, but also predominant industrial constituents of simulated textile wastewater given in Table 1. Higher than 50% COD removal percent was obtained in 28 runs, which had also over 98% color removal while more than 95% color and more than 70% turbidity removal were achieved in 41 and 31 batch runs, respectively. As a general trend, increase in electrolyte concentration and applied potential resulted in enhanced COD, color and turbidity removals in all runs.

In Table 3, run 5 specifically gave the best removal percent for COD as 93.9% while removal of color and turbidity was achieved as 99.5% and 82.9%, respectively, in the same run. Fig. 1 shows COD, color and turbidity removal percents and pH time profiles of this run. In 10 min of reaction time 98% of color removal and in 120 min COD and turbidity removals were achieved as 90% and 75%, respectively. The pH of the reaction medium raised from 11.4 to 13.1, which was observed in most of the runs, was most likely due to the production of hydroxyl ions and hydrogen gas evolution on the cathode. In the study, the conductivity of textile wastewater was adjusted using NaCl, the main salt in textile dye baths used for the optimal fixation of the dyes on the textile substrate. Current density is one of the most important parameters in carrying out electrochemical processes which can be increased by elevated electrolyte concentration and applied potential. Increasing applied potential also increases the amount of gas discharged on the electrodes and production. During electrochemical treatment organic molecules are electrooxidized at the anode or electroreduced at the cathode into small molecules.  $\text{Fe}(\text{OH})_3$  coagulation and  $\text{H}_2/\text{O}_2$  flotation also remove most of the organic molecules and suspended solids [4].

#### 3.1. Evaluation of experimental results with design expert

The experimental results were evaluated by Design-Expert 6.0 software using approximating functions of dependent variables COD ( $y_1$ ), color ( $y_2$ ) and turbidity ( $y_3$ ) removal percents.

The approximating functions of COD, color and turbidity removal percents obtained by Design-Expert software are given in Eqs. (2)–(4), respectively.

$$\begin{aligned}
 y_1 = & -31.221 - 1.448x_1 + 1.027x_2 + 1.098x_3 + 1.585x_4 \\
 & + 0.586x_5 + 0.017x_1^2 + 0.398x_2^2 - 0.012x_3^2 \\
 & + 8.168 \times 10^{-3}x_4^2 - 1.035 \times 10^{-3}x_5^2 - 0.050x_1x_2 \\
 & - 0.023x_1x_3 - 1.916 \times 10^{-3}x_1x_4 + 2.414 \times 10^{-4}x_1x_5 \\
 & + 0.135x_2x_3 - 0.076x_2x_4 + 5.216 \times 10^{-3}x_2x_5 \\
 & + 0.020x_3x_4 - 2.971 \times 10^{-4}x_3x_5 - 6.593 \times 10^{-3}x_4x_5
 \end{aligned} \quad (2)$$

$$\begin{aligned}
 y_2 = & -19.924 - 0.125x_1 + 7.608x_2 + 1.340x_3 - 1.663x_4 \\
 & + 1.403x_5 + 3.994 \times 10^{-3}x_1^2 + 0.519x_2^2 \\
 & - 6.904 \times 10^{-3}x_3^2 + 0.086x_4^2 - 2.848 \times 10^{-3}x_5^2 \\
 & - 0.012x_1x_2 + 9.374 \times 10^{-3}x_1x_3 - 0.013x_1x_4 \\
 & - 2.143 \times 10^{-4}x_1x_5 - 0.051x_2x_3 - 0.217x_2x_4 \\
 & - 0.024x_2x_5 - 0.020x_3x_4 - 2.488 \times 10^{-3}x_3x_5 \\
 & - 0.010x_4x_5
 \end{aligned} \quad (3)$$

$$\begin{aligned}
 y_3 = & 247.533 - 0.352x_1 - 49.298x_2 + 6.826x_3 - 10.320x_4 \\
 & + 1.315x_5 - 0.018x_1^2 + 1.009x_2^2 - 0.052x_3^2 + 0.092x_4^2 \\
 & - 2.430 \times 10^{-3}x_5^2 + 0.219x_1x_2 + 0.027x_1x_3 \\
 & + 7.969 \times 10^{-3}x_1x_4 + 9.974 \times 10^{-4}x_1x_5 - 0.260x_2x_3 \\
 & + 0.904x_2x_4 - 2.542 \times 10^{-3}x_2x_5 - 0.064x_3x_4 \\
 & - 8.136 \times 10^{-3}x_3x_5 - 0.011x_4x_5
 \end{aligned} \quad (4)$$

In Eqs. (2)–(4)  $y_1$ ,  $y_2$  and  $y_3$  correspond to response of COD, color and turbidity removal percents;  $x_1$ ,  $x_2$ ,  $x_3$ ,  $x_4$  and  $x_5$  correspond to independent variables of pollution load, applied potential, electrolyte concentration, reaction temperature and reaction time, respectively. ANOVA results of these quadratic models presented in Table 4 indicated that these quadratic models could be used to navigate the design space. In Table 4, the model  $F$ -values of 7.46, 3.03 and 3.86 imply the models are significant for COD, color and turbidity removal percents, respectively. Adequate precision measures the signal to noise ratio and a ratio greater than four is desirable. Therefore, in the quadratic models of COD, color and turbidity removal percents, the ratios of 12.650, 9.192 and 8.795 indicate adequate signals for the models to be used to navigate the design space. The values of  $P > F$  less than 0.0500 indicate model terms are significant, because values greater than 0.1000 indicate that the model terms are not significant. For all models,  $P > F$  is less than 0.0001, indicating that terms are significant in all models. For Eq. (3), lack of fit  $F$ -value of 6187.82 implies the significance for color removal, and the value of 12.22 for Eq. (4), implies that lack of fit is insignificant for turbidity removal per-

Table 4  
ANOVA results of the quadratic models

Source	Sum of squares	Degrees of freedom	Mean square	$F$ value	$P > F$
COD removal % <sup>a</sup>					
Model	15066.32	20	753.32	7.46	<0.0001
Residual	2928.00	29	100.97		
Lack of fit	1903.42	22	86.52	0.59	0.8370
Pure Error	1024.57	7	146.37		
Color removal % <sup>b</sup>					
Model	9059.51	20	452.98	3.03	0.0033
Residual	4332.87	29	149.41		
Lack of fit	4332.65	22	196.94	6187.82	<0.0001
Pure error	0.22	7	0.032		
Turbidity removal % <sup>c</sup>					
Model	29843.87	20	1492.19	3.86	0.0005
Residual	11199.74	29	386.20		
Lack of fit	10915.50	22	496.16	12.22	0.0012
Pure error	284.24	7	40.61		

<sup>a</sup>  $R^2 = 0.84$ ,  $R^2_{\text{adj}} = 0.73$ , adequate precision = 12.650.

<sup>b</sup>  $R^2 = 0.68$ ,  $R^2_{\text{adj}} = 0.45$ , adequate precision = 9.192.

<sup>c</sup>  $R^2 = 0.73$ ,  $R^2_{\text{adj}} = 0.54$ , adequate precision = 8.795.

cent. Also for all models normal % probability and studentized residuals graphs for responses  $y_1$ ,  $y_2$  and  $y_3$  yielded fairly straight lines, proving normal distribution of the data (graphs were not shown).

### 3.2. Optimization of experimental conditions

The experimental results were optimized by Design-Expert software using the approximating functions of COD, color and turbidity removal percents in Eqs. (2)–(4). In this study, a cost driven approach was preferred in the range of 25–45 °C reaction temperature within 0–240 min; applied potential and electrolyte concentration were to be minimized so as to save energy and electrolyte, whereas COD, color and turbidity removals were maximized at 100% pollution load. The optimization results are shown in Table 5, whereas AP, EC,  $T$ ,  $t$  and  $D$  corresponding to applied potential, electrolyte concentration, reaction temperature, reaction duration and desirability, respectively.

Optimized conditions under specified cost driven constraints were obtained at 100% pollution load for the highest desirability as, 25 g/L electrolyte concentration, 30 °C reaction temperature and 8 V applied potential (35.5 mA/cm<sup>2</sup> current density) within 183 min of reaction time. At these optimum conditions, 66.7% COD removal, 72.6% turbidity removal and complete color removal were foreseen by the program optimization. Then a specific batch run was performed under these optimum conditions in order to test the estimated performance and COD, turbidity and color removals were achieved as 61.6%, 66.4% and 99.6%, respectively, denoting a reasonable prediction of the model. This result also showed that the relationship developed between the responses and the independent variables in Eqs. (2)–(4) was satisfactory.

Table 5  
Optimization results

Solution no.	AP (V)	EC (g/L)	T (°C)	t (min)	COD removal (%)	Color removal (%)	Turbidity removal (%)	D
1	7.71	23.56	30.5	183	66.7	100	72.6	0.81
2	7.72	23.60	30.5	183	66.7	100	72.6	0.81
3	7.68	23.62	30.5	183	66.7	100	72.6	0.81
4	7.69	23.58	30.4	183	66.6	100	72.5	0.81
5	7.71	23.64	30.5	183	66.7	100	72.6	0.81
6	7.69	23.55	30.4	183	66.7	100	72.4	0.81
7	7.72	23.59	30.5	183	66.7	100	72.7	0.81
8	7.72	23.52	30.5	183	66.7	100	72.6	0.81
9	7.70	23.56	30.5	183	66.7	100	72.4	0.81
10	7.69	23.55	30.5	183	66.7	100	72.6	0.81

### 3.3. Effects of operational parameters at optimum conditions

Eqs. (2)–(4) have been used to visualize the effects of experimental factors on responses under optimized conditions in 3D graphs of Figs. 2–6, where initial COD of simulated wastewater was 3505 mg/L (100% load).

In Fig. 2, the effect of applied potential and electrolyte concentration on COD removal at 100% pollution load and 30 °C is shown. The increase in applied potential enabled higher half cell voltage and current density increase for oxidation reactions resulting in enhanced COD removal within 240 min. Above 4.5 V applied potential (14.2 mA/cm<sup>2</sup> current density) and between 5 and 44 g/L electrolyte concentration, a region of more than 60% COD removal was obtained within 240 min. Maximum 65% of COD removal (causing 2278 mg/L COD drop) obtained at 25 g/L electrolyte under 8 V applied potential (35.5 mA/cm<sup>2</sup> current density). COD removal also increased with the increase in NaCl concentration up to 25 g/L due to increase in the amount of strong oxidants and conductance as well.

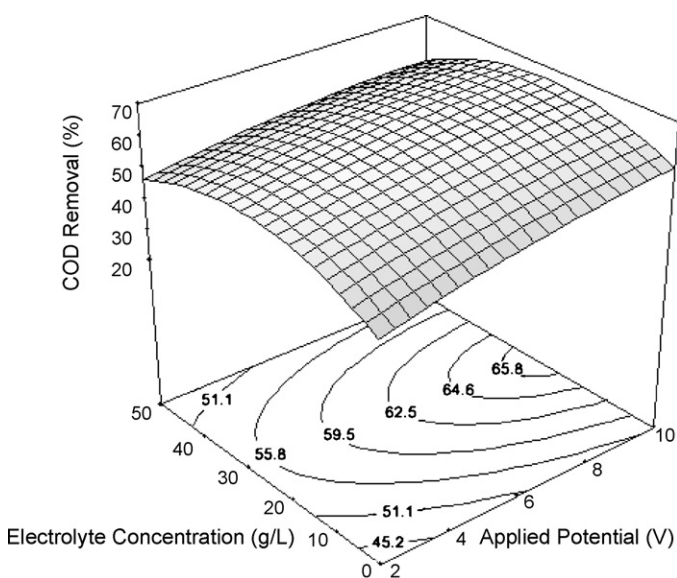


Fig. 2. The effect of electrolyte concentration and applied potential on COD removal (pollution load: 100%; reaction temperature: 30 °C; reaction time: 240 min).

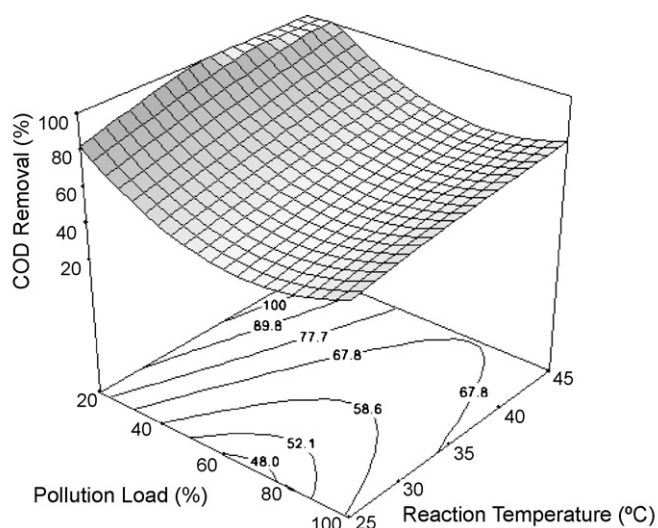


Fig. 3. The effect of pollution load and reaction temperature on COD removal (applied potential: 8 V (35.5 mA/cm<sup>2</sup> current density); electrolyte concentration: 25 g/L; reaction time: 240 min).

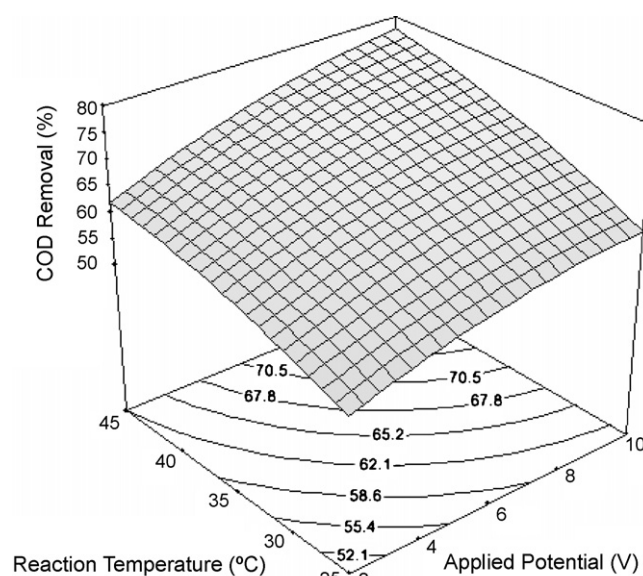


Fig. 4. The effect of reaction temperature and applied potential on COD removal (pollution load: 100%; electrolyte concentration: 25 g/L; reaction time: 240 min).

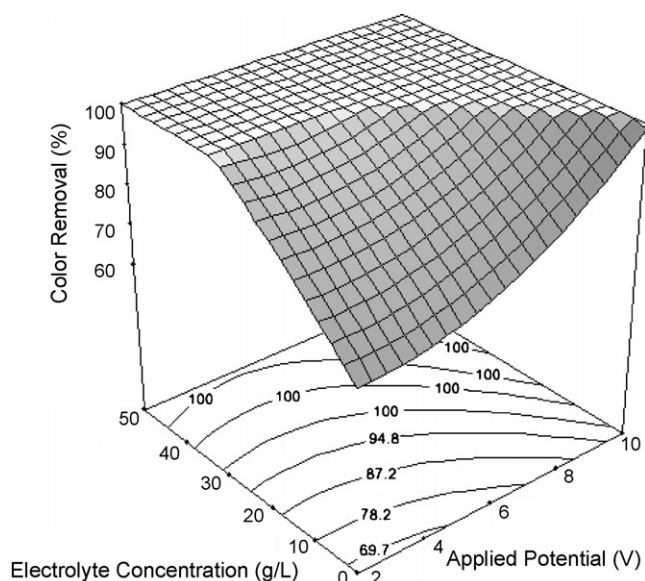


Fig. 5. The effect of electrolyte concentration and applied potential on color removal (pollution load: 100%; reaction temperature: 30 °C; reaction time: 90 min).

It is well known that the electrolysis of NaCl solution results in very strong oxidants of HOCl/CIO<sup>-</sup> ensuring indirect oxidation in the solution [23,35–40] while electrochemical degradation proceeds by direct redox reactions on the electrodes [15]. To quantify the contribution of indirect oxidation, Szpyrkowicz et al. [21] compared the results of an electrochemical treatment process with chemical oxidation by hypochlorite on the destruction of disperse dyes [21]. The authors concluded that the results obtained during hypochlorite oxidation were not satisfactory at all with 35% color reduction. Their trials proved that the electrochemical oxidation is much more efficient under acidic pH, and 79% COD elimination and 90% color removal

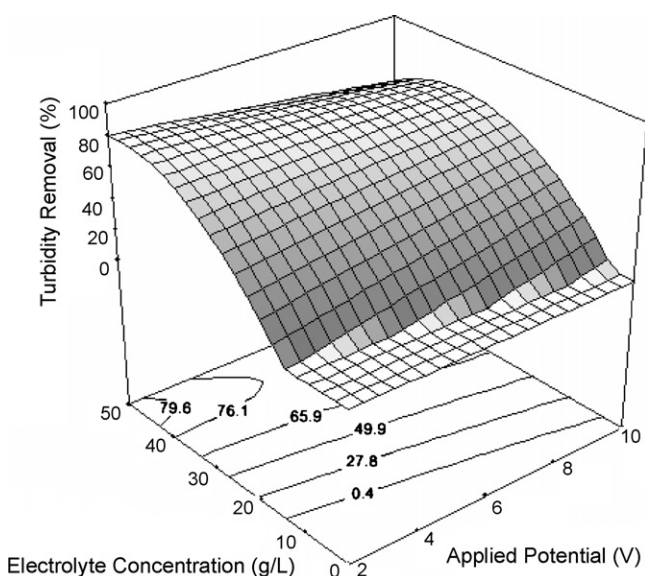


Fig. 6. The effect of electrolyte concentration and applied potential on turbidity removal (pollution load: 100%; reaction temperature: 30 °C; reaction time: 90 min).

in 40 min electrolysis time were achieved using Ti/Pt–Ir anodes [21].

In Fig. 3, the change of COD removal with reaction temperature and pollution load is depicted at 8 V applied potential (35.5 mA/cm<sup>2</sup> current density) and 25 g/L electrolyte concentration. COD removal generally increased with the decrease in pollution load while slightly increased with increasing reaction temperature. A region of more than 70% COD removal was achieved below 40% pollution load (causing 1400 mg/L COD drop) between 30 and 45 °C reaction temperature within 240 min. Shen et al. [11] reported that the enhancement of temperature lead to proportional increase of color removal [11], which in fact proportional increase of COD removal in their studies. This inference for reaction temperature is also seen in Fig. 4. In our study, above 35 °C, complete COD removal was obtained below 30% pollution load (causing 1052 mg/L COD drop). Daneshvar et al. [12] studied electrocoagulation color removal of C.I. Basic Red 46 (BR46) and C.I. Basic Blue 3 (BB3) and they concluded that the initial concentration of dye in solutions should not be higher than 80 mg/L in order to achieve high color removal [12].

Fig. 4 shows the change of COD removal with reaction temperature and applied potential at 100% load with 25 g/L electrolyte concentration. The increase in reaction temperature and applied potential both increased the COD removal. Maximum 77.6% of COD removal (causing 2720 mg/L COD drop) was obtained at 45 °C reaction temperature under 10 V applied potential (48.4 mA/cm<sup>2</sup> current density). Cerón-Rivera et al. [18] studied the electrochemical treatment of Basic Yellow 28 (SLY) and Reactive Black 5 (CBWB) methine and sulfoazo textile dyes and obtained 95% color removal and COD removal up to 65–67% in the case of CBWB dye solution treated with the copper and iron electrodes by applying applied potentials between 1.0 and 2.5 V [18]. Nevertheless, their reaction solution was basically made of dye, which was easily degradable at the concentration 615 mg/L COD [18].

The effect of electrolyte concentration and applied potential on color removal is shown in Fig. 5 at 30 °C with 100% pollution load. Color removal increased both with the increase in electrolyte concentration and applied potential. The rapid decoloration indicates that initial azo group dyes are fully degraded, giving smaller and colorless organic or inorganic products, which can further be treated for complete mineralisation. It was also reported in the literature that the chromophore groups of dyes are easily destroyed by direct and indirect oxidation, later the subsequent intermediates and other organics undergo further anodic oxidation at a much lower rate [6]. In electrochemical degradation of textile dye solutions, the rate of color removal was higher than the COD removal due to the faster azo bond degradation [6,15,17,18]. In this study, above 4 V applied potential (12.0 mA/cm<sup>2</sup> current density) and 19.3 g/L electrolyte concentration more than 90% color removal was achieved within 90 min. Reaction conditions higher than 4 V (12 mA/cm<sup>2</sup> current density) and 19.3 g/L electrolyte concentration assured the complete color removal. Alinsafi et al. [16] studied the electrocoagulation of Drimarene K2LR CDG Blue and they achieved 90–95% decoloration with 30–36% COD removal at optimal



105 min electrolysis time and 12 mA/cm<sup>2</sup> current density [16]. Shen et al. [11] stated that increasing the electrolyte concentration and voltage above 3.0 V increased the color removal, where they obtained between 30 and 40% color removal [11]. Daneshvar et al. [12] reported that an increase in the current density up to 6–8 mA/cm<sup>2</sup> enhanced the color removal efficiency [12]. Sakalis et al. [15] investigated the electrolytic degradation of Reactive Orange 91, Reactive Red 184, Reactive Blue 182 and Reactive Black 5 azodyes and obtained complete decoloration both using NaCl and Na<sub>2</sub>SO<sub>4</sub> electrolytes for all dyes. They obtained 94.4% dye removal after real wastewater treatment under 12 V applied potential and 45% COD removal [15].

Turbidity removal increased with the increase in electrolyte concentration while slightly changed with increasing applied potential at 100% load and 30 °C in Fig. 6. Turbidity removal increased up to 40 g/L NaCl and further increase in electrolyte concentration did not have a significant effect. It could be concluded that the maximum NaCl concentration should not exceed 40 g/L for satisfactory turbidity removal within 90 min. Above 40 g/L NaCl, the highest turbidity removal was obtained below 4 V applied potential (12.0 mA/cm<sup>2</sup> current density) as 80%. Any further increase either in applied potential or in electrolyte concentration may lead to increase in the formation of by-products and low molecular weight organic compounds, which may possibly contribute to turbidity.

Compared to literature data, reasonably successful results were obtained in this study under relatively mild conditions for electrochemical treatment of a highly polluted industrial textile wastewater, indicating that electrochemical degradation could be an effective treatment alternative to the traditional wastewater treatment methods.

#### 4. Conclusion

The electrochemical treatment of simulated industrial textile wastewater was studied using iron electrodes in the presence of NaCl electrolyte in a batch electrochemical reactor. The literature data showed that the real textile wastewater was successfully simulated. In the runs, highest removal for COD, color and turbidity were achieved as 93.9%, 99.5%, and 82.9%, respectively. The approximating functions for COD, color and turbidity were obtained with satisfactory degrees of fit. Using these functions, electrochemical treatment of industrial textile wastewater was optimized with the constraints of minimum applied potential, electrolyte concentration and reaction duration within 25–45 °C; maximizing COD, color and turbidity removals. The optimum conditions were found at 30 °C reaction temperature, 8 V applied potential applied (35.5 mA/cm<sup>2</sup> current density) at 100% load and 25 g/L electrolyte concentration within 183 min of reaction time. Under these conditions, COD, turbidity and color removals were predicted as 66.7%, 72.6% and 100%, respectively, which were achieved in the order 61.6%, 66.4% and 99.6% in the test run. According to these results, the electrochemical method could be a strong alternative to conventional physicochemical methods for the treatment of industrial textile wastewater with further research.

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