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Simulated textile dye wastewater treatment by electrochemical oxidation: application of response surface methodology (RSM)

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ABSTRACT

One of the main problems linked with wastewater from textile industries is colour. Reactive dyes in industrial discharge are difficult to manage as they are not readily amenable to biological treatment. The present study employs an electrochemical method using cast iron electrodes and sodium chloride (NaCl) as electrolyte to decolourize synthetic wastewater containing reactive red dye (Cibacron Red CR). Response surface methodology was employed to assess individual and interactive effects of operational parameters; electrolyte concentration (0.6–1.0 g/l), current density (1–3 mA/cm^2), reaction time (20–60 min) and initial dye concentration (20–100 mg/l) on dye degradation. The range of NaCl concentrations studied did not show any effect on dye removal indicating that the concentrations were higher than the optimum level required. Under optimum process conditions (NaCl concentration 0.6 g/l, current density 1.4 mA/cm^2 and reaction time 60 min), initial dye concentration of 100 mg/l could be almost completely removed (≥99%).

Keywords: Textile effluent; Electrochemical treatment; Reactive red dye; Cast iron electrodes; Response surface methodology

1. Introduction

Textile industries are one of the largest producers of wastewater; originating mainly from dyeing, finishing, slashing and other operations. Colour of the effluent is a major concern as even small amount of residual dye can cause a significant visual effect [1–3]. Many dyes used in textile processes can be biologically transformed to toxic species and could cause interference in natural photosynthetic processes. Some dyes are carcinogenic and mutagenic because they were earlier made from hazardous chemicals, such as benzidine and metals. Thus, these effluents have to be treated properly before discharge to receiving waterways [3,4].

Textile wastewater is typically characterized by strong colour, high COD, high SS, high temperature, high salt content, variable pH and low biodegradability. Several techniques have been applied for the removal of dyes from textile effluents; including biological processes, adsorption, membrane filtration, coagulation-flocculation, photo-catalytic oxidation and chemical oxidation. These methods, however, are associated with disadvantages like incomplete elimination of colour, relatively high operating cost, adsorbent regeneration problem and high energy requirement [2,5].

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In recent years, electrochemical oxidation has been used successfully to treat various kinds of wastewaters including landfill leachate [6,7], oil-in-water emulsion [8], textile wastewater [1,9] and tannery wastewater [10]. Electrochemical degradation of pollutants in the presence of electrolyte occurs through the following two mechanisms [11]:

(1) Direct anodic oxidation – where the pollutants are adsorbed on the anode surface and destroyed by the anodic electron transfer reactions. The following simultaneous reactions occur when iron is used as electrode material

Oxidation reaction at anode,

$$\mathrm{Fe(s)} \leftrightarrow \mathrm{Fe^{2+}} + 2\mathrm{e^-} \tag{1}$$

Chemical reaction,

$$\mathrm{Fe^{2+}} + 2\mathrm{OH^-} \leftrightarrow \mathrm{Fe(OH)_2(s)} \tag{2}$$

Reduction reaction at the cathode,

$$2\mathrm{H_2O} + 2\mathrm{e^-} \leftrightarrow \mathrm{H_2} + 2\mathrm{OH^-} \tag{3}$$

Overall reaction,

$$\mathrm{Fe(s)} + 2\mathrm{H_2O} \leftrightarrow \mathrm{Fe(OH)_2(s)} + \mathrm{H_2} \tag{4}$$

(2) Indirect oxidation in the bulk liquid; the presence of NaCl (electrolyte) leads to generation of Cl_2 gas, hypochlorite ion (OCl^-) and hypochlorous acid (HOCl). The hypochlorous acid is a strong oxidant that oxidizes pollutants in wastewater. Oxidation reactions in the bulk solution are:

$$2\mathrm{Cl^-} \leftrightarrow \mathrm{Cl_2} + 2\mathrm{e^-} \tag{5}$$

$$\mathrm{Cl_2} + \mathrm{H_2O} \leftrightarrow \mathrm{HOCl} + \mathrm{H^+} + \mathrm{Cl^-} \tag{6}$$

$$\mathrm{HOCl} \leftrightarrow \mathrm{H^+} + \mathrm{OCl^-} \tag{7}$$

$$6\mathrm{OCl^-} + 3\mathrm{H_2O} \leftrightarrow \left(\frac{3}{2}\right)\mathrm{O_2} + 6\mathrm{H^+} + 4\mathrm{Cl^-} + 2\mathrm{ClO_3^-} + 6\mathrm{e^-} \tag{8}$$

Reactive dyes are water-soluble, anionic dyes that require relatively simple dyeing methods. They attach to their substrates through formation of covalent bonds and are mainly used for dyeing cellulosic fibres (like cotton and rayon), silk, wool, nylon and leather. As well as imparting colour to the receiving water stream, reactive dyes are associated with problems such as toxicity to aquatic life and health risk to human beings [12]. This study is focused on the electrochemical removal of a commercial Reactive Red dye (Cibacron Red CR) from synthetic textile wastewater using NaCl as electrolyte and cast iron electrodes. The effects of electrolyte concentration, contact time, current density and initial dye concentration on dye removal were investigated. The operational parameters were optimized with response surface methodology (RSM).

2. Materials and methods

2.1. Dye and electrodes

Commercial reactive red dye (Cibacron Red CR), available in powder form, was used in this study. An amount of 0.5 g of reactive Red CR was accurately weighed using an analytical balance (model HM 300, Japan) and dissolved in 0.5 litre of deionized water to prepare the dye stock solution. The stock solution was kept in a cool dark room to avoid possible decolourization by light until use. Samples were analysed by measuring absorbance at wavelength 525 nm using a scanning UV–visible spectrophotometer (spectroquant NOVA 60, Germany). A standard graph of absorbance vs. dye concentration was prepared for 0–100 mg/l dye. The graph was used for determination of dye concentration remaining in samples after treatment.

Cast iron electrodes (each 8 cm × 4 cm and 1 mm thick) with effective surface area 64 cm^2 were used in this study. The material selection was made primarily based on its low cost and good process performance.

2.2. Experimental set-up

Dye degradation tests were conducted in a 600 mL batch electrolytic reactor equipped with a magnetic stirrer to keep its contents well mixed during the experiment. Two cast iron electrodes were used as anode and cathode. The electrodes were connected to a DC digital power supply (model DE-670, class 2.5, China) using wires and crocodile clips.

2.3. Experimental procedure

The anode and cathode were positioned vertically and parallel to each other, 5 cm apart, in the electrolytic reactor containing 500 mL of test sample. Pre-decided amounts of sodium chloride (NaCl) were added to the samples before each experiment. Initial pH of the samples was adjusted to 7 using dilute sodium hydroxide or sulphuric acid. Current was switched on and set according to the desired current density to start electrochemical treatment of the dye. At the end of each run, the supernatant was filtered through GC-50 glass fibre filters prior to determination of final dye concentrations. The electrodes were cleaned with sand paper before each experiment.

2.4. Experimental design and analysis

Design Expert 6.0.7 software was used for the statistical design of experiments and data analysis based on RSM. RSM is an empirical modelling technique employed to assess the relationship between dependent (response) and independent (operational) variables as well as to optimize the relevant processes [13–16].

Four significant independent variables considered in this study were: electrolyte (NaCl) concentration (A), current density (B), reaction time (C) and initial dye concentration (D). Final dye concentration of the treated synthetic wastewater was chosen as the response. Each independent variable was coded at 3 levels i.e. −1, 0, and +1. The operational ranges of variables (Table 1) were determined by conducting some preliminary tests before the factorial design experiments. Initial dye concentration was chosen based on literature [12,17,18]. The total number of experiments required was 3^k (k = number of factors) plus six replicates of the centre point. Thus, a total of 87 experiments were conducted.

The polynomial model shown in Eq. (9) was used for estimation of the response function.

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum\sum_{i<j} \beta_{ij} X_i X_j + e_i \tag{9}$$

where Y is the response, X_i and X_j are coded independent variables, β_0 is a constant coefficient, β_j, β_{jj} and β_{ij} are interaction coefficients of linear, quadratic and the second-order terms, respectively, k is the number of studied factors and e_i is the error [13,15].

Table 1
Operational variables of the experimental design

Variable	Factor	Level −1	Level 0	Level +1
A	NaCl conc., g/l	0.6	0.8	1.0
B	Current density, mA/cm^2	1	2	3
C	Reaction time, min	20	40	60
D	Initial dye conc., mg/l	20	60	100

Analysis of variance (ANOVA) was used for statistical analysis of the data. The quality of fit of the polynomial model was expressed by the coefficient of determination R^2 and R^2_{adj}. Statistical significance of the model was determined based on adequate precision ratio, F and P values.

3. Results and discussion

3.1. Analysis of variance

The response (final dye concentration) from the 87 tests conducted varied from 0.5 to 97 mg/l, yielding a maximum to minimum ratio of 158. As this ratio was greater than 10, a response transformation for better approximation was adopted. In this case, the base 10-log transformation, which yielded the highest coefficient of determination (R^2 = 0.8148), was used with a quadratic approximating function for data analysis and model generation.

Table 2 shows the ANOVA results of regression parameters of the predicted response surface quadratic model for final dye concentrations obtained.

The model F-value of 49.66 and a very low probability value (Prob > F = 0.0001) indicate that the model is suitable for final dye concentration prediction. The adequate precision value of greater than 4 indicates that the model is desirable. In this study, B, C, D, B^2, BC, BD, and CD are significant

Table 2
ANOVA results of the quadratic model for Log$_{10}$ (final dye concentration)

Source	Sum of squares	DF	Mean square	F value	Prob > F	
Model	18.08	7	2.58	49.66	<0.0001	Significant
B	2.79	1	2.79	53.60	<0.0001	
C	10.41	1	10.41	200.18	<0.0001	
D	1.40	1	1.40	26.83	<0.0001	
B^2	0.43	1	0.43	8.31	0.0051	
BC	1.98	1	1.98	38.08	<0.0001	
BD	0.80	1	0.80	15.37	0.0002	
CD	0.27	1	0.27	5.23	0.0249	
Residual	4.11	79	0.05			
Lack of fit	3.84	73	0.05	1.15	0.4793	Not significant
Pure error	0.27	6	0.05			

SD = 0.23, R^2 = 0.8148, R^2_{adj} = 0.7984, Adeq precision = 28.44.

model terms. Insignificant model terms which do not influence the model viz., A, A^2, C^2, D^2, AB, AC, and AD were excluded to simplify the model. The final quadratic regression model in terms of coded factors is expressed by the following second-order polynomial equation:

$$log_{10}\left(\text{final dye conc.}, \frac{\text{mg}}{\text{l}}\right) = 0.23 - 0.23B - 0.44C + 0.16D + 0.15B^2 + 0.23BC - 0.15BD - 0.087CD \quad (10)$$

Fig. 1 shows the normal probability plot of the studentized residuals for response. A normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. Some scatter is expected even with normal data. It can be concluded from Fig. 1 that the data are normally distributed.

3.2. Effect of operational variables on the degradation of reactive red dye

The effects of operational variables on dye removal are shown as 3D surface plots (Figs. 2–5). For Fig. 2, the response surface was developed as a function of reaction time and current density whereas the initial dye and electrolyte concentrations were constant at 60 min and 1.0 g/l, respectively. The figure indicates that the final dye concentration decreased when the reaction time and current density increased. The final dye concentration of 1 mg/l obtained at 60 min reaction time and 3.0 mA/cm^2 of current density, show that 99% dye removal was achieved with these experimental conditions. The minimum predicted dye removal efficiency of 53.2% was obtained at 1 g/l sodium chloride, 1 mA/cm^2 current density, 20 min reaction time, and 100 mg/l initial dye concentration.

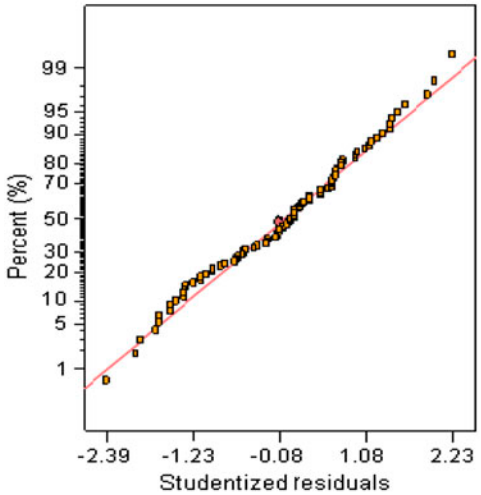

Fig. 1. Normal probability plot of the studentized residuals for Log$_{10}$ (final dye concentration).

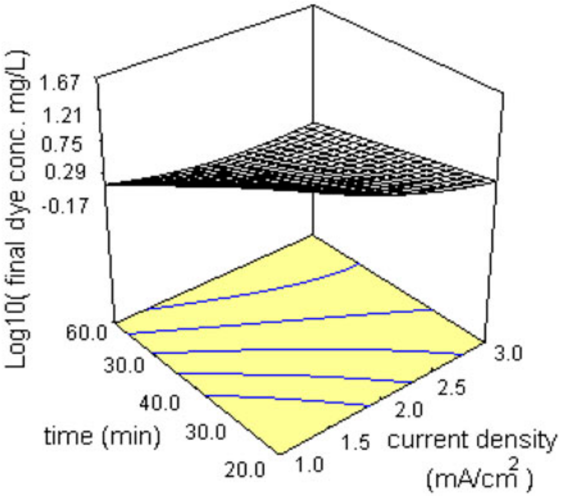

Fig. 2. 3D surface plot for the effect of reaction time and current density on final dye conc. (1.0 g/l NaCl, 100 mg/l initial dye conc.).

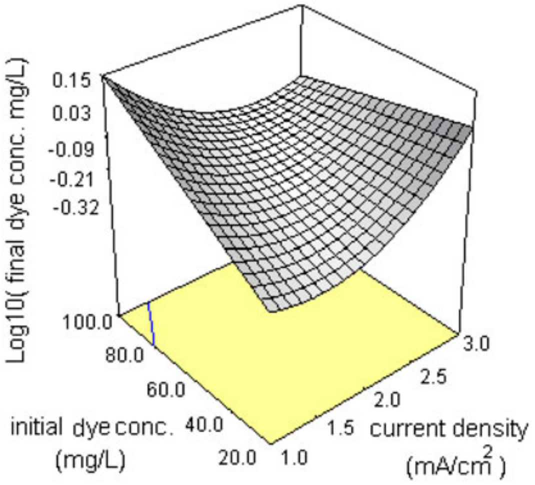

Fig. 3. 3D surface plot for the effect of initial dye conc. and current density on final dye conc. (1 g/l NaCl, 60 min reaction time).

Fig. 3 shows the effect of initial dye concentration and current density on dye removal. Sodium chloride concentration and reaction time were constant at 1.0 g/l and 60 min, respectively; initial dye concentration and current density were varied within the experimental range (Table 1). Generally, the final dye

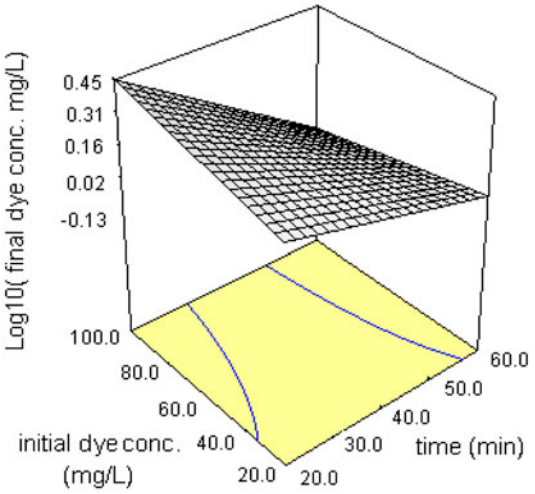

Fig. 4. 3D surface plot for the effect of initial dye conc. and reaction time on final dye conc. (1 g/l NaCl, 3 mA/cm^2 current density).

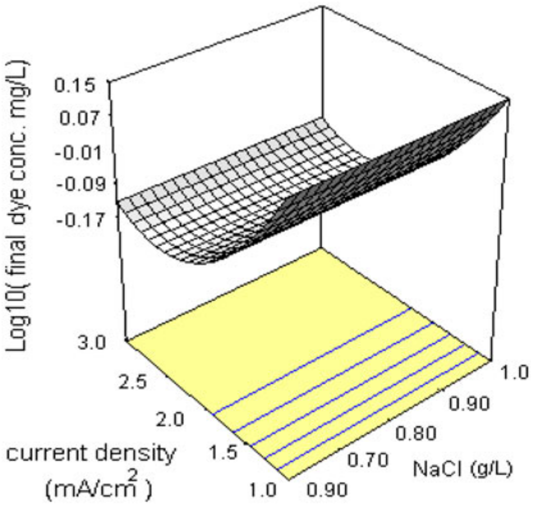

Fig. 5. 3D surface plot for the effect of current density and NaCl dosage on final dye conc. (100 mg/l initial dye conc., 60 min reaction time).

concentration decreased when the initial dye concentration was decreased. With higher initial dye concentration, higher current density and longer reaction time are required to get the same final dye concentration.

The effect of initial dye concentration and reaction time on final dye concentration is shown in Fig. 4. The final dye concentration is seen to decrease with increasing reaction time and decreasing initial dye concentration. In general, generation of chlorine/hypochlorite increases with increase in reaction time and current density; thus, enhancing electrochemical oxidation [8]. Hence, with longer reaction time and higher current density, higher colour removal efficiency can be obtained.

The increase in electrolyte (NaCl) concentration in the medium and current density directly increase the concentration of strong oxidants (HOCl and ClO^-) in the medium. This will enhance the electrochemical decolourization [8,19]. However in this study, the change in NaCl concentration did not produce any apparent effect on the response (Fig. 5). It is concluded that the range of NaCl concentration used in this study was higher than the optimum level required.

3.3. Optimization of operational conditions

Numerical optimization using the Design-Expert software 6.0.7 was carried out for maximum reduction of reactive dye. It was found that an initial dye concentration of 100 mg/l can be reduced by over 99%, if reaction time is 60 min and current density is greater than, 1.4 mA/cm^2. This is applicable to the range of NaCl concentrations tested in this study i.e. 0.6 to 1 g/l.

4. Conclusions

In the present study, removal of reactive red dye by electrochemical treatment using cast iron electrodes in the presence of sodium chloride as electrolyte was investigated. A significant (R^2 = 0.8148, p < 0.0001) quadratic polynomial model was generated. The data were shown to fit the model well. Statistical analysis indicated that RSM is a reliable tool to optimize electrochemical oxidation of reactive red dye. Under optimum conditions, an initial dye concentration of 100 mg/l could be reduced to less than 1 mg/l.

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