

Response surface optimization of electrochemical treatment of textile dye wastewater

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Abstract

The electrochemical treatment of textile dye wastewater containing Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes was studied on iron electrodes in the presence of NaCl electrolyte in a batch electrochemical reactor. The wastewater was synthetically prepared in relatively high dye concentrations between 400 mg/L and 2000 mg/L. The electrochemical treatment of textile dye wastewater was optimized using response surface methodology (RSM), where current density and electrolyte concentration were to be minimized while dye removal and turbidity removal were maximized at 28 °C reaction temperature. Optimized conditions under specified cost driven constraints were obtained for the highest desirability at 6.7 mA/cm², 5.9 mA/cm² and 5.4 mA/cm² current density and 3.1 g/L, 2.5 g/L and 2.8 g/L NaCl concentration for Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive textile dyes, respectively.

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Keywords: Electrochemical wastewater treatment; Textile wastewater; Dye removal; Optimization; Response surface methodology (RSM)

1. Introduction

Dyeing is the application of color to the textile material with some degree of colorfastness, and may take place at any of several stages in the manufacturing process with continuous and batch processes [1]. Dyeing operations generate a large portion of the industry's total wastewater [2,3]. Three major problems that face cotton dyers are water-use reduction and elimination of color and salt from dye wastewater [3]. Reactive dyes are most commonly in use today for cotton dyeing having a fixation rate of 60–90% in a typical dyeing process [2], and require large amounts of water for application and washoff [3]. The primary source of wastewater in dyeing operations is spent dye bath and rinsing processes which typically contains residual dye, salt and auxiliary chemicals [2,3] and generate about 125–150 L wastewater/kg of product [2].

Environmental concerns about fiber reactive dyes focus on color and salt. Color is a hard-to-treat textile waste originating primarily from dyeing or printing operations is being increas-

ingly regulated and is widely recognized as a significant problem [3]. Effluent from most textile dyeing operations generally has a dark reddish-brown color that is aesthetically displeasing when discharged to receiving waters. Salt is used mostly to assist the exhaustion of ionic dyes and particularly anionic dyes, such as fiber reactive dyes on cotton. Typical cotton batch dyeing operations use quantities of salt that range from 20% to 80% of the weight of goods dyed, and the usual salt concentration in wastewater is 2–3 g/L [3], where sodium chloride is used as one of a common salt [2,3].

The relatively low fixation efficiency of the dyes results in effluent color, which is not easily removed in treatment systems. Although many methods of color removal exist, none of them works in every case [3]. Color can interfere with the transmission of light in receiving waters; high doses of color can interrupt photosynthesis and aquatic life. Color can also interfere with ultraviolet (UV) disinfection of treated wastewater. Decoloration of the effluent is difficult because of the low level of aerobic biodegradation and/or adsorption of the dye color onto activated sludge during treatment. The conventional treatment systems are not effective in removing salt in order to meet salt discharge limits because of large amounts of salt are using to exhaust the dyes. Dyeing contributes essentially all of the salt and color in effluent from textiles operations [3].

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Electrochemical oxidation is becoming an alternative wastewater treatment method and replacing the conventional processes, because many industrial processes produce toxic wastewaters, which are not easily biodegradable and requiring costly physical or physicochemical pretreatments [4]. Many researchers had investigated the electrochemical oxidation of various types of wastewater containing 1,4-benzoquinone [4], phenol [5–8], aniline [9], olive oil [10,11], vinasse [12], chlorophenols [13], *p*-chlorophenol and *p*-nitrophenol [14], low level nuclear waste [15,16], human waste [17] and tannery wastewater [18].

The electrochemical treatment of textile dye wastewater has also been studied in the literature [19–34]. Although the electrochemical methods used for dye degradation have been successful, this study meets the lack of data on the electrochemical degradation of commercial Levafix CA reactive dyes. In the study, Levafix CA reactive dyes were chosen because of increasing regional use due to their high fastness profile and meet most requirements set by textile manufacturers for fastness to light, perspiration, chlorine and repeated washing. The use of Levafix CA dyes are extending for most of dyeing processes in the textile industry and they have a wide range of favorable dyeing properties, including a high fixation yield and washoff properties.

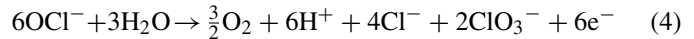
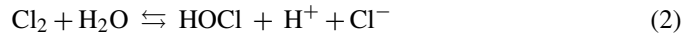
In this study, the electrochemical treatment of textile dye wastewater containing Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes was investigated, and the effect of operating parameters of current density, electrolyte concentration, initial dye concentration and electrolysis time on COD removal, dye removal and turbidity removal efficiency were analyzed to optimize the electrochemical treatment conditions in order to maximize the rates of dye removal and COD removal was aimed from batch runs using response surface methodology (RSM). The textile dye wastewater was synthetically prepared for the standardization throughout the study. In the study, no any coagulant addition or no any further physicochemical processes employed in order to enhance the electrochemical treatment performance.

2. Theoretical approach

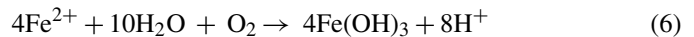
2.1. Chemistry of the electrochemical process

In the study, the electrochemical treatment of textile dye wastewater was investigated in the presence of NaCl electrolyte using iron electrodes. The electrochemical reactions that take place during the electrolysis of NaCl solution are rather complicated, only assumptions can be made based on the products that can be determined as Cl₂, ClO₂, O₃, OH[•], O[•], H₂O₂, O₂, H₂ and CO₂ [11,12]. The possible electrochemical reactions are shown in Eqs. (1)–(11). The discharged chlorine gas on the anode was in excess amount in the reactor for textile dye wastewater treatment in the presence of NaCl and the irreversible reactions of hydrolysis and ionization take place. Firstly, reaction (1) occurs [11,12,35–37] and Cl₂ gas is discharged on the anode rapidly. Hydrolysis reaction (2) [35,36,38] and ionization reaction (3) [36,38] occur when Cl₂ gas is introduced into the water. HOCl is

replenished in the medium with the electrochemical reaction of NaCl in solution. Hypochlorous acid, HOCl, is a strong oxidant, which oxidizes the wastewater while OCl[−] is also consumed by reaction (4) [11,12,39]:

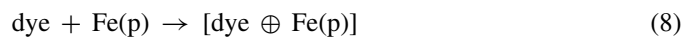
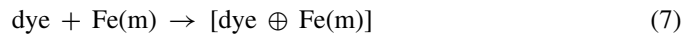


Moreover, with sufficient power supply, Fe²⁺ ions added to the solution by the anodic reaction (5), and some of the organic molecules and suspended solids removed by Fe(OH)₃ sedimentation or H₂ flotation [19]:

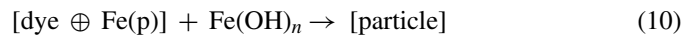
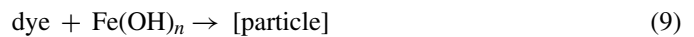


Two major mechanisms of precipitation (pH < 6.5) and adsorption (pH > 6.5) are considered between dye molecules and electrolysis by-products in Eqs. (7)–(10) [28,32], Fe(m) and Fe(p) are corresponding to monomeric Fe and polymeric Fe, respectively.

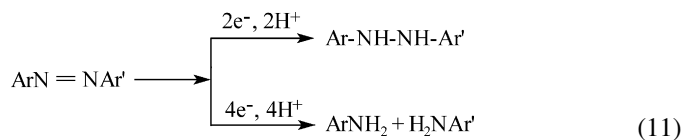
Precipitation:



Adsorption:



In electrochemical reactions azo linkage also electroreduce, where Ar and Ar' are aryl groups in Eq. (11) [40]:



2.2. Experimental design and optimization

In this study, response surface methodology (RSM) was used for the experimental design and optimization. RSM, is essentially a particular set of mathematical and statistical methods for designing experiments, building models, evaluating the effects of variables, and searching optimum conditions of variables to predict targeted responses [41–43]. RSM is an important branch of experimental design and a critical technology in developing new processes, optimizing their performance, and improving design and formulation of new products. 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 [41–43].

Table 1
Experimental design of electrochemical treatment of textile dye wastewater

Independent variable	Coded levels				
	-2	-1	0	+1	+2
Initial dye concentration (mg/L)	400	800	1200	1600	2000
Current density (mA/cm ²)	1.0	3.5	6.0	8.5	11.0
Electrolyte concentration (g/L)	0	1	2	3	4
Electrolysis time (min)	0	10	20	30	40

Reactive dyes: Levafix Blue CA, Levafix Red CA and Levafix Yellow CA.

The researcher is often interested in finding a suitable approximating function for the purpose of predicting and determining the future response. 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 [41–43]. The most popular class of second-order designs called central composite design (CCD) was used for the RSM in the experimental design. The CCD was first introduced by Box and Wilson in 1951, and is well suited for fitting a quadratic surface, which usually works well for the process optimization [41–43]. The CCD is an effective design that is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points [41–43].

Therefore, the central composite design with four factors at five levels was applied using Design-Expert 6.0 (trial version) 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 at 28 °C reaction temperature, where the independent variables were initial dye concentration: 400–2000 mg/L, current density: 1.0–11.0 mA/cm², NaCl electrolyte concentration: 0–4 g/L and electrolysis time: 0–40 min as shown in Table 1. In the study, maximum NaCl concentration was determined as 4 g/L, since in typical cotton dyeing operations 2–3 g/L NaCl electrolyte exist in the textile wastewater as a remaining dye-bath additive [3].

The four-factor designed experiments were augmented with six replications at the design center to evaluate the pure error and were carried in randomized order as required in many design procedures. Performance of the process was evaluated by analyzing the response of dye removal and turbidity removal.

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:

$$\eta = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i < j=2}^k \sum \beta_{ij} x_i x_j + e_i \quad (12)$$

where, η is the response, x_i and x_j are variables, β_0 is constant coefficient, β_j 's, β_{jj} 's and β_{ij} 's are interaction coefficients of linear, quadratic and the second-order terms, respectively, and e_i is the error. In the study, dye removal and turbidity

removal data were processed for Eq. (12) 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_{adj}^2 , and statistical significance was checked by the F -test in the program. For optimization, a module in Design-Expert 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 dye removal and turbidity removal at minimum required current density and electrolyte concentration.

3. Materials and methods

3.1. Chemicals and materials

Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes (DyStar) and sodium chloride (Merck) were obtained in extra pure grade and double distilled water was used for the preparation of synthetic textile dye wastewater. The Levafix CA reactive dyes are bifunctional and CA (combined anchor) refers to the use of chlorine-free tri-fluoropyrimidine, mono-fluorotriazine and new vinyl sulphone anchor groups. The dyes had COD concentrations of 950 mg/g, 690 mg/g and 740 mg/g, respectively, with pH values between 6 and 8. The chemical structures of commercial Levafix CA reactive dyes are not disclosed.

3.2. Experimental set-up and procedure

The synthetic textile dye wastewater was prepared in relatively high dye concentrations between 400 mg/L and 2000 mg/L, whereas dye content of textile wastewater used in the literature was as 373 mg/L [26], 60 mg/L [27], 20–100 mg/L [28], 10–200 mg/L [29], 50 mg/L [32], 20–360 mg/L [33] and 100 mg/L [34].

The electrochemical reactor shown in Fig. 1 was designed in our laboratory and used batch-wise in the experiments designed in accord with central composite design (CCD). 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 (OD = 12 mm) were used as anode and cathode and placed

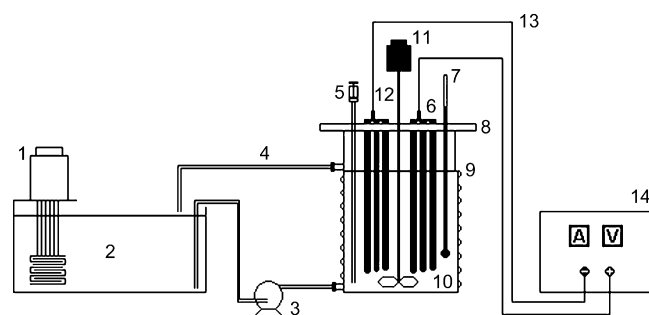


Fig. 1. Batch reactor system (1: heater; 2: heating/cooling tank; 3: heating/cooling pump; 4: feed lines; 5: sampling cell; 6: electrodes; 7: thermometer; 8: plexiglas reactor cover; 9: heating/cooling coil; 10: electrochemical reactor; 11: driving motor; 12: glass mixer; 13: connections; 14: DC power source).

Table 2
ANOVA results of the quadratic models of Levafix CA reactive dye removal and turbidity removal

Source	Sum of squares	Degrees of freedom	Mean square	F-Value	P > F
Dye removal ^a (%)					
Model	119652.40	32	3739.14	22.04	<0.0001 (significant)
Residual	9670.00	57	169.65		
Lack of fit	9669.96	50	193.40	27970.95	<0.0001 (significant)
Pure error	0.0484	7	0.0069		
Turbidity removal ^b (%)					
Model	89591.22	32	2799.73	6.49	<0.0001 (significant)
Residual	24746.06	57	434.14		
Lack of fit	24744.58	50	494.89	2327.49	<0.0001 (significant)
Pure error	1.488	7	0.2126		

^a $R^2 = 0.93$; $R^2_{\text{adj}} = 0.88$; adequate precision = 16.39.

^b $R^2 = 0.78$; $R^2_{\text{adj}} = 0.66$; adequate precision = 9.56.

15 mm apart on a Plexiglas[®] reactor cover. A glass stirrer with two blades 3 cm diameter impeller was driven with a Heidolph-RZR1 model mixer for homogenization at 750 rpm. The reaction temperature was monitored with a glass thermometer immersed inside the reactor. The reaction temperature was controlled with circulating water recycled from a temperature controlled water bath (New Brunswick, G-86). The current was applied by a constant voltage/current controlled DC power source, NETES NPS-1810D.

The synthetic textile dye 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 and turbidity prior to reaction. The reaction started with the application of specified current density, and the recycling water for temperature control was pumped through the reactor coil. At appropriate time intervals, samples of 5 mL were taken from the reactor in order to analyze the specimen during electrochemical degradation.

3.3. Analysis

During the reaction 5 mL samples were taken from the electrochemical reactor at appropriate time intervals and centrifuged at 5000 rpm for 10 min to have supernatant for analysis and measurements. The color of the reaction medium was monitored by a Labomed UV-vis double beam UVD-3200 model spectrophotometer at 610 nm, 526 nm and 416 nm for Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes, respectively. The turbidity was measured by a Hach 2100 AN IS model turbidimeter at 860 nm. COD analysis performed with Palintest PL464 test kits after color and turbidity analysis. In the Palintest COD method, the water sample is oxidized by digesting in a sealed reaction tube with sulphuric acid and potassium dichromate in the presence of a silver sulphate catalyst. The amount of dichromate reduced is proportional to the chemical oxygen demand (COD). The absorbance of the COD samples was read at 605 nm at Labomed UV-vis double beam UVD-3200 model spectrophotometer and the COD values was calculated using a calibration curve prepared previously.

4. Results and discussion

In the first phase of the study, the effect of operating variables of initial dye concentration, current density, electrolyte concentration and electrolysis time on the dye removal was investigated using response surface methodology according to central composite design (CCD). In the second phase, the main objective was to select the current density and NaCl electrolyte concentration in order to achieve optimal COD removal, dye removal and turbidity removal.

The batch runs were conducted in CCD designed experiments to visualize the effects of independent factors on responses and the results along with the experimental conditions. As a general trend, increase in current density and NaCl concentration resulted in enhanced dye removal and turbidity removal in the runs.

The experimental results were evaluated and obtained approximating functions of dye removal are given in Eqs. (13)–(16), respectively:

$$y_{\text{Levafix Blue CA}} = 827.778 - 0.380x_1 + 101.212x_2 - 189.927x_3 - 54.572x_4 + 8.305x_5 + \Theta \quad (13)$$

$$y_{\text{Levafix Red CA}} = 580.286 - 0.392x_1 + 100.236x_2 - 203.118x_3 - 44.088x_4 + 8.061x_5 + \Theta \quad (14)$$

$$y_{\text{Levafix Yellow CA}} = 902.234 - 0.367x_1 + 95.802x_2 - 178.510x_3 - 57.069x_4 + 8.035x_5 + \Theta \quad (15)$$

$$\begin{aligned} \Theta = & -9.50 \times 10^{-6}x_1^2 - 0.556x_2^2 - 3.900x_3^2 + 0.752x_4^2 \\ & - 0.094x_5^2 - 0.006x_1x_2 + 0.015x_1x_3 + 0.013x_1x_4 \\ & + 0.002x_1x_5 - 1.058x_2x_3 - 2.658x_2x_4 - 0.064x_2x_5 \\ & + 7.543x_3x_4 - 0.718x_3x_5 - 0.074x_4x_5 \end{aligned} \quad (16)$$

In Eqs. (13)–(16), y 's are Levafix CA reactive dye removal percents; x_1 , x_2 , x_3 , x_4 and x_5 are corresponding to independent

Table 3
Optimization results of electrochemical treatment and the performance of electrochemical treatment of textile dye wastewater at optimum conditions

Reactive dye	Optimum current density (mA/cm ²)	Optimum NaCl concentration (g/L)	COD removal at optimum (%)	Dye removal at optimum (%)	Turbidity removal at optimum (%)
Levafix Blue CA	6.7	3.1	32	100	82
Levafix Red CA	5.9	2.5	37	100	88
Levafix Yellow CA	5.4	2.8	33	100	94

variables of initial dye concentration, current density, NaCl electrolyte concentration, reaction temperature and reaction time, respectively. ANOVA results of these quadratic models presented in Table 2 indicating that these quadratic models can be used to navigate the design space. In Table 2, the model *F*-values of 22.04 and 6.49 imply the models are significant for dye removal and turbidity removal, respectively. Adequate precision measures the signal to noise ratio and a ratio greater than 4 is desirable. Therefore, in the quadratic models of dye removal and turbidity removal, the ratios of 16.39 and 9.56 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, whereas the values greater than 0.1000 are not significant. For all models, $P > F$ is less than 0.0001, indicating that terms are significant in all models. For Eqs. (13)–(16), lack of fit *F*-values of 9669.96 and 24744.58 implies the significance for dye removal and turbidity removal, respectively.

The experimental results were optimized using the approximating functions of dye removal in Eqs. (13)–(16). In this study, a cost driven approach was preferred at 28 °C reaction temperature within 0–40 min of reaction time; current density and NaCl concentration were to be minimized so as to save energy and electrolyte, whereas dye removal and turbidity removal were maximized between 400 mg/L and 2000 mg/L textile dye concentration.

The objective was to determine the optimal pair current density and electrolyte concentration to achieve both good decoloration and organic matter removal expressed as COD. Several scenarios examined in order to find the optimal conditions and the optimization results shown in Table 3. In Table 3, optimized conditions under specified constraints at 28 °C reaction temperature were obtained for the highest desirability at 6.7 mA/cm², 5.9 mA/cm² and 5.4 mA/cm² current density and 3.1 g/L, 2.5 g/L and 2.8 g/L NaCl concentration for Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive textile dyes, respectively. Then specific batch runs were performed in order to test the optimum conditions and COD removal, dye removal and turbidity removal obtained at optimized conditions were shown in Table 3.

Eqs. (13)–(16) have been used to visualize the effects of experimental factors on responses under optimized conditions in response surface graphs of Figs. 3–5. The model adequacy checking is an important part of the data analysis procedure, which the approximating model would give poor or misleading results if it were an inadequate fit. The residual plots should always be examined for the approximating model [41–44]. The quadratic models for dye removal percents well satisfied the assumptions of the analysis of variance (ANOVA) according to

normal probability, studentized residuals and outlier-t residual plots, which are not shown here. The residual plots indicated a normal distribution, in which case there was no response transformation need and no apparent problem with normality. In the study, the outlier-t values lied below the interval of ± 3.50 indicated that the approximation of the fitted model to the response surface was fairly good with no any data recording error.

The actual and the predicted dye removal and turbidity removal plots are shown in Fig. 2. Actual values are the measured response data for a particular run, and the predicted values

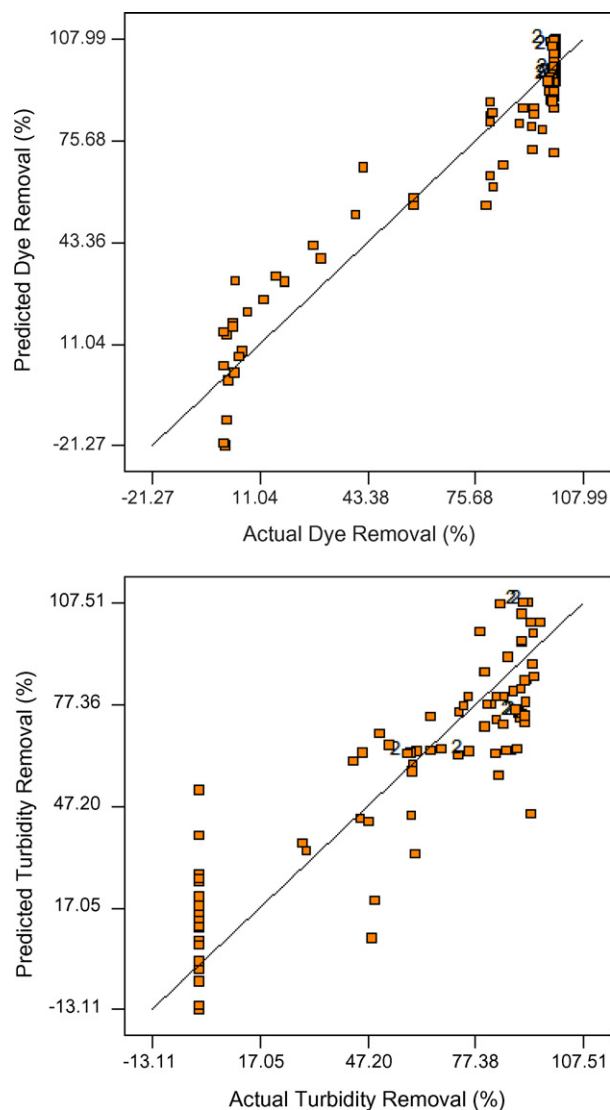


Fig. 2. The actual and predicted plot for dye removal and turbidity removal.

evaluated from the model and generated by using the approximating functions. In Fig. 2, the values of R^2 and R^2_{adj} evaluated as 0.93 and 0.88; 0.78 and 0.66 for dye removal and turbidity removal, respectively. The correlation coefficient found for actual and predicted turbidity removal was not high, and this result is most likely due to the possible formation of low molecular weight complex side products during the electrochemical treatment, which was also resulted in fluctuating turbidity values during the electrochemical treatment.

The effect of operating parameters of current density, NaCl concentration, initial dye concentration and electrolysis time on Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dye removal are shown in the response surface graphs in Figs. 3–5. The analysis conditions kept constant for all reactive dyes at 28 °C reaction temperature, 2000 mg/L initial dye concentration except the effect of initial dye concentration investigated in Fig. 3, and the electrolysis time was 30 min except the effect of electrolysis time investigated in Fig. 5.

Azodyes are synthetic products and show rather low biodegradability, which traditional biological processes are not able to fully decolorize azodyes wastewater [31]. Pollutants can be destroyed by direct anodic oxidation, indirect oxidation or cathodic reduction processes during electrochemical treatment, and all of the processes play an important role in the electrochemical treatment of textile dye wastewater.

In the study, the formation of colorless compounds obtained with the degradation of azo groups in the dye molecule and the degree of dye decomposition is much higher in the presence of chloride ion. 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 [22].

The effect of current density and initial dye concentration on dye removal for Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes are shown in Fig. 3a–c, respectively. In all electrochemical processes, current density is the most important parameter for controlling the reaction rate within the electrochemical reactor. In order to investigate the effect of current density on the efficiency of dye removal and COD removal, electrolysis process was carried out between 1.0 mA/cm² and 11.0 mA/cm² current densities. Fernandes et al. [33] studied the electrochemical oxidation of C.I. Acid Orange 7 between 1.25 mA/cm² and 10 mA/cm², and Awad and Galwa [29] investigated the electrocatalytic degradation of Acid Blue and Basic Brown dyes between 0 mA/cm² and 45 mA/cm² current densities.

In Fig. 3a and c, the dye removal of Levafix Blue CA and Levafix Yellow CA reactive dyes increased with both increase in dye concentration and current density. The complete removal of Levafix Blue CA and Levafix Yellow CA reactive dyes obtained above 7.6 mA/cm² current density at all dye concentrations as shown in Fig. 3a and c at optimum 3.1 g/L and 2.8 g/L NaCl, respectively. In Fig. 3b, the removal of Levafix Red CA reactive dye increased with the increase in current density and increased with the decrease in dye concentration above 3.4 mA/cm² current density. The complete removal of Levafix

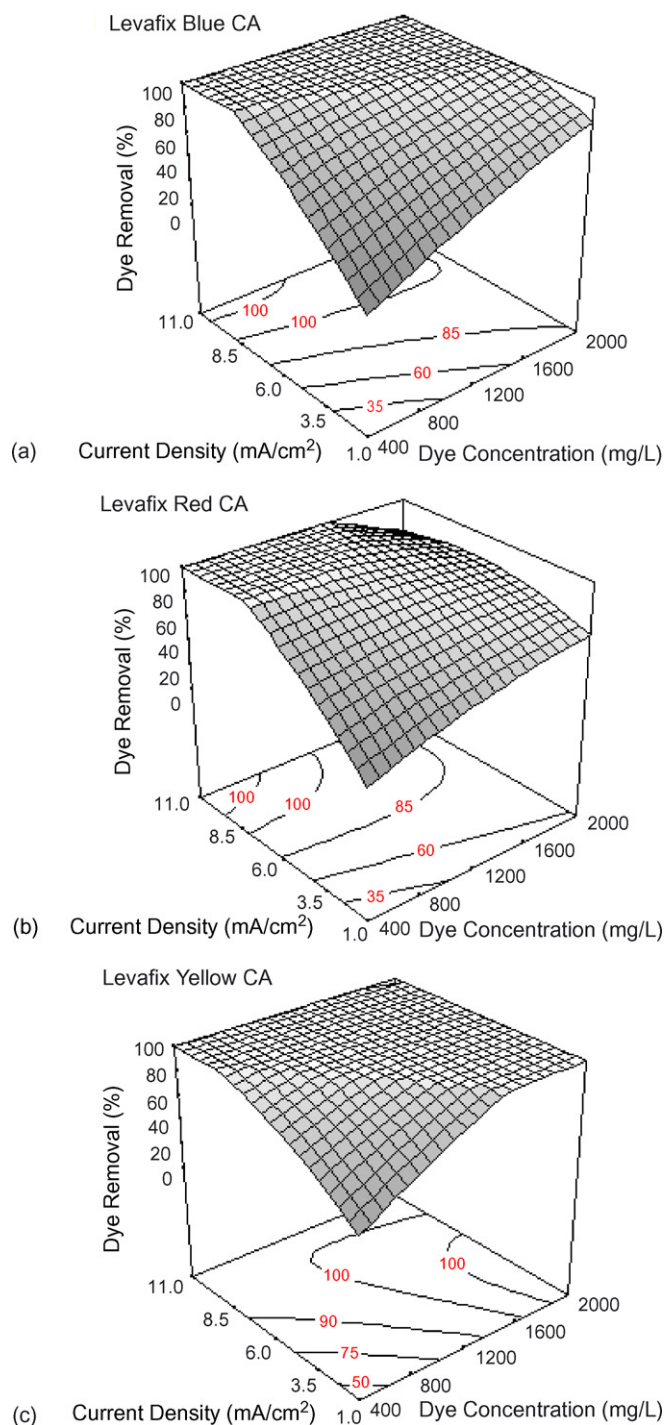


Fig. 3. The effect of current density and dye concentration on dye removal: (a) Levafix Blue CA (NaCl: 3.1 g/L; T : 28 °C; t : 30 min), (b) Levafix Red CA (NaCl: 2.5 g/L; T : 28 °C; t : 30 min) and (c) Levafix Yellow CA (NaCl: 2.8 g/L; T : 28 °C; t : 30 min).

Red CA obtained above 7.3 mA/cm² current density between 400 mg/L and 1400 mg/L dye at optimum 2.5 g/L NaCl as shown in Fig. 3b. Daneshvar et al. stated that an increase in the current density up to 6–8 mA/cm² enhanced the color removal efficiency in their study [28].

The rapid decoloration indicates that initial dyes are fully degraded, giving smaller and colorless organic or inorganic

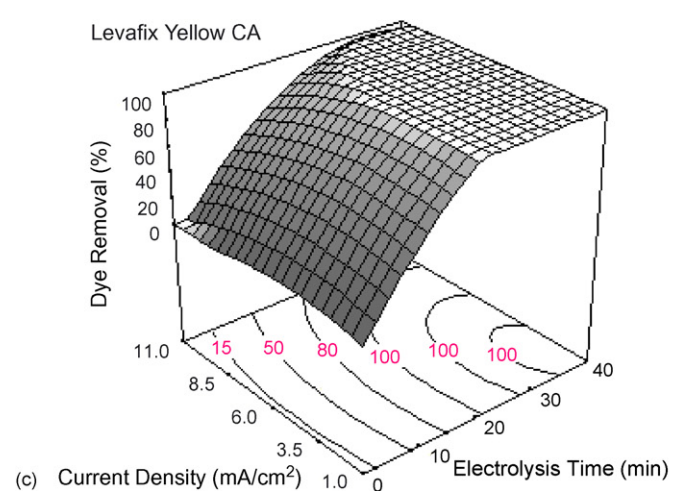
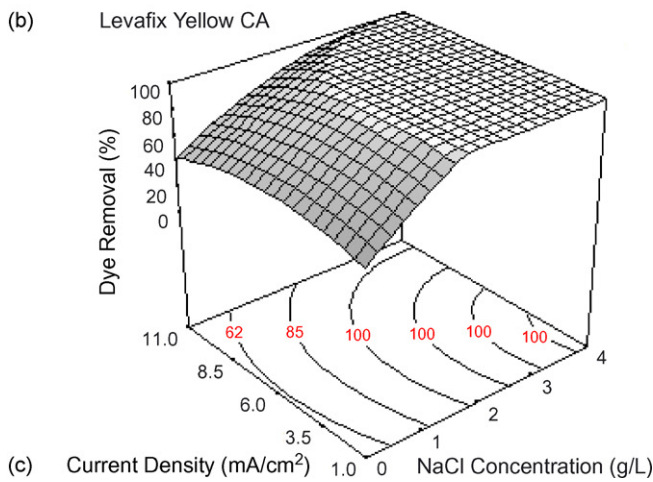
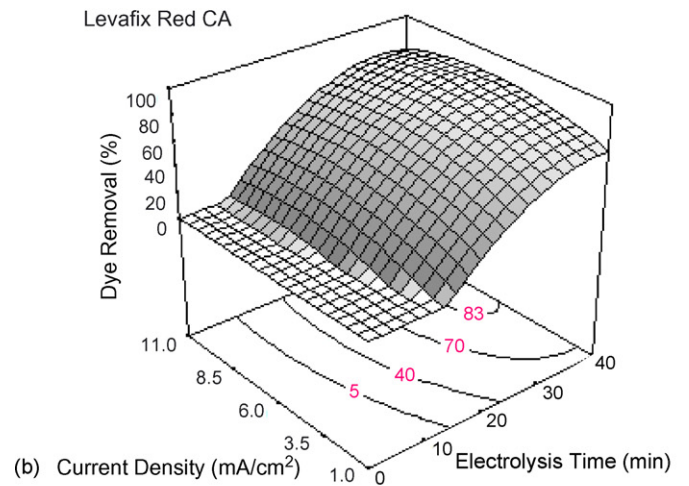
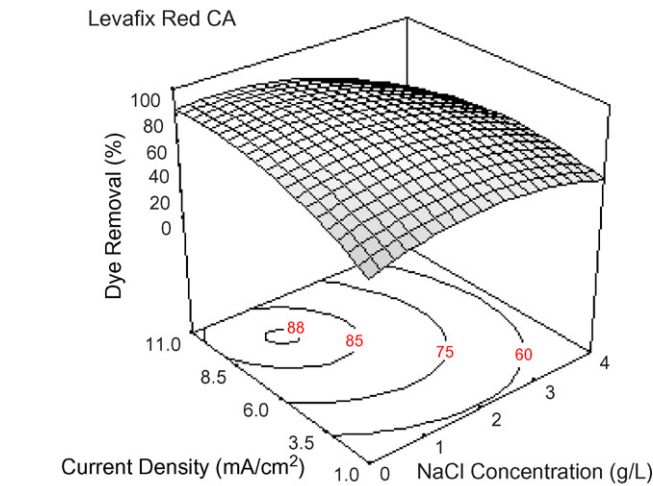
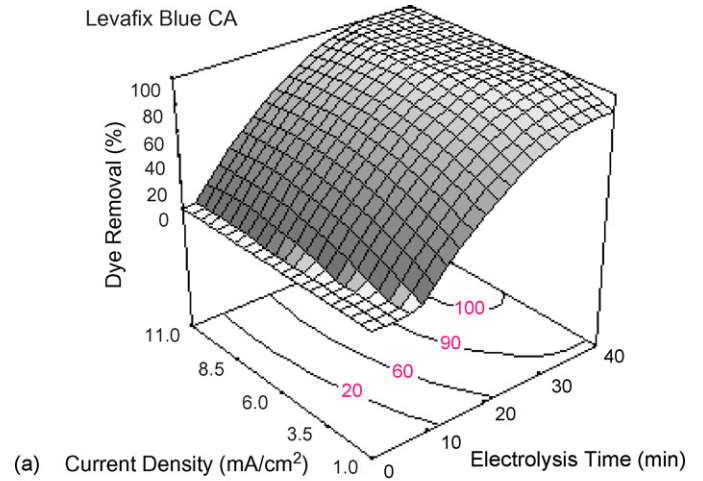
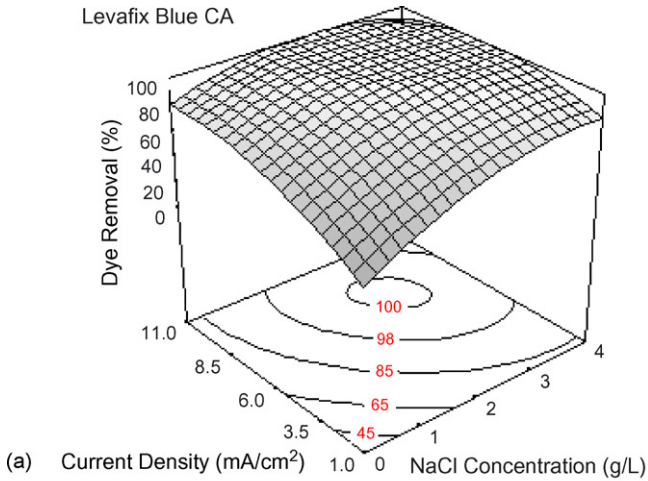


Fig. 4. The effect of current density and NaCl electrolyte concentration on on dye removal: (a) Levafix Blue CA (dye: 2000 mg/L; T : 28 °C; t : 30 min), (b) Levafix Red CA (dye: 2000 mg/L; T : 28 °C; t : 30 min) and (c) Levafix Yellow CA (dye: 2000 mg/L; T : 28 °C; t : 30 min).

Fig. 5. The effect of current density and electrolysis time on on dye removal: (a) Levafix Blue CA (NaCl: 3.1 g/L; dye: 2000 mg/L; T : 28 °C), (b) Levafix Red CA (NaCl: 2.5 g/L; dye: 2000 mg/L; T : 28 °C) and (c) Levafix Yellow CA (NaCl: 2.8 g/L; dye: 2000 mg/L; T : 28 °C).

products, which can further be treated for complete mineralisation. In the study, the complete degradation of the initial dye obtained with the presence of some organic side products according to COD analysis in Table 3. The decrease of COD shows that further degradation of the initial colorless products

took place along with the decoloration during the electrochemical treatment. It could be concluded that the rate of COD removal is lower than that of color, indicating the azo bond degradation is the first step of the electrochemical degradation mechanism with the comparison of COD removal and color

removal which is also stated in the literature [22,31,33,34]. The COD values in Table 3 indicates the removal degree for Levafix CA reactive dyes treated using iron electrodes that color disappearance does not mean complete degradation or complete removal of pollutants in wastewater. In terms of COD removal, some of literature studies apparently achieved better results than this work, however, the initial dye concentrations used in this study were relatively high in contrast to those in the literature [26–29,32–34].

The degradation products in the electrochemical oxidation of azo dyes are typically carbon dioxide, nitrate and sulphate, with the possible formation of aromatic esters, phenols, aromatic carboxylic acids, cyclic and aliphatic hydrocarbons as intermediates [22]. Usually, the oxidation of the azo group occurs, followed by the oxidation of the decomposition products [33]. Nitro compounds are very resistant to decomposition by anodic oxidation [22]. The decomposition of nitro compounds involves cathodic reduction of the nitro group to an amino group, which is more readily oxidized by chlorine. Also diazo groups are reduced to amines by hydrogen generated on cathode. The indirect anodic oxidation of organic compounds can lead to the production of many chloroderivatives, which can be more harmful than the compounds present in the effluents [22].

The effect of current density and electrolyte concentration on dye removal for Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes are shown in Fig. 4a–c, respectively. In textile dye baths, NaCl is the main salt used for the optimal fixation of the dyes on the textile substrate. Therefore, the real textile wastewater contains the required quantity of NaCl [3,31] to carry out the electrochemical treatment without any further addition of electrolyte, which would increase the ionic strength.

The conductivity of dye solutions was adjusted using NaCl in the range of 0–4 g/L in the present study. The addition of NaCl into textile dye wastewater increases conductance and electric current of electrochemical process. Increasing solution conductivity resulted in the reduction of cell voltage that caused a decrease in electrical energy consumption. Also, solution resistance and the potential in solution decrease with the enhancement of electrolyte concentration [27].

In the study, the removal of reactive dyes increased with the increase in NaCl concentration. The complete Levafix Blue CA reactive dye removal obtained above 1.4 g/L NaCl and 4.4 mA/cm² current density. At 2000 mg/L dye, 80% Levafix Blue CA removal obtained without NaCl addition at 11.0 mA/cm² current density as shown in Fig. 4a. In Fig. 4b, higher Levafix Red CA reactive dye removal achieved at lower NaCl concentrations. At the optimum point, 89% Levafix Red CA reactive dye removal obtained at 1 g/L NaCl and 8.9 mA/cm² current density. About 86% Levafix Red CA removal obtained without NaCl addition at 9.6 mA/cm² current density as shown in Fig. 4b. In Fig. 4c, the complete Levafix Yellow CA reactive dye removal obtained above 1.3 g/L NaCl between 1.0 mA/cm² and 11.0 mA/cm² current densities. At 2000 mg/L dye, 60% Levafix Yellow CA removal obtained without NaCl addition at 5.7 mA/cm² current density as shown in Fig. 4c. Awad and Galwa obtained the highest electrocatalytic activity in the presence of 2 g/L NaCl in which the degradation of Acid Blue and

Basic Brown dyes occurred by both direct and indirect oxidation. The authors concluded that the electrocatalytic effect with NaOH and H₂SO₄ was not as good as that in NaCl due to the absence of chloride [29].

It is known that almost all azodyes are polysulphonated compounds in order to be water-soluble. These anions together with other ionic degradation products cause the increase of the current, however NaCl enhances the decoloration process [31]. It is well known that the electrolysis of NaCl results in very strong oxidants of HOCl/ClO⁻ ensuring indirect oxidation [11,12,35–39]. The whole decoloration proceeds mainly by direct redox reactions on the electrodes, enhanced by indirect redox reactions by the produced oxidants or reductants. The better enhancement could be achieved with the stronger oxidants and reductants [31].

The results of the present investigation have shown that the electrodegradation of Levafix CA reactive dyes occurred very efficiently in the presence of NaCl as a conductive electrolyte. Do and Yeh was reported that oxygen evolution was the major reaction in the absence of chloride, but the oxygen formation in solution did not produce significant oxidation [36]. It could be concluded that the degradation of Levafix CA reactive dyes is faster when NaCl used as electrolyte in the study.

In most cases, high concentrations of supporting NaCl electrolyte is required for satisfactory results leading to high concentrations of hypochlorite anions and free chlorine [22,31]. However, the use of NaCl involves the possibility of the formation of organochloride compounds, mainly due to the presence of OCl⁻ as a possible side reaction [22,28,31,33]. In the case of the formation of undesirable side compounds can only be prevented if the complete mineralisation of the organic compounds is ensured at high enough times of electrolysis also with the use of electrocatalytic electrodes.

The effect of current density and electrolysis time on dye removal for Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes are shown in Fig. 5a–c, respectively. The electrolysis time necessary for degradation depends mainly upon the concentration and stability of the solutes when other factors as initial dye concentration, current density and electrolyte concentration have been optimized.

In the study, the dye removal increased throughout the reaction duration. In Fig. 5a and b, Levafix Blue CA and Levafix Red CA reactive dye removal increased with the increase in current density, where higher Levafix Yellow CA reactive dye removal achieved at lower current densities as shown in Fig. 5c. In Fig. 5a, the complete Levafix Blue CA reactive dye removal obtained after 26 min reaction time between 3.2 mA/cm² and 11.0 mA/cm² current density at optimum 3.1 g/L NaCl. In Fig. 5b, maximum Levafix Red CA reactive dye removal of 84% obtained at 7.2 mA/cm² current density after 36 min reaction time with optimum 2.5 g/L NaCl. The complete Levafix Yellow CA reactive dye removal obtained between 1.0 mA/cm² and 10.7 mA/cm² current density after 17 min reaction time with optimum 2.8 g/L NaCl as shown in Fig. 5c.

Raising current density causes a corresponding increase in the oxidized iron production from electrodes, which is also stated in the literature [28,32]. In fact, when current density increases,

there is an increase in the amount of iron dissolved in the liquid phase and an increase in the production of $\text{Fe}(\text{OH})_3$ [32]. It could be concluded that the increase in current density greatly enhances the degradation effect at low potential differences. At high voltages most of current is consumed by oxygen evolution and side reactions [27]. Electrolyte decomposition and gas evolution secondary reactions can also take place during the mineralisation of organic compounds, resulting in a loss of current efficiency and leading to a decreasing of the removal yield [33]. The results showed that an increase in the current density increased the color removal efficiency, which is also stated in the literature [28,29,31,33].

5. Conclusion

The electrochemical degradation of Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes was investigated in textile dye wastewater using iron electrodes. The effect of operating parameters on COD removal, dye removal and turbidity removal was optimized using response surface methodology (RSM), and the approximating functions of dye removal were obtained with satisfactory degrees of fit. Under specified cost driven constraints determined for highest desirability, complete dye removal obtained within COD removal and turbidity removal of 32% and 82%, 37% and 88%, 33% and 94% for Levafix Blue CA, Levafix Red CA and Levafix Yellow CA reactive dyes, respectively. During the electrochemical treatment, rapid decoloration achieved throughout the study indicating that the reactive dyes were completely degraded into smaller and colorless organic and inorganic molecules without any coagulant addition or any further physicochemical processes in order to enhance the electrochemical treatment performance. Since in typical cotton dyeing operations 2–3 g/L NaCl electrolyte exist in the textile wastewater as a remaining dye-bath additive, such investigated electrochemical treatment process could be employed to the real textile dye wastewater. In this study, a pilot plant electrochemical process was proposed achieving almost complete decoloration and satisfactory COD reduction requiring no further addition of supporting electrolyte. The results of this study indicate that this electrochemical reactor could be a feasible and an effective alternative system for the electrochemical treatment of textile dye wastewater and it could also be used at an oxidation pretreatment stage. Although high electrolyte concentration, high current density and low initial dye concentration is improving treatment effect, some more research is required on this subject in order to mineralize organic pollutants and side products completely.

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