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Application of response surface methodology on COD removal from textile wastewater by anodic chlorination and cathodic electro-Fenton process

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ABSTRACT

This study applied response surface methodology to investigate chemical oxygen demand (COD) removal from dyeing wastewater by coupling anodic chlorination using Ti/Pt anode and cathodic electro-Fenton oxidation using activated carbon fiber cathode. The COD was removed by electrogenerated HOCl in the anodic compartment, while in the cathodic compartment the COD was removed by $OH^•$ produced by combing the cathodically generated H_2O_2 with Fe^{2+}. A face-centered central composite experimental design was used to obtain the main variables, such as current density, initial chloride concentration, Fe^{2+} concentration and solution pH, on the individual response surface for anodic chlorination and cathodic electro-Fenton COD removal efficiencies. Two mathematical models that can describe the individual COD removal response were obtained. Analysis of variance showed a high coefficient of determination value (R^2) and insignificant lack of fit for both anodic and cathodic quadratic response surface models. The Pareto analysis gave the percentage effect of each variable on the response. For the anodic chlorination, the current density and the added chloride concentration were the most important two factors. On the other hand, the solution pH played the most important part for cathodic electro-Fenton oxidation.

Keywords: COD removal; Anodic chlorination; Electro-Fenton oxidation; Response surface methodology

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1. Introduction

Textile dyeing industries cause serious environmental and health problems in Taiwan. It is difficult for successful treatment of dyeing wastewater because of its high color and chemical oxygen demand (COD) content. Till now, most of textile dyeing factories in Taiwan still use a large amount of oxidants, such as NaOCl and Cl_2, to preliminarily destroy the pollutants in the wastewater. However, the further treatment is required because of the secondary pollution resulting from high chemical doses. In recent years, advanced oxidation processes (AOPs) are thought to be one of the promising techniques for treating recalcitrant compounds such as dyes. Electrochemical methods including anodic oxidation and electro-Fenton oxidation have been identified as one of the AOPs. The electrochemical technology is an intrinsic environmentally friendly method to treat pollutants in wastewater; thus in recent years, its treatment of wastewater has been largely developed [1–6]. Rajkumar and Kim [3] used anodic oxidation and found the COD removal percentages were 39.5%–82.8% for different reactive dyes. Panizza and Cerisola [4] compared the anodic oxidation efficiency of different anode materials and found that using boron-doped diamond (BDD) as anode material achieved complete COD removal of methyl red because of its extremely high oxygen overvoltage. Vlyssides et al. [5] used Pt/Ti anode to treat the real textile wastewater, and found that COD decreased by 86%

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at a very high chloride concentration. In addition to anodic oxidation, the use of H_2O_2 electrogenerated at cathodes in the presence of Fe^{2+} to oxidize pollutants has been proposed [7]. Because the oxidative power of H_2O_2 is sometimes not high, increasing the oxidative power of H_2O_2 is crucial to the practical application. The oxidative power of H_2O_2 can be increased via the production of hydroxyl free radicals while adding metal catalysts (Fenton chemistry). According to this theory, the electro-Fenton technology, which combines Fe^{2+} with cathodically generated H_2O_2 to generate $OH^{\bullet}$, has received an increasing amount of attention [8–12]. Wang et al. [10] investigated the treatment of acid red 14 by electro-Fenton's reagent and found that 70% of TOC was removed after 360 min electrolysis. In our previous study [13], the color removal efficiency reached 70.6% by using electro-Fenton technology after 150 min treatment of real textile wastewater. Theoretically, the high-power oxidants can be in situ electrochemically generated from both anodic and cathodic reactions. Therefore, coupling of the electrochemical reactions to treat pollutants in wastewater was promising.

The previous investigations of electrochemical wastewater treatment usually used the traditional one-factor-at-a-time (OFAT) approach, which varies only one factor or variable at a time while keeping others fixed. However, interactions of factors are not estimable from OFAT experiments. A designed experiment is a more effective way to determine the impact of two or more factors on a response than an OFAT experiment and requires fewer resources (experiments, time, material, etc.) for the amount of information obtained. Moreover, the estimates of the effects of each factor are more precise using designed experiment technique. The response surface methodology (RSM) uses mathematical and statistical techniques for the modeling and analysis of problems in which a response of interest is influenced by several variables [14]. The objective of RSM is to evaluate the relative significance of several affecting factors and finally obtain the best operating conditions by optimizing this response. RSM had been successfully used in several processes, including adsorption [14,15], electrocoagulation [16,17], chlorine disinfection [18], Fenton-related process [19], electrochemical oxidation [20–22] and electro-Fenton [23–25].

This study used RSM to investigate the coupling of anodic chlorination and cathodic electro-Fenton oxidation for removing COD from real textile dyeing wastewater in a divided electrochemical reactor. In the anodic compartment, electrochlorination of pollutants has been proposed from the chloride ion oxidation at the anodes. On the same time, two-electron productions of H_2O_2 in the cathodic compartment from reduction of oxygen combined with the added Fe^{2+}, leading to the generation of hydroxyl free radicals cause the degradation of dyes in the water. In this divided electrochemical cell, several variables that can affect the COD removal efficiencies by anodic oxidation and electro-Fenton oxidation were studied and the interactions among factors were elucidated by RSM. Consequently, two individual mathematical models were obtained in the present study.

2. Materials and methods

All chemicals were of analytical grade and used as-received without further purification. The Ti/Pt plate anode, 3 cm × 5 cm, was supplied by a local electroplating company. The Ti/Pt plate was pickled in alkaline (1 M NaOH) and acidic (1 M H_2SO_4) solutions alternatively for cleaning and then rinsed with deionized water before the experiment was conducted. Activated carbon fiber (ACF), used at cathode, was cut into the desired dimensions of 3 cm × 5 cm and was then heated with boiling deionized water, produced from a deionized water purification system, for 30 min and finally dried in a 60°C oven. The apparent current densities of anode and cathode are the same during the electrochemical operation because both have the same electrode surface areas.

The electrochemical generation of HOCl and H_2O_2 was conducted in a H-type divided cell, made of 0.1 cm thick glassy material with 15 cm height, 10 cm long, and 10 cm width, as seen in Fig. 1.

The anodic and the cathodic compartments of equal volume were separated using the perforated plastic separator, 0.1 cm thick. A cation permeable membrane Nafion® 117 was used to keep the anolyte and catholyte from mixing. Therefore, the COD removal efficiency by the anodic oxidation in the anodic compartment and the electro-Fenton reactions in the cathodic compartment could be separately investigated and calculated. The distance between the ACF cathode and the Ti/Pt anode was 4 cm. The electrochemical cell was placed inside a constant temperature bath (25°C). A stirrer from the Global Company (Model s-110) was used to enhance the anolyte flow in the anodic compartment. The agitation speed was 250 rpm. Oxygen gas was sparged into the cathodic compartment at a rate of 0.4 dm^3/min to increase the dissolved oxygen concentration and enhance catholyte mixing. The voltage was supplied by a DC power supply (GW, GPR-25H30D). To accurately measure the voltage and the current, a voltmeter and ammeter were connected to the

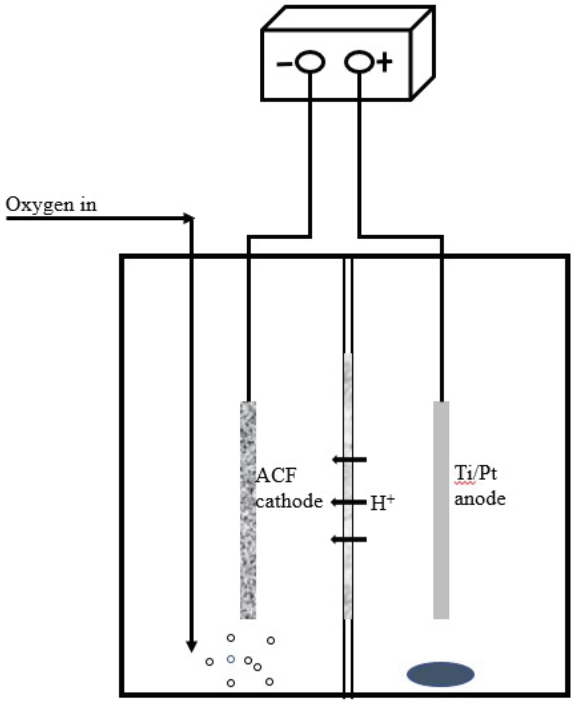

Fig. 1. Experimental setup.

circuit. All the electrolytic experiments were conducted in constant-current mode.

The wastewater sample used was taken from a textile dyeing plant located at Tainan County in Taiwan and was kept in a dark environment. The suspended particles of colloidal ranges in the wastewater were first removed by filtration with cellulose acetate filter papers (0.45 μm in pore diameter). The wastewater was then diluted to the desired initial COD value of 720 mg/dm^3 before conducting the electrolytic experiments. The pH was adjusted to the desired value using 0.5 M $H_2SO_{4(aq)}$. The total solution volume of each experiment was 0.6 dm^3 and it was equally divided between the anodic and cathodic compartments. The electrolytic time of each experiment was 120 min.

Measurement of the COD was conducted using a Hach spectrophotometer (DR5000) and a Hach COD reactor. The pH of the solution was measured using a pH/ORP/conductivity meter (Myron L, Ultrameter II). In this study, the COD removal efficiency was calculated using the following definition:

$$\text{COD removal efficiency (\%)} = \frac{\text{COD}_{\text{original}} - \text{COD}_{\text{treated}}}{\text{COD}_{\text{original}}} \times 100\% \tag{1}$$

The experimental design was performed using the face-centered central composite design to create a set of designed experiments by Design-Expert software (version 7, trial). To conduct RSM, the selected main factors were designed. We chose current density (X_1), added Cl$^-$ concentration (X_2) and initial pH (X_4) as the main factors for direct and indirect anodic oxidation. For cathodic electro-Fenton oxidation, current density (X_1), added Fe^{2+} concentration (X_3) and initial pH (X_4) were used as the main input factors to design the matrix. The current densities (X_1) of the electrodes and the initial pHs (X_4) used in both compartments were of the same values. In the anodic compartment, chloride ions (X_2) were added for anodic liberation of chlorine gas. The added Fe^{2+} (X_3) of different concentration was used to catalyze the cathodic generation of H_2O_2 in the cathodic compartment. The ranges of these factors (independent variables) selected for this study were current density (X_1), 0.5–2.0 A/dm^2, Cl$^-$ concentration (X_2) 500–4,500 mg/dm^3, Fe^{2+} concentration (X_3) 2–6 mg/dm^3 and pH (X_4) 2–4. It is appropriate to use coded variables for describing these factors in the (–1, 1) interval according to the following definition:

$$X_i = \frac{x_i - x_0}{\Delta x_i} \tag{2}$$

where X_i is the dimensionless coded value of the ith independent variable, x_i is the uncoded value of the ith independent variable, x_0 is the uncoded value of the ith independent variable at the center point, and Δx_i is the step change value between low level (–1) and high level (+1). When there is a curvature in the response surface, a second-order model is useful to approximate a portion of the true response surface. Therefore, the mathematical relationship of the response Y on these independent variables X_i was approximated by a second-order polynomial equation as shown below:

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum b_{ii} X_i^2 \tag{3}$$

where Y is the predicted response for anodic oxidation (Y_a) or electro-Fenton oxidation (Y_c); b_0 is the intercept parameter and b_i, b_{ii} and b_{ij} are parameters for linear, quadratic and interaction factor effects, respectively. The analysis of variance (ANOVA) was used to obtain the interaction between the process variables and the responses. Examination of the fitted model is important if the model provides an adequate approximation of the true response surface. This study used normality, ANOVA, regression analysis and lack of fit test to examine the response model.

3. Results and discussion

Two kinds of anode are generally used in anodic oxidation. Pt, IrO_2 and RuO_2 based anodes are so-called active anodes. In contrast, PbO_2, BDD can promote high contents of physisorbed OH$^\bullet$ are called non-active anodes [4]. In anodic oxidation of chloride-containing wastewater, chlorine-based oxidants are probably generated following a complex cycle of chloride–chlorine–hypochlorite (hypochlorous acid)–chloride [2]. Several studies have reported that the chlorine-based mechanism (electrochlorination) plays the main role in the treatment of real wastewater [5,6]. The reaction scheme for the production of chlorine-based oxidants involves the following electrochemical and chemical reactions [6,22]:

$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \tag{4}$$

$$\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \tag{5}$$

$$\text{HOCl} \leftrightarrow \text{ClO}^- + \text{H}^+ \tag{6}$$

Within the acidic pH range, the HOCl ($E° = 1.49$ V/SHE) predominates [2], and is the main oxidant because the pH variation of this operation was kept in this acidic range in the present study.

It is known that hydrogen peroxide can be produced at cathode through the two-electron reduction of dissolved oxygen. Therefore, electro-Fenton technology combined cathodically produced H_2O_2 and externally added Fe^{2+} to produce OH$^\bullet$ to oxidize pollutants in acidic solution. The main mechanisms of electro-Fenton technology were as follows [10–13,22]:

$$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \tag{7}$$

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^\bullet \tag{8}$$

H_2O_2 is continuously produced at cathode and Fe^{2+} can be regenerated by reduction of Fe^{3+} at cathode. Consequently, the catalytic reaction, Eq. (8), is propagated to produce OH$^\bullet$.

Therefore, pollutants in wastewater were completely or partially destroyed by OH•.

In this study, we coupled anodic chlorination and cathodic electro-Fenton oxidation with the same current densities and initial pHs for removing COD in a divided electrochemical reactor. A face-centered central composite experimental design with a total number of 20 experiments was used for RSM modeling, as seen in Table 1. The highest removal efficiency for anodic chlorination was 93.77% at the condition of 2 A/dm^2 current density, 4,500 mg/dm^3 chloride concentration and pH 4. For cathodic electro-Fenton oxidation, the operating condition of 2 A/dm^2 current density, 6 mg/dm^3 Fe^{2+} concentration and pH 2 reached the highest removal efficiency of 67.74%. The finding indicated that the quadratic model was the most suitable regression equation because the quadratic model is useful in approximating a portion of the true response surface with parabolic curvature.

The ANOVA of this study confirms the adequacy of the quadratic model (the model Prob > F is less than 0.05). Tables 2 and 3 show the probability values for each individual term in the quadratic model for anodic chlorination and electro-Fenton oxidation, respectively. The model F values of 171.00 for anodic chlorination and 509.13 for electro-Fenton oxidation imply these two quadratic models are significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise for each model. Values of "Prob > F" less than 0.05 indicate model terms are significant. Therefore, for anodic chlorination X_1, X_2, X_4, X_1X_2, X_1X_4, X_2X_4, X_2^2 are significant model terms. For electro-Fenton oxidation, X_1, X_4, X_1X_4, X_3X_4, X_4^2 are significant model terms. In addition, we used the "Lack of Fit Tests", also shown in tables, to compare residual error with "Pure Error" from replicated design points. Theoretically, if there is significant lack of fit, as shown by a low probability value ("Prob>F"), then care should be taken when using the model as a response predictor. The "Lack of Fit F-value" of 3.18 for anodic oxidation and 0.12 for electro-Fenton oxidation imply each lack of fit is not significant relative to the pure error. Consequently, both the quadratic models, identified earlier as the likely models, do not show significant lack of fit.

How well the estimated model fits the experimental data are measured by the value of R^2. As R^2 is closer to 1, the estimation of regression model better fits the experimental data. In this study, both the quadratic models show best results, because they exhibit low standard deviations (2.27 for anodic chlorination and 0.77 for electro-Fenton oxidation) and high R^2 values (0.9935 for anodic chlorination and 0.9978 for electro-Fenton oxidation). Fig. 2 shows the comparison of experimental and predicted values of COD removal efficiency for anodic chlorination and electro-Fenton oxidation, respectively. It can be seen that each of the present model fits well the experimental data and consequently we can use the model to predict the COD removal efficiency in the experimental range of variables.

A good estimated regression model shall explain the variation of the dependent variable in the sample. Tests of hypotheses about the model parameters can help the measurement of the effectiveness of the model. These tests require for the error term to be normally and independently distributed with mean zero and variance. We used normal plot of the internally studentized residuals to check the normality of the experimental data, shown in Fig. 3. The studentized residuals are normally distributed if the data points are approximately linear. When a non-linear pattern

Table 1
COD removal percentage for anodic chlorination and cathodic electro-Fenton

Run	X_1 (current density, A/dm^2)	X_2 (Cl$^-$, mg/dm^3)	X_3 (Fe^{2+}, mg/dm^3)	X_4 (pH)	Removal percentage (anodic, %)	Removal percentage (cathodic, %)
1	1.25	500	4.0	3.0	19.03	43.48
2	2.00	500	2.0	2.0	25.11	60.14
3	2.00	2,500	4.0	3.0	59.23	45.13
4	0.50	500	6.0	2.0	5.62	60.72
5	0.50	4,500	2.0	2.0	13.24	53.90
6	1.25	2,500	4.0	3.0	36.65	41.82
7	2.00	4,500	6.0	2.0	59.17	67.74
8	1.25	2,500	4.0	3.0	37.42	43.56
9	0.50	2,500	4.0	3.0	13.26	40.45
10	1.25	2,500	4.0	4.0	44.88	30.08
11	0.50	500	2.0	4.0	8.90	25.80
12	1.25	2,500	4.0	2.0	28.32	62.85
13	1.25	4,500	2.0	3.0	44.84	40.09
14	1.25	2,500	4.0	3.0	37.94	44.19
15	1.25	2,500	4.0	3.0	38.18	44.68
16	2.00	4,500	2.0	4.0	93.77	28.78
17	1.25	2,500	6.0	3.0	37.94	45.16
18	0.50	4,500	6.0	4.0	20.98	29.06
19	2.00	500	6.0	4.0	39.80	32.42
20	1.25	2,500	4.0	3.0	34.32	42.71

Table 2
ANOVA for anodic chlorination

Source	Sum of squares	df	F Value	p Value Prob > F	
Model	7,909.69	9	171.00	<0.0001	Significant
X_1, current density	4,625.94	1	900.05	<0.0001	
X_2, Cl^- concentration	1,783.29	1	346.97	<0.0001	
X_4, pH	590.90	1	114.97	<0.0001	
X_1X_2	583.62	1	113.55	<0.0001	
X_1X_4	183.07	1	35.62	0.0001	
X_2X_4	74.24	1	14.44	0.0035	
X_1^2	0.10	1	0.02	0.8894	
X_2^2	46.57	1	9.06	0.0131	
X_4^2	0.83	1	0.16	0.6959	
Residual	51.40	10			
Lack of fit	39.11	5	3.18	0.1149	Not significant
Pure error	12.29	5			

Table 3
ANOVA for cathodic electro-Fenton oxidation

Source	Sum of squares	df	F Value	p Value Prob > F	
Model	2,702.55	9	509.13	<0.0001	Significant
X_1, current density	29.42	1	49.89	<0.0001	
X_3, Fe^{2+} concentration	0.52	1	0.88	0.3713	
X_4, pH	1,263.53	1	2,142.32	<0.0001	
X_1X_3	0.17	1	0.29	0.6050	
X_1X_4	5.99	1	10.15	0.0097	
X_3X_4	7.07	1	11.99	0.0061	
X_1^2	1.37	1	2.33	0.1582	
X_3^2	2.09	1	3.54	0.0893	
X_4^2	24.24	1	41.09	<0.0001	
Residual	5.90	10			
Lack of fit	0.63	5	0.12	0.9819	Not significant
Pure error	5.27	5			

exists, it indicates non-normality in the error term and thus response should be corrected. Fig. 3 shows the normality assumptions in the present models for anodic oxidation and electro-Fenton oxidation were satisfied.

Consequently the ultimate RSM models, in terms of the coded factors, for the removal efficiencies for anodic chlorination and electro-Fenton oxidation can be described as:

$$\begin{aligned} Y_a &= 36.56 + 21.51X_1 + 13.35X_2 + 7.69X_4 + 8.54X_1X_2 \\ &\quad + 4.78X_1X_4 + 3.05X_2X_4 + 0.19X_1^2 - 4.11X_2^2 + 0.55X_4^2 \end{aligned} \tag{9}$$

$$\begin{aligned} Y_c &= 45.21 + 2.57X_1 + 1.79X_3 - 16.86X_4 + 0.29X_1X_3 \\ &\quad - 0.87X_1X_4 - 1.88X_3X_4 - 0.71X_1^2 - 3.49X_3^2 + 2.97X_4^2 \end{aligned} \tag{10}$$

A positive coefficient of a factor results in a increase in the removal efficiency when the factor level increases. On the contrary, a negative coefficient of a factor means the removal efficiency decreases with increasing the factor level. Therefore, increasing the current density, chloride concentration and pH increased the removal efficiency for anodic oxidation. However, for electro-Fenton oxidation, the removal efficiency was increased only with increasing the applied current density and Fe^{2+} concentration and the pH had a negative efficiency on removal efficiency in the experimental ranges. The Pareto analysis describes the percentage effect of each factor on the response according to the coefficient of coded equation and determined the significance of the variables affecting COD removal:

$$P_i\ (\%) = \left(\frac{b_i^2}{\sum b_i^2}\right) \times 100 \quad (i \neq 0) \tag{11}$$

Table 4 shows the result of the Pareto analysis. For the anodic chlorination, the current density and the chloride concentration were the most important two factors. On the other hand, the solution pH played the most important part for electro-Fenton oxidation.

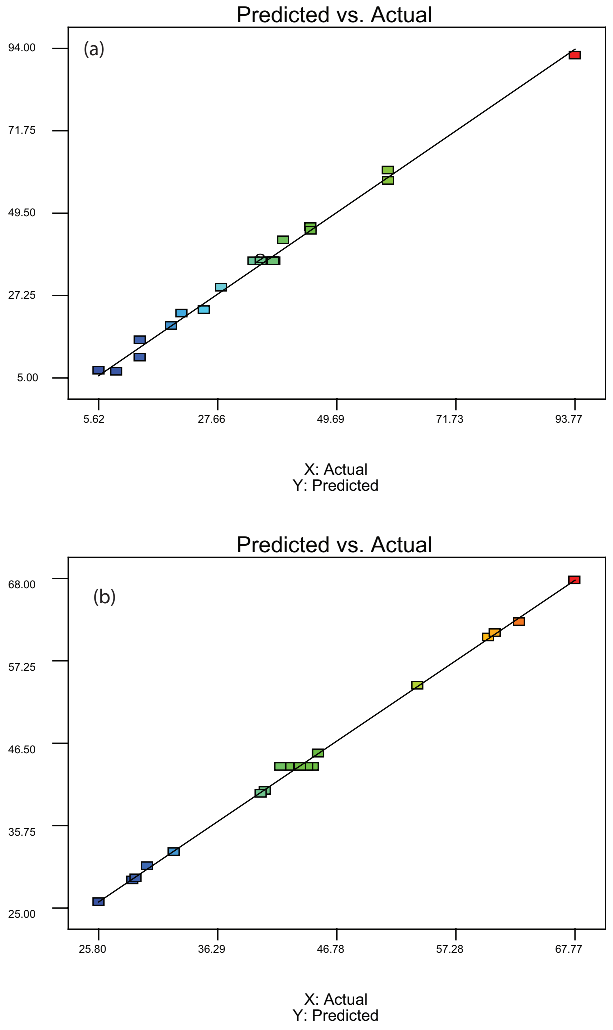

Fig. 2. Predicted vs. actual values for COD removal efficiency: (a) for anodic chlorination and (b) for cathodic electro-Fenton oxidation.

The contour plot can show contour lines of variable pairs that have the same response value. Interaction effects were usually determined by plotting the response surface contour. In addition, the behavior of response with respect to simultaneous change in two variables can be seen in contour plots. Figs. 4(a) and (b) show the 3D response surface graph and the contour plot, respectively, at initial pH 3 using the current density and the added chloride concentration, the most important two, as seen in Pareto analysis, as the variables for anodic oxidation. The removal percentage significantly increased with increasing the current density and chloride concentration. Increase in current density means the direct oxidation at the anode probably increases if mass transfer limitation of pollutant does not exist. Also, this Ti/Pt anode is a good catalytic electrode to liberate chlorine from chloride-concentration solution, causing higher rate of the hypochlorous acid production, and consequently bringing about more oxidation of pollutants.

Figs. 5(a) and (b) show the 3D response surface graph and the contour plot, respectively, at 1.25 A/dm^2 current density using the added Fe^{2+} concentration and the solution initial pH as the variables for electro-Fenton oxidation. The slightly positive effect of Fe^{2+} concentration on the

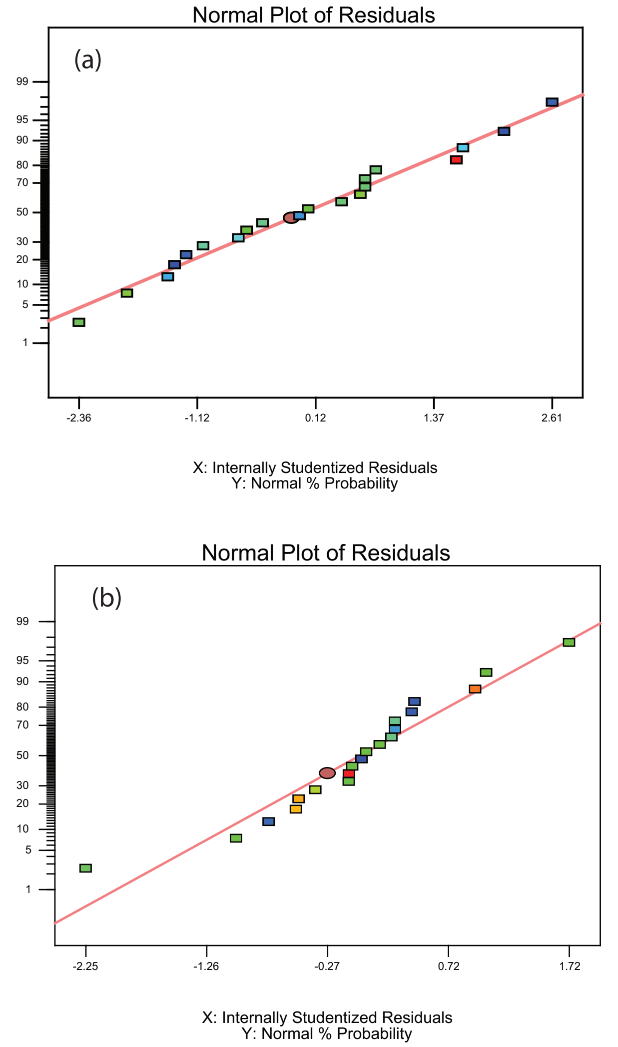

Fig. 3. Normal probability plot of the internally studentized residuals: (a) for anodic chlorination and (b) for cathodic electro-Fenton oxidation.

Table 4
Pareto analysis for anodic chlorination and electro-Fenton oxidation

Anodic oxidation (%)		Electro-Fenton oxidation (%)	
X_1	56.2630	X_1	2.0644
X_2	21.6723	X_3	1.0014
X_4	7.1911	X_4	88.8453
X_1X_2	8.8687	X_1X_3	0.0263
X_1X_4	2.7784	X_1X_4	0.2366
X_2X_4	1.1312	X_3X_4	1.1047
X_1^2	4.39E–03	X_1^2	0.1576
X_2^2	2.0541	X_3^2	3.8069
X_4^2	0.0368	X_4^2	2.757

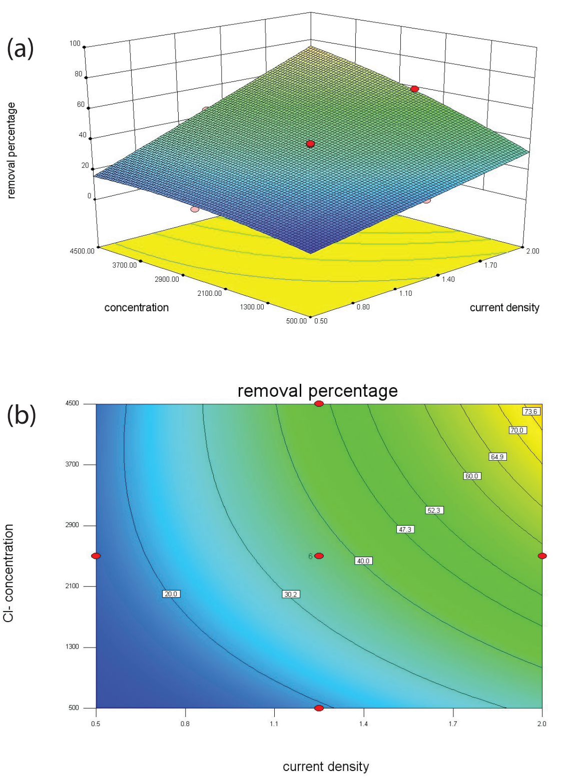

Fig. 4. The 3D response surface graph and the contour plot of COD removal efficiency using the current density and the added chloride concentration as the variables for anodic chlorination; initial pH: 3. (a) Red point and (b) design point.

removal percentage was observed between 2 and 6 mg/dm^3. The pH effect on removal percentage was more observable. The value of pH 2–3 was mostly considered to be the optimal value for Fenton chemistry. Higher pH can lead to the hydroxide precipitation of Fe species and thus the catalytic effect is reduced [26,27]. For electro-Fenton oxidation process, the pH is not only a crucial factor for Fenton oxidation efficiency, but also a chief parameter for electrochemical generation of H_2O_2. Considering the theoretical aspect of H_2O_2 production, a low pH is favorable for producing hydrogen peroxide because the conversion of dissolved oxygen to hydrogen peroxide consumes protons in acidic solution, as seen in Eq. (7). The more amount of H_2O_2 generated, the more hydroxyl radicals are produced according to Eq. (8). Therefore, the removal efficiency increased with decreasing pH in this study.

4. Conclusions

The electrochemical treatment of dyeing wastewater was studied in a divided reactor. According to the present study, anodic chlorination using Ti/Pt anode and cathodic electro-Fenton oxidation using ACF cathode were effective for COD removal. The use of RSM enabled modeling the influence of a number of variables, with a limited number of experiments, for COD removal. Central composite design was adopted to obtain the response surfaces of COD removal efficiency as a function of current density, added chloride concentration, added Fe^{2+} concentration and solution pH for anodic chlorination and cathodic electro-Fenton oxidation. Agreement of each quadratic model with the experimental data was satisfactory from the ANOVA analysis. For the variable ranges studied, findings showed the applied current density and the solution pH were the most important factors for anodic oxidation and cathodic electro-Fenton oxidation, respectively.

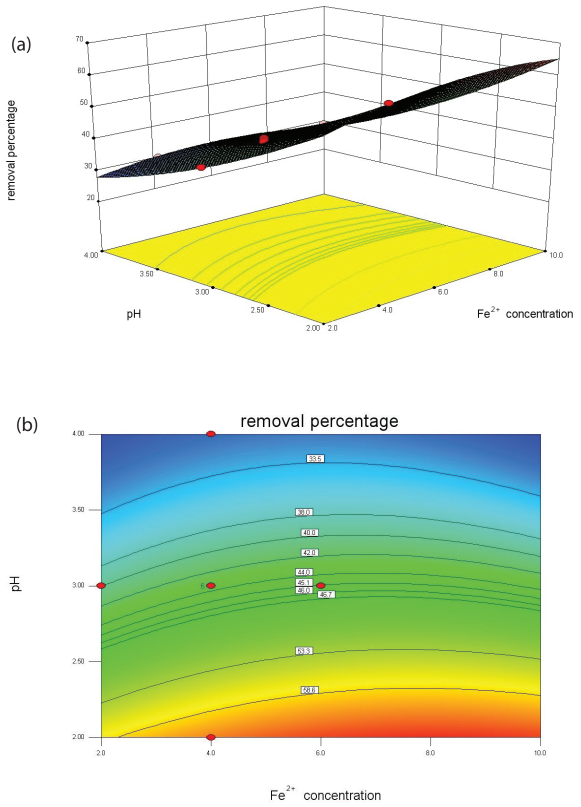

Fig. 5. The response surface graph and the contour plot of COD removal efficiency using the added Fe^{2+} concentration and the solution initial pH as the variables for electro-Fenton oxidation; current density: 1.25 A/dm^2. (a) Red point and (b) design point.

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