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Optimization and analysis of homogenous Fenton process for the treatment of dry-spun acrylic fiber manufacturing wastewater

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ABSTRACT

In this study, the homogenous Fenton process was employed for the pretreatment of dry-spun acrylic fiber (DAF) manufacturing wastewater. Central composite design and response surface methodology (RSM) were used for the design and optimization of the Fenton process. A second-order polynomial regression equation was developed to describe the chemical oxygen demand (COD) removal efficiency of Fenton process and validated by the analysis of variance and residual techniques. The interaction effects of the operational parameters were investigated using response surface analysis. The optimum parameters were determined as 90.00 mM H_2O_2, 30.00 mM Fe^{2+}, pH of 3.14, and reaction time of 114 min. Under the optimum reaction conditions, the COD removal efficiency was 47.1%, which was highly consistent with the value predicted by the model equation, with a deviation of 2.89%. Furthermore, the biodegradability and toxicity of raw and treated wastewater were compared; the results showed that the (BOD_5)/COD (B/C) ratio increased from 0.35 to 0.67, whereas the light loss of *Vibrio fisheri* bacteria decreased from 92 to 31%. The Fenton process was an effective method for pretreating DAF wastewater, and RSM was suitable for process design and optimization.

Keywords: Fenton; Dry-spun acrylic fiber wastewater; Response surface methodology; Central composite design; Optimization

1. Introduction

Over the past several decades, the acrylic fiber industry has grown rapidly in many developing countries. Presently, wet-spun and dry-spun acrylic fiber (DAF) manufacturing technologies are the two main production processes used in China. Of these two technologies, the DAF is the preferred product for its high quality and versatility. However, the effluents from DAF manufacturing process contain a large

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amount of organic and inorganic pollutants [1]. Some of these pollutants are highly toxic and biorefractory, which may cause serious environmental problems if improperly treated and discharged to receiving waterbodies. For wastewater treatment, most DAF manufacturing factories have adopted traditional biological treatment or biological treatment followed by physicochemical treatment such as coagulation, neutralization, and adsorption. The effluents of biological treatment still contain high concentrations of chemical oxygen demand (COD), ammonia nitrogen (NH_4^+-N), and toxic substances. Biochemical treatment is inadequate for the removal of organic pollutants considering increasingly strict environmental standards [1–3]. Therefore, it is necessary to develop an effective and feasible pretreatment for DAF wastewater prior to biological treatment.

The Fenton reaction process is a common advanced oxidation process (AOP) used as a pretreatment to improve the biodegradability and reduce the toxicity of refractory wastewater prior to biological treatment [4,5]. In the Fenton reaction process, free hydroxyl radicals (·OH), which are powerful oxidizing agents (2.80 V oxidation–reduction potential, second only to fluorine), are generated in the catalytic oxidation reaction of hydrogen peroxide (H_2O_2) with ferrous ions (Fe^{2+}). In addition to the main reaction, a series of chain reactions are also possible, in which ferrous ions, ferric ions, hydrogen peroxide, superoxide, and hydroxyl radicals are involved. In these reactions, refractory or toxic organic compounds can be oxidized and transformed into biodegradable small molecules or carbon dioxide and water [6]. Additionally, ferrous ions are oxidized to ferric ions and ferric complexes, and the resultant flocculation improves the treatment efficiency of the Fenton process [7]. Due to its simplicity and high removal efficiency for recalcitrant pollutants, Fenton oxidation has been successfully applied to the degradation of landfill leachate [8], the enhancement of anaerobic digestibility [9], the discoloration of textile-dying wastewater [10], the treatment of petrochemical wastewater [11], and the removal of antibiotics in aqueous solution [12]. Nonetheless, the application of the Fenton process as the pretreatment of DAF manufacturing wastewater has not yet been studied.

Response surface methodology (RSM) is a statistical-based method that is widely used in design, modeling, and analysis [13,14]. The main objective of this study was to investigate the application of homogenous Fenton process in the pretreatment of DAF manufacturing wastewater and optimize the process parameters. Central composite design (CCD) and RSM were employed to evaluate the effects of the key ariables including H_2O_2 dosage, Fe^{2+} dosage, initial pH value, and reaction time. A regression quadratic model was developed with the experimental data, and the significance of each variable on the performance of Fenton process was determined and the optimal Fenton reaction condition was obtained and validated. Additionally, the biodegradability and toxicity of raw and treated DAF manufacturing wastewater were also evaluated.

2. Materials and methods

2.1. Raw wastewater

The wastewater used in this study was obtained from a DAF manufacturing factory located in Liaoning Province, China. Wastewater samples were collected from the DAF manufacturing department, stored at 4℃ during transportation to the laboratory, and then immediately analyzed. The characteristics of the DAF manufacturing wastewater used in this study are listed in Table 1.

2.2. Experimental procedure

The experiments were conducted in 500 mL batch reactors at 25℃, and continuous mixing was provided by mechanical stirring. In each process, 300 mL of wastewater was transferred to the reactor and the initial pH was adjusted to the desired value with H_2SO_4 (3.0 M). A weighed amount of $FeSO_4·7H_2O$ was added to the wastewater and dissolved in the solution. The Fenton oxidation was initiated with the addition of H_2O_2 solution (30%, w/w). Samples were withdrawn from the reactor at determined times, and the reaction was stopped by adjusting the pH to 10.0 using NaOH (5.0 M), which instantaneously consumed the residual H_2O_2. Finally, the stirring was stopped and the solution was left undisturbed for 30 min to settle out the flocs. The supernatant was withdrawn and filtered for analyses.

Table 1
Characteristics of DAF manufacturing wastewater

Parameter	Unit	Value
COD	mg O_2/L	1,091.5
BOD	mg O_2/L	382.8
TOC	mg /L	326.3
TN	mg/L	160.0
NH_3-N	mg/L	21.6
SO_4^{2-}	mg/L	776.8
pH	–	6.56
Conductivity	μS	1,421
Turbidity	NTU	46.6

2.3. Analytical methods

COD and biochemical oxygen demand (BOD_5) were measured according to the standard method [15]. The sample ecotoxicity was analyzed using bioluminescent marine bacteria *Vibrio fischeri*, provided by America SDI, using the Microtox DeltaTox II system according to the international standard process (DIN/EN/ISO 11348-2) [16]. Prior to the tests of BOD_5 and ecotoxicity, the pH of wastewater samples was adjusted to 7.0–8.0. The wastewater pH was measured with a pH meter (OHAUS Starter 3C, America).

2.4. Central composite design

CCD was used to optimize the Fenton process. To estimate the influence of operational parameters on COD removal efficiency, four key controlling parameters were chosen: H_2O_2 dosage (X_1), Fe^{2+} dosage (X_2), initial pH (X_3), and reaction time (X_4). Experimental parameter ranges and levels of the independent variables for COD removal are given in Table 2. The experimental data were analyzed using software Design-Expert 8.0 (Stat-Ease Inc., America).

3. Results and discussion

3.1. Central composite design model

The four-factor experimental design and the COD removal efficiencies are shown in Table 3. A second-order polynomial equation (Eq. (1)) was used to correlate the dependent and independent variables.

$$Y = b_0 + \sum b_i x_i + \sum b_{ii} x_i^2 + \sum b_{ij} x_i x_j \qquad (1)$$

where Y is the response variable of COD removal efficiency; b_0 is the constant coefficient; b_i, b_{ii}, and b_{ij} indicate the regression coefficients; and x_i and x_j indicate the levels of the process independent variables [17].

Table 2
Experimental ranges and levels of the independent variables for response surface methodology

Variables	Symbol	Ranges and levels −2	−1	0	+1	+2
H_2O_2 dosage (mM)	X_1	30	60	90	120	150
Fe^{2+} dosage (mM)	X_2	7.5	15	22.5	30	37.5
Initial pH values	X_3	1.0	2.0	3.0	4.0	5.0
Reaction time (min)	X_4	30	60	90	120	150

Table 3
CCD experimental design and results of COD removal efficiency

Run	$[H_2O_2]$ X_1 (mM)	$[Fe^{2+}]$ X_2 (mM)	Initial pH X_3	Reaction time X_4 (min)	Response COD removal (%) Actual	Predicted
1	−2	0	0	0	30.49	31.08
2	0	0	2	0	39.92	37.42
3	1	−1	−1	−1	25.62	26.35
4	0	0	0	0	44.47	44.47
5	1	1	1	1	48.05	51.12
6	−1	−1	−1	1	24.64	23.91
7	0	0	0	−2	33.09	33.19
8	0	0	0	0	44.47	44.47
9	0	0	−2	0	30.49	29.02
10	0	0	0	0	44.47	44.47
11	2	0	0	0	50.65	46.09
12	1	−1	1	−1	34.07	35.30
13	0	0	0	0	44.47	44.47
14	1	−1	1	−1	29.84	28.08
15	0	0	0	0	44.47	44.47
16	0	0	0	2	45.12	41.05
17	−1	−1	−1	−1	23.34	23.76
18	0	−2	0	0	21.39	20.67
19	−1	1	1	−1	31.47	33.19
20	−1	1	−1	1	37.00	39.26
21	0	0	0	0	44.47	44.47
22	1	−1	−1	1	26.92	28.69
23	1	1	−1	−1	39.92	41.21
24	0	2	0	0	47.40	44.13
25	1	−1	1	1	37.97	39.52
26	1	1	1	−1	42.20	43.42
27	−1	1	1	1	38.95	38.70
28	−1	−1	1	1	27.89	30.10
29	1	1	−1	1	44.80	47.05
30	−1	1	−1	−1	36.67	35.61

Based on the results in Table 3, the relationship between the COD removal response and operational variables was attained and expressed by the following second-order polynomial regression equation (Eq. (2)):

$$\begin{aligned} \mathrm{Y} = {} & -8362220 + 0.30389x_1 + 3.87067x_2 + 20.57029x_3 \\ & + 0.43326x_4 + 0.038607x_1x_3 - 0.22487x_2x_3 \\ & - 1.63686{x_1}^2 - 0.053644{x_2}^2 - 2.81428{x_3}^2 \\ & - 2.04326{x_4}^2 \end{aligned} \qquad (2)$$

It should be noted that the insignificant regression coefficients ($p > 0.05$) were excluded from the model.

3.2. CCD model validation and residuals analysis

The coefficient of determination (R^2) evaluates the correlation between the experimental data and the predicted values. The experimental results and model predictions (Eq. (2)) are shown in Table 3. The plot of the predicted values vs. the experimental values of COD removal response is shown in Fig. 1. The values calculated using the second-order model was in good agreement with the experimental values, with satisfactory correlation.

The obtained R^2 value of 0.9500 suggested a good agreement with the experimental results; namely, 95.00% of the variation in the COD removal efficiency could be explained by the independent variables. This high R^2 value indicated that the regression model was able to well estimate the COD removal response in the studied range.

The reaction residual is another important indicator for evaluating the adequacy of the model in addition to the regression coefficient. The residuals are essentially elements of the variation unexplained by the fitted model and should conform to a normal distribution [18]. The normal probability plot is a suitable graphical method for judging the normality of the residuals. As shown in Fig. 2, a normal distribution was acquired according to the plots of the observed residuals against the expected values. Generally, the residuals obtained by analysis should be normally distributed. However, moderate deviations from normality generally do not seriously affect the results for balanced designs or a large number of observations. The normal probability plot of the residuals should roughly follow a straight line. Fig. 2(a) reveals reasonably well-behaved residuals from the trends. Fig. 2(b) shows the residuals vs. the predicted values. Based on this plot, the residuals appear to be randomly scattered around zero. Fig. 2(c) illustrates the residuals in the order of the corresponding observations; the residuals in the plot fluctuated randomly around the center line.

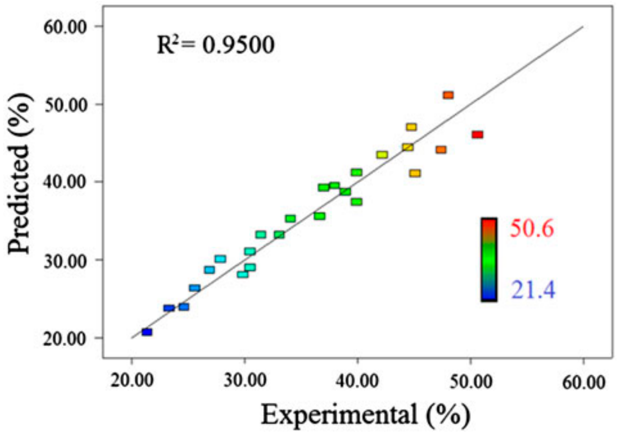

Fig. 1. Predicted vs. experimental values of COD removal efficiencies.

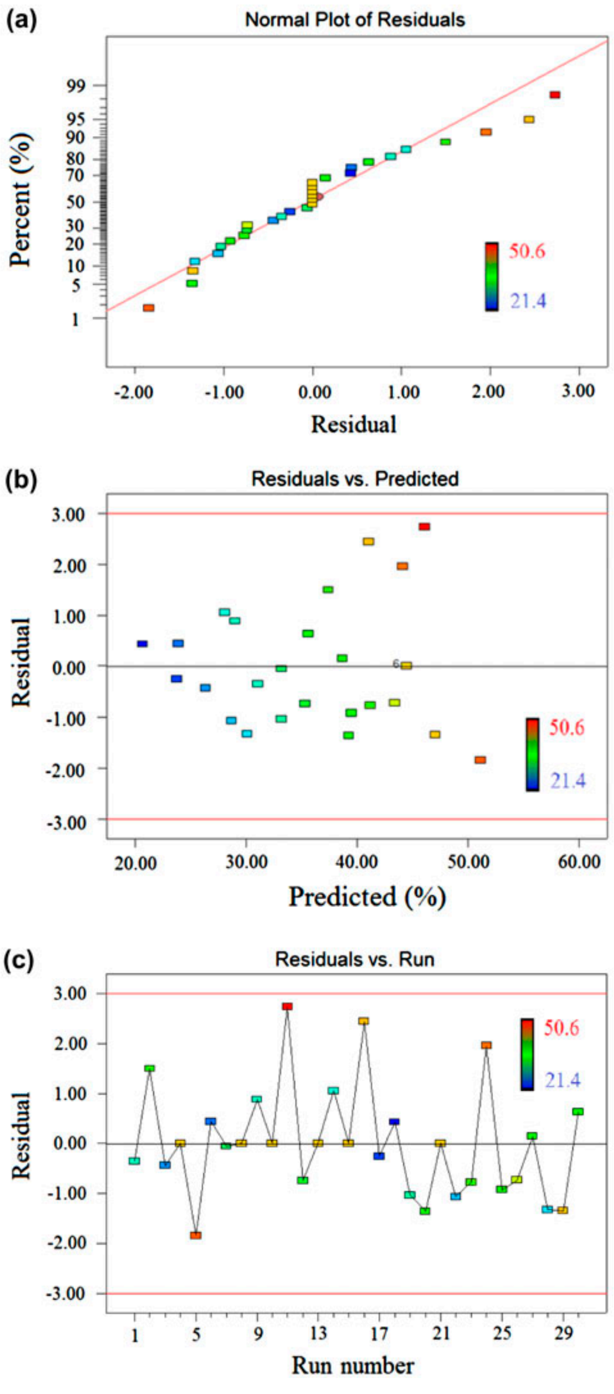

Fig. 2. Residual plots for COD removal efficiency of DAF wastewater.

3.3. Analysis of variance

Analysis of variance (ANOVA) is an important tool for checking the significance and adequacy of the model [19]. Table 4 summarizes the ANOVA results of the quadratic response surface model for the COD removal from DAF manufacturing wastewater using the Fenton process. Based on the statistical analysis of the data in Table 4, the model *F* value of 27.49 implied that the model was significant for the COD removal efficiency; indeed, there was only a 0.01% chance that a model *F* value this large could occur due to noise. The *F* values for H_2O_2 dosage, Fe^{2+} dosage, pH, and reaction time were 49.31, 120.49, 15.44, and 13.51, respectively, which implied that the influence of Fe^{2+} dosage on the Fenton oxidation of DAF manufacturing wastewater was the most significant, followed by H_2O_2 dosage, pH, and reaction time, orderly.

The probability value (*P* value) was equivalent to the proportion of the area under the curve of the *F*-distribution that lies beyond the observed *F* value [20]. A smaller *P* value indicates a higher significance of the corresponding coefficient. A *P* value >0.10 indicates that the model term was insignificant [21]. In this study, the *P* value <0.0001 for the regression model indicated that the quadratic model was highly significant and adequate for representing the actual relationship between the response and the variables. Furthermore, the individual variables effects (X_1, X_2, X_3, and X_4) and interaction terms (X_1^2, X_2^2, X_3^2, X_4^2, X_1X_3, and X_2X_3) for the COD removal efficiency were also significant.

Table 4
ANOVA for the regression model equation and coefficients

Source	SS	Df	MS	*F*	*P*
Model	1,883.96	10	188.40	27.49	<0.0001
X_1	337.93	1	337.93	49.31	<0.0001
X_2	825.73	1	825.73	120.49	<0.0001
X_3	105.81	1	105.81	15.44	0.0009
X_4	92.01	1	92.01	13.51	0.0016
X_1X_3	21.46	1	21.46	3.13	0.0928
X_2X_3	45.51	1	45.51	6.64	0.0185
X_1^2	59.53	1	59.53	8.69	0.0083
X_2^2	249.74	1	249.74	36.44	<0.0001
X_3^2	217.24	1	217.24	31.70	<0.0001
X_4^2	92.75	1	92.75	13.54	0.0016
Residual	130.20	19	6.85		
Lack of fit	130.20	14	9.30		
Pure error	0.000	5	0.000		
Cor total	2,014.16	29			

Note: SS, sum of square; Df, degrees of freedom; MS, mean square; *P*, probability.
$R^2 = 0.9500$, adjusted $R^2 = 0.9034$.

3.4. Response surface analysis

To estimate the effect of each operational variable on COD removal, response surface plots were created to investigate the interaction effect of two variables on the COD removal efficiency (Fig. 3(a)–(f)). According to Fig. 3(a), (d), and (e), the COD removal efficiency significantly increased when the Fe^{2+} dosage increased from 15.0 to approximately 25.0 mM. However, further increases in the Fe^{2+} dosage from 25.0 to 30.0 mM did not significantly promote COD removal. This phenomenon may be caused by the redox reaction between high active ·OH and excess Fe^{2+} inducing a self-scavenging effect of ·OH, which reduces the degradation efficiency of pollutants [22]. As shown in Fig. 3(a)–(c), increasing H_2O_2 concentrations led to a steady increase in the COD removal efficiency. The probable reason for this behavior is that the ·OH concentration increased with the increase in the H_2O_2 concentration, which enhanced the oxidation capability of the Fenton system, thereby increasing the COD removal efficiency [23]. Fig. 3(c), (e), and (f) shows that the COD removal efficiency increased rapidly at the beginning of the reaction and then slowed nearer the maximum efficiency at approximately 110 min. No significant increase in the COD removal was observed with further increase in contact time. Fig. 3(b), (d), and (f) shows that pH 3.0–4.0 is the optimum pH range for the Fenton reaction, with lower or higher pH values having a negative effect on COD removal. The results closely agreed with the literatures [24,25].

3.5. Determination of optimum conditions

The main objective of the optimization was to determine the optimum values of the variables of the Fenton process based on the obtained model. The desired goal in terms of COD removal efficiency was defined as "maximize" to achieve the maximum treatment efficiency. The optimum values of the variables for the maximum COD removal efficiency were as follows: 90.00 mM H_2O_2, 30.00 mM Fe^{2+}, pH 3.14, and 114 min reaction time. According to the prediction of the polynomial quadratic equation model, the COD removal efficiency was as high as 48.5% under the optimum reaction conditions. To verify the optimization results, three parallel experiments were carried out under the predicted optimum values. The average experimental value (47.1%) was highly consistent with the predicted value of the model equation, with a deviation of 2.89%. These results imply that RSM is a powerful method for optimizing the operational conditions of COD removal efficiency by the Fenton process.

3.6. Biodegradability and toxicity analysis

In this experiment, biodegradability and toxicity tests were conducted to assess the biotreatability and toxicity of the raw and treated DAF wastewater. The effluent is typically considered biodegradable when the BOD_5/COD (B/C) ratio is above 0.4 [26,27]. Considering its B/C ratio of 0.35, the raw DAF wastewater is clearly refractory and difficult to biodegrade using biological treatment. The test result shows that the B/C ratio of DAF wastewater increased from 0.35 to 0.67 after 2.0 h of Fenton oxidation under the optimum conditions, indicating a high biodegradability of the treated wastewater. Associated with the biodegradability improvement, the *Vibrio fisheri* bacteria light loss reduced significantly from 92 to 31%, which corresponds to a remarkable decrease in the wastewater ecotoxicity. Therefore, it can be confirmed that Fenton oxidation is effective in improving the biodegradability of DAF wastewater and is promising as pretreatment prior to biological treatment.

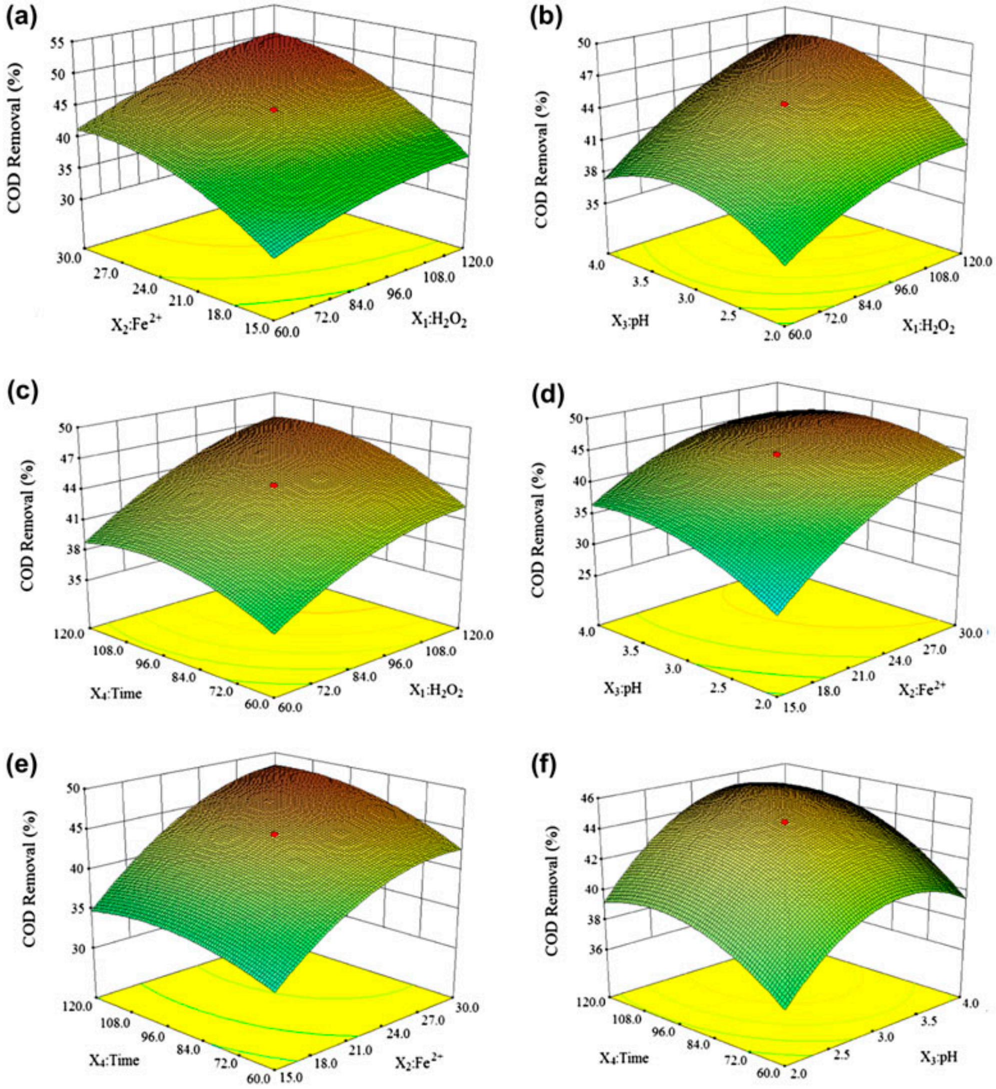

Fig. 3. Response surface plot for COD removal in DAF production wastewater by the Fenton process: effect of process parameters. (a) COD removal vs. H_2O_2 and Fe^{2+} doses. (b) COD removal vs. H_2O_2 dose and pH. (c) COD removal vs. H_2O_2 dose and reaction time. (d) COD removal vs. Fe^{2+} dose and pH. (e) COD removal vs. Fe^{2+} dose and reaction time. (f) COD removal vs. reaction time and pH.

4. Conclusions

In this study, the homogenous Fenton process was used for the pretreatment of DAF manufacturing wastewater. CCD and RSM were employed for the optimization and analysis of the Fenton process. The following conclusions could be drawn:

(1) The second-order response surface model was adequate for predicting the COD removal efficiency of DAF wastewater with four independent variables: H_2O_2 dosage, Fe^{2+} dosage, initial pH, and reaction time.

(2) ANOVA yielded a high coefficient of determination ($R^2 = 0.9500$ and adjusted $R^2 = 0.9034$), ensuring a satisfactory adjustment of the second-order regression model with the experimental data.

(3) The effect of the experimental parameters on the COD removal efficiency was established by the response surface plots. The optimum values of the variables for the maximum COD removal (48.5%) developed by the response surface model were found as follows: 90.0 mM H_2O_2, 30.0 mM Fe^{2+}, pH 3.14, and 114 min reaction time.

(4) After the treatment under the optimum conditions, the B/C ratio increased from 0.35 to 0.67, while the *V. fisheri* bacteria light loss ratio reduced from 92 to 31%, indicating a significant biodegradability improvement and toxicity reduction of the DAF manufacturing wastewater.

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