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Optimization of Fenton oxidation process for treatment of hexogeon industrial wastewater using response surface methodology

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ABSTRACT

Fenton oxidation technology was applied to treat hexogeon industrial wastewater and response surface methodology was used to optimize the effects of the $FeSO_4$ concentration, H_2O_2 concentration, pH value, and temperature. A quadratic model was obtained as the result of this design. In the optimization, the coefficient of variation is only 3.17%, indicating a good precision and reliability of the experimental. The coefficient of association (R^2) and adj-R^2 for quadratic model were evaluated quite satisfactorily as 0.98 and 0.96, respectively. The predicted optimum conditions were determined as 763 mg L^{-1} of $FeSO_4$ concentration, 107 mg L^{-1} of H_2O_2 concentration, 2.64 of pH, and 19˚C with 83.5% of chemical oxygen demand removal. The experimental result was 82.92% under optimizing reaction factors.

Keywords: Hexogeon industrial wastewater; Fenton; Response surface methodology; Optimization

1. Introduction

Hexogeon (hexahydro-1,3,5-trinitro-1.3.5-triazine, RDX), as an important energetic material, has become an indispensable explosive applied to the national defense worldwide. However, the emissions of organic wastewater from RDX industrial are huge [1,2]. The characteristics of the organic wastewater are strong chromaticity, non-transparent, high chemical oxygen demand (COD), and low biochemical oxygen demand (BOD)/COD ratio. The RDX-containing wastewater would pollute water, contaminate the fish, and harm to human health [3]. This high toxic organic wastewater therefore must be treated before emission in order to prevent pollution of ecological environment.

Nowadays, Fenton's reagent is used in the typical advanced oxidation technology to deal with many types of organic wastewater [4–6]. It is great at dealing with the wastewater which is high-chroma, poor biodegradability, and containing toxic substances. The degradation mechanism is shown in Fig. 1. A mixture of Fe^{2+} catalyst and H_2O_2 can form highly reactive hydroxyl radicals ($^{\bullet}OH$) which can damage organic contaminants [7,8]. Fe^{2+} dosage and H_2O_2 dosage must have the proper values controlled in Fenton oxidation processing. It have been reported that RDX wastewater was treated by Fenton oxidation [9–11]. However, to the best of our knowledge, the treatment of actual wastewater from RDX factory by Fenton oxidation has been not found in literature yet.

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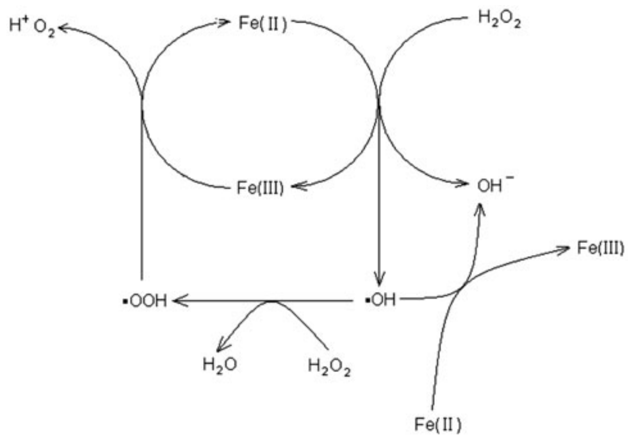

Fig. 1. Mechanism of Fenton's reagent in acid aqueous.

Response surface methodology (RSM) is a statistical method to analyze and optimize processing parameters and solve multi-variable problems. The mathematical model established can accurately describe the relationship between the factor and the response values, determine optimum operating parameters, and predict the experimental results. Thus, RSM has broad applications in the design of experiments, data analysis, and experimental prediction [12–15]. Gozzi et al. used electro-Fenton method to optimize operating parameters for Acid Yellow 36 decolorization by RSM [5]. Zhu et al. optimize Fenton and electro-Fenton process for treatment coking wastewater using RSM [13]. Bashir et al. used RSM to optimize the removal of ammoniacal nitrogen from semi-aerobic landfill leachate [16].

In this study, the actual wastewater from Chinese RDX factory was treated by Fenton oxidation. The effects of initial $FeSO_4$ concentration, initial H_2O_2 concentration, pH value, and temperature were investigated in detail and optimized using RSM.

2. Materials and methods

2.1. Chemicals

$FeSO_4{\cdot}7H_2O$, $K_2Cr_2O_7$, H_2SO_4, $(NH_4)_2Fe(SO_4)_2{\cdot}7H_2O$, Ag_2SO_4, H_2O_2(30% in H_2O), NaOH were all purchased from Beijing Chemical Reagent Company (China). All of the chemicals were of analytical reagent grade.

2.2. Wastewater

The RDX industrial wastewater used in this study was obtained from an explosive mill. It was analyzed that the sample wastewater contained some toxic or colored organic contaminants, such as RDX, dye, fatty, and soluble salt, in which COD content was about 44,000 mg L^{-1}. In this study, water sample was diluted 50 times and initial COD of wastewater was 880 mg L^{-1}.

2.3. Procedures and analysis

Fenton oxidation was processed using a 100 mL wastewater in a beaker. The wastewater was stirred by a magnetic stirrer. The pH of wastewater was adjusted using H_2SO_4. The quantitative $FeSO_4$ and H_2O_2 were added to the wastewater. After 2 h, pH was adjusted to 10 using NaOH to terminate the oxidation at the end of reaction. COD of wastewater was tested by $K_2Cr_2O_7$ method. COD removal was determined using following equation:

$$\text{COD Removal}\ (\%) = \frac{\text{COD}_0 - \text{COD}_f}{\text{COD}_0} \times 100\% \quad (1)$$

where COD_0 is the initial COD of wastewater and COD_f is the final COD after Fenton oxidation.

2.4. Experimental design for Fenton process to treat the RDX wastewater

This study used the RSM with central composite design (CCD) to optimize each reaction parameters of Fenton oxidation. There were four main factors in this experiment: the $FeSO_4$ dosage, the H_2O_2 dosage, pH value and temperature. On the basis of experimental results, thirty experiments were designed using CCD. The levels of the variables for Fenton oxidation is shown in Table 1. For four variables ($n = 4$), the design was performed with 30 experiments: 16 factorial points, 8 axial points, and 6 center points [12–14].

In RSM theory, the response variable Y exists with a set of input variables $x_1, x_2, x_3, \ldots, x_k$. It can be written as an empirical model $Y = f(x_1, x_2, x_3, \ldots, x_k)$. Generally, the second polynomial is deduced to describe the f. polynomial as shown by Eq. (2):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} {x_i}^2 + \sum_{i}^{i<j} \sum_{j}^{k} \beta_{ij} x_i x_j \quad (2)$$

where Y is the predicted response (COD Removal, %). The x_i and x_j are independent variables. The β_0 is the regression intercept and β_i, β_{ii}, β_{ij} are the regression coefficients. Design expert software version 8.06 was used to perform the regression analysis and analysis of variance (ANOVA).

Table 1
Levels of the variables for CCD experimental design

Variables	Code	Unit	Levels				
			−2	−1	0	+1	+2
$FeSO_4$ concentration	*A*	mg L	300	500	700	900	1,100
H_2O_2 concentration	*B*	mg L	20	60	100	140	180
pH value	*C*	–	1.5	2	2.5	3	3.5
Reaction temperature	*D*	℃	10	15	20	25	30

3. Results and discussion

3.1. ANOVA analysis

The 30 designed experimental points for the experimental values of COD removal are presented in Table 2. The values of COD removal range from 47.29 to 83.76%. The regression analysis is a mathematical statistic method, which adopts the principle of the least square method and uses mathematical statistics methods to establish regression equation between influencing factors (the independent variable) and prediction object (the dependent variable) on the basis of a large number of the collected response variable data. Design Expert 8.06 was used to analysis the experimental results. Quadratic model obtained for each response is expressed in Eq. (3), which takes their coded value.

$$\text{COD Removal} = 80.69 + 4.27A + 5.29B + 3.28C - 1.15D + 1.02AB - 0.28AC - 0.012AD - 0.52BC - 0.09BD + 0.13CD - 5.77A^2 - 5.07B^2 - 2.42C^2 + 0.019D^2 \quad (3)$$

ANOVA is used to made significant test for the mean difference of two or more samples. Summaries of the ANOVA are tabulated in Table 3. From Table 3, the Model *F*-value of 42.55 implied the model as significant because there was only a 0.01% chance that a "Model *F*-value" as large as this could occur due to noise. Values of "Prob > *F*" less than 0.0500 could determine model terms as significant. Values greater than 0.1000 indicated the model terms as not significant. For treatment of RDX industrial wastewater by Fenton oxidation, the model terms *A*, *B*, *C*, *D*, A^2, B^2, C^2 significantly affected the measured response of the system (COD removal). It was also observed that the concentration of $FeSO_4$ (*A*), the concentration of H_2O_2 (*B*), pH value (*C*), and their quadratic terms A^2, B^2, C^2 have large effects on the COD removal on account of the high *F*-value. A significant lack of fit suggests that there may be some systematic variation unaccounted in the hypothesized model. This may be due to the exact replicate values of the independent variable in the model that provide an estimate of pure error [16,17].

Table 2
Experimental design matrix and results for process optimization

Run	*A*	*B*	*C*	*D*	COD removal (%)
1	−1	1	1	1	70.45
2	1	1	1	−1	80.53
3	1	1	−1	−1	75.15
4	1	−1	1	1	68.45
5	0	2	0	0	73.96
6	0	0	0	0	80.91
7	−1	1	−1	1	61.57
8	0	0	2	0	75.22
9	−1	1	1	−1	72.12
10	2	0	0	0	69.48
11	1	1	1	1	78.24
12	−1	−1	1	1	63.12
13	0	−2	0	0	48.43
14	0	0	0	0	80.42
15	0	0	0	0	79.96
16	0	0	0	0	81.01
17	1	−1	1	−1	70.65
18	−1	1	−1	−1	64.42
19	0	0	0	0	81.09
20	0	0	−2	0	68.36
21	0	0	0	2	79.35
22	0	0	0	−2	83.76
23	−1	−1	−1	1	53.89
24	1	−1	−1	1	59.44
25	−2	0	2.5	0	47.29
26	0	0	0	0	80.75
27	−1	−1	−1	−1	56.43
28	1	−1	−1	−1	61.14
29	−1	−1	1	−2	65.33
30	1	1	−1	1	71.87

Table 3
ANOVA for response surface quadratic model

Source	*SS*	*df*	*MS*	*F*-value	Prob > *F*
Model	2937.37	14	209.81	42.55	<0.0001
A	437.93	1	437.93	88.81	<0.0001
B	671.62	1	671.62	136.21	<0.0001
C	258.07	1	258.07	52.34	<0.0001
D	31.65	1	31.65	6.42	0.0229
AB	16.65	1	16.65	3.38	0.0860
AC	1.23	1	1.23	0.25	0.6244
AD	2.500E−003	1	2.500E−003	5.070E−004	0.9823
BC	4.33	1	4.33	0.88	0.3638
BD	0.13	1	0.13	0.026	0.8734
CD	0.25	1	0.25	0.051	0.8249
A^2	914.17	1	914.17	185.39	<0.0001
B^2	705.22	1	705.22	143.02	<0.0001
C^2	160.88	1	160.88	32.63	<0.0001
D^2	0.010	1	0.010	2.088E−003	0.9642
Residual	73.96	15	4.93		
Lack of fit	73.04	10	7.30	39.69	0.0004
Pure error	0.92	5	0.18		
Cor total	3011.33	29			

Notes: *SS*—sum of squares; *df*—degree of freedom; *MS*—mean square.

The coefficient of determination (R^2) is the index of the degree of covariant between variables, equaling to the ratio of the regression sum of squares to the total sum of squares, namely the square of the correlation coefficient. The bigger the determination coefficient, the greater the contribution regression sum of squares make to the overall sum of squares and the better the effect of regression. In this study, R^2 for Fenton oxidation treating the wastewater-containing RDX was as great as 0.9754, indicating that the obtained model gave a good system response estimates within the studied range.

Coefficient of variation (CV), is another statistic to estimate the ratio of the standard deviation and the averages for observed results and measure the degree of variation for each observation. It also is a kind of evaluation profile of model reproducibility. As a general rule, a model can be considered reasonably reproducible when CV is not greater than 10% [18]. CV for this model was 3.17%, showing a good precision and reliability of the experimental runs. Moreover, adequate precision value (Adeq Precision) of 21.66 for the model was above four, which indicated adequate model discrimination [19].

Several diagnostic plots were analyzed to check on the models adequacy. Fig. 2 showed the normal plot of residuals for Fenton oxidation treatment of the RDX industrial wastewater, which revealed the residuals falling on a straight line. This indicated that errors were normally distributed for all the responses. Fig. 3 showed the plot of studentized residuals versus predicted COD removal. The plot implied a random scatter without any obvious patterns and unusual structure. This indicated that the model proposed is adequate. Fig. 4 showed the predicted versus actual plot for COD removal of Fenton oxidation, which implied that the predicted values were close to the experimental values. We can give a conclusion that

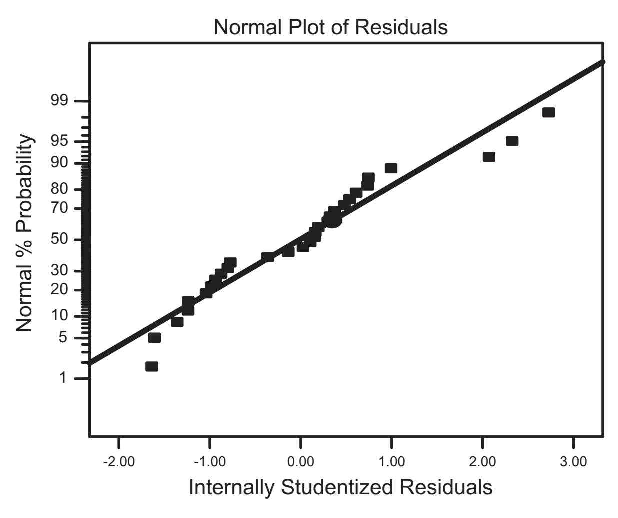

Fig. 2. Normal plot of studentized residuals for COD removal.

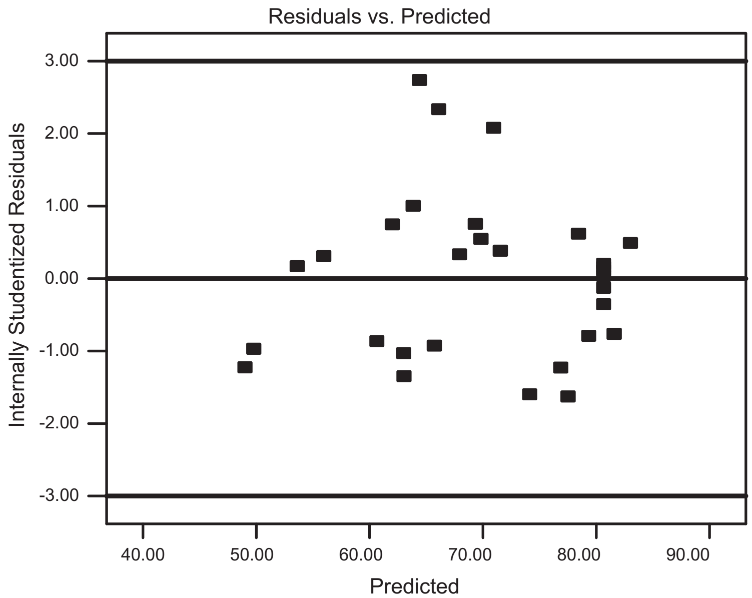

Fig. 3. Studentized residuals vs. predicted COD removal.

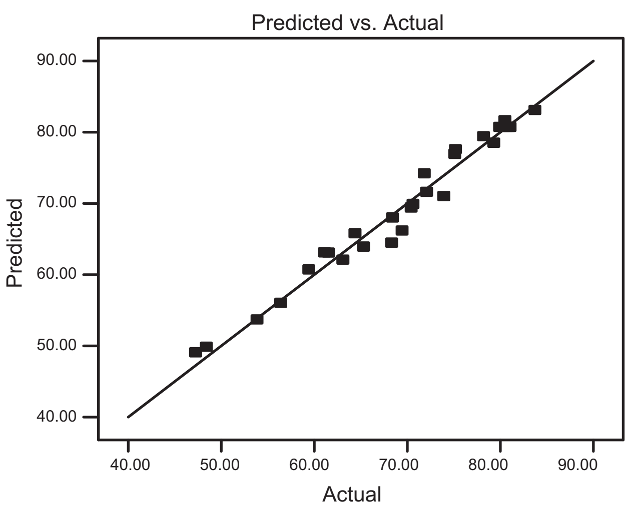

Fig. 4. Predicted vs. actual plot for COD removal.

the model developed was able to successfully capture the correlation between the reaction condition variables and the COD removal.

3.2. Model analysis

Fig. 5 showed three-dimensional response surface plot and contour plot on the effects of the Fenton process condition variables, which were $FeSO_4$ concentration (*A*), H_2O_2 concentration (*B*), pH value (*C*), and temperature (*D*) on the COD removal.

Fig. 5(a) showed the effects of $FeSO_4$ concentration (*A*) and H_2O_2 concentration (*B*) at zero level of pH value and temperature. It can be seen that COD removal increased with the increasing of $FeSO_4$ concentration. However, when the initial dosage of $FeSO_4$ was above a certain value, COD removal showed a declining trend. Fe^{2+} would react (Eq. (4)) with H_2O_2 in the acidic condition and generated $^{\bullet}OH$, which had a strong oxidizing ability. The gradual increasing of Fe^{2+} concentration would promote the Eq. (4) to the direction of the positive reaction, but it also increased the reaction showed in Eq. (5). Excessive Fe^{2+} would make response trend in Eq. (5) significantly increased, which could consume some $^{\bullet}OH$ and decrease the effect of Fenton's reagent. Thus, the COD removal was reduced.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (4)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (5)$$

Similarly, the concentration of $FeSO_4$ maintained a certain value, COD removal of the wastewater increased and then fall along with the increasing of the H_2O_2 concentration. The increasing of H_2O_2 dosage was conducive to the positive reaction of Eq. (4) at lower concentration of H_2O_2. This made the concentration of $^{\bullet}OH$ increase, so that the COD removal increased significantly. However, when the H_2O_2 concentration reach a certain value, the excess free radicals react with H_2O_2 (Eqs. (6) and (7)), and some

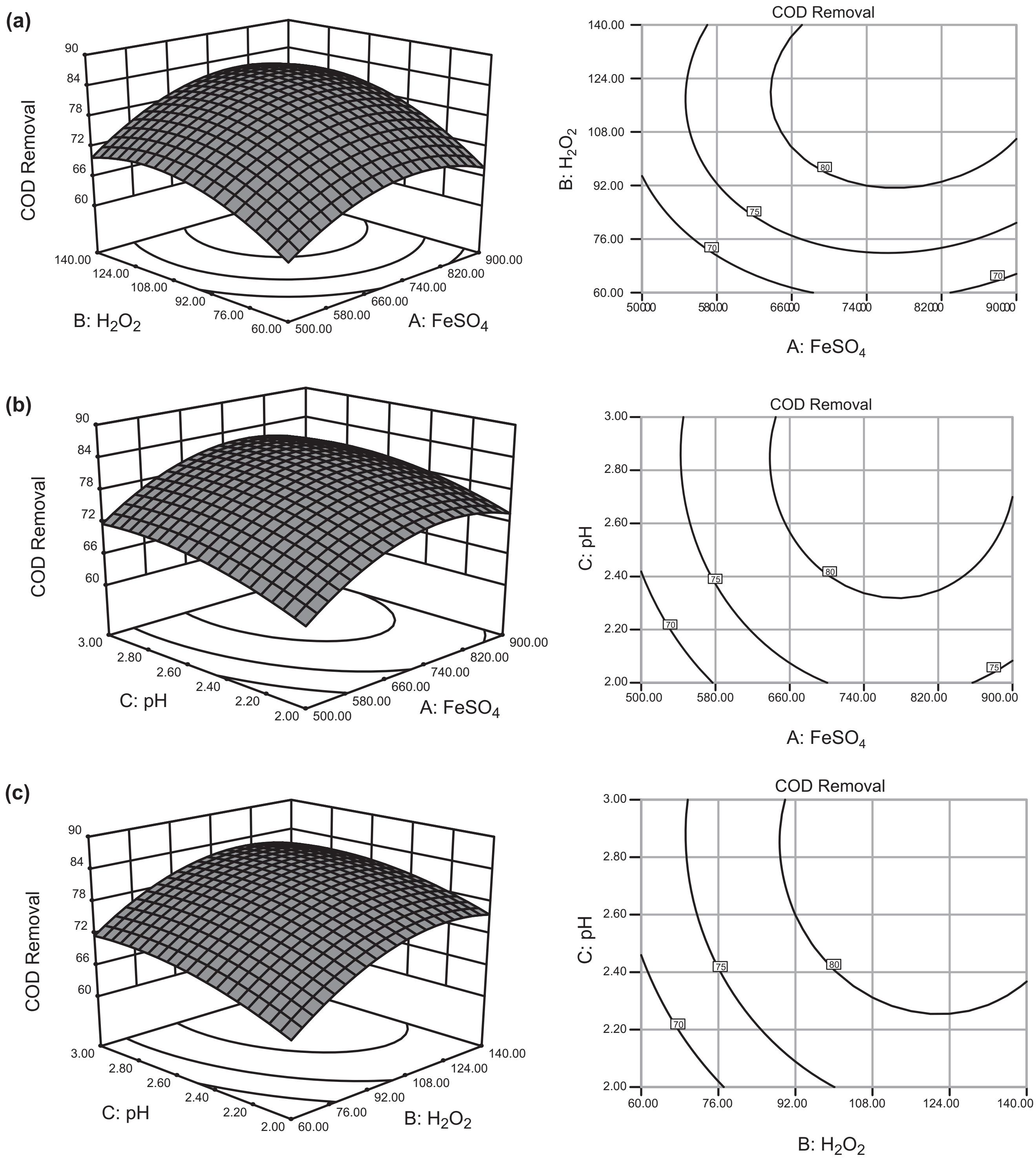

Fig. 5. Three-dimensional response surface plot and contour plot of COD removal for Fenton oxidation.

intermediates and by-products were difficult to be decomposed during reaction, which could weaken the Fenton process. Generally speaking, there will be different ratio of H_2O_2/Fe^{2+} for Fenton reagent dealing with different wastewater and the COD removal would be the highest in this ratio.

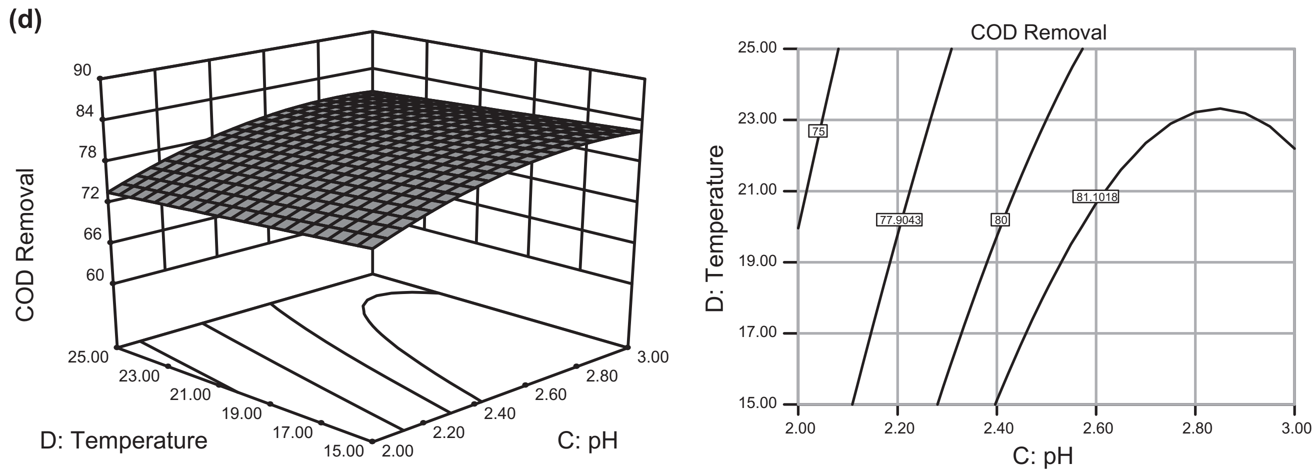

Fig. 5. (*Continued*).

$$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}OOH + H_2O \quad (6)$$

$$OH + {}^{\bullet}OOH \rightarrow H_2O + {}^{\bullet}O_2 \quad (7)$$

The pH of the solution is another important parameter for Fenton oxidation processing [20]. The effect of pH on the decomposition of wastewater containing RDX by Fenton reagent is shown in Fig. 5(b–d). It could be seen that the addition of pH from 1.5 to 2.64 could increase the COD removal of wastewater. But the further addition of pH from 2.64 to 3.0 could decrease the COD removal. Therefore, pH of 2.64 was believed as the optimum value for Fenton oxidation. At low pH ($pH < 2.64$), the COD removal was limited because the free radicals ($^{\bullet}OH$) could be consumed by the excessive H^+ (Eq. (8)) [21]. When pH of the water samples was more than 2.64, the COD removal would be reduced for three reasons. Firstly, the high pH value can reduce the stability of H_2O_2 and it will be broken down. Secondly, the ferrous catalyst will be inactivated because of the formation of ferric hydroxyl complexes in relative partial alkaline environment [22]. Thirdly, this condition is bad for Eq. (1) reaction to the positive direction so that the free radicals of the solution will be reduced according to Le Chatelier principle.

$$^{\bullet}OH + H^+ + e^- \rightarrow H_2O \quad (8)$$

The effect of reaction temperature on Fenton oxidation processing is shown in Fig. 5(d). As seen in figures, the removal rate of COD had certain decline with increasing temperature. Though the rising in temperature was conducive to raise reaction speed, it was a disadvantage for hydrolyzed effects. At high temperature, H_2O_2 was very instable and accelerated to be decomposed by itself, and Fe^{2+} was easily hydrolyzed. COD removal of wastewater had a great reduce with rise of reaction temperature. Although high temperature was not helpful for the removal of COD, low temperature would reduce the rate of chemical reaction. It was thus advisable to take room temperature for the reaction temperature of Fenton oxidation processing.

3.3 Process optimization of Fenton oxidation

To keep all the variables in range of the experimental values, numerical optimization method was used to optimize the desired response of the system, which was the COD removal. The optimized conditions and predicted COD removal are shown in Table 4. Using this optimized solution, the experimental run for Fenton oxidation dealing with the RDX

Table 4
Optimization criteria for Fenton oxidation

Reaction conditions	Fenton
$FeSO_4$ concentration (mg L^{-1})	763
H_2O_2 concentration (mg L^{-1})	107
pH (–)	2.64
Reaction temperature (°C)	19
Predicted COD removal (%)	83.50
Experimental COD removal (%)	82.92

industrial wastewater was conducted according to verification and an experimental value obtained was 82.92%. The optimized COD removal was 83.5% according to RSM. The result implied that the experimental value obtained was close to the value calculated from the model and the error rate was only 0.7%, which consequently verified the model capability.

4. Conclusions

Fenton oxidation was successfully applied to treat RDX industrial wastewater and RSM based on CCD was used to optimize the $FeSO_4$ concentration, H_2O_2 concentration, pH value, and temperature. The CV was only 3.17% indicating a good precision and reliability of the experiment. The coefficient of association (R^2) and adj-R^2 for quadratic model were evaluated as satisfactorily as 0.98 and 0.96, respectively. Through RSM analysis method, the predicted optimum condition for Fenton oxidation to treat the RDX industrial wastewater was determined as $763\,mg\,L^{-1}$ of $FeSO_4$ concentration, $107\,mg\,L^{-1}$ of H_2O_2 concentration, 2.64 of pH, and 19℃ with 83.50% of COD removal. The experimental result under optimizing reaction factors was 82.92%. The experimental data and model predictions were in good agreement with only 0.7% declination.

Acknowledgments

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