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Analyzing the kinetics of degradation of Acid Red B dye through Fenton oxidation with online monitoring system

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ABSTRACT

Fenton oxidation method was employed in Acid Red B (AR B) wastewater treatment, and the degradation process was monitored by means of online spectrophotometry. Under the optimal experimental reaction conditions determined by response surface methodology (RSM), we analyzed the reaction kinetics of AR B degradation, evaluated the biodegradability of the treated AR B wastewater, and preliminarily probed the possible AR B degradation mechanism using UV-Vis spectrum analysis and ion chromatography analysis. AR B concentration was 25 mg/L in the simulated wastewater, the reaction time and reaction temperature were set at 300 s and 20°C, respectively, in the Fenton treatment process. Analysis of the RSM result showed that (1) the optimum reaction conditions were H_2O_2 dosage (3.56 mmol/L), Fe^{2+} dosage (0.35 mmol/L), pH (2.63), under which the color removal rate could reach 96.8%. (2) The Fenton reaction process included two reaction stages, that is, rapid degradation stage (reaction time < 10 s) and slow degradation stage (reaction time > 10 s). Both stages followed the first-order reaction kinetics, and the reaction rate constants (K) were 0.159 and 0.0030 s^{-1} for rapid and slow stage, respectively. (3) Fenton reaction would significantly improve the biodegradability of AR B dye wastewater. (4) When the reaction time proceeded for 300 s, Fenton process could successfully destroy the molecular structure of AR B, rather than completely mineralize them.

Keywords: Acid Red B; Fenton oxidation; Online spectrophotometry; Reaction kinetics; Response surface methodology

1. Introduction

Organic dye wastewater (ODW), characterized by the low pH value, high chemical oxygen demand (COD) and salt content, poor biodegradability and complex composition, is one of the main harmful industrial wastewaters [1,2]. The quality and quantity of the ODW varied considerably, and its chromaticity is about tens of thousands to hundreds of thousands of times. ODW is difficult to treat by conventional methods, and the aromatic agents, metals and chlorides contained in it are toxic to aquatic organisms, human beings and even biosphere [3]. The discharge of untreated high concentration ODW will induce the excessive consumption of dissolved oxygen in natural water and reduce the water transparency [4], which may deteriorate the aquatic habitats, harm the living organisms, and seriously damage the urban landscape. Once the organic dye contaminated water is used for irrigation,

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it is bound to reduce the crop yields leading to economic losses. Moreover, when the contaminants deposit in the aquatic sediment, they may produce toxic gases and hence pollute the atmospheric environment [5]. Because of their stable chemical properties, organic dyes present similar eco-chemical behaviors and toxicological characteristics of persistent organic pollutants after entering environmental media such as water and soil. Briefly, contaminants in ODW can migrate and transform in water–soil–plant system, impairing the whole ecosystems and human health. Therefore, it is urgent to treat the ODW effectively in order to avoid the pollution and destruction of water resources, alleviate the serious shortage of water resources, and protect the ecological environment and human health in China.

The advanced oxidation technologies are widely applied in degradation of organic contaminants in industrial wastewater [6–12]. Hydroxyl radicals ($^\bullet$OH), having strong oxidation ability, are generated during the oxidation process. They can convert some organic macromolecules into nontoxic and harmless, biodegradable low-molecular substances, and hence improve the biodegradability of wastewater [7]. The advanced oxidation processes can degrade pollutants efficiently and have low selectivity to target contaminants [13]; furthermore, the catalyst consumption is low, and consequently it will not produce sludge during the oxidation reaction. In Fenton process [14,16], $^\bullet$OH generated through the reaction of H_2O_2 and Fe^{2+} ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^-$), can oxidize and degrade pollutants in wastewater, transforming organic pollutants into CO_2 and H_2O. Fenton oxidation ($Fe^{2+}/H_2O_2/H^+$) technology has received intensive attention in wastewater treatment due to its superior degradation efficiency, rapid reaction speed and moderate investment [15]. Under certain acidic conditions, Fe^{2+} is oxidized by H_2O_2 to form Fe^{3+}; $^\bullet$OH and OH^- [2] can produce highly reactive $^\bullet$OH, and thereby destroy the molecular structure of organic dyes, achieving the aim of dye wastewater decolorization.

Online spectrophotometric monitoring technology is an accurate, fast and convenient method for detecting instantaneous absorbance variation of dye at continuous reaction time during ODW treatment [5,9]. The key part of the device is special flow pool colorimetric dish in UV-Vis spectrometer. It is connected to a peristaltic pump and a reactor, and then the reactant can be continuously degraded and goes through measuring instruments. Thus, it can record the instant mass concentration change of the dye [9,16] and monitor the instantaneous state of the dye decolorization during the Fenton oxidation process. The experimental values are accurate.

Response surface methodology (RSM), comprising a collection of mathematical statistical methods [17,18], has been proved as an effective approach to explore the effects of independent variables and their interactions [19–21]. RSM can discriminate the sample points in the actual experiment and fit the continuous response surface function. Compared with the orthogonal test merely dealing with discrete values, RSM determines the optimum experimental conditions according to the accurate regression equation and has good predictive ability [22,23]. RSM was employed to investigate the optimum experimental conditions for degrading Acid Red B (AR B) dye via Fenton process, and predict the optimal degradation rate of AR B. Online spectrophotometry system was applied to record the real-time reaction process. Based on the RSM results, we studied the reaction kinetics in AR B removal, evaluated the biodegradability of the treated AR B wastewater, and explored the potential AR B degradation mechanism preliminarily using UV-vis spectrum analysis and ion chromatography analysis.

2. Materials and methods

2.1. Chemical reagents

The chemical structure of AR B is presented in Fig. 1. The AR B was purchased from Shijiazhuang Dyestuffs Company (China). Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (H_2O_2) were purchased from Tianjin Damao Chemical Reagent Company (Tianjin, China). Sodium hydroxide (NaOH) was purchased from Tianjin Senchang Reagent Factory (Tianjin, China). Sulfuric acid (H_2SO_4) was purchased from Modern Chemical Reagent Company (Shijiazhuang, China). All chemicals used were of reagent analytical grade. The simulated AR B wastewater was configured with ultrapure water.

2.2. Experimental procedure

The online spectrophotometry experiment device consisted of three parts: reaction device, photometric measuring device and data recording device. The reaction device was composed of magnetic agitator and reaction beaker. The photometric measuring device was comprised by peristaltic pump, UV-Vis spectrometer (UNICO 2802, Shanghai, China) and special colorimetric dish. A computer was utilized to record the absorbance data. The flow rate of peristaltic pump was set at 0.5 mL/s. The data recording frequency and duration was 1 Hz and 300 s, respectively. Fenton oxidation process was performed in a 500 mL vessel. The simulated ODW was pumped into the cuvette of UV-Vis spectrophotometer by peristaltic pump. The optimum experimental conditions were determined via RSM. The COD and BOD_5 apparatus were used for measuring the biodegradability. UV-Vis spectroscopy and ion chromatography (IC) were employed to analyze the AR B degradation mechanism.

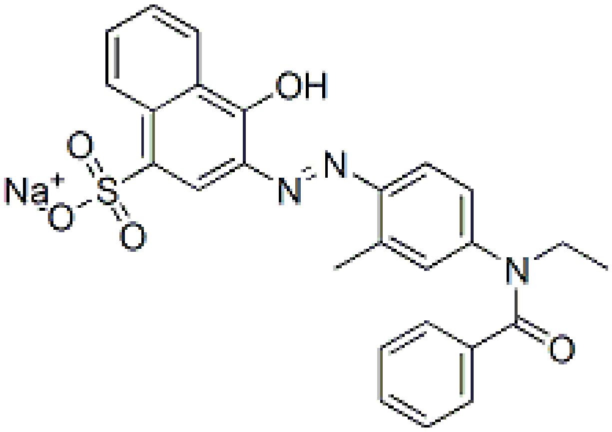

Fig. 1. Chemical structure of AR B.

2.3. Feasibility analysis of online monitoring technology

The simulated AR B wastewater was scanned at 200–800 nm and the absorbance peak was around 515 nm. The fitted standard curve is shown in Fig. 2. The simulated AR B wastewater and AR B (Fe^{2+} + Fe^{3+} + H^+) were scanned at 200–800 nm. The results are given in Fig. 3. The waveforms and absorption coincide at 400–600 nm, so online spectrophotometric monitoring at 515 nm is feasible. The linear relationship between the absorbance (A) at 515 nm and the AR B concentration (C) could be described by the function: $A = 0.02689C + 0.0049$ ($R^2 = 0.99995$).

2.4. Experimental condition optimized by RSM

The selected variables and their numerical ranges were selected according to our previous single factor experimental analysis. In this study, Box–Behnken design (BBD) was used for choosing the optimal reaction conditions (Fe^{2+} dosage, H_2O_2 dosage, and pH value) of the Fenton oxidation process for the AR B wastewater. To construct the response surface model, three variables with three levels, that is, Fe^{2+} dosage (0.2, 0.3, 0.4 mmol/L), H_2O_2 dosage (2, 3, 4 mmol/L), and pH value (2, 2.5, 3), were set as independent variables; and dye degradation rate was set as response variable. BBD was implemented in Design-Expert Software (version 10.0, Stat-Ease Inc., Minneapolis, MN, USA). Levels of each factor were represented as –1, 0, +1 indicating low, intermediate and high values, respectively. The levels and codes of BBD factors are displayed in Table 1. The BBD matrix of the 17 AR B wastewater treatment experiment is demonstrated in Table 2. The variables were coded according to Eq. (1):

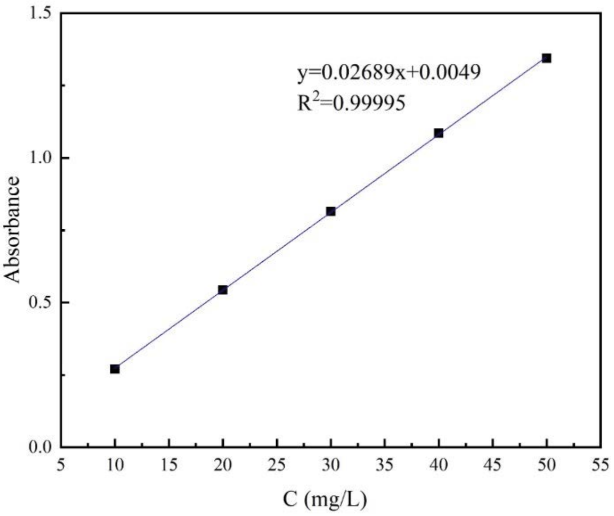

Fig. 2. Standard curve of concentration and absorbance of AR B.

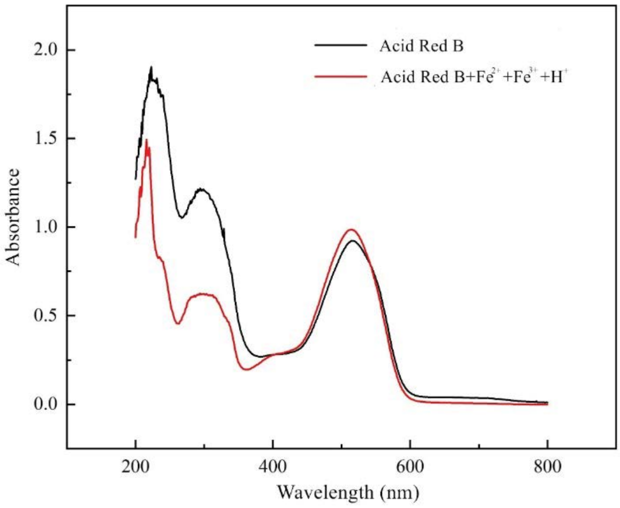

Fig. 3. Comparison of the UV-vis spectra between AR B dye and AR B (+H_2SO_4+Fe^{2+}+Fe^{3+}).

$$X_i = \frac{(x_i - x_0)}{(\Delta x)} \quad i = 1,2,3 \tag{1}$$

where X_i is the coded value of the independent variable; x_i is the actual value of the independent variable; x_0 is the actual value of the independent variable at center point; and Δx is the step change value of the independent variable. To predict the optimized conditions, a second-order polynomial model was fitted to portray the relationship between independent variables and the response. The quadratic equation is shown in Eq. (2) as follows:

$$\eta = \beta_0 + \sum_{i=1}^{3} \beta_1 X_1 + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i<j}^{3} \beta_{ij} X_i X_j \tag{2}$$

where η is the predicted response; β_0 is the intercept; $\beta_{1\sim3}$ are linear regression coefficients; β_{12}, β_{13}, and β_{23} are cross-product coefficients; and β_{11}, β_{22}, β_{33} are the quadratic coefficients.

3. Results and discussion

Based on the results of previous single factor experiment, the optimal experimental conditions for treating AR B wastewater using Fenton oxidation could be summarized as follows: Fe^{2+} concentration is 0.3 mmol/L, H_2O_2 concentration is 3 mmol/L and pH value is 2.5. Additionally, combining the results of single-factor analysis and Fenton reaction mechanism analysis, we would find some significant interactions among these foregoing factors, implying that the removal rate of AR B must be controlled by the covariation of the selected factors.

Table 1
Factor levels and code of variables in Box–Behnken design (unit: mg/L, except pH)

Variables	Code	Levels		
		–1	0	+1
Concentration of H_2O_2	X_1	2	3	4
Concentration of Fe^{2+}	X_2	0.2	0.3	0.4
pH value	X_3	2	2.5	3

3.1. Response surface experimental analysis

3.1.1. ANOVA analysis

The matching degree and the significance of each coefficient of binary regression equation can be obtained more clearly and the validity of model matching. Analysis of variance (ANOVA) was performed to evaluate the significance of the regression model and the parameters. The AR B degradation rate, corresponding to the 17 designed experimental points, is presented in Table 2, ranging from 64.00% to 96.86%. The regression analysis adopts mathematical statistics methods to establish regression equation between influencing factors and prediction value on the basis of a large number of the collected response variable data. ANOVA is used to made significant test for the mean difference of two or more samples. According to the ANOVA results listed in Table 3, the regression model, shown in Eq. (3), was reliable ($p < 0.001$) for determining the optimal experimental conditions of AR B wastewater treatment by Fenton oxidation.

The Prob. > *F* in model is less than 0.0001 and the model fits well. The missing fitting item Prob. > *F*-value is 0.8253, being higher than the test level (0.05), and this indicates that the fitting item Prob. > *F*-value of the prediction model is not significant. Therefore, this model can be used to analyze and predict the condition optimization test for the Fenton oxidation of AR B wastewater. The response value and the variables were predicted by the following Eq. (3):

The degradation rate is given as follows:

$$\eta = 94.08 + 0.31X_1 + 5.43X_2 + 6.43X_3 - 0.23X_1X_2 + 0.49X_1X_3 - 5.06X_2X_3 + 0.65X_1^2 - 2.81X_2^2 - 6.86X_3^2 \quad (3)$$

3.1.2. Interaction analysis of Fe^{2+} concentration and pH

Compared with traditional experimental design method, RSM is superior in identifying the impact of interactions between variables on experimental index. During the AR B wastewater treatment process using Fenton reagents, we examined the influences of variable interactions on decolorization rate, while keeping other variables at the optimal levels. The schematic diagram of the influence of Fe^{2+} concentration and pH interaction analysis on the removal rate of AR B is shown in Fig. 4. Other conditions are H_2O_2 dosage of 3.56 mmol/L, reaction temperature of 20°C, and AR B dosage of 25 mg/L in 300 s. As shown in Table 3 and Fig. 4, pH value and Fe^{2+} concentration jointly controlled the AR B degradation rate. The removal rate reached the maximum at pH value of 2.63, which is similar to the results of a single-factor experiment, and Fe^{2+} concentration of 0.35 mmol/L.

It has been proved that pH value plays an important role in determining the Fenton oxidation efficiency [24]. The contour plot and response surface plot of the interaction between Fe^{2+} concentration and pH show that the removal rate trends of AR B when Fe^{2+} concentration is within the range of 0.2–0.4 mmol/L and pH is in the range of 2–4. It is shown that the degradation rate of wastewater increases as pH is from 2 to 2.63. But the further addition of pH to 4 would result in decreasing the degradation rate. Therefore, pH of 2.63 was believed as the optimum value for Fenton oxidation. This is similar to the single factor result. When the pH was lower than 2.63 in the experiment, the $^{\bullet}OH$ might be consumed by excessive hydrogen ion ($^{\bullet}OH + H^+ + e^- \rightarrow H_2O$) [25], thus decreasing the degradation rate; when the pH was higher than 2.63, the Fenton-oxidation capacity decreased as well, due to the self-decomposition

Table 2
Experimental scheme and results

Standard sequence	Operation sequence	X_1	X_2	X_3	Degradation rate
		H_2O_2 (mmol/L)	Fe^{2+} (mmol/L)	pH	
10	1	3.00	0.40	2.00	91.66%
11	2	3.00	0.20	3.00	87.20%
4	3	4.00	0.40	2.50	96.57%
13	4	3.00	0.30	2.50	94.04%
15	5	3.00	0.30	2.50	94.19%
8	6	4.00	0.30	3.00	94.63%
7	7	2.00	0.30	3.00	95.08%
5	8	2.00	0.30	2.00	82.00%
1	9	2.00	0.20	2.50	88.98%
14	10	3.00	0.30	2.50	93.89%
16	11	3.00	0.30	2.50	94.33%
3	12	2.00	0.40	2.50	93.59%
12	13	3.00	0.40	3.00	96.86%
17	14	3.00	0.30	2.50	93.74%
2	15	4.00	0.20	2.50	90.62%
9	16	3.00	0.20	2.00	64.00%
6	17	4.00	0.30	2.00	81.10%

Table 3
Analysis of variance (ANOVA) result of the regression equation

Source	Sum of squares	Degrees of freedom	Mean square	*F*-value	Prob. > *F*	
Model	909.10	9	101.01	7.81	<0.0001	Significant
X_1	0.79	1	0.79	0.061	0.0815	Unsignificant
X_2	235.55	1	235.55	18.21	0.0037	Significant
X_3	328.83	1	328.83	25.42	0.0015	Significant
X_1X_2	0.20	1	0.20	0.016	0.9040	Unsignificant
X_1X_3	0.94	1	0.94	0.073	0.7952	Unsignificant
X_2X_3	102.31	1	102.31	7.91	0.0261	Significant
X_1X_1	1.78	1	1.78	0.14	0.7218	Unsignificant
X_2X_2	33.19	1	33.19	2.57	0.1532	Unsignificant
X_3X_3	198.02	1	198.02	15.31	0.0058	Significant
Residual	90.56	7	12.94			
Loss of fit	90.34	3	30.11	2.893	0.8253	Unsignificant
Pure error	0.22	4	0.055			
Cor. total	999.66	16				

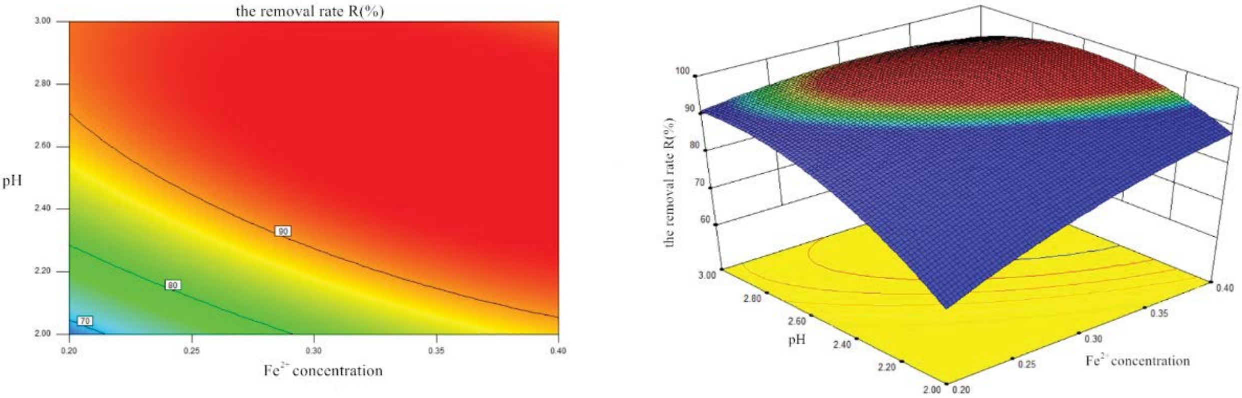

Fig. 4. Contour plot and 3D response surface plot describing the influence of Fe^{2+} concentration and pH interaction on the removal rate of AR B.

of hydrogen peroxide (H_2O_2) and the deactivation of ferrous catalyst, which will conduct the generation of ferric hydroxide complexes and thereby reduce the amount of $^{\bullet}OH$ radical [26], the Fenton oxidizing ability also decreased. These results showed that the Fenton oxidation had the best activity in a weakly acidic environment.

With pH increasing from 2 to 4, Fe^{2+} concentration increases from 0.2 to 0.35 mmol/L, and the removal rate of AR B increases. However, the degradation rate of AR B in wastewater decreased till the Fe^{2+} concentration exceeded the threshold level (0.35 mmol/L), implying that redundant Fe^{2+} probably inhibited the decolorization of AR B during Fenton oxidation process. This may be because the excess ferrous ion (Fe^{2+}) tends to compete the hydroxyl radical $^{\bullet}OH$ with the dye molecules ($Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$) [16,25]. Therefore, the Fe^{2+} dosage of 0.35 mmol/L can be chosen as an optimum dosage for efficient AR B degradation from aqueous solutions. The response surface graph shows the significant interaction between Fe^{2+} concentration and pH value.

3.1.3. Interaction analysis of other factors

The interaction between H_2O_2 concentration and pH value and between H_2O_2 concentration and Fe^{2+} concentration is not significant (Fig. 5). This is the same as the response surface ANOVA result. The possible reason for this phenomenon is that the horizontal span of H_2O_2 concentration may be too small as the response surface experiment level was designed.

3.1.4. Process optimization and model verification

By using the model simulation and analytical prediction of the Design-Expert 10 software, the boundary conditions were obtained from the results of the optimal experimental conditions, as shown in Table 4. The above boundary conditions were applied to make the model prediction, and the predicted optimal values are H_2O_2 of 3.56 mmol/L, pH of 2.63, and Fe^{2+} of 0.35 mmol/L, and the degradation rate of

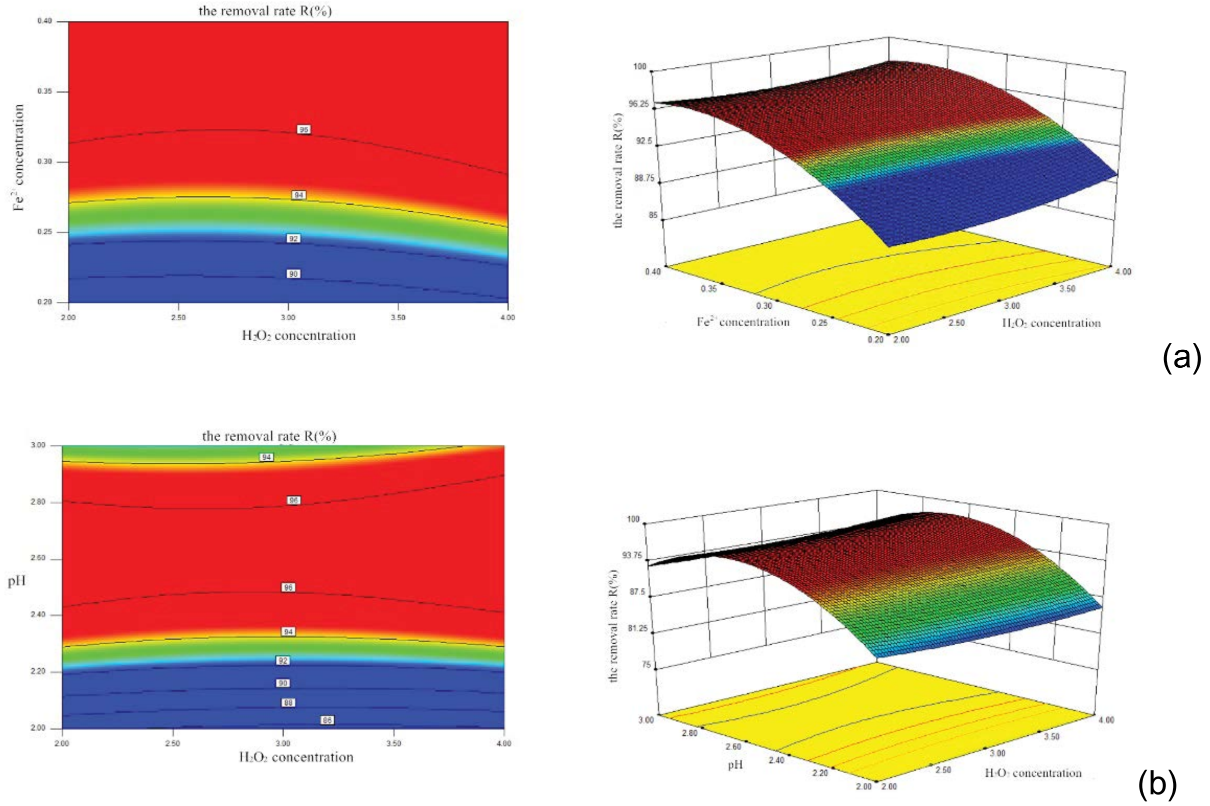

Fig. 5. Contour plot and 3D response surface plot describing the influence of (a) Fe^{2+} concentration and H_2O_2 concentration interaction, and (b) H_2O_2 concentration and pH interaction on the removal rate of AR B.

Table 4
Boundary conditions obtained by optimal experimental conditions

Index	Target	Lower limit	Upper limit	Weight	Significance
H_2O_2 concentration	In range	2	4	1	3
Fe^{2+} concentration	In range	0.2	0.4	1	3
pH	In range	2	3	1	3
Degradation rate	Maximize	64	100	1	3

97.02% (96.2% of confidence degree). Three parallel experiments were carried out to verify the optimal experimental conditions predicted by the RSM. The average removal rate of AR B was 96.80% (Table 5), remarkably close to the predicted value (97.02%). Consequently, RSM is suitable for predicting the Fenton oxidation effect of AR B dye wastewater.

3.2. Reaction kinetics analysis

It is of great significance to study the characteristics of Fenton reaction kinetics in ODW degradation, which can reveal the Fenton reaction process in essence, optimize the experimental conditions. It is of great significance to scientific research and practical application. To analyze the reaction kinetics of the AR B degradation, the online spectrophotometry system was utilized for monitoring the absorbance variation with time, under the optimal reaction conditions. The reaction process, as presented in Fig. 6, included two stages: the rapid reaction phase in the first 10 s and the subsequent slow degradation phase.

The reaction order of each reaction stage was determined by scrutinizing the relationship between concentration and reaction time. First-order reaction kinetics was more appropriate for depicting both reaction stages. Specifically, the correlation coefficient (CC) and the rate constant (*K*) were 0.98938 and 0.159 s^{-1}, respectively, in the rapid reaction phase (Fig. 7–9; Table 6); and the CC and *K* were 0.99563 and 0.0030 s^{-1} in the slow reaction phase (Fig. 10–12; Table 7).

We studied the effects of Fe^{2+}, H_2O_2 concentration, and pH on the reaction rate constant. When other conditions remain constant, the first-order and second-order reaction kinetic model fitting results (Fe^{2+}) of the rapid degradation stage under different Fe^{2+} concentrations are

Table 5
Verification of experimental results (unit: mg/L, except pH; reaction time: 300 s)

H_2O_2	Fe^{2+}	pH	Temperature	Dye concentration	AR B removal rate (%)			
					1	2	3	Average
3.56	0.35	2.63	20°C	25	96.82	96.89	96.68	96.80

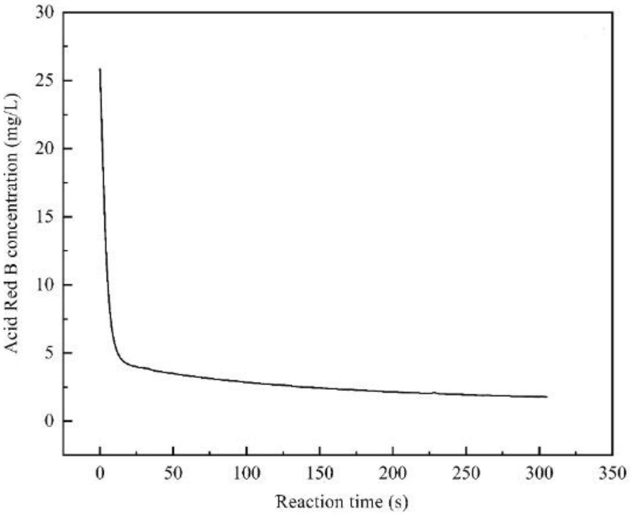

Fig. 6. Relationship between reaction time and dye concentration during Fenton oxidation process.

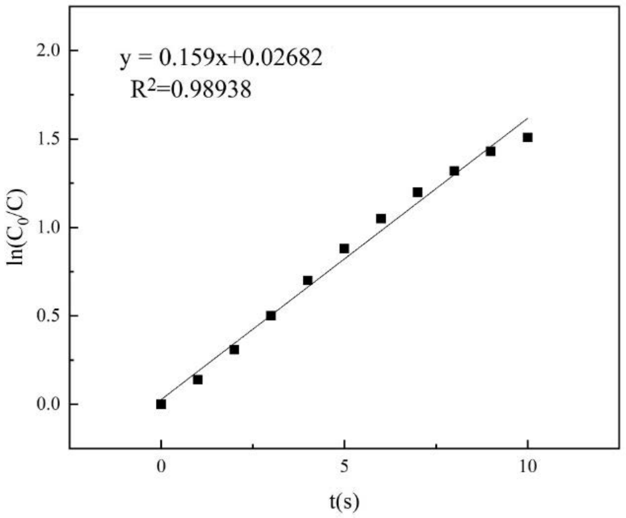

Fig. 8. First-order reaction fitting results in the rapid degradation stage.

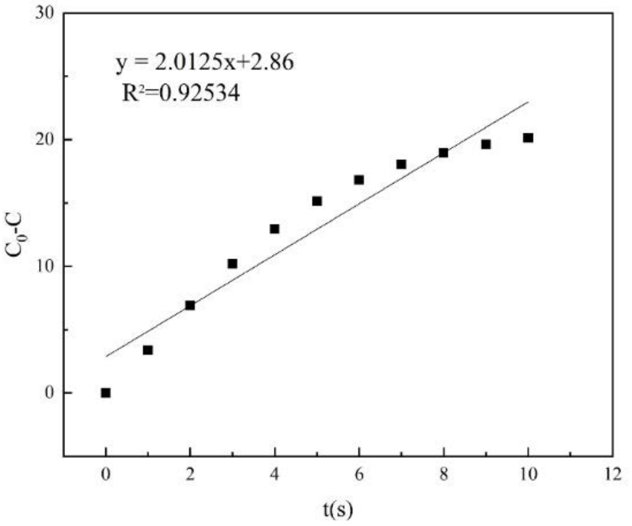

Fig. 7. Zero-order reaction fitting results in the rapid degradation stage.

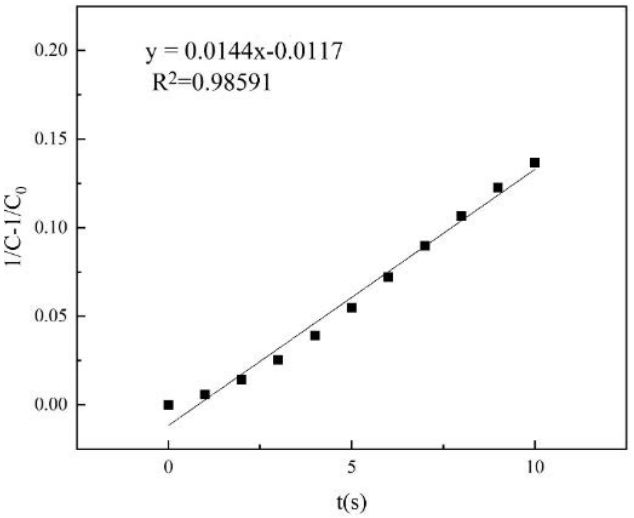

Fig. 9. Second-order reaction fitting results in the rapid degradation stage.

shown in Fig. 13 and 14, respectively. The fitting results of H_2O_2 and pH impact factors were also given in figures under the same operating conditions. The fitting correlation coefficient (R^2) comparison shows that the first-order reaction kinetic model can describe the AR B reaction kinetic degradation process well. The R^2 ranges of first-order reaction kinetic model are about 0.93–0.98 for Fe^{2+}, 0.94–0.97 for H_2O_2, and 0.98–0.99 for pH, and these of second-order reaction kinetics are about 0.80–0.88 for Fe^{2+}, 0.84–0.95 for H_2O_2, and 0.94–0.95 for pH, respectively. Therefore, the first-order reaction kinetics model is used to describe the reaction kinetics of AR B degradation process more accurately.

Table 6
Results of reaction kinetics fitting in the rapid degradation stage

Reaction order	Reaction kinetics equation	Rate constant (*K*)	Correlation coefficient
Zero	$C_0 - C = 2.0125t + 2.86$	2.0125 mg L^{-1} s^{-1}	0.92534
First	$\ln\frac{C_0}{C} = 0.159t + 0.0268$	0.159 s^{-1}	0.98938
Second	$\frac{1}{C} - \frac{1}{C_0} = 0.0144t - 0.0117$	0.0144 mg^{-2} L^2 s^{-1}	0.98591

Table 7
Results of reaction kinetics fitting within the slow degradation stage

Reaction order	Reaction kinetic equation	Rate constant (*K*)	Correlation coefficient
Zero	$C_0 - C = 0.008t + 21.9759$	0.008 mg L^{-1} s^{-1}	0.88511
First	$\ln\frac{C_0}{C} = 0.0030t + 1.8646$	0.0030 s^{-1}	0.99563
Second	$\frac{1}{C} - \frac{1}{C_0} = 0.00115t - 0.1916$	0.0012 mg^{-2} L^2 s^{-1}	0.99189

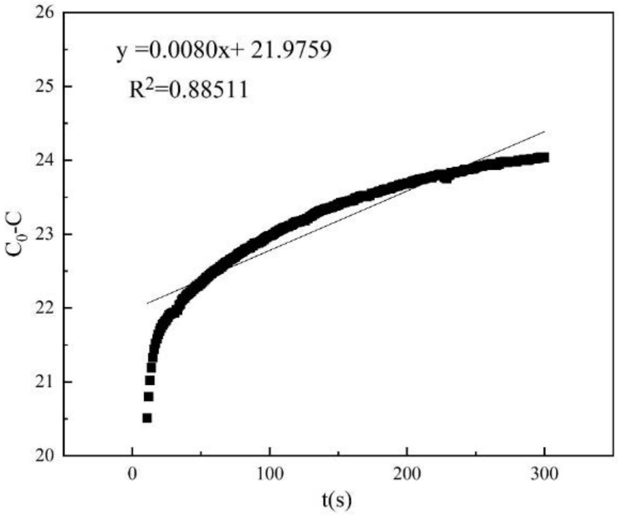

Fig. 10. Zero-order reaction fitting results at the slow degradation stage.

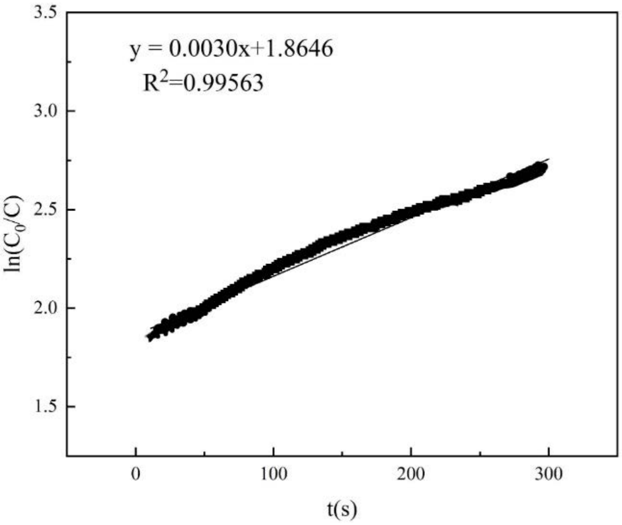

Fig. 11. First-order reaction fitting results at the slow degradation stage.

3.3. Biochemical characteristic analysis

Treatment of ODW is a great challenge due to its poor biodegradability. Fenton oxidation, as a pretreatment method, has been confirmed to improve the biodegradability of ODW. In the simulated wastewater with the AR B concentration of 25 mg/L, the initial COD and BOD_5 concentrations were, respectively, 11.29 and 2 mg/L (BOD_5/COD = 0.18 < 0.3), indicating a low biodegradability. After pretreated by Fenton reagents, of which the reaction concentration was optimized by RSM, the BOD_5/COD ratio elevated to 0.72 (8.28 mg/L of COD and 6 mg/L of BOD_5), suggesting that the wastewater biodegradability was greatly improved. Fenton oxidation method is, therefore, practicable as a pretreatment approach in AR B wastewater degradation.

3.4. Preliminary analysis of degradation mechanism

Understanding the degradation mechanism is essential in advancing the treatment effect and efficiency. The UV-vis spectrogram of the raw and treated AR B wastewater, shown in Fig. 15, could help reveal the transformation process of AR B dye during the Fenton treatment. First, there was a sharp absorption peak at 400–700 nm in the initial AR B wastewater, hinting the existence of aromatic group or the chromogenic group (–N=N–). The absorption peak, however, disappeared after a 300-s treatment with Fenton reagents, demonstrating that the chemical structure of AR B dye has been destroyed. Second, the absorbance peak in ultraviolet region, which was even higher in the treated AR B wastewater, probably implies the generation of some intermediate products in the Fenton reaction. Lastly, although the molecular structure of AR B was damaged after the treatment, it might transform into other organic state

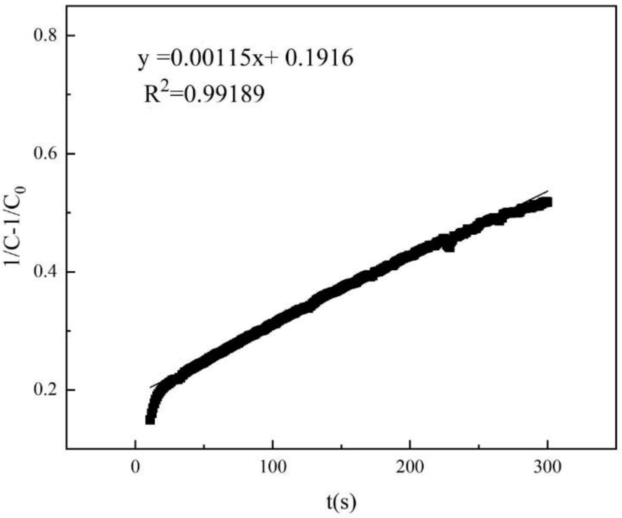

Fig. 12. Second-order reaction fitting results at the slow degradation stage.

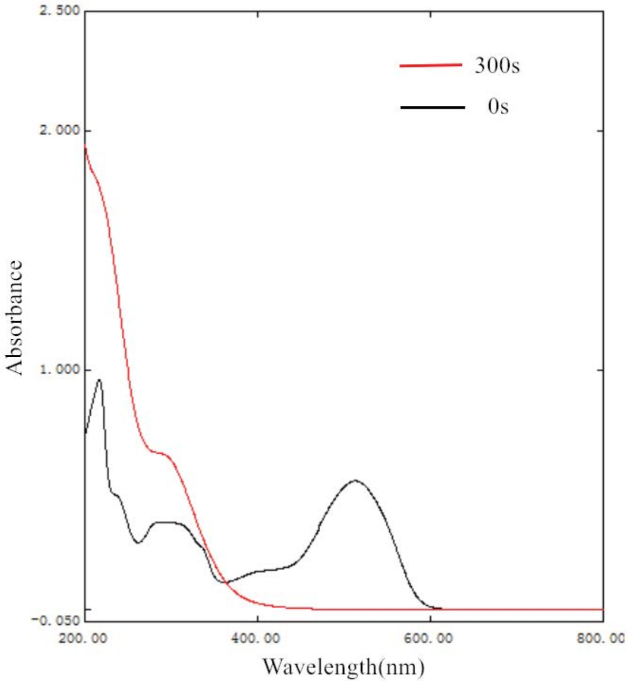

Fig. 15. UV-vis spectra of the raw and treated AR B wastewater.

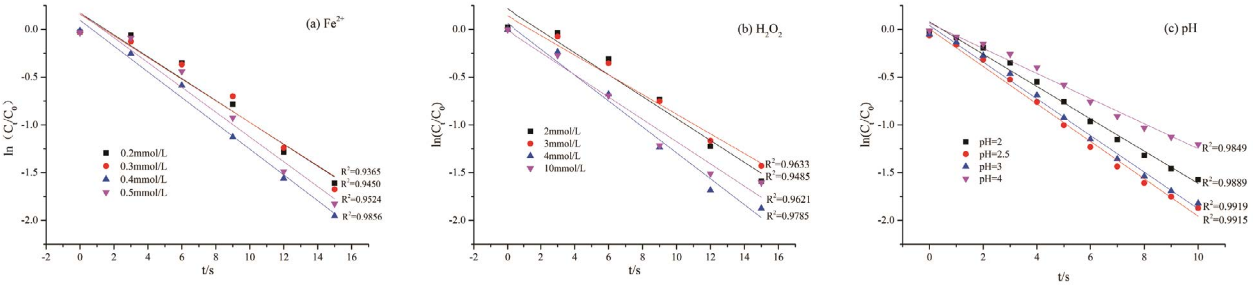

Fig. 13. First-order reaction kinetic model fitting results (Fe^{2+}, H_2O_2, and pH), respectively.

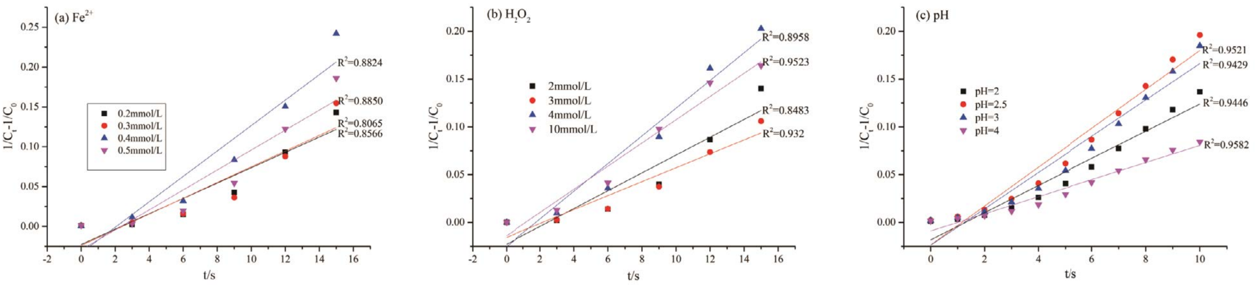

Fig. 14. Second-order reaction kinetic model fitting results (Fe^{2+}, H_2O_2, and pH), respectively.

(such as nitro), rather than been completely mineralized into NO_3^- and NO_2^-, because these elements were not identified in the treated wastewater by ion chromatography (IC). The mineralization rate of AR B wastewater was 26.7% after a 300 s treatment with Fenton reagents. The specific intermediate products of degradation need to be further studied.

4. Conclusions

Fenton reagent can degrade the ODW, and the reaction process is feasible and effective to be monitored in real time by online spectrophotometric system. Based on the optimum experimental conditions for treating AR B wastewater determined by RSM, we discussed the reaction kinetics of the degradation process, the biodegradability of the treated ODW, and the potential degradation mechanism. The key findings of this study are summarized as follows:

- According to the RSM analysis results, the degradation rate could reach 97.02%, and the optimum conditions for degrading the AR B wastewater by Fenton oxidation process were determined as 0.35 mmol/L for $FeSO_4$ concentration, 3.56 mmol/L for H_2O_2 concentration, and 2.63 for pH value. The experiment result under the optimum level of each variable was 96.80%, indicating that the difference between experimental data and model prediction was only 0.22%, thus confirming the reliability of RSM in experimental design and prediction.
- Fenton oxidation process in treating the ODW consisted of two stages, that is, rapid degradation stage (reaction time < 10 s) and slow degradation stage (reaction time > 10 s). Both stages followed the first-order reaction kinetics, but their *K*-values were quite different, which was 0.159 and 0.0030 s^{-1} in the rapid and slow degradation stage, respectively.
- The biodegradability of AR B wastewater was improved after the Fenton oxidation treatment.
- By analyzing the characteristics of AR B wastewater before and after the Fenton treatment using UV-Vis spectrum and IC, we found that Fenton process could merely destruct the molecular structure of AR B rather than completely mineralize it, when the reaction time reached 300 s. The degradation intermediate products, however, remain to be identified in the future.

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