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Influence Factors and Kinetics on Crystal Violet Degradation by Fenton and Optimization Parameters using Response Surface Methodology

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Abstract: This work investigated influence factors and kinetics on crystal degradation violet dye by Fenton. For $FeSO_4$ dose, fitted the date of crystal violet concentration and time, it conformed to first-order kinetic. At 0.1ml H_2O_2, decolorization rate was 98.2% and it increased to 98.7% when H_2O_2 was raised to 0.2ml at 15 min. However, H_2O_2 doses higher than 0.4ml, no obvious increased in the removal was observed. An important pH effect was found, reaching its degradation at pH 2.0 with decolorization rate of 97% at 30min. However, when pH was 4 and 6, the removal was only 79% and 72% at 40min. The Box-Behnken Response Surface Methodology was utilized for mathematical modeling for decolorization rate as a response by Fenton. The determinate coefficient of model was 0.9851. The optimum operating conditions were that $FeSO_4$ dose was 4.55ml, H_2O_2 dose was 0.20ml and reaction time was 15min. Under such conditions, the error of the model predicted and experimental values was 1.85%.

Keywords: Response surface methodology, Box-Behnken design, crystal violet, decolorization

1. Introduction

Colored wastewater and dyes can cause toxic problems in several type of receiving media. Therefore removal of dyes from wastewater is a significant environmental issue[1]. Crystal violet is a kind of polycyclic aromatic hydrocarbon and a synthetic dye. It is stable and nondegradable. Therefore, the conventional treatment methods are not suitable for treatment the crystal violet wastewater[2]. Fenton's treatment that is one of the advanced oxidation processes, is effective in treating dyeing wastewater[3]. Compared with other oxidation methods, Fenton is an efficient, non-selective and does not require a special reaction system. Response surface methodology (RSM) is a useful mathematical and statistical technique for designing experiments, building models, evaluating relative significance of several influencing factors and determining optimum conditions for desirable responses[2,4]. In the present study, we investigated influence factors and kinetics on crystal violet dye degradation by Fenton. The three-factor and three-level Box-Behnken was utilized for mathematical modeling with decolorization rate as a response by Fenton. At the same time, the objective of this study was to obtain the optimum operating conditions for crystal violet decolorization.

2. Materials and methods

2.1. Materials

All reagents and chemicals used in the study were of AR grade. The molecular formula of crystal violet was $C_{25}H_{30}N_3Cl$[5]. It was purchased from Harbin, China. H_2O_2 (30%) and $FeSO_4{\cdot}7H_2O$, used during experiments, were purchased from Harbin.

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2.2. Fenton process methodology and analytical measurements

For each experimental run, 400ml of crystal violet dye solution of 50 mg/l initial concentration were taken in 500ml flasks. The concentration of $FeSO_4$ was 0.2mol/l. The pH was adjusted by diluted sulphuric acid and sodium hydroxide. Required dosage of $FeSO_4$ and H_2O_2 were added into the sample and stirring was applied[3,5]. The decolorization rate of crystal violet dye by Fenton at any time (t) was calculated as:

$$\text{Decolorization\%}=(C_0-C_t)/\ C_0 \qquad (1)$$

where C_0 is the initial absorbance and C_t is the measured absorbance after time, respectively.

2.3. Box-Behnken design

A Box-Behnken design with three factors and three levels was used for fitting a second order response model[6,7]. The fit quality of the polynomial model equation can be evaluated by coefficient of determination R^2[6]. According to Box-Behnken design, the dosage of $FeSO_4$ (X_1), the dosage of H_2O_2 (X_2) and reaction time (X_3) were selected as the independent variables because they were three important parameters affecting crystal violet dye decolorization by Fenton, and decolorization rate (Y) was considered as the response[4]. The pH of the wastewater was kept at 2.5, at room temperature. Experimental range and levels of independent variables for crystal violet dye degradation by Fenton were presented in Table 1. In this study, fifteen experiments were performed. Experimental results were analyzed using Design Expert 7.0 software.

Table 1 Experimental range and levels of independent variables.

Independent variable	Factors	Range levels		
		-1	0	1
$FeSO_4$（mL）	X_1	3	4	5
H_2O_2（mL）	X_2	0.2	0.3	0.4
Reaction time（min）	X_3	5	10	15

3. Results and discussion

3.1. Influence factors and kinetics of crystal violet degradation dye by Fenton

3.1.1 Influence of $FeSO_4$ dosage

The effect of $FeSO_4$ dosage on crystal violet dye decolorization rate was examined by changing the $FeSO_4$ dosage from 1ml to 4ml when keeping the dosage of H_2O_2 and pH at 0.4ml and 2.5, respectively (Fig.1). It was seen in Fig. 1 that the decolorization rate was 96% when the $FeSO_4$ dosage was 4ml at 5min. However, it was only 32% when the $FeSO_4$ dosage was 1ml. Because higher ferrous doses could lead to the generated more hydroxyl radicals so that the decolorization rate increased[3]. With increasing the reaction, the degradation velocity increased slowly at the 3ml and 4ml of $FeSO_4$ dosage. The decolorization rate remained constant at around 92% to 98%. But the decolorization rate was from 71% to 97% at the reaction time from 5min to 40min at the 2ml. Therefore, the $FeSO_4$ dosage was more, the degradation rate was increased. The $FeSO_4$ reached to a certain extent, H_2O_2 became the limiting condition for further hydroxyl radicals generation[3]. In particular, the $FeSO_4$ of overdose maybe cause waste and residue iron. At same time, an excess of ferrous ions would consume hydroxyl radicals by the following nonoxidizing reaction[3]. Fitted the date of crystal violet concentration and time, it conformed to first-order kinetic(Fig.2).

3.1.2. Influence of H_2O_2 dosage

The effect of H_2O_2 dosage on Fenton reagent was investigated in the dosage of H_2O_2 range 0.1 to 0.8ml when $FeSO_4$ dose was kept at 4ml. pH of the wastewater was kept at 2.5, at room temperature(Fig.3). At 0.1ml H_2O_2, decolorization rate was 98.2% and it increased to 98.7% when H_2O_2 was raised to 0.2ml at 15 min. However, H_2O_2 doses higher than 0.4ml, no obvious increased in the removal was observed. With overdose H_2O_2, it was inhibited the hydroxyl radicals doses in Fenton reagent. At the same time, ferrous ion concentration became deficient for reacting with H_2O_2. For H_2O_2 doses, fitted the date of crystal violet concentration and time, it could proposed by a second order model (Fig.4).

3.1.3. Influence of pH

To analyze the effect of pH, crystal violet dye solutions with initial pH of 1.0, 2.0, 4.0 and 6.0 were degradated when initial dosage of $FeSO_4$ and H_2O_2 were 4ml and 0.2ml, respectively. The results were illustrated in Fig.5. A significance pH effect was found for the Fenton process, reaching its great degradation at pH 2.0 with decolorization rate of 97% at 30 min. The optimum pH was 2 to 3. At very acidic pH, iron ion was not favorably deoxidized to ferrous ion. Consequently less hydroxyl radicals were produced by reaction[8]. Therefore, when pH was 1, the decolorization rate was 94% at 30 min. At pH above 4.0 the degradation rate decreased because the oxidation potential of hydroxyl radicals and the dissolved fraction of iron species decreased[3,8]. When pH was 4 and 6, the decolorization rate was only 79% and 72% at 40 min.

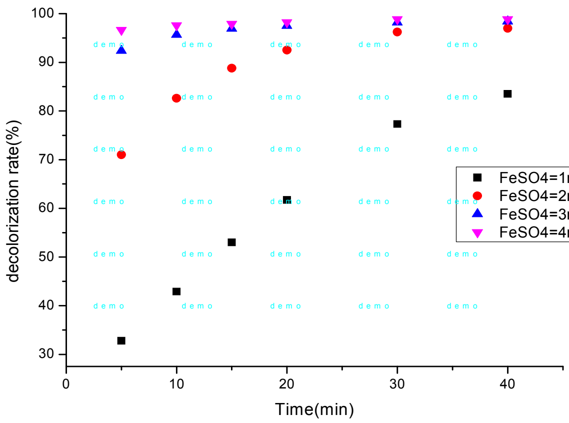

Fig.1: Influence of $FeSO_4$ dosage on decolorization rate.

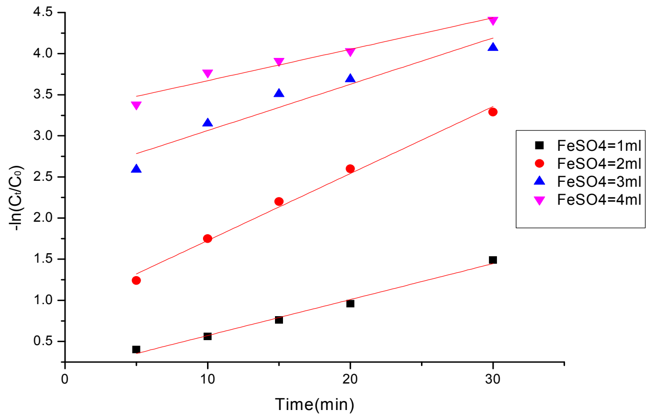

Fig.2: First order rate plots of crystal violet concentration and reaction time by different dosage $FeSO_4$.

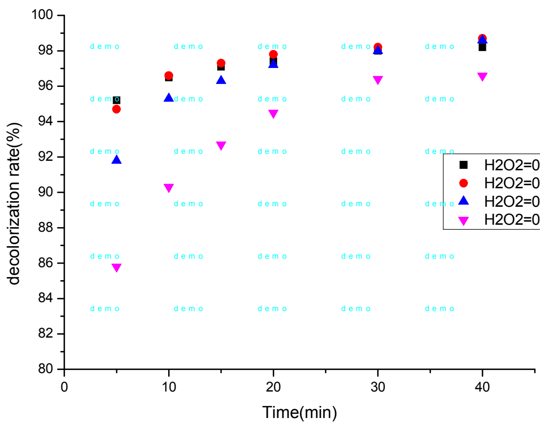

Fig. 3: Influence of H_2O_2 dosage on decolorization rate.

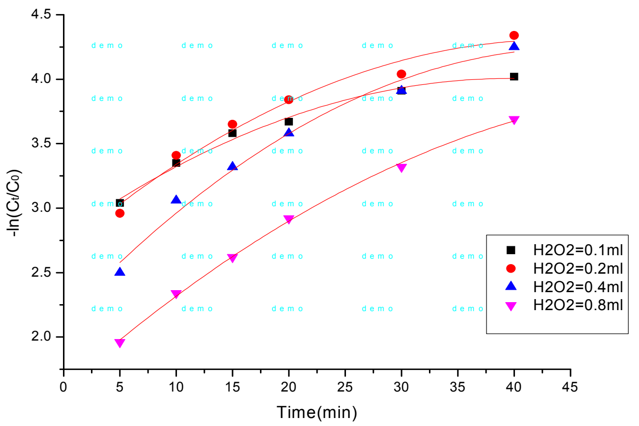

Fig. 4: Rate plots of crystal violet concentration and reaction time by different dosage H_2O_2.

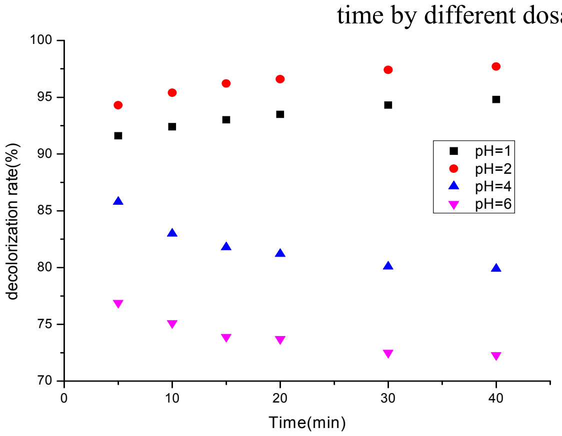

Fig.5: Influence of pH on crystal violet decolorization rate.

3.2. Response surface methodology

3.2.1. Experimental design and quadratic model

Fifteen designed batch runs were performed according to Box-Behnken design. The decolorization rate results was evaluated and given in Eq. (2).

$$Y_1=95.867+4.51X_1-0.975X_2+0.96X_3-3.68X_1X_1+1.275X_1X_2+0.9X_1X_3+0.19X_2X_2+0.675X_2X_3-0.333X_3X_3 \quad (2)$$

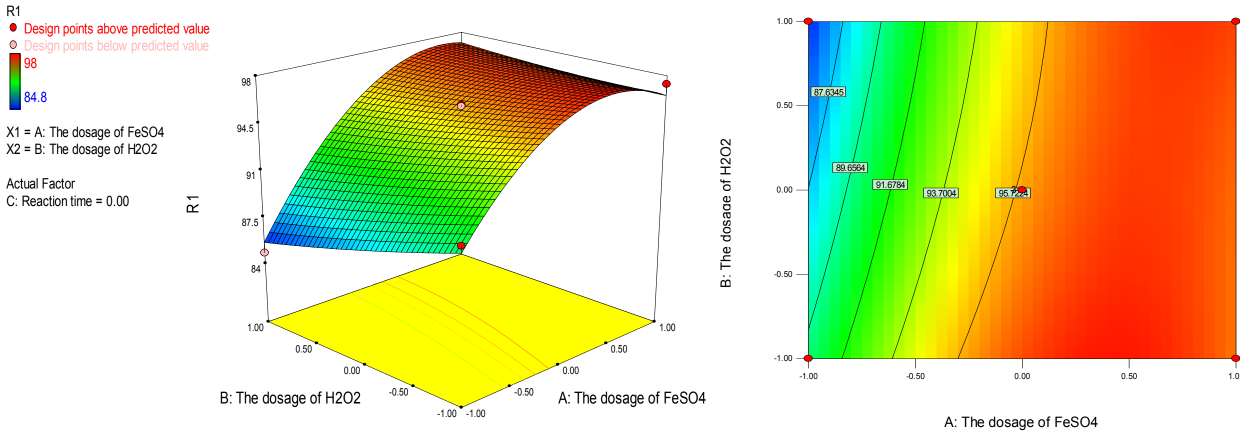

Fig.6: Response surface plot and contourline showing the effect of the dosage of $FeSO_4$ and H_2O_2.

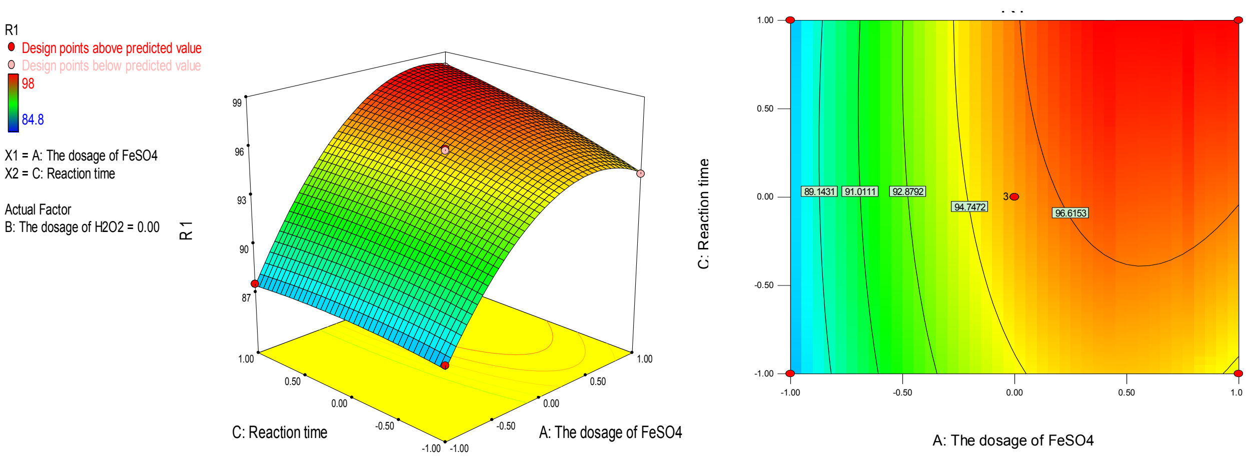

Fig7: Response surface plot and contourline showing the effect of the dosage of $FeSO_4$ and reaction time.

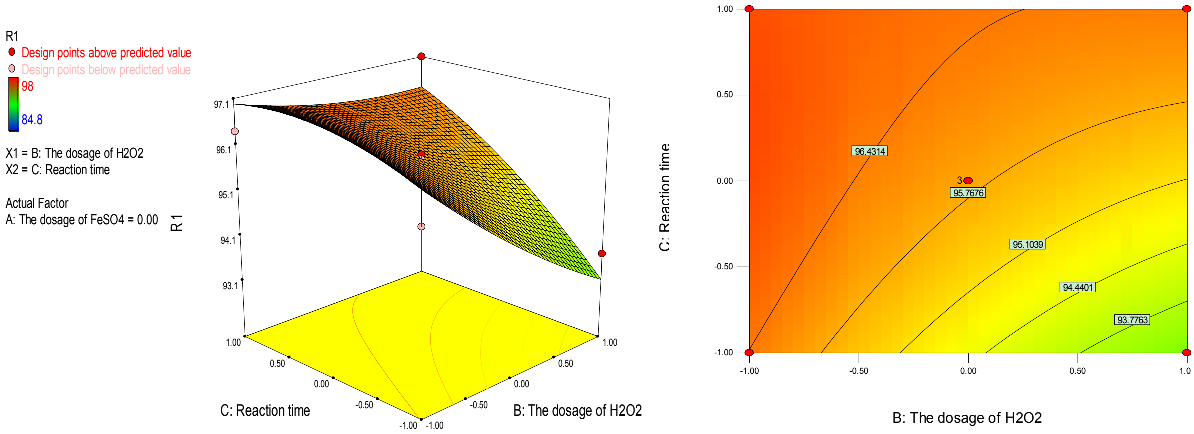

Fig.8: Response surface plot and contourline showing the effect of the dosage of H_2O_2 and reaction time.

The model R^2 value was 0.9851. It could provide an well explanation of the relationships between the independent variable and the response[7]. Factors or interaction factors with p-values lower than 0.05 was significant[7]. In this case, X_1, X_2, X_3 and X_1X_2 were significant. In the case, F-value of 36.81 implies the model was significant for decolorization of crystal violet. The p-value was less than 0.05. It showed that the model terms were significant at 95% of probability level.

3.2.2. Optimization conditions and response surface analysis

In order to gain the optimum operating conditions, Eq.(2) was differentiated with independent variable and three equations could be obtained[4]. The optimum operating conditions were that the $FeSO_4$ dose was

4.55ml, H_2O_2 dose was 0.20ml and reaction time was 15min. Predicted decolorization rate of 96.75% could be achieved under the optimum operating conditions[4]. Response surfaces and contourline were given to investigate the interactive effect of two variables on crystal violet decolorization rate (Fig.6 to Fig.8). The interaction of $FeSO_4$ and H_2O_2 dose was significant factors. In the choice of test range, it could be seen that decolorization rate increased with increasing $FeSO_4$ dose from 3.0 to 4.5ml. However, when $FeSO_4$ dose increased over the optimum value, the decolorization rate declined. As shown in Fig. 6, $FeSO_4$ dose had a more significant effect than H_2O_2 dose and reaction time. Because the surface slope of $FeSO_4$ dose was more great than the other factors. At the same time, Fig.7 and Fig.8 showed that decolorization rate increased with increasing reaction time. Also when H_2O_2 concentration increases over the optimum value, it could cause adverse effect for crystal violet decolorization[4].

3.2.3. Model validation and experimental confirmation

In order to validate the validity of regression equation, additional three runs were carried out under the optimum conditions obtained through Box-Behnken RSM. The decolorization rate of 96.3% was achieved at the condition. The error of the model-predicted and experimental values of decolorization rate was 1.85%.

4. Conclusion

For $FeSO_4$ dose, fitted the date of crystal violet concentration and time, it conformed to first-order kinetic. At 0.1ml H_2O_2, decolorization rate was 98.2% and it increased to 98.7% when H_2O_2 was raised to 0.2ml at 15 min. However, H_2O_2 doses higher than 0.4ml, no obvious increased in the removal was observed. The optimum pH was 2 to 3. The dosage of $FeSO_4$ and H_2O_2, reaction time, the interaction of $FeSO_4$ and H_2O_2 were significant factors. The determinate coefficient of model was 0.9851. The optimum three operating conditiones were that $FeSO_4$ dose was 4.55ml, H_2O_2 dose was 0.20ml and reaction time was 15min. Under such conditions, the error of the model predicted and experimental values was 1.85%. It indicated that the Box-Behnken RSM was reliable for optimizing the decolorization process of crystal violet by Fenton.

5. Acknowledgements

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