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Response surface optimization for decolorization of Basic Blue 41 by Fenton's reagent

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Abstract: In this paper, response surface methodology was used to optimize the operation parameters for the decolorization of Basic Blue 41 (BB41) dye in aqueous solutions using advanced oxidation process with Fenton's reagent. The variables considered for process optimization were H_2O_2 concentration, Fe^{2+} concentration, and pH. This methodology allowed assessing and identifying the effects of the independent variables and their interactions on color removal which were considered as the objective functions to be maximized. The results indicated that optimum conditions for degradation of BB41 were H_2O_2 concentration, Fe^{2+} concentration, and pH of 8.65 mM, 0.45 mM, an 3.2. Under these conditions, about 97.05% of color was removed. The analysis of variance (ANOVA) and regression with R^2 values of 0.978 for color removal illustrate that the experimental results are in good agreement with the predicted values, and the model which developed in this study can be used for predicting the conditions for degradation of BB41 in the aqueous solution using Fenton's reagent.
Keywords: Advanced oxidation process; Fenton's reagent; Basic Blue 41; RSM; Oxidation.

1. Introduction

In Vietnam, textile is one of the mainstream industries with important strategic position in the development of the national economy.[1] However, due to the specific characteristics of a complex manufacturing industry that utilizes much water, chemicals, materials… the risk of environmental pollution caused by the textile industry is inevitable. Wastewater from the textile industry, can be collected from different manufacturing utitary operations including bleaching, dyeing, soaping and softening, is one of major environmental problems not only in Vietnam, but also in other countries.[1-5] The dyes have to be removed from textile wastewater before discharge because the environmental pollution due to the textile industry can cause serious problems not only to the land mass fertility but also to the natural flora, fauna, as well as the aquatic bodies.[1]

We can use some techniques including biological, physical and chemical processes for treatment of textile wastewater. However, a number of biological and physicochemical methods showed low performance for removing dyes. The treatment processes based on the production of free hydroxyl radicals, which called as advanced oxidation processes (AOPs), have been known as the alternative techniques for dye removal. Fenton's reagent consisting of Fe^{2+} and H_2O_2 is one of the most effective advanced oxidation agent for degradation of organic dyes compounds. In the Fenton process, the effects of some important parameters including Fe^{2+} concentration, H_2O_2 concentration, and pH of the solution on the treatment efficiency have been reported. However, these their interactions on the treatment performance have been limited in the literatures.

In this study, our interest lies in determining the optimal conditions for degradation of Basic Blue 41, a very stable dye which widely used in textile factories in Vietnam, by Fenton's reagent and evaluating the effects and/or interactions of variables on the treatment performance. For the development of an acceptable process in shortest time using minimum number of experiments, we employ the response surface methodology (RSM), which is a reliable statistical tool in the investigation of various processes and can be widely applied for process modeling and optimization.[4,5]

2. Experimental Section

2.1. Degradation experiment

All experiments were performed in a batch reactor with a capacity of 500 mL. Uniform mixing was provided using a magnetic stirrer. The reactor was filled with 250 mL of dye solution containing Basic Blue 41 (Figure 1) at the concentration of ca. 200 mg/L. The pH of the solution was then adjusted by using diluted H_2SO_4. Iron (II) salt (98%) was injected into the dye solutions, and mixed well before adding hydrogen peroxide solution (30% v/v aqueous solution). The reactor was open to the atmosphere at room temperature. During the reaction, the change of temperature was negligible. The color removal was determined after 120 min of treatment.

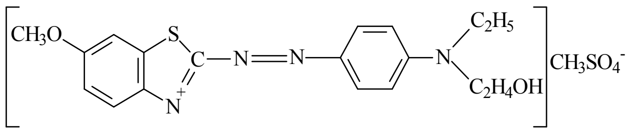

Figure 1. The chemical structure of Basic Blue 41 (BB41).

2.2. Analysis procedure

The concentration of BB41 in water is determined by the photometric method at a wavelength of 609 nm,[4] using an UV-1650 PC UV-Visible Spectrophotometer (Shimadzu, Japan). Color removal performance is determined by the following formula:

$$R\,(\%) = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

where R (%), C_o, and C_t are decolorization performance, BB41 concentrations in the aqueous solutions before and after treatment, respectively. The color removal performance was used as a response in a CCD model.

3. Response Surface Methodology

In this study, the optimal conditions for the degradation of BB41 by Fenton's reagent were obtained by response surface methodology (RSM) using MODDE software (Umetrics, Sweden). Table 1 shows the ranges and levels of independent variables used in this study.

Table 1. Levels of the parameters studied

Variables	Symbol	Unit	Coded variable levels				
			-1.682	-1	0^a	+1	+1.682
H_2O_2	x_1	mM	1.59	5	10	15	18.41
Fe^{2+}	x_2	mM	0.057	0.18	0.36	0.54	0.663
pH	x_3	-	0.977	2	3.5	5	6.023

[a] Center point

The relationships among the screened variables are expressed mathematically in the form of quadratic polynomial equation under RSM. The experiments were conducted in the central composite design (CCD) fashion with three center points and fitted by an empirical, full second-order polynomial model representing in the form of response surface over a relatively wide range of variables. Equation (2) was used to fit the experimental data of decolorization performance to construct the RSM model:

$$Y=\beta_o+\sum_{i=1}^{n}\beta_i X_i+\sum_{i=1}^{n}\beta_{ii}X_i^2+\sum_{i=1}^{n}\sum_{j=1}^{n}\beta_{ij}X_iX_j+\varepsilon \quad (2)$$

where Y represents the response (the decolorization performance, %), β_o is the constant, β_i, β_{ij}, β_{ii} are the linear, interaction, and quadratic term coefficients, respectively; X_i is the coded value of i^{th} independent variable, n is the number of factors, and ε is the random error. In this study, the relation of real and coded values of H_2O_2 concentration (x_1), Fe^{2+} concentration (x_2) and pH (x_3) can be described by the following formulas:

$$X_1=\frac{x_1-10}{5} \quad (3); \qquad X_2=\frac{x_2-0.36}{0.18} \quad (4) \qquad X_3=\frac{x_3-3.5}{1.5} \quad (5)$$

4. Results and Discussion

4.1. RSM model

The effects of operating parameters including pH, the concentration of Fe^{2+}, and the concentration of H_2O_2 on the decolorization performance were investigated by using RSM method using MODDE software. The experimental results indicated that the decolorization performance increased from 59.01% to 96.12% depending on the experimental conditions. The effects of three operating parameters and their interactions on the response can be described by the following equation:

$$Y = 95.4539 - 2.79539\ X_1 + 6.76119\ X_2 - 3.96969\ X_3 - 5.9196\ X_1^2 - 6.2554\ X_2^2 - 10.3591\ X_3^2 - 1.2425\ X_1 X_2 - 0.647502\ X_1 X_3 + 0.45\ X_2 X_3 \quad (6)$$

where Y is the decolorization performance; X_1, X_2, and X_3 are corresponding to coded values of the concentrations of H_2O_2, Fe^{2+}, and pH, respectively. This results also indicated that the effects of three independent variables on the response decreased as the following order: $X_2 > X_3 > X_1$. The detail results in the Table 2 suggested that the interaction between the independent variables on the response are small.

The fit of the model was evaluated by analysis of variance (ANOVA) and coefficient of correlation (R^2). The developed model showed the F-value of the Regression of 34.2519, indicating that the model is highly significant. Besides, the p value of 0.000, is lower than 0.05, suggesting the model is considered to be statistically significant. For ANOVA, the value of R^2 of 0.978 indicates adequacy of the applied model, 97.8% of the response variability is explained by the model. The value of R^2 also confirms the model is good predictability, for which at least $R^2 = 0.80$ is suggested.[6]

Table 2. Coefficients and statistical measures for decolorization performance (R, %)

	Coeff. SC	Std. Err.	*p*	Conf. int (±)[a]
Constant	95.4539	1.59402	9.50689e-011	3.7693
H_2O_2	-2.79539	0.748514	0.00731458	1.76998
Fe^{2+}	6.76119	0.748514	4.16591e-005	1.76998
pH	-3.96969	0.748515	0.0011192	1.76998
H_2O_2 * H_2O_2	-5.9196	0.82376	0.000179618	1.94791
Fe^{2+} * Fe^{2+}	-6.2554	0.82376	0.000126945	1.94791
pH * pH	-10.3591	0.82376	4.64054e-006	1.94791
H_2O_2 * Fe^{2+}	-1.2425	0.978031	*0.244532*	2.31271
H_2O_2 * pH	-0.647502	0.978031	*0.529126*	2.31271
Fe^{2+} * pH	0.45	0.978031	*0.65939*	2.31271
N = 17			Cond. no. =	4.9932
DF = 7	R^2 =	0.978	Y-miss =	0
	R^2 Adj. =	0.949	RSD =	2.7663
			Conf. lev. =	0.95

4.2. Effect of independent variables and their interaction

In order to access the relationship between the process variables and the response, three-dimention response surface plots of the response were also obtained using MODDE software. As can be seen from the Figures 2-4, the process variables may show a positive or negative effect on the decolorization performance depending on their values.

The effect of concentration of Fe^{2+} and pH on the decolorization performance was shown in the Figure 2. As can be seen from the Figure 2, at low level of pH, when the concentration of Fe^{2+} increased from 0.18 mM to 0.428 mM, the decolorization efficiency increases from 76.6% to 90.7%. However, the decolorization efficiency decreases to 89.2% if the concentration of Fe^{2+} increased to ca. 0.54 mM. Similar to the effect of Fe^{2+} concentration, the decolorization increased from 76.6% to 83.7% when pH increased varied from 2 to 3, but decreased to about 67.7% when pH increased to 5.0. The highest value of decolorization performance of 97.6% reached at the concentration of Fe^{2+} and pH were ca. 0.45 mM and 3, respectively.

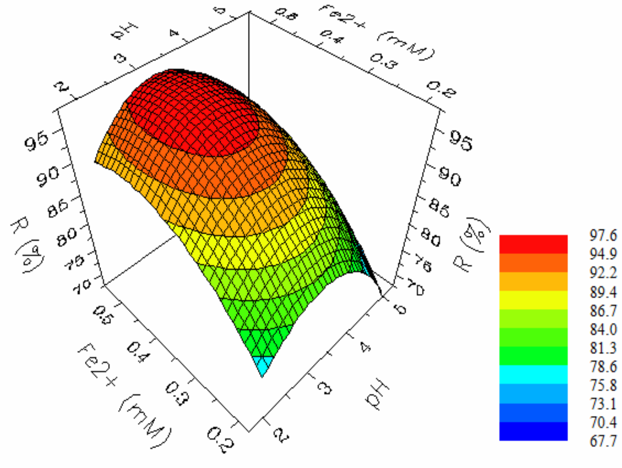

Figure 2. Three-dimensional response surface plots showing the effects of Fe^{2+} concentration and pH on the decolorization performance.

Figure 3 showed the effects of pH and the concentration of H_2O_2 on the response. The result in the Fugure 3 indicated that the effect of H_2O_2 is very similar to Fe^{2+} effect. The decolorization performance increased from 85.4% to 89.3% (at low level of pH and center level of Fe^{2+}) when the contrentation of H_2O_2 increased from 5 mM to ca. 9 mM. The response's values decreases to ca. 81% when the H_2O_2 concentration increased to 15 mM. At low level of H_2O_2 concentration, the decolorization performance increased from 85.3% to 92.7% if pH variated from 2 to ca. 3.23. At the center level of Fe^{2+}, the decolorization performance reached the highest value of 96.1% at the concentration of H_2O_2 and pH were 9 mM and 3, respectively. The results in the Figure 3 also confirmed that the effects of pH is significant higher compared to H_2O_2 concentration.

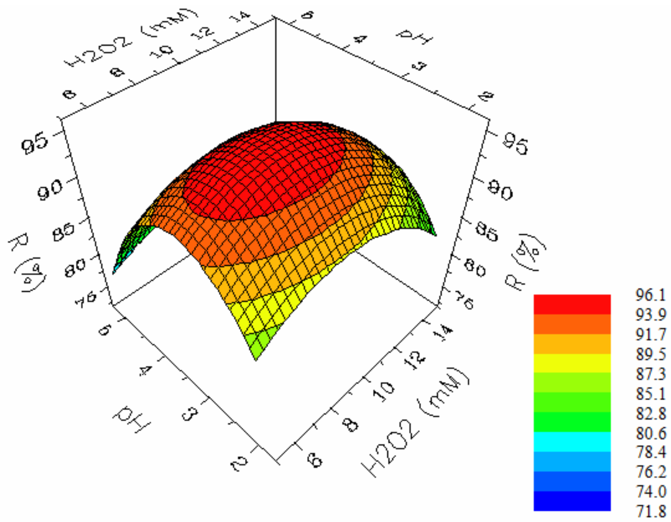

Figure 3. Three-dimensional response surface plots showing the effects of pH and H_2O_2 concentration on the decolorization performance.

The result in the Figure 4 showed the effects of the concentrations of Fe^{2+} and H_2O_2 on the decolorization performance. As can be seen from the Figure 4, Fe^{2+} concentration showed the higher effect than H_2O_2 concentration. At the center level of pH, the decolorization performance will be reached the highest value of 97.8% when the concentrations of H_2O_2 and Fe^{2+} of ca. 8.4 mM and 0.46 mM, respectively.

4.3. Optimum conditions

Based on the experimental data and the developed model for simulating the decolorization performance, the optimum conditions for the maximum value of the decolorization efficiency can be determined by using MODDE software. The criteria for three variables in correspondence with decolorization performance were shown in the Table 3. The developed model in this study predicted that the optimum conditions for the highest color removal performance were: H_2O_2 concentration of 8.65 mM, Fe^{2+} concentration of 0.45 mM, and pH of 3.2. Under the optimum conditions, the decolorization efficiency was 97.05% which very close with the predicted value of 98.09%. The validity of the model for the decolorization performance of Basic Blue 41 was confirmed by the good agreement between the experimental and predicted values.

Table 3. Properties of solid sorbent prepared under the optimum conditions

Optimum condition			Color removal (R, %)		
H_2O_2 (mM)	Fe^{2+} (mM)	pH	Predicted (%)	Experimental[a] (%)	Error (%)
8.65	0.45	3.2	98.09	97.05	1.05

[a] Measured after 120 min of treatment.

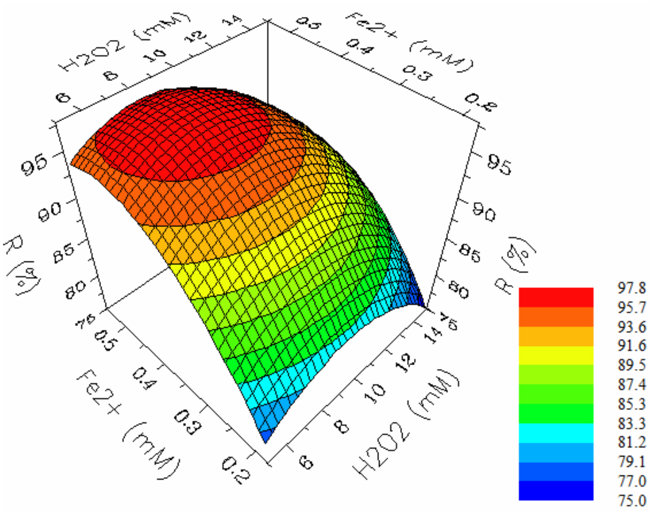

Figure 4. Three-dimensional response surface plots showing the effects of concentrations of Fe^{2+} and H_2O_2 on the decolorization performance.

4. Conclusions

The effects of some key operating parameters for the decolorization of BB41 with the Fenton's reagent were investigated by response surface methodology with MODDE software. The optimum conditions for highest decolorization performance were determined including pH, the concentration of H_2O_2 and Fe^{2+} of 3.2; 8.65 mM and 0.45 mM, respectively. Under the optimum conditions, about 97.05% color was removed. The experimental data of the response was found to agree satisfactorily with the values predicted by the model. The experimental results confirmed that the response surface methodology is a useful tool and it can be used for prediction the suitable conditions for decolorization of BB41 by Fenton's reagent.

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