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Optimization of Fenton-Like Degradation Conditions of Acid Red 14 Azo Dye Under Low Frequency Ultrasonic Irradiation

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Response surface methodology (RSM) was applied to evaluate individual and interactive effects of the three main independent parameters (initial pH, temperature and time of ultrasound) and optimizing the operating conditions in the process of Fenton-like reaction with low frequency ultrasonic irradiation. Analysis of variance (ANOVA) showed a high coefficient of determination value ($R^2 = 0.9575$). Effect of experimental parameters was established by the response surface and contour plots. Results showed that degradation of acid red 14 increased with increasing temperature and reaction time of ultrasound. The interactive effects were showed among three parameters (initial pH, temperature and time of ultrasound) by keeping the other constant. The optimum initial pH, temperature and time of ultrasound were found to be 6, 35 ºC and 10 min, respectively. Under the optimal value of process parameters, high removal (> 99 %) was obtained from the proposed model for acid red 14.

Key Words: Fenton-like, Azo dye, Ultrasonic irradiation, Response surface methodology.

INTRODUCTION

Azo dyes are characterized by presence of chromatographic group (–N=N–). The colour of dyes is due to azo bond and associated chromophores[1,2]. Due to their biological recalcitrance, conventional biological treatment processes such as activated sludge process are ineffective to remove these dyes from wastewater[3,4]. As an alternative method, ultrasonic irradiation aiming at degrading organic pollutants including dyes has received much attention[5-7].

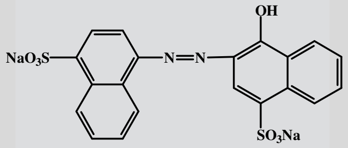
In the present study, Fenton-like reactions by cast iron in the presence of low frequency ultrasonic irradiation were used for degradation of azo dye acid red 14. Response surface methodology (RSM) based on Box-Behnken design was applied to optimize the degradation process. The objective of this study is to obtain the optimum operating condi-tions for acid red 14 degradation by investigating the single and interactive effects of three significant operating variables *i.e.*, pH value of dye solution, temperature and reaction time of ultrasonic irradiation. The processes were designed in accordance with Box-Behnken design and carried out in batches. A quadratic model was proposed to describe the relationship between the degradation rate and the operating variables.

EXPERIMENTAL

AR14 azo dye was obtained from Shenyang Zhongshan Chemical Reagents Co. (Shenyang, China), the molecular structure of it is presented in Table-1. Cast iron (0.2-0.9 mm) was obtained from the experimental plant of Institute of Metal Research, Chinese Academy of Sciences (Shenyang, China). Hydrochloric acid and sodium hydroxide were all obtained from Sinopharm Chemical Reagents Co. (Shanghai, China). All chemicals were of analytical grade and were used without any further purification. Distilled water was used throughout this study.

Procedures: All experiments were carried out in 250 mL beakers, which were placed in a SK250LH ultrasonic cavitation cleaner (Shanghai Kedao instructual Co. Ltd.) water bath with constant temperature. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by the addition of cast iron and dilution with distilled water to 100 mL. Solution pH values were adjusted to the desired level using hydrochloric acid and sodium hydroxide, which were measured by a pH meter (PHS-3C). The reactions were initiated by adding cast iron to the beaker. Samples were taken out from the beaker periodically using a pipette and were imme-

TABLE-1
CHEMICAL STRUCTURE AND CHARACTERISTICS OF ACID RED 14

Chemical structure	Color index number	λ_{max} (nm)	$\varepsilon\lambda_{max}$ ($l\ mol^{-1}\ cm^{-1}$)	Chemical class	M_w ($g\ mol^{-1}$)
	14720	515	32.658×10^3	Monoazo	502

diately analyzed and then returned back to the beaker. Each experiment was replicated three times or more.

Detection method: The dye concentration was determined using a UV-VIS spectrophotometer (Lambda 25, Perkine Elmer) at 515 nm. The equation used to calculate the degradation rate in the treatment experiments was:

$$\text{Decolourization efficiency (\%)} = \frac{A_0 - A}{A_0} \times 100\ \% \qquad (1)$$

where A_0 and A are the initial absorbance and the measured absorbance, respectively.

Experimental design and optimization: Response surface methodology based on Box-Behnken design was applied to optimize the experimental conditions for acid red 14 azo dye degradation. Three critical parameters affecting acid red 14 azo dye degradation: pH value of dye solution (X_1), temperature (X_2) and reaction time of ultrasonic irradiation (X_3) were selected as the independent variables based on the preliminary experiments and degradation rate (Y) was considered as the dependent variable. Each independent variable was coded as xi according to the following relationship[8-10]:

$$x_i = \frac{X_i - X_0}{\Delta X} \times 100 \qquad (2)$$

Experimental range and levels of independent variables for acid red 14 removal were presented in Table-2.

TABLE-2
EXPERIMENTAL RANGE AND LEVELS
OF INDEPENDENT VARIABLES

Independent variable	Factor	Range and levels		
	x_i	-1	0	+1
pH value	X_1	2	4	6
Temperature (ºC)	X_2	20	27.5	35
Reaction time (min)	X_3	6	8	10

RESULTS AND DISCUSSION

Model results for degradation of acid red 14: In the optimization process, the responses can be simply related to chosen variables by linear or quadratic models. A quadratic model, which also includes the linear model, is given below:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \varepsilon \qquad (3)$$

where Y is the response and x_1, x_2 and x_3 are the independent variables effects. x_1^2, x_2^2 and x_3^2, are the square effects. x_1x_2, x_1x_3 and x_2x_3 are the interaction effects. β_1, β_2 and β_3 are the linear coefficients. β_{11}, β_{22} and β_{33} are the squared coefficients. β_{12}, β_{12} and β_{23} are the interaction coefficients. β_0 and ε are the constant and the random error, respectively. This model is preferred because a relatively few experimental combinations of the independent variables are adequate to estimate potentially complex response function.

Experimental results were analyzed using Design Expert 7.1.4 software and a regression model was proposed. Analysis of variance (ANOVA) was performed based on the proposed model to find out the interaction between the variable and the response. The quality of the fit for the regression model was expressed by the coefficient of determination (R^2) and statistical significance was checked by the F-test in the same program. Model terms were selected or rejected based on the probability value with 95 % confidence level. Finally, three-dimensional response surfaces were drawn in order to visualize the individual and the interactive effects of the independent variables on acid red 14 degradation.

The experimental results and predicted values for degradation are presented in Table-3. Based on these results, an empirical relationship between the response and independent variables was attained and expressed by the following second-order polynomial equation:

TABLE-3
EXPERIMENTAL AND PREDICTED DEGRADATION RATE

Run	pH	Temp. (ºC)	Time (min)	Degradation rate (%)	
				Actual value	Predicted value
1	0	-1	1	90.63	91.65
2	0	0	0	87.72	88.09
3	-1	-1	0	90.63	90.27
4	-1	0	1	94.94	93.91
5	0	0	0	88.64	89.09
6	1	0	1	86.62	86.73
7	1	0	-1	94.36	93.25
8	0	1	1	95.15	94.71
9	0	0	0	88.48	88.01
10	-1	0	-1	88.85	88.76
11	0	-1	-1	92.03	92.11
12	1	1	0	93.32	93.79
13	-1	1	0	88.5	87.3
14	1	-1	0	85.79	85.3
15	0	1	-1	87.62	87.3

$$Y = 87.3036 + 0.0221x_2 + 1.1102x_2 + 2.7829x_3 + 1.8015x_1x_2 + 0.7032x_1x_3 + 0.2315x_2x + 2.1032x_1^2 + 1.5764x_2^2 + 1.7913x_3^2 \qquad (4)$$

ANOVA results of this model presented in Table-4 indicate that it can be used to navigate the design space. In Table-4, the model F-value of 4.9679 implies the model is significant for

TABLE-4
ANOVA RESULTS OF THE QUADRATIC MODEL OF DECOLORIZATION OF AR14 BY USING US-CAST IRON

Source	Sum of squares	Degree of freedom	Mean square	F-Value	*p*-Value Prob > F
Model	119.4896	9	13.2766	4.9679	0.0461
A-X1	0.0038	1	0.0038	0.0015	0.9710
B-X2	9.8618	1	9.8618	3.6901	0.1128
C-X3	61.9594	1	61.9594	23.1843	0.0048
AB	12.9825	1	12.9825	4.8578	0.0787
AC	1.9783	1	1.9783	0.7403	0.4289
BC	0.2143	1	0.2143	0.0802	0.7884
A^2	16.3335	1	16.3335	6.1117	0.0564
B^2	9.1764	1	9.1764	3.4337	0.1231
C^2	11.8479	1	11.8479	4.4333	0.0891
Residual	13.3623	5	2.6724	–	–
Lack of Fit	9.5392	3	3.1797	1.6634	0.3968
Pure Error	3.8231	2	1.9115	–	–
Cor Total	132.8521	14	–	–	–

$R^2 = 0.89$, Adj $R^2 = 0.72$, Adeq precision = 5.83.

degradation of acid red 14 and there is only a 4.61 % chance that a model F-value this large could occur due to noise. In the degradation of acid red 14 model, the adequate precision ratio of 5.83 indicates an adequate signal where it measures the signal to noise ratio; a ratio greater than four is desirable. The *p*-values less than 0.0500 indicate that the model terms are significant, whereas the values greater than 0.1000 are usually considered as non-significant. Table-3 showed the results of this model when applied to removal rate of acid red 14. The terms are significant according to *p*-values.

Fig. 1 shows a comparison between calculated and experimental values of the response variable of degradation rate by using resulted second-order polynomial equation (eqn. 4). This plot has correlation coefficient of 0.957, which confirm that the experimental values are in good agreement with the predicted values.

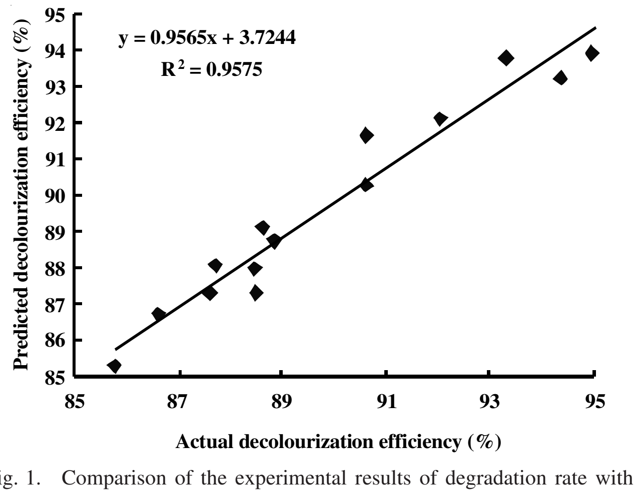


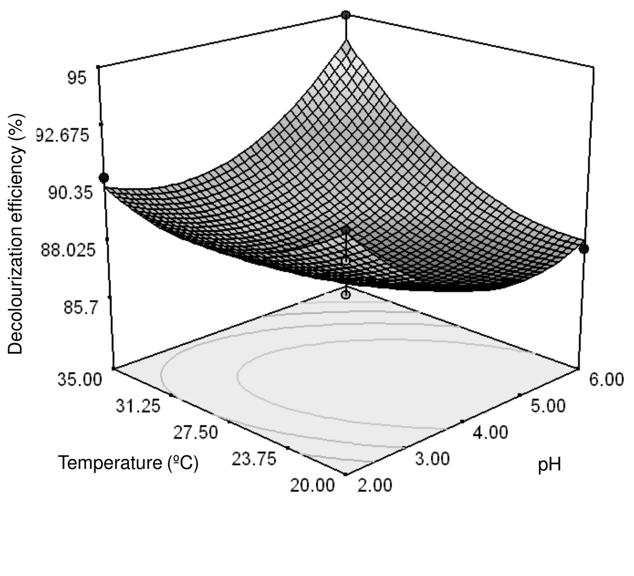
Fig. 1. Comparison of the experimental results of degradation rate with those calculated *via* response surface design resulted equation

Response surface and contour plots for dccolourization of acid red 14: The response surface and contour plots of the model-predicted responses, while two variables kept at constant and the others varying within the experimental ranges, were obtained and utilized to assess the interactive relationships between the process variables and treatment outputs for degradation of AR14.

Response surface plots provide a method to predict the degradation rate for different values of the tested variables and the contours of the plots help in identification of the type of interactions between these variables[11]. Each contour curve represents an infinite number of combinations of two tested variables with the other two maintained at their respective zero level. A circular contour of response surfaces indicates that the interaction between the corresponding variables is negligible. In contrast, an elliptical or saddle nature of the contour plots indicates that the interaction between the corresponding variables is significant[12].

Effect of initial pH and temperature on degradation rate: Fig. 2 illustrates the effect of initial pH of acid red 14 solution and temperature on degradation rate for reaction time of 8 min and initial dye concentration of 50 mg/L. As can be seen from Fig. 2, much higher degradation rate can be got with relative lower pH (2-3). The surface and elliptical nature of contour plot for acid red 14 in Fig. 2 show the interactive effect of pH and temperature by keeping reaction time constant.

Effect of initial pH and reaction time on degradation rate: The response surface contour plots to estimate the removal efficiency surface over independent variables pH and reaction time shown in Fig. 3. The contour and response surface plots given in the figure show the relative effects of two variables when temperature value is kept constant (27.5 ºC).



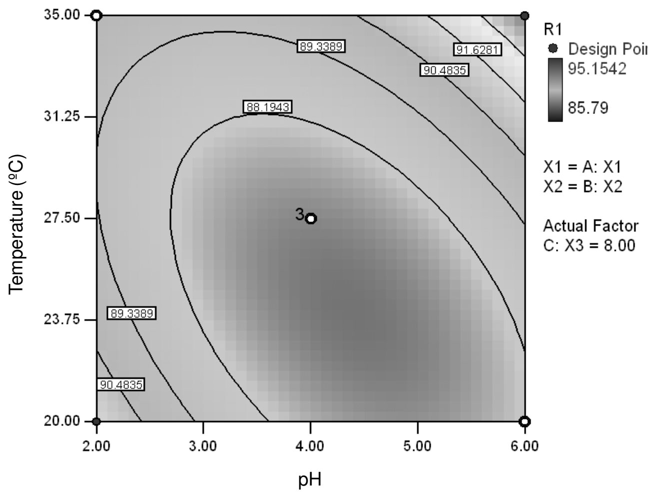


Fig. 2. Response surface and contour plot showing the effect of pH and temperature at 8 min, fixed dye concentration 50 mg/L and US (59 kHz, 250 W)

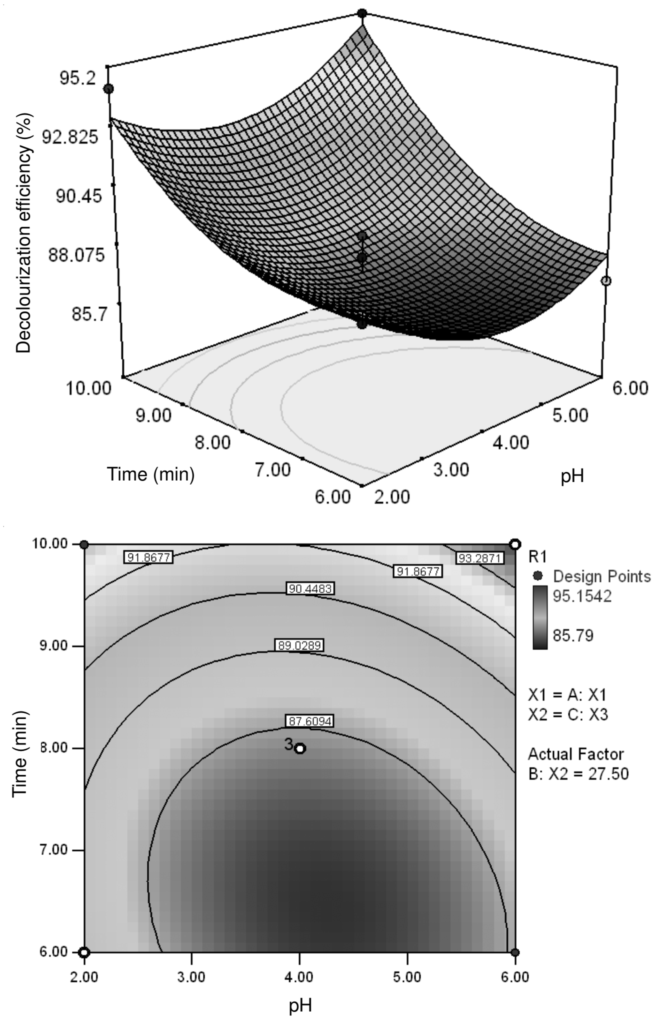


Fig. 3. Response surface and contour plot showing the effect of pH and reaction time of ultrasound at 27.5 ºC, dye concentration 50 mg/L and US (59 kHz, 250 W)

Effect of temperature and reaction time on degradation rate: Fig. 4 shows the response surface and contour plots for degradation rate as a function of temperature and reaction time at pH = 4 and initial concentration of 50 mg/L. This figure

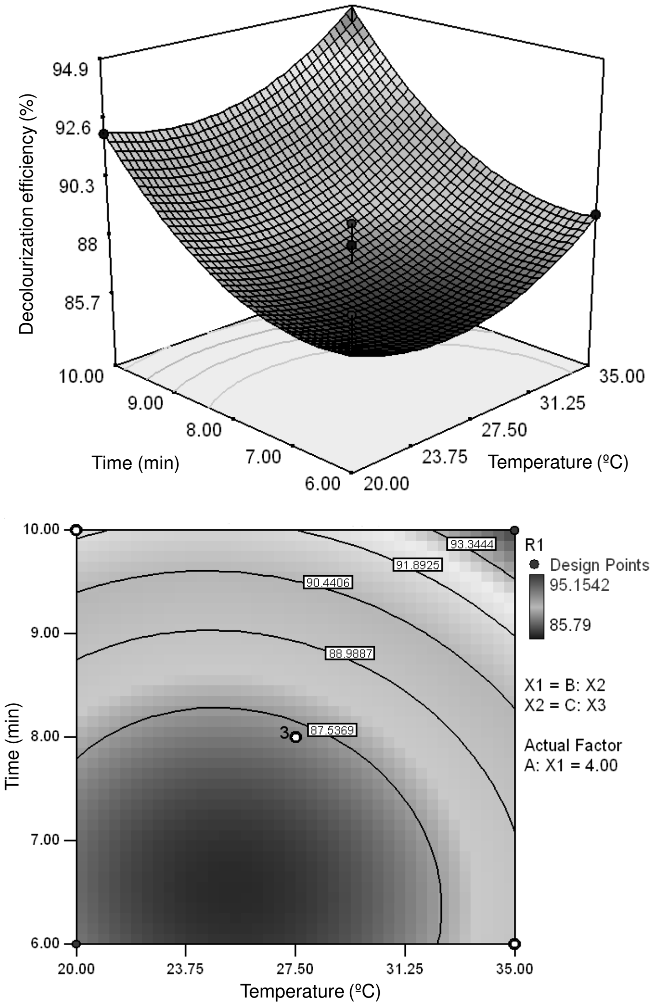


Fig. 4. Response surface and contour plot showing the effect of temperature and reaction time of ultrasound at pH = 4, dye concentration 50 mg/L and ultrasound (59 kHz, 250 W)

shows that degradation rate increases with the increase of reaction time of ultrasound and temperature. The degradation rate relates to the probability of formation of $OH^{\bullet}$ radicals and its reaction with dye molecules[13-16]. At the high temperature and long reaction time, amount of hydroxyl radicals will be enough to increase removal efficiency.

Determination of optimal conditions for the degradation of acid red 14: The desired goal in term of degradation rate was defined as "maximize" to achieve highest treatment performance. The optimum values of the process variables for the maximum degradation rate are shown in Table-5. After verifying by a further experimental test with the predicted values, the result indicated that the maximal degradation rate was obtained when the values of each parameter were set as the optimum values, which was in good agreement with the value predicted from the model. It implies that the strategy to optimize the degradationconditions and to obtain the maximal

TABLE-5
OPTIMUM VALUES OF THE PROCESS PARAMETERS FOR MAXIMUM DEGRADATION RATE

Desirability factor	pH	Temp. (ºC)	Time (min)	Predicted degradation rate (%)
0.9596	6	35	10	99.42637

degradation rate by response surface methodology for the degradationof the dye acid red 14 with US-Cast iron in this study is successful.

Conclusion

Degradation of acid red 14 by cast iron in the presence of low frequency ultrasonic irradiation has been optimized by using response surface methodology based on Box-Behnken design. A regression model was proposed to describe the effects of independent variables and their interactions on degradation of acid red 14. ANOVA indicated the proposed regression model based on Box-Behnken design is agreement with the experimental case with R^2 and R^2_{adj} correlation coefficients of 0.89 and 0.72, respectively. The optimum initial pH, temperature and time of ultrasound were found to be 6, 35 ºC and 10 min, respectively.Under the optimal value of process parameters, 99.4 % of degradation was obtained from the proposed model for acid red 14. This study clearly showed that response surface methodologybased on Box-Behnken design was one of the suitable methods to optimize the operating conditions and maximize degradation rate of acid red 14.

ACKNOWLEDGEMENTS

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