Removal of Congo Red and Rhodamine B Dyes from Aqueous Solution by Fenton Process: Optimization of Operational Parameters

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ABSTRACT: *Dye discharge in industrial effluents is a major source of concern, as its existence and accumulation can be harmful or carcinogenic to living organisms. This research focuses on using the Fenton process to treat dyes, Congo Red (CR) and Rhodamine B (RB), in aqueous solutions. The effects of the three independent variables considered for the optimization of the oxidative process: temperature, Fe (II), and H_2O_2 concentrations were evaluated using Response Surface Methodology (RSM). The experimental results are reported in terms of the degradation percentage of the dye. The optimal reaction conditions to degrade the congo red from aqueous solutions were: pH 3; T 298 K; 1.03 mM Fe^{2+} and 11.77 mM H_2O_2. The optimal reaction conditions to degrade the rhodamine B from aqueous solutions were: pH 3; T 298 K; 1.038 mM Fe^{2+} and 12.14 mM H_2O_2. Under these conditions and with a 120 min treatment, it was possible to reach 74.75 and 97.63 % of decolorization efficiency, for CR and RB, respectively. The model (R^2) correlation coefficients for CR (congo red) and RB (rhodamine B) were 0.979 and 0.986, respectively, in the optimization. The Fenton process also showed a higher removal efficiency of RB compared to RC. RSM was clearly demonstrated to be one of the most effective methods for optimizing operating conditions in this study.*

KEYWORDS: *Central composite design; Congo red; Decolorization; Fenton process; Rhodamine B.*

INTRODUCTION

Synthetic dyes are commonly used to color goods in a variety of industries, including textiles, paper, leather tanning, plastic, carpet, fruit, and cosmetics [1, 2]. Dye discharge in industrial effluents is a major source of concern, as its existence and accumulation can be harmful or carcinogenic to living organisms [3,4]. It's impossible to get rid of those compounds at such low levels. Textile dyes are expected to be discharged in such industrial effluents at a rate of 280.000 tons per year [5]. While effective for color removal in many cases, physical processes wastewater treatment methods simply move contaminants to other media, resulting in secondary waste [6-9].

Advanced Oxidation Processes (AOPs) have been identified as effective methods for obtaining high oxidation yields from a variety of organic compounds in recent years [10, 11].

Hydroxyl radicals (•OH) play a key role in AOPs, which can target a wide range of contaminants in an unspecific and effective manner [12–14].

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The Fenton process is the AOP that involves the reaction of Fe^{2+} species with H_2O_2 under strong acid conditions to generate highly reactive hydroxyl radicals (•OH) (2.8V vs.NHE) and is known as Fenton-like equations [15–17]:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \quad (2)$$

The Fenton reaction is a potentially practical, cost-effective, and environmentally friendly wastewater treatment process [18]. The Fenton method has received a lot of attention [19–22]. The Fenton processes are influenced by several factors, including temperature, H_2O_2, Fe^{2+} concentrations and pH. pH is a very important factor in AOPs and especially in the Fenton process, as it directly influences the rate of degradation of the pollutant. Several studies on Fenton processes have shown that the pH must be between 2.8 and 3.0 [23, 24], for optimal degradation of organic pollutants.

The increase in iron concentration always leads to an increase in the rate of reaction. However, this increase is not always proportional, and the rate ends up stabilising at high concentrations. Stabilise at higher concentrations, the homogeneous Fenton reactions occur between hydrogen peroxide and between hydrogen peroxide and Fe^{2+} or Fe^{3+} and lead to the production of highly reactive hydroxyl radicals that attack and destroy organic molecules.

The influence of the oxidant concentration on the kinetics has been studied by several authors and their conclusions can be summarised by the fact that there is a range of concentration range for hydrogen peroxide, too low a concentration leads to a reduction in reaction rate, too high a concentration leads to the hydroxyl radicals to react preferentially with H_2O_2 rather than with the pollutant.

Temperature improves the speed of the reactions involved in the oxidation mechanism, but it also promotes the decomposition of H_2O_2 into oxygen and water. Generally there is no consensus on the effect of temperature.

In this paper, we have optimized the removal of congo red (CR) and rhodamine B (RB) as a model dyes from aqueous solutions using the Fenton process

The effect of various operating parameters such as the effect of temperature, H_2O_2 and Fe^{2+} concentrations on the oxidation of CR and RB in terms of degradation (%), have been evaluated. The present study aims to determine the optimum reaction conditions of degradation (to degrade) of the CR and RB by Fenton process using Response Surface Methodology (RSM).

EXPERIMENTAL SECTION

Chemicals

Iron sulphate ($FeSO_4.7H_2O$, Merck 99,5%) and hydrogen peroxide (H_2O_2 Panreac 33% (w/v)) were used to obtain hydroxyl radical, ·OH. Concentrated sulphuric acid and sodium hydroxide solutions were used to achieve desired pH values (pH = 3) in working solutions.

Since several experiments have shown that the optimal pH for Fenton's reaction is in the range of 2.8-3.0, pH 3.0 was chosen [23, 24]. For pH values below pH 3, inhibiting Fe (III) complexation with H_2O_2 results in a decrease in activity. At higher pH values, low activity is observed due to a decrease in free iron species due to ferric oxyhydroxide precipitation, the development of different complex species, and the breakdown of H_2O_2 to O_2 and H_2O_2.

To study the degradation of the dyes (RB, RC) by the Fenton process, we used the experimental setup shown in Fig.1. The treatment time was 120 min. The H_2O_2 and Fe (II) concentrations are in accordance with stoichiometric requirements. The RB and CR concentrations in these preliminary experiments were 30 mg/L (0.0626 mM) and 50 mg/L (0.071 mM), respectively

The dye removal efficiency was determined using the following expression [25]:

$$\%\,R = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (3)$$

Where C_0 and C_t represent the initial and final concentrations of dye in mg/L, respectively.

Table 1 shows the structure of the investigated dyes. Stock solutions of dyes were prepared by dissolving the powder in double distilled water. Dye solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

Experimental design

For the optimization conditions for dye degradation under Fenton conditions, Central Composite Design (CCD), a commonly used type of RSM, was used in this study. Three key factors were chosen to test the effect

Table 1: Characteristics of dyes.

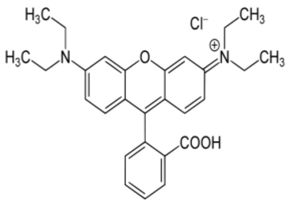
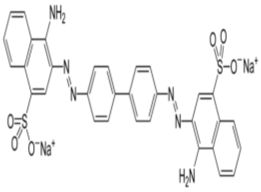
Generic name	Rhodamine B	Congo red
Chemical formula	$C_{28}H_{31}N_2O_3Cl$	$C_{32}H_{22}N_6O_6S_2$
Molar mass (g/mol)	479.02	696.7
λ_{max} (nm)	554	494
Ionisation	Basic	Acid
Structure		

Table 2: Levels of the parameters studied in CCD statistical experiment of CR.

Variable	Coded variable				
	-1.68	-1	0	+1	+1.68
T (K)	286	298	315.5	333	345
$[H_2O_2]$ (mM)	3.72	6.46	10.48	14.50	17.24
$[Fe^{2+}]$ (mM)	0.426	0.646	0.97	1.29	1.51

Table 3: Levels of the parameters studied in CCD statistical experiment of RB.

Variable	Coded variable				
	-1.68	-1	0	+1	+1.68
T (K)	286	298	315.5	333.0	345.0
$[H_2O_2]$ (mM)	7.582	9.14	11.425	13.71	15.268
$[Fe^{2+}]$ (mM)	0.842	0.914	1.0195	1.125	1.197

Fig.1: Schematic of the Fenton process experimental setup.

of operating parameters on the decolorization efficiency of RB and CR: temperature (X1), initial H_2O_2 concentration (X2), and initial concentration Fe (II) (X3)

A total of 20 experiments were employed in this work for each dye. Each experiment was repeated three times. The experimental ranges and the levels of the independent variables for dyes color removal are given in Tables 2, 3.

RESULTS AND DISCUSSION

Statistical analysis

The second-order polynomial response equation (4) was used to correlate the dependent and independent variables.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (4)$$

Where Y is a response variable of decolorization efficiency. The b_i are regression coefficients for linear effects; b_{ii} are the regression coefficients for squared effects; b_{ik} are the regression coefficients for interaction effects and x_i are coded experimental levels of the variables (Temperature, H_2O_2, and Fe (II) concentrations).

Based on these results, an empirical relationship

Table 4: Central composite design matrix: Response factor results (% of decolorization efficiency) of congo red.

Essai	T (K)	$[H_2O_2]$ mM	$[Fe^{2+}]$ mM	Y (%) Experimental	Y (%) Predicted
1	298	6.46	0.646	36.4	40.37
2	333	6.46	0.646	36.6	38.01
3	298	6.46	1.29	41.2	43.41
4	333	6.46	1.29	40.8	42.99
5	298	14.5	0.646	50.6	53.01
6	333	14.5	0.646	51.3	51.29
7	298	14.5	1.29	60	60.81
8	333	14.5	1.29	60.4	58.65
9	286	10.48	0.97	69.2	64.68
10	345	10.48	0.97	59.5	60.88
11	315.5	10.48	0.426	48.5	45.013
12	315.5	10.48	1.51	53.3	53.75
13	315.5	3.72	0.97	27.1	23.85
14	315.5	17.24	0.97	49.4	49.623
15	315.5	10.48	0.97	70.8	71.34
16	315.5	10.48	0.97	71.2	71.34
17	315.5	10.48	0.97	70.8	71.34
18	315.5	10.48	0.97	72.3	71.34
19	315.5	10.48	0.97	71.6	71.34
20	315.5	10.48	0.97	70.8	71.34

between the response and independent variables was attained and expressed by the following second-order polynomial equation:

$$Y_1(\text{\%decolorization of congo red, after 120 min Fenton treatment}) = 71.34 - 1.13\ X_1 + 7.67\ X_2 + 2.6\ X_3 - 3.03\ X_1^2 - 12.26\ X_2^2 - 7.78\ X_3^2 + 0.16\ X_1X_2 - 0.11\ X_1X_3 + 1.19\ X_2X_3 \quad (5)$$

$$Y_2(\text{\%decolorization of Rhodamine B, after 120 min Fenton treatment}) = 94.7 - 1.32\ X_1 + 9.42\ X_2 + 3.01\ X_3 - 5.24\ X_1^2 - 15.42\ X_2^2 - 9.59\ X_3^2 + 0.46\ X_1X_2 + 0.11\ X_1X_3 + 1.29\ X_2X_3 \quad (6)$$

From equations (5) and (6), we predicted the decolorization efficiencies.The obtained results are presented in Table 4 and Table 5. These results indicated good agreements between the experimental and the predicted values of decolorization efficiency.

Six of the experiments were conducted at the central points. For such replicates (runs 15-20), the dye removal efficiency reduction lies between 70.8 and 72.3% for CR and between 94.2 and 95.4% for RB. The analysis of variance (ANOVA) was used to test the suitability of the model. Table 6 shows the results of the quadratic response surface model fitting in the form of analysis of variance (ANOVA).

ANOVA subdivides the total variation of the results into two components: Variation associated with the model and variation associated with the experimental error. These show whether the variation from the model is significant or not when compared with the ones associated with residual error [26, 27]. If the model is a good predictor of the experimental results, the F-value should be greater than

Table 5: Central composite design matrix: Response factor results (% of decolorization efficiency) of Rhodamine B.

Essai	T (K)	$[H_2O_2]$ mM	$[Fe^{2+}]$ mM	Y(%) Experimental	Y (%) Predicted
1	298	9.14	0.914	53.2	55.25
2	333	9.14	0.914	53.5	51.42
3	298	9.14	1.125	58.5	58.42
4	333	9.14	1.125	57.9	55.08
5	298	13.71	0.914	67.4	70.54
6	333	13.71	0.914	68.2	68.6
7	298	13.71	1.125	76.5	78.92
8	333	13.71	1.125	79.1	77.42
9	286	11.425	1.0195	86.4	82.13
10	345	11.425	1.0195	73.8	77.69
11	315.5	11.425	0.842	64.4	62.57
12	315.5	11.425	1.197	71.2	72.69
13	315.5	7.582	1.0195	33.3	35.35
14	315.5	15.268	1.0195	69.3	67
15	315.5	11.425	1.0195	94.8	94.7
16	315,5	11.425	1.0195	94.2	94.7
17	315.5	11.425	1.0195	94.8	94.7
18	315.5	11.425	1.0195	94.3	94.7
19	315.5	11.425	1.0195	95.4	94.7
20	315.5	11.425	1.0195	94.6	94.7

Table 6: ANOVA results for % of decolorization efficiency under Fenton treatment of CR and RB.

	Source	df	SS	MS	F-ratio	P-value
Congo red	Model	9	3739.55	415.51	51.74	< 0.0001
	Residual	10	80.31	8.03		
	Total	19	3819.86	423.54		
	$R^2 = 0.979$	$R^2_{adj} = 0.96$				
Rhodamine B	Model	9	5877.56	653.06	77.44	< 0.0001
	Residual	10	84.33	8.43		
	Total	19	5961.81	661.49		
	$R^2 = 0.986$	$R^2_{adj} = 0.973$				

the tabulated value of the F-distribution for a certain number of degrees of freedom in the model at a level of significance. A F-ratios obtained, 51.74 and 77.44 for CR and RB, respectively, is clearly greater than the Fisher's F-value $F_{9,10}$ (3.02 at 95% significance) confirming the adequacy of the model fits. The quality of the fit of the polynomial model was expressed by the correlation coefficient (R^2). From $R^2 = 0.979$ for RC and $R^2 = 0.986$ for RB, we can say that 97.9% and 98.6.0% of the response variability is explained by the model. For which at least $R^2 = 0.80$ is suggested [28].

Response surface

In Fig. 2, the response surface plots were presented

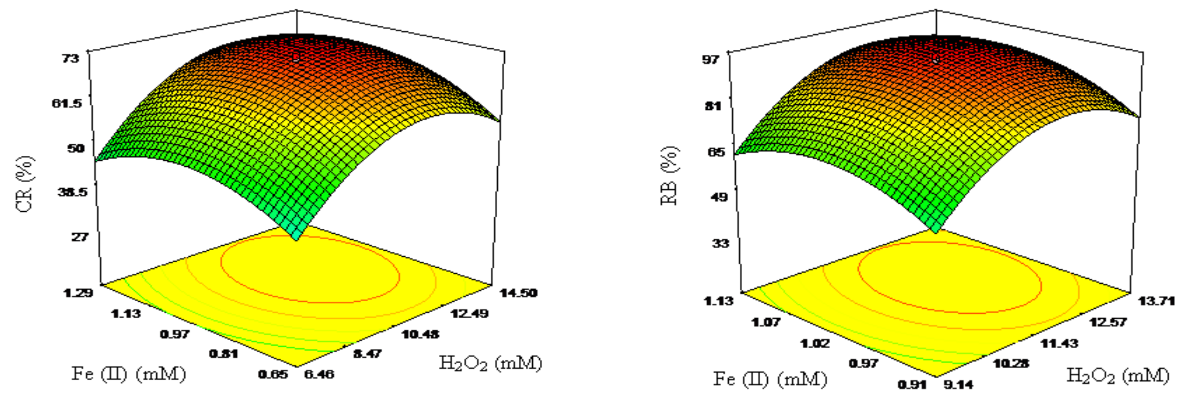


Fig. 2: Response surface for of the decolorization efficiency (CR, RB %) after 120 min Fenton treatment, as a function of [H_2O_2] and [Fe (II)].

as a function of H_2O_2 and Fe (II) concentrations; the temperature was kept constant at 298 K and pH was maintained at 3.

The key parameter for decolorization efficiency as a function of H_2O_2 and Fe (II) concentrations can be deduced from Fig. 2. The surface of a response is part of a sphere, the percentage of degradation of the dyes passes through a maximum whose values are respectively 72.92% (X2= 0.321, X3 = 0.193), 96.52 % (X2 = 0.315, X3 =0.177), for congo red and rhodamine B.

Above these values, the percentage of dye degradation decreases due to the scavenging power of Fe^{2+} (equation 1), which in high concentrations destroys the $HO^{\bullet}$ radicals produced [29], and by the acceleration of parasitic reactions that consume hydroxyl radicals (Eqs (2, 3)):

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^{-} \qquad (1)$$

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (2)$$

$$HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2 \qquad (3)$$

Fig. 3 shows the decolorization efficiency response surface plots as a function of temperature and H_2O_2 concentration.By varying the H_2O_2concentration from 7.582 to 15.268 mM for RB and from 3.72 to 17.24 mM for CR, the maximum decolorization efficiency was achieved when H_2O_2 concentrations were held at about 11.77 mM for CR and 12.14 mM for RB. Other researchers have also noted a similar observation for the decolorization of C.I. Acid Red 66 and C.I. Direct Blue 71 dyes by the Fenton process [30].

Fig. 4 shows the decolorization efficiency response surface as a function of temperature and initial Fe(II) concentration. According to the results of this study, the concentration of Fe (II) is one of the most critical factors affecting the dye removal efficiency of the Fenton process.

By varying the Fe (II) concentration from 0.842 to 1.197 mM for RB and from 0.426 to 1.51 mM for CR, as can be shown, as the amount of Fe (II) increases, the decolorization efficiency decreases. The maximum decolorization efficiency was achieved when Fe (II) concentrations were held at about 1.03 mM for CR and 1.038 mM for RB. When Fe (II) ions are in excess, then there is an inhibition effect because there is competition between the excess Fe (II) ions and the dye molecules for $HO^{\bullet}$ radicals [31]. At very low concentrations of Fe (II) ions, the catalytic effect of Fe (II) ions was limited and resulted in lesser decomposition of H_2O_2 to form $HO^{\bullet}$Radicals [18]. The temperature, on the other hand, has only a minor effect.

Response optimization and confirmation

To achieve the best treatment results, the desired target in terms of decolorization efficiency was described as "maximize." After 120 minutes of treatment with optimum Fenton, the decolorization efficiency of the CR and RB was calculated. For CR and RB, the obtained values were 74.75 and 97.63 %, respectively (Fig.4). It means that the strategy of using a Central Composite Design (CCD) to optimize decolorization conditions and achieve maximum decolorization efficiency for the Fenton process removal of CR and RB was efficient.

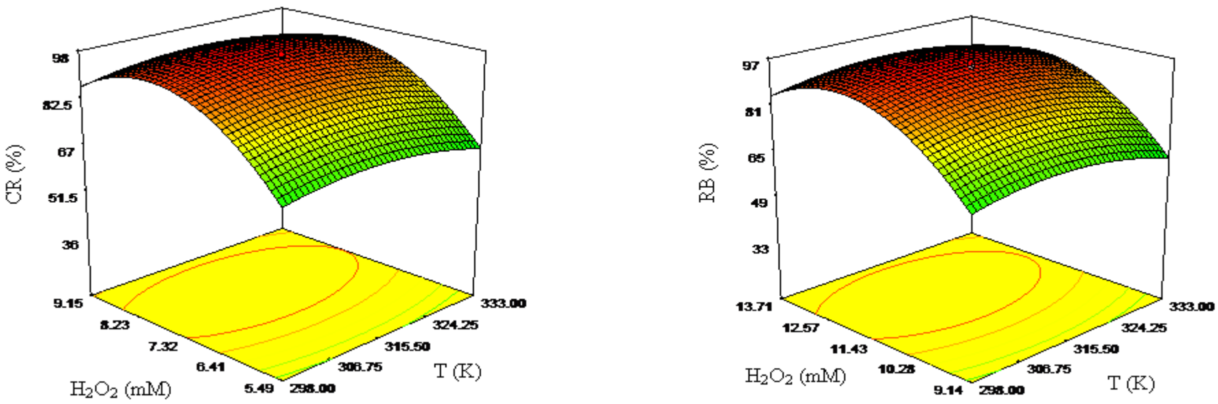


Fig. 3: Response surface for of the decolorization efficiency (CR, RB %) after 120 min Fenton treatment, as a function of [H_2O_2] and temperature.

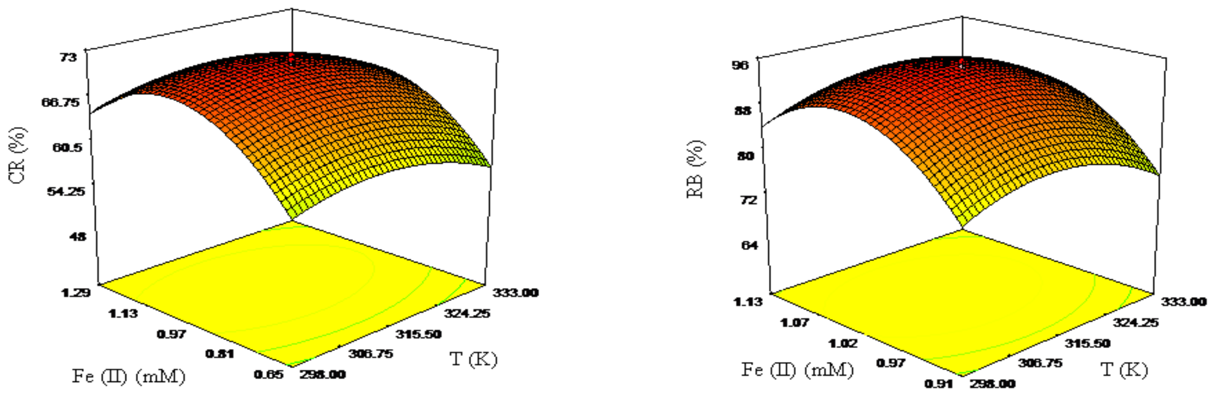


Fig. 4: Response surface for of the decolorization efficiency (CR, RB %) after 120 min Fenton treatment, as a function of [Fe (II)] and temperature.

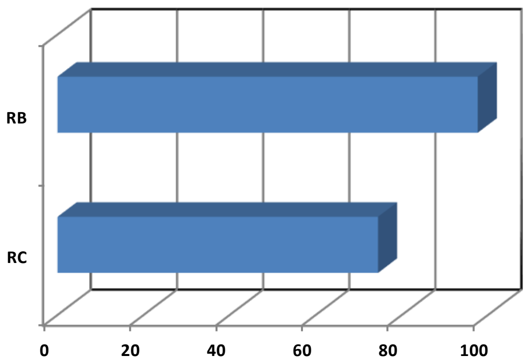


***Fig. 5:** Evolution of the decolorization efficiency under optimal conditions.*

CONCLUSIONS

In this study, the Fenton process was used to study the removal of CR and RB as model dyes from aqueous solutions. The effects of the three independent variables considered for the optimization of the oxidative process: Temperature, Fe (II), and H_2O_2 concentrations were evaluated using Response Surface Methodology (RSM).

The experimental results are reported in terms of the degradation percentage of the dye. The optimal reaction conditions to degrade the congo red from aqueous solutions were: pH 3; T 298 K; 1.03 mM Fe^{2+} and 11.77 mM H_2O_2. The optimal reaction conditions to degrade the rhodamine B from aqueous solutions were: pH 3; T 298 K; 1.038 mM Fe^{2+} and 12.14 mM H_2O_2. Under these conditions and with a 120 min treatment, it was possible to reach 74.75 and 97.63 % of decolorization efficiency, for CR and RB, respectively.

The model (R^2) correlation coefficients for CR (Congo Red) and RB (Rhodamine B) were 0.979 and 0.986, respectively, in the optimization. The Fenton process also showed a higher removal efficiency of RB compared to RC. RSM was clearly demonstrated to be one of the most effective methods for optimizing operating conditions in this Study.

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