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EFFECT OF OPERATING PARAMETERS ON DECOLOURIZATION OF REACTIVE RED 35 BY UV/H_2O_2 PROCESS: OPTIMIZATION THROUGH RESPONSE SURFACE METHODOLOGY

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ABSTRACT

In this paper, decolourization of reactive red 35 was studied using advanced photo-oxidation process (UV/H_2O_2). The effect of operating parameters such as solution pH (3-11), H_2O_2 dosage (10-60 mM), and initial dye concentrations (100-200 mg/L) was studied on % decolourization. The operating parameters were optimized using response surface methodology. The global optimal parameters are: 46.6 mg/L of initial reactive red concentration, pH of 7.6 and H_2O_2 concentration of 20.5 mM.

Key words: Reactive dye, Photo-oxidation, H_2O_2, Optimization.

INTRODUCTION

Dyes are used in the textile, printing and many other industries to colour their end products. A significant portion of dyes remains unconsumed and therefore let out to the environment[1]. The presence of dyes in aqueous effluents poses threat to living organisms. It reduces light penetration and reoxygenation capacity of water and there by disturbing the metabolic activity of aquatic life[2]. Reactive dyes are widely used in the textile industries due to its simple dyeing procedure and good stability during washing process[3]. They are representing a class of organic pollutants, which are proven to be potentially carcinogenic[4].

Different approaches have been used to remove dyes from aqueous solution such as physical adsorption, chemical coagulation/precipitation, and biological anaerobic/aerobic decomposition[5-7]. But these processes only transfer the contaminant from liquid phase to

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solid phase. Alternative solution to the conventional treatment have been developed, including electrochemical treatment, chemical oxidation, ozonation and other advanced oxidation processes (AOPs). AOPs are able to oxidize a wide range of compounds that are otherwise difficult to degrade. Among the AOP methods, the use of ultraviolet (UV) radiation in the presence of hydrogen peroxide (H_2O_2) is a very promising technique[8]. In UV/H_2O_2 process the photolysis of hydrogen peroxide generates effective oxidizing species hydroxyl radical ($^{\bullet}OH$) species. The oxidation potential of hydroxyl radical is 2.8 eV, which can completely destroy the pollutants present in waste water[9]. These reactive radicals can decompose and even mineralize the organic contaminants with high efficiency[10,11]. In this work, we studied the treatment of model dye reactive red 35 by UV/H_2O_2 process. Reactive red 35 was chosen, since it has been the topic of only a few articles and the nature of by-products remains a matter of conjecture. The effects of the key operating parameters such as pH, H_2O_2 concentration and initial dye concentration on percentage decolourization were studied.

In contrast to the classical optimization processes, which did not account the effect of different combination of parameters, response surface methodology (RSM) provides elaborative vision over various combinations of parameters[12]. RSM is essentially a particular set of mathematical and statistical methods for designing experiments, building models, evaluating the effects of variables, and searching optimum conditions of variables to predict targeted responses[13,14]. RSM shows promising results in industrial research, especially where large number of variables influences the system; hence influencing parameters were optimized using RSM technique[15].

EXPERIMENTAL

Materials and methods

The reactive red 35 dye was purchased from Micro Fine Chemicals, Chennai and used as received without further purification. Analytical grade of Na_2CO_3 (Reachem) and H_2SO_4 (Reachem) were used to adjust the solution pH. The dye solutions of desired concentration were prepared by dissolving requisite quantity of dye in deionized water. H_2O_2 (30% w/w) was purchased from Reachem and used as received.

Photoreactor

Batch experiment of UV/H_2O_2 process was performed in a photoreactor. The cylindrical reactor of 1.2 L capacity made of borosilicate glass was used. The temperature of reactor was maintained by cooling water passed through the jacket around the reactor. An

UV lamp (11 watts) emitting radiation at 254 nm was located in center of the cylindrical reactor. The dye solution was continuously stirred using magnetic stirrer and air was supplied continuously through pump.

Decolorization experiments

The dye solution (1L) of known concentration was loaded into photoreactor and irradiated for a definite period of time. Samples were withdrawn at periodic intervals and analyzed with UV-Vis spectrophotometer (Systronics, India) at a wavelength of 530 nm. The effect of pH (3-11), dye concentration (100, 150, 200 mg/L) and H_2O_2 dosage (10-60 mM) on percentage decolourization were studied.

Experimental design and optimization by central composite design (CCD)

Optimum experimental condition for the photo decolorization of reactive red 35 was determined by using RSM and second-order central composite design (CCD). Optimization studies were carried out by considering the effect of three different variables such as, initial dye concentration, pH and H_2O_2 dosage of the dye solution. To describe the effect of different operating parameters, 20 sets of experiments were performed. The independent variables chosen in this study were coded as shown in Eq. 1.

$$X_i = \frac{X_i - X_o}{\Delta X} \quad \ldots(1)$$

Where X_i is the dimensionless coded value of the ith independent variable, X_o is the value of X_i at the center point and ΔX is the step change value. The experimental design and results of CCD are shown in Table 1. The behavior of the system is explained by the following third-order polynomial model.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{23}X_2X_3 + b_{31}X_3X_1 \quad \ldots(2)$$

Where Y is the predicted response (% decolorization after 10 min of reaction); X_1, X_2 and X_3 are the code forms of the input variables such as initial dye concentration, pH and H_2O_2 dosage, respectively; b_0 is a constant; b_1, b_2 and b_3 are the linear coefficients; b_{11}, b_{22} and b_{33} are the quadratic coefficients; b_{12}, b_{23} and b_{31} are cross-product coefficients. A statistical program package was used for regression analysis to estimate the coefficients of polynomial equations. Analysis of variance (ANOVA) was used for graphical analysis and to obtain interaction between operating variables with the response. The R^2 values are determined to find the quality of model proposed.

Table 1: RSM design for photochemical decolourization

S. No.	Initial dye conc. (mg/L)	pH	H_2O_2 dosage (mM)	% Decolourization at 10 min (Experimental)	% Decolourization at 10 min (Predicted)
1	300	8	20	37.39	37.56
2	100	4	20	95.22	90.27
3	200	6	40	50.83	49.55
4	200	6	40	46.8	49.55
5	100	8	60	81.33	80.2
6	300	4	60	41.02	44.79
7	200	2.734	40	68.72	68.67
8	363.3	6	40	38.33	32.81
9	200	9.266	40	60.78	61.27
10	200	6	72.66	61.5	57.58
11	200	6	7.34	44.06	48.42
12	200	6	40	52.6	50.15
13	200	6	40	49.06	50.15
14	36.7	6	40	99.87	105.83
15	100	8	20	83.56	79.48
16	300	4	20	33.7	34.52
17	200	6	40	48.39	49.66
18	200	6	40	51.22	49.66
19	100	4	60	93	92.52
20	300	8	60	43.41	47.40

RESULTS AND DISCUSSION

Effect of initial dye concentration

The variation of percentage decolourization at various initial dye concentrations (100, 150 and 200 mg/L) with respect to time is shown in Fig. 1. These results clearly showed that the percentage decolourization was decreased with an increase in initial concentration of the dye. With 100 mg/L, nearly 95% of colour was removed in 10 min, while with 150 mg/L the percentage decolourization was 75% and 45% with initial dye concentration of 200 mg/L. Degradation of dye is mainly due to hydroxyl radicals generated by photolytic effect. Moreover, increase in initial dye concentration increases the organic loading in to the system. This prolongs the decomposition process and it is evident that the initial dye concentration has significant influence on the decolourization process. Several studies confirm that the initial dye concentration has a remarkable effect on photolytic decolourization rate and the higher the concentration, the lower the decolourization rate[16].

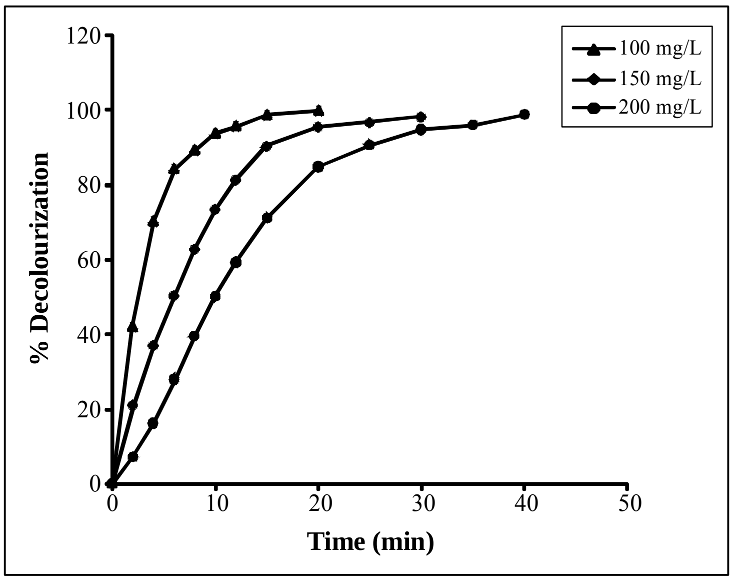

Fig. 1: Effect of dye concentration on % decolourization (Conditions: pH: 6, H_2O_2 concentration: 50 mM)

Effect of pH

The effect of initial pH on photo decolourisation of reactive red 35 is shown in Fig. 2. From the figure, it is observed that the decolourization was increased as the pH increased from 3 to 7, further increase in pH did not enhance the decolourization, instead the % decolourization decreases. This is due to the self-decomposition of hydrogen peroxide as shown in Eq. (3).

$$2H_2O_2 \rightarrow H_2O + O_2 \qquad \ldots(3)$$

Eq. (3) is strongly dependent on the pH value of the aqueous solution[16]. Its rate constant increases with increased pH. With the consumption of H_2O_2, the lower the amount of $^{\bullet}OH$ radical produced. Further, the oxidation potential of O_2 is lower than that of $^{\bullet}OH$. Thus increase in pH enhances the direct photolysis, at the same time it also enhances the self-decomposition of H_2O_2, which leads to a lower production $^{\bullet}OH$ and subsequently with a decreased contribution to the decolourization.

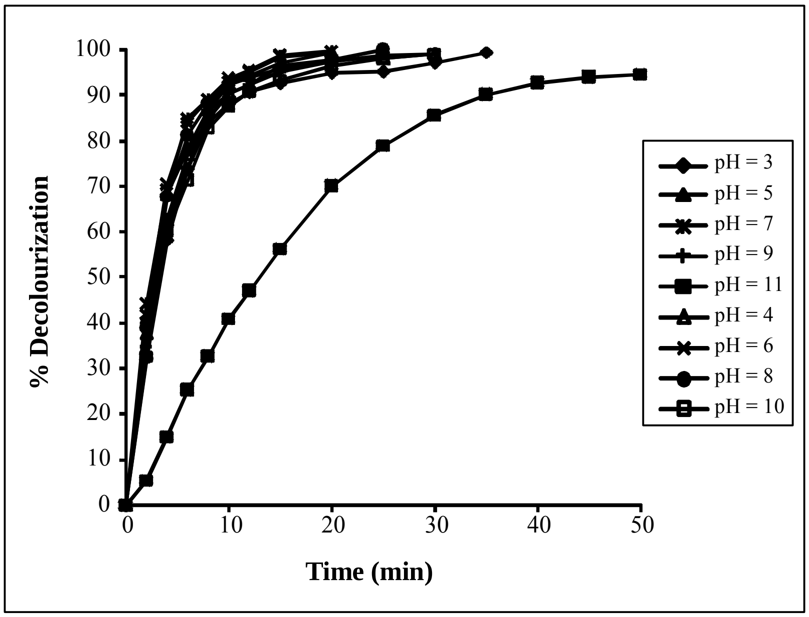

Fig. 2: Effect of pH on % Decolourization
(Conditions: Initial dye concentration: 100 mg/L, H_2O_2 concentration: 50 mM)

Effect of H_2O_2 dosage

The effect of H_2O_2 dosage on the decolourisation of reactive red 35 was investigated over a range of 10-60 mM at pH 6 and 100 mg/L of initial dye concentration and the results are shown in Fig. 3. From the Figure, it can be seen that the percentage decolourization was increased when hydrogen peroxide dosage increases, however, the effect of H_2O_2 is negative for H_2O_2 dosage higher than 40 mM. The reason may be due to either the reaction of $^{\bullet}OH$ and H_2O_2 or the combination of two hydroxyl radicals to form H_2O_2. Both reactions reduced the probability of dye being attacked by $^{\bullet}OH$ and causing decreased dye decolourisation[16].

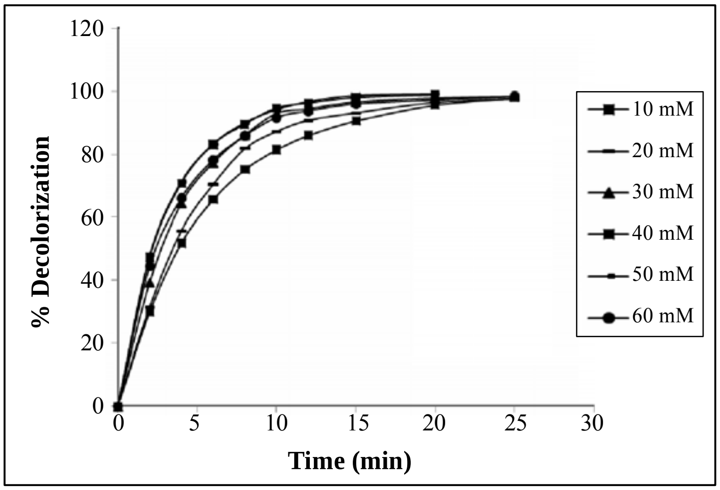

Fig. 3: Effect of H_2O_2 dosageon % decolourization (Conditions: pH 6, initial dye concentration 100 mg/L)

Optimization studies

Experimental design analysis

Percentage dye decolourization was influenced by pH, H_2O_2 dosage and initial dye concentration. Due to these varied effects on overall decolourization, there should exist optimum conditions. Therefore a search for optimum conditions was performed using stastical methods. A custom defined response surface design was used for this purpose. Initial dye concentration, pH and H_2O_2 dosage were used as process parameter. The proposed model Eq. (2) was solved using Minitab 14. Batch runs were conducted with experiments designed through CCD to visualize the effects of independent factors on responseand the results were evaluated. Regression equation for reactive red 35 given in Eq. (4).

$$\begin{aligned}\text{\% Decolourization} = {} & 208.729 - 0.665909 \text{ dye concentration} - 21.3206 \text{ pH} - 0.271604 \text{ } H_2O_2 \\ & \text{dosage} + 0.000718958 \text{ (Dye concentration)}^2 + 1.38959 \text{ pH}^2 + \\ & 0.00267408 \text{ } (H_2O_2 \text{ dosage})^2 + 0.0183813 \text{ dye concentration* pH} + \\ & 0.00111187 \text{ (Dye concentration)* } (H_2O_2 \text{ dosage}) - 0.00409375 \text{ pH*} \\ & H_2O_2 \text{ dosage} \end{aligned} \quad \ldots(4)$$

ANOVA results of these quadratic models are presented in Table 2, indicating that these quadratic models can be used to navigate the design space. The global optimal solution for this system was found to be 46.6 mg/L initial dye concentration, initial pH of 7.64 and H_2O_2 dosage of 20.57 mM. These values render 100% decolorization when testified for regression polynomial equation model.

Table 2: Analysis of variance for % decolourization

Source	Degree of freedom	Seq. SS	Adj. SS	Adj. MS	F	P
Blocks	2	1.45	1.45	0.73	0.03	0.970
Regression	9	8006.29	8006.29	889.59	37.75	0.000
Linear	3	6837.28	6837.28	2279.09	96.72	0.000
Square	3	1021.12	1021.12	340.37	14.44	0.001
Interaction	3	147.89	147.89	49.30	2.09	0.180
Residual error	8	188.51	188.51	23.56		
Lack-of-fit	5	170.12	170.12	34.02	5.55	0.095
Pure error	3	18.39	18.39	6.13		

Effect plot

The effect of variables on response (% decolourization) could be analysed from the main effect plots. The individual significance of the variables can be predicted from the Fig. 4.

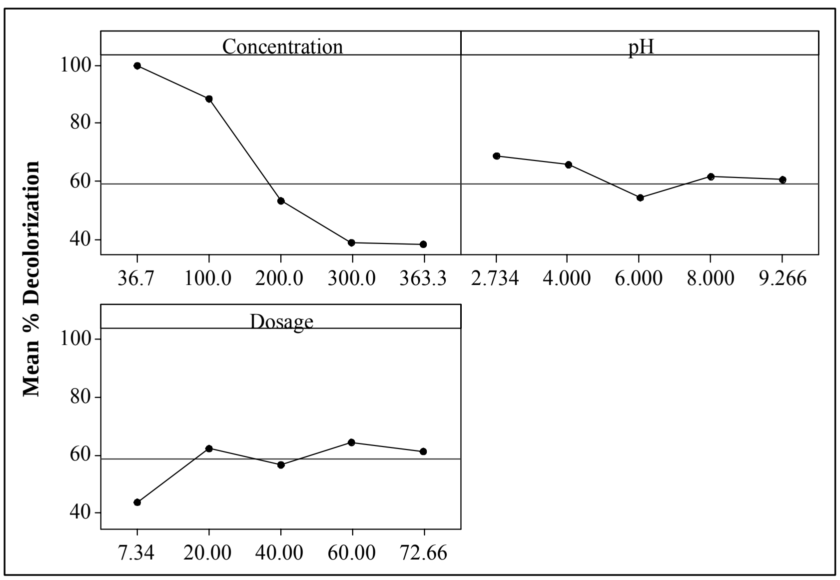

Fig. 4: Main effects plot for % decolourization

It was observed that, as the initial dye concentration increase the % decolourisation decreased. The combined effect of pH, initial dye concentration and H_2O_2 dosage was also analyzed on % decolourization. The plot implies that change in initial dye concentration, H_2O_2

dosage and pH of dye solution influences the % decolourization significantly. There was a decrease in % decolourization when the pH increases upto 6. Further increase in pH increases the % decolourization. The % decolourization also increases with increase in H_2O_2 dosage.

Response surface and contour plot

The Response surface area and the Response surface contour plot are shown in Fig. 5a, b, c. and Fig. 6a, b, c, respectively. The contour plots given in Fig. 6a, b, c show the relative effects of variables on % decolourization. The plot implies that the % decolourization reaches the level of 100% at pH below 3.2 and an initial concentration of 130 mg/L. More than 90% decolourization could be achieved below the initial concentration of 160 mg/L and pH level of 4.1 and more than 90% decolourization could be achieved at all H_2O_2 dosage studied at a initial dye concentration below 100 mg/L.

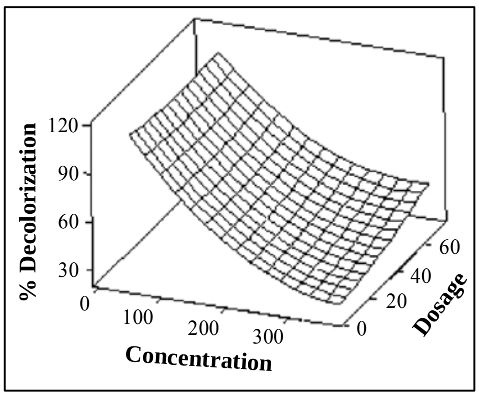

Fig. 5 (a): Response surface plot of % decolourization, initial concentration and H_2O_2 dosage

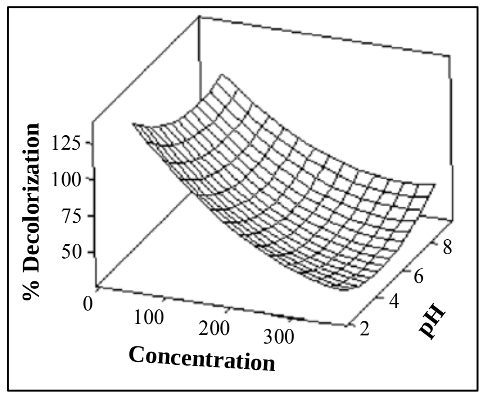

Fig. 5 (b): Response surface plot of % decolourization, pH and initial dye concentration

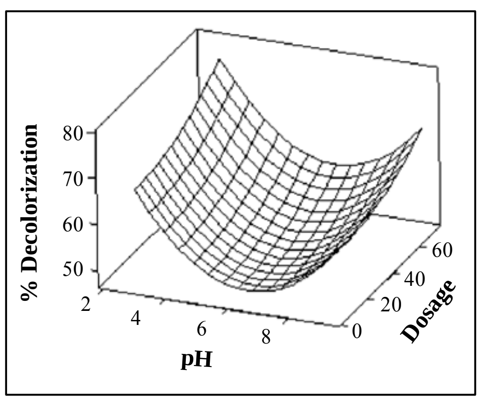

Fig. 5 (c): Response surface plot of % decolourization, pH and H_2O_2 dosage

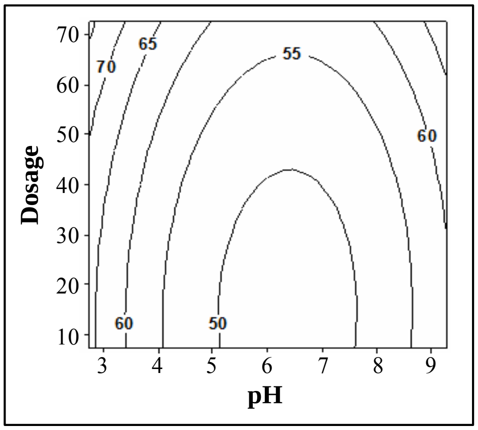

Fig. 6 (a): Response contour plot of % decolourization, pH and H_2O_2 dosage

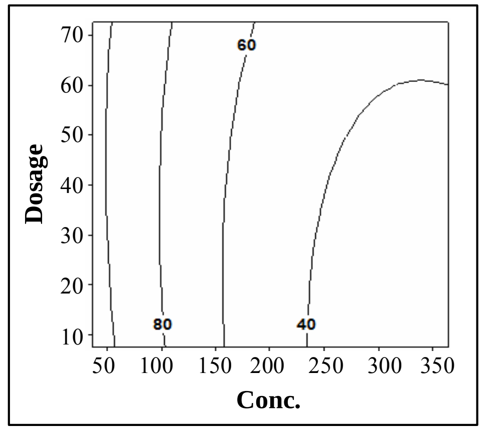

Fig. 6 (b): Response contour plot of % decolourization, initial dye concentration, H_2O_2 dosage

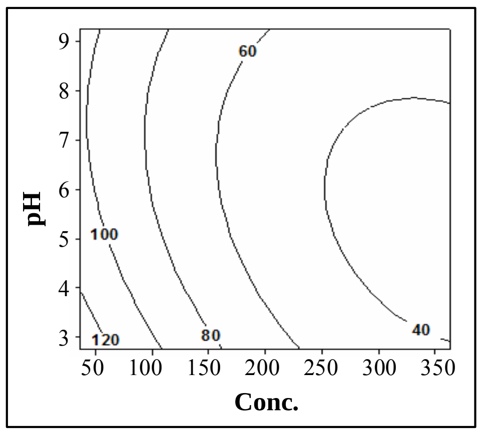

Fig. 6 (c): Response contour plot of % decolourization, pH and initial dye concentration

CONCLUSION

This study involves the decolourization of reactive red 35 using UV/H_2O_2 process. The preliminary studies showed that the decolourization using this method is much effective and would take minimum time (within 10 min) for all studied concentrations. Furthermore, the RSM studies show that the global solutions for the decolourization are: initial dye concentration of 46.6 mg/L, pH of 7.6 and H_2O_2 dosage of 20.5 mM. Thus, this method was proved to be efficient for treating industrial wastewaters, which contains reactive dyes.

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