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Determination of optimum operating conditions of carmine decoloration by UV/H_2O_2 using response surface methodology

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ABSTRACT

In this study, the photolytic decoloration of carmine (C.I. Natural Red 4) via UV radiation in the presence of H_2O_2 was optimized using response surface methodology (RSM). According to analysis of variance (ANOVA) results, the proposed model can be used to navigate the design space. It was found that the response of carmine degradation is very sensitive to the independent factors of carmine concentration, H_2O_2 concentration, pH and reaction time. The proposed model for D-optimal design fitted very well with the experimental data with R^2 and R^2_{adj} correlation coefficients of 0.998 and 0.997, respectively.

1. Introduction

Synthetic dyes are an important class of chemicals which are used in many industrial processes. The main users of these dyes are the textile industry, paper and printing, plastics, etc. Presently the world production of dyes is estimated to be around 450,000 tons annually. Out of this, 50,000 tons are being lost in effluents during application and manufacturing steps. 1–15% of dyes are discharged as effluent thus causing a potential threat to the environment [1]. Most of the dyestuffs used are highly structured polymers with low biodegradability. Reactive dyes cause special environmental problems due to their precursors and of their degradation products; for example, aromatic amines are considered highly carcinogenic [2,3]. Many different techniques have been suggested to tackle the issue of removing these dyes from solution. These include activated carbon adsorption [4], chemical coagulation [5], nanofiltration [6], sedimentation [7], etc. However, these traditional methods mainly transfer the contaminants from wastewater to solid wastes. Therefore, neither simple chemical nor biological treatment has proved adequate for decoloration and for sufficient reduction of organic matter. Among the other chemical oxidation processes investigated for the treatment of dyes and effluents from dyeing plants, advanced oxidation processes (AOPs) are effective (under appropriate conditions) for color removal, detoxification, and mineralization of the effluents from textile dyeing mills [8,9]. To date, ultraviolet (UV)/H_2O_2 oxidation, the photo-Fenton and Fenton-like processes, have been reported to destroy various dye molecules [10,11]. The process in general demands the generation of $^{\bullet}OH$ radicals in solution in the presence of UV light. These radicals can then attack the dye molecules to destroy them or convert into simple harmless compounds [12].

Carmine is a representative example of an organic dye which belongs to the “natural” class of dyes, and is used in paints. Since dyes are suspected to be carcinogenic in nature, any presence of them in wastewater would have detrimental effects on marine and human life. The objective of the present study is to use response surface methodology (RSM) for the experimental design and optimization of carmine decoloration and use the reported experimental values of carmine decoloration study to verify the optimized conditions and see the reliability of the reported data. The statistical planning of the experiment is needed to analyze the collected data by statistical methods which result in valid and objective conclusions. Therefore, the statistical approach to experimental design is necessary to draw meaningful conclusions from the experimental data.

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]. Its greatest applications have been in industrial research, particularly in situations where a

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large number of variables influence the system feature. This feature termed as the response and normally measured on a continuous scale, represents the most important function of the systems [13,14].

Although the RSM was initially developed for the purpose of determining optimum operating conditions in the chemical industry, it is now used in various fields and applications in the physical sciences and engineering as well as in biological, clinical and social sciences [15]. In this study, response surface design was selected because it provides a reasonable distribution of data points throughout the region of interest, allows model adequacy including lack of fit, allows designs of higher order to be built up sequentially and provides an internal estimate of error. Response surface designs do not require a large number of runs and also do not require too many levels of the independent variables [13,14]. The success of the RSM depends on the approximation of response function by a low order polynomial in some region of the independent variables.

2. Materials and methods

2.1. Experimental

Carmine (C.I. name Natural Red 4, C.I. number 75470 and λ_{max} = 500 nm) was obtained from Fluka and was used as such. Deionized water was used to make the dye solutions of desired concentration. The structure of this dye is shown in Fig. 1. Hydrogen peroxide (35%, w/w) was obtained from Merck and was diluted in water right before use. UV–vis studies were carried out on a CARY 50 UV–vis spectrophotometer, using a 1 cm cell. For photolytic experiments, the samples were irradiated with a UV lamp (Upland model UVGL-58) with an output at 254 nm and operates at 50–60 Hz with a current intensity of 0.12 A. Since the purpose of studying photolytic oxidation of this dye is to extend the results to actual waste effluents present at normal temperatures, therefore no temperature changes were made during the course of the experiments and the present studies were carried out at room temperature (25 ± 2 °C).

2.1.1. Preparation of samples and decoloration studies

Carmine stock solution of 1×10^{-3} M was prepared in 100 mL of deionized water in a 250-mL flask. Necessary dilutions of this stock were done with deionized water to obtain a series of dye solutions with varying concentrations. An aliquot of the diluted solution was mixed with a given amount of H_2O_2 and the mixture was irradiated with UV light. After a certain time interval (2–5 min), the absorbance of the solution was monitored instantaneously on a spectrometer. The percent decoloration was found in the usual way [16]. Photolytic oxidation studies were carried out at 25 ± 2 °C. In order to obtain the optimized conditions of pH effect, initially the pH values were changed till the optimized conditions were obtained. For studying the effect of pH on dye decoloration, the pH of the dye solution was altered by adding incremental amounts of either diluted HCl or diluted NaOH. The solution was then subjected to UV light and change in absorbance value was noted to calculate the percent decoloration using the following equation:

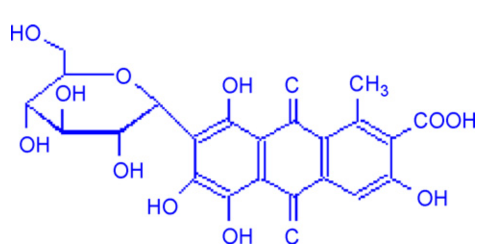

Fig. 1. Molecular structure of carmine.

Table 1
Experimental design of photolytic degradation of carmine dye with H_2O_2

Factor name	Low actual value	High actual value
[Carmine] (μM)	20	160
[H_2O_2] (mM)	0.83	6.64
pH	2	10
Reaction time (min)	0	30

$$\text{percent decoloration} = \left[\frac{A(\text{initial}) - A(\text{final})}{A(\text{initial})}\right] \times 100 \quad (1)$$

Complete experimental findings are reported elsewhere [16].

2.2. Experimental design and optimization

In this study, the photolytic decoloration of carmine via UV radiation in the presence of H_2O_2 was optimized using RSM by utilizing Design-Expert 7.1. The runs were designed in accordance with D-optimal design and carried out batch-wise. The D-optimal criterion can be used to select points for a mixture design in a constrained region. This criterion selects design points from a list of candidate points so that the variances of the model regression coefficients are minimized [13,14,17].

The main purpose in the present study was to find a suitable approximating function in order to predict and determine the future response, and to investigate the operating conditions in a region for the factors at a certain operating specifications. The independent variables of carmine concentration, H_2O_2 concentration, pH and reaction time was coded with low and high levels in D-optimal design as shown in Table 1, while decoloration of carmine dye was the response (dependent variable). The D-optimal designed experiments were augmented with three replications in order to evaluate the pure error and were carried in randomized order as required in many design procedures. Performance of the process was evaluated by analyzing the response of percentage decoloration. In the optimization process, the response can be simply related to chosen factors by linear or quadratic models. A quadratic model, which also includes the linear model, is given as

$$\eta = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} x_i x_j + e_i \quad (2)$$

where η is the response, x_i and x_j are variables, k is the number of independent variables (factors), β_0 is the constant coefficient, β_j, β_{jj} and β_{ij} are interaction coefficients of linear, quadratic and the second-order terms, respectively, and e_i is the error. In this study, decoloration/degradation percent data were processed by Eq. (2) including analysis of variance (ANOVA) to obtain the interaction between the process variables and the response. The quality of the fit of polynomial model was expressed by the coefficient of determination R^2 and R^2_{adj} in Eqs. (3) and (4), respectively. The statistical significance was checked with adequate precision ratio in Eqs. (5) and (6), and by the F-test in the program [17,18].

$$R^2 = 1 - \frac{SS_{residual}}{SS_{model} + SS_{residual}} \quad (3)$$

$$R^2_{adj} = 1 - \frac{SS_{residual}/DF_{residual}}{(SS_{model} + SS_{residual})/(DF_{model} + DF_{residual})} \quad (4)$$

$$\text{adequate precision} = \frac{\max(\hat{Y}) - \min(\hat{Y})}{\sqrt{\bar{V}(\hat{Y})}} \quad (5)$$

$$\bar{V}(\hat{Y}) = \frac{1}{n}\sum_{1=1}^{n} V(\hat{Y}) = \frac{p\sigma^2}{n} \quad (6)$$

In Eqs. (3)–(6), SS is the sum of squares, DF is the degrees of freedom, p is the number of model parameters, σ^2 is the residual mean square from ANOVA table, and n is the number of experiments.

3. Results and discussion

The decoloration studies were attempted by observing changes in the absorbance of the dye at 500 nm. Initially, experiments were carried out with either UV light or H_2O_2. The results showed that mere UV light or H_2O_2 alone did not result in any significant decoloration of this dye. However, when the dye solutions of various concentrations were mixed with H_2O_2 prepared in aqueous media and subjected to UV light, the dye started degrading immediately in the presence of H_2O_2 and the UV radiation. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time.

The batch runs were conducted in D-optimal designed experiments to visualize the effects of independent factors on the response and the results along with the experimental conditions. D-optimal is a good design choice because unlike the Central Composite and Box-Behnken designs, where there is a specific pattern to the design points, points in this design are chosen mathematically that satisfies statistical criteria called D-optimality.

A D-optimal design minimizes the determinant of the $[\mathbf{X}'\mathbf{X}]^{-1}$ matrix, which minimizes the volume of the confidence ellipsoid for the coefficients [13,14,18]. $[\mathbf{X}'\mathbf{X}]$ matrix has a special structure that the diagonal elements of $[\mathbf{X}'\mathbf{X}]$ are the sums of squares of the elements in the columns of $[\mathbf{X}]$, and the off-diagonal elements are the sums of cross-products of the elements in the columns of $[\mathbf{X}]$. The optimization in this study was performed to minimize the general variance of the coefficients in the model. D-optimal point selection chooses points from the candidate point set that are spread throughout the design region. The main key is that these designs are built algorithmically to provide the most accurate estimates of the model coefficients [13,14,18].

The experimental results were evaluated according to D-optimal design and approximating function of carmine degradation percent obtained in Eq. (7). The method of least squares was used to estimate the parameters in the approximating polynomial, and then the response surface analysis was done in terms of the fitted surface. The analysis of fitted surface is approximately equivalent to analysis of the actual system if the fitted surface is an adequate approximation of the true response function [13,14]. In most cases, the second-order model is adequate.

$$\hat{y} = -25.564 + 0.270x_1 + 13.160x_2 - 5.96x_3 + 3.418x_4 - 2.250 \times 10^{-3}x_1^2 - 1.196x_2^2 + 0.674x_2^2 - 0.054x_4^2 \quad (7)$$

In Eq. (7), $\hat{y}$ is the carmine degradation percent; x_1, x_2, x_3, and x_4 are corresponding to independent variables of carmine concentration (μM), H_2O_2 concentration (mM), pH and reaction time (min), respectively.

ANOVA results of this model presented in Table 2 indicate that it can be used to navigate the design space. The appropriate procedure for testing the equality of several means is the ANOVA which has a much wider application. It is probably the most useful technique in the field of statistical inference [13,14].

In Table 2, the model F-value of 741.33 implies that the model is significant for carmine degradation and there is only a 0.01% chance that a model F-value this large could occur due to noise. The model adequacy checking is an important part of the data analysis procedure. In general, it is always necessary to examine the fitted model to ensure that it provides an adequate approximation to the true system, and to verify that none of the least squares regression assumptions are violated. The regression model gives poor or misleading results unless it is an adequate fit [13,14]. In carmine degradation model, the adequate precision ratio of 108.17 indicates an adequate signal-to-noise ratio; a value greater than 4 is desirable. The P-values less than 0.0500 indicates that the model terms are significant, whereas the values greater than 0.1000 are not significant. In Table 2, all the terms are significant according to P-values.

Eq. (7) was used to visualize the effects of experimental factors on degradation percent response in Figs. 2–9. In Figs. 2–5, the residual plots were examined for the model adequacy checking. The normal % probability and studentized residuals plot is shown in Fig. 2 for carmine dye degradation. In Fig. 2, residuals show how well the model satisfies the assumptions of the ANOVA where the studentized residuals measure the number of standard deviations separating the actual and predicted values. This figure also shows that neither response transformation was needed nor there was any apparent problem with normality.

Fig. 3 shows the studentized residuals versus predicted carmine decoloration percent. The general impression is that the plot should be a random scatter, suggesting the variance of original observations to be a constant for all values of the response. This plot often exhibits a funnel-shaped pattern when the variance of the response depends on the mean level of $\hat{y}$ [13,14]. This also implies that there was no need for transformation of the response variable.

The actual and the predicted carmine decoloration percent is shown in Fig. 4. Actual values are the measured response data for

Table 2
ANOVA results of the quadratic model of photolytic degradation of carmine dye with H_2O_2

Source	Sum of squares (SS)	Degrees of freedom (DF)	Mean square (MS)	F-value	P-Value
Model	5472.81	8	684.10	741.33	<0.0001
A: [carmine] (μM)	209.77	1	209.77	227.32	<0.0001
B: [H_2O_2] (mM)	350.30	1	350.30	379.61	<0.0001
C: pH	144.50	1	144.50	156.59	<0.0001
D: reaction time (min)	3670.83	1	3670.83	3977.91	<0.0001
A^2	164.86	1	164.86	178.66	<0.0001
B^2	136.71	1	136.71	148.15	<0.0001
C^2	163.06	1	163.06	176.70	<0.0001
D^2	219.57	1	219.57	237.94	<0.0001
Residual	8.30	9	0.92		
Lack of fit	8.30	6	1.38		
Pure error	0	3	0		

R^2 = 0.998; R^2_{adj} = 0.997; adequate precision = 108.17 (>4).

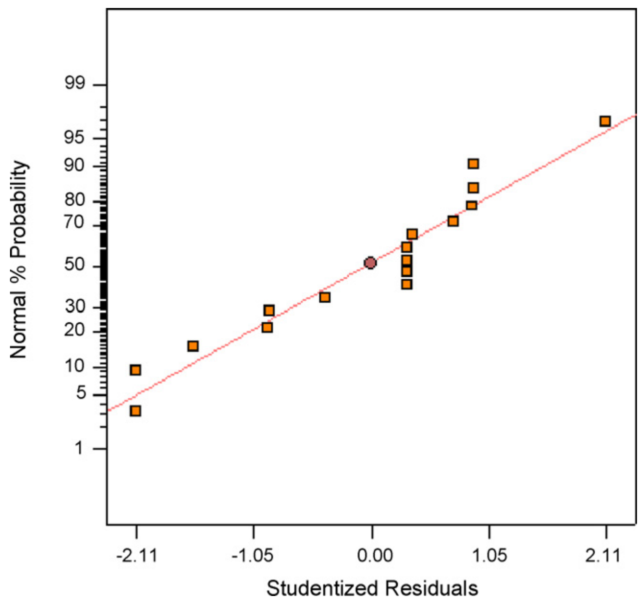

Fig. 2. The studentized residuals and normal % probability plot of photolytic degradation of carmine dye.

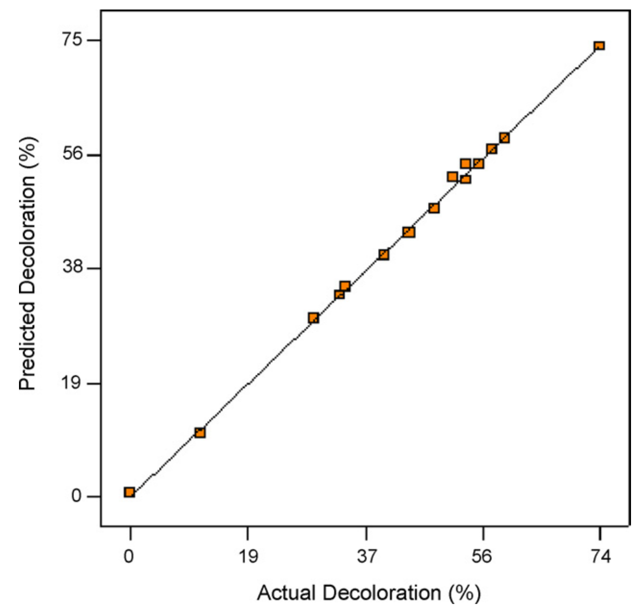

Fig. 4. The actual and predicted decoloration plot of carmine degradation (R^2 = 0.998, $R^2_{adj} = 0.997$).

a particular run, and the predicted values were evaluated from the model and generated by using the approximating function. In designed experiments, R^2 is a measure of the amount of reduction in the variability of the response obtained by using the independent factor variables in the model. However, a large value of R^2 does not necessarily imply that the regression model is a good one. Adding variable to the model always increases R^2, regardless of whether the additional variable is statistically significant or not. Thus it is possible for models that have large values of R^2 to yield poor predictions of new observations or estimates of the mean response. Although R^2 always increases on adding terms to the model, using an adjusted R^2 is preferred as defined in Eq. (4). In general, the adjusted R^2 does not always increases as variables are added to the model. In fact, if unnecessary terms are added, the value of R^2_{adj} often decreases. There is a good chance that insignificant terms have been included in the model when R^2 and R^2_{adj} differ dramatically [13,14]. The proposed model for D-optimal design fitted very well to the experimental data with R^2 and R^2_{adj} correlation coefficients of 0.998 and 0.997, respectively.

The sum of squares for regression always increases with the addition of a variable to the regression model. Therefore, the sufficiency of the increase in the regression sum of squares must be decided. Furthermore, adding an unimportant variable to the model can actually increase the mean square error, thereby decreasing the usefulness of the model [13,14].

In designed experiments, the outliers should be carefully examined, because they may represent something as simple as a data recording error or something of more serious concern, such as a region of the independent factor variable space where the fitted

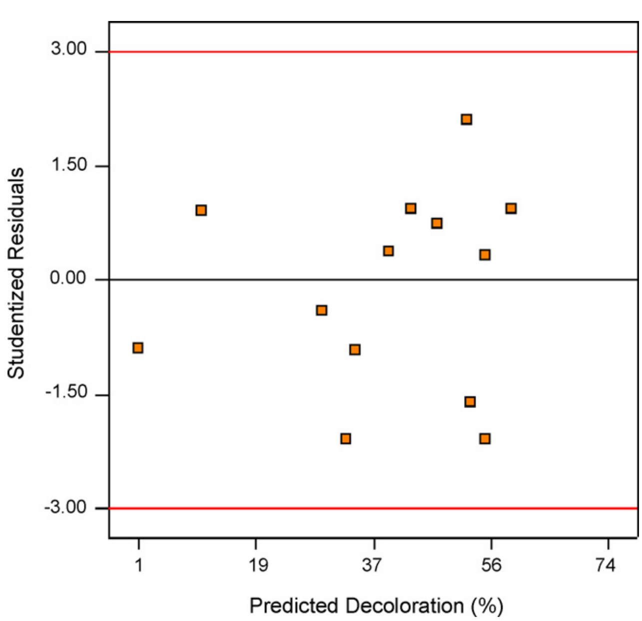

Fig. 3. The predicted decoloration of carmine dye and studentized residuals plot.

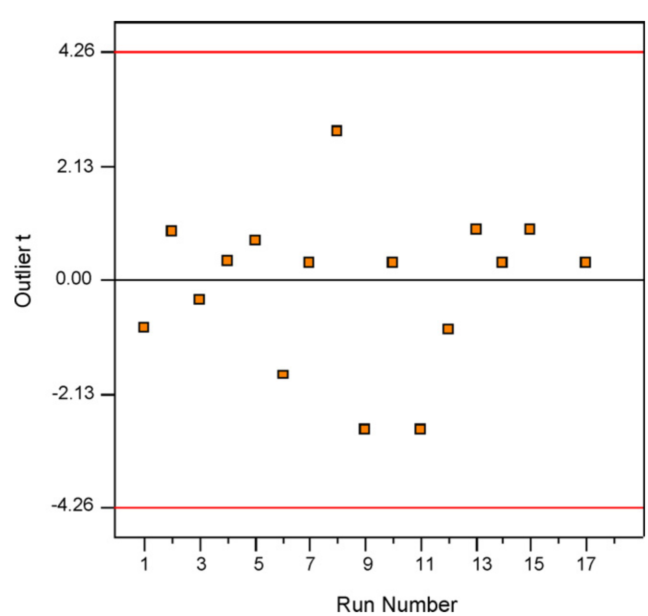

Fig. 5. The outlier t plot of decoloration of carmine dye.

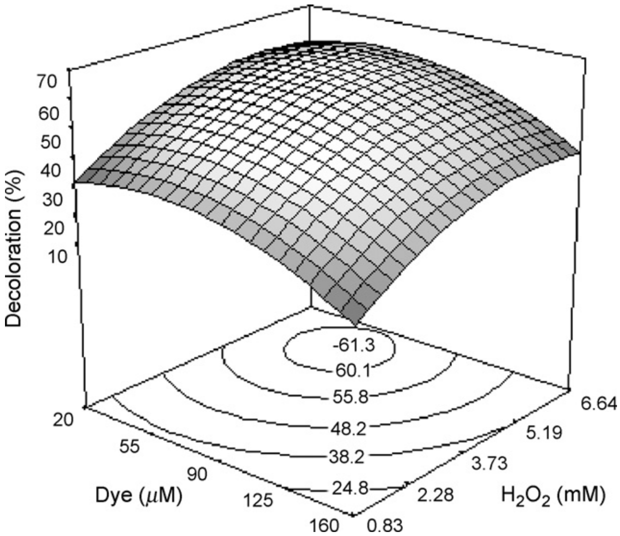

Fig. 6. The effect of carmine concentration and H_2O_2 concentration on carmine degradation (pH: 6; reaction time: 30 min).

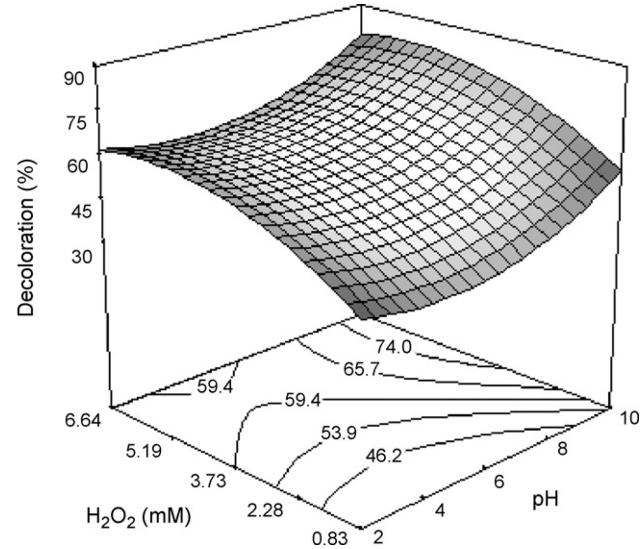

Fig. 8. The effect of H_2O_2 concentration and pH on carmine degradation ([carmine]: 62 μM; reaction time: 30 min).

model is a poor approximation to the true response surface [13,14]. In Fig. 5, outlier *t* plot for the batch runs of carmine dye decoloration is shown. The outlier *t* is a measure of how many standard deviations the actual value deviates from the predicted value. Most of the standard residuals should lie in the interval of ±3.50 and any observation with a standardized residual outside of this interval is potentially unusual with respect to its observed response [13,14]. In Fig. 5, the outlier *t* values below the interval of ±3.50 indicated that the approximation of the fitted model to the response surface was fairly good with no data recording error.

The response surface graphs for carmine degradation are shown in Figs. 6–8. In Fig. 6, the effect of carmine concentration and H_2O_2 concentration on carmine degradation is shown at pH 6. The semi-spherical response surface of decoloration slightly increased with increasing H_2O_2 concentration from 0.83 to 5.50 mM, and then decreased slightly above 5.50 mM. Similar trend was also observed at other carmine concentrations. The maximum value of decoloration was determined to be 61.3% at 62 μM carmine dye and 5.50 mM H_2O_2. In the scope of operational cost, the optimum dye and H_2O_2 concentration values were decided to be 62 μM and 5.50 mM, respectively.

The effects of initial carmine dye concentration and initial H_2O_2 concentration versus pH on carmine degradation within 30 min of reaction time are shown in Figs. 7 and 8. In Fig. 7, carmine decoloration percent increased with the increase in pH, whereas it decreased with the increase in dye concentration at optimum concentration of H_2O_2 (5.50 mM). Carmine decoloration percent increased with the increase in H_2O_2 concentration at optimum value of 62 μM carmine concentration as shown in Fig. 8.

In the perturbation plot (Fig. 9) the effects of all the factors at the optimal run conditions in the design space are compared. The perturbation plot helps to compare the effect of all the factors at a particular point in the design space. The response is plotted by changing only one factor over its range while holding the other factors constant. The plot was obtained for 62 μM carmine dye,

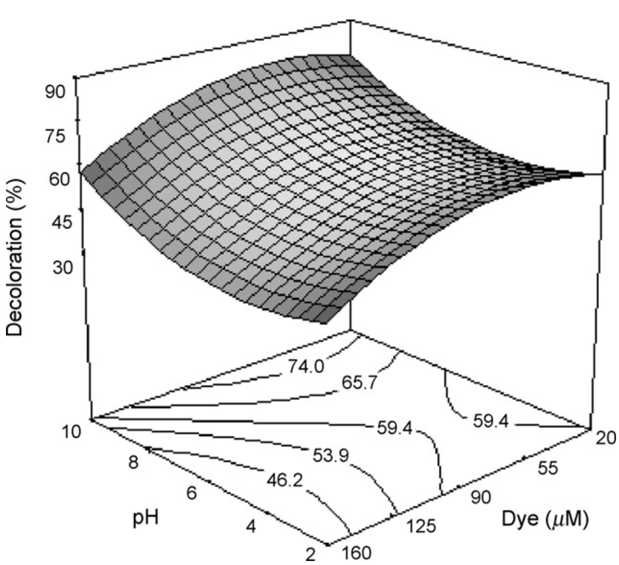

Fig. 7. The effect of carmine concentration and pH on carmine degradation ([H_2O_2]: 5.50 mM; reaction time: 30 min).

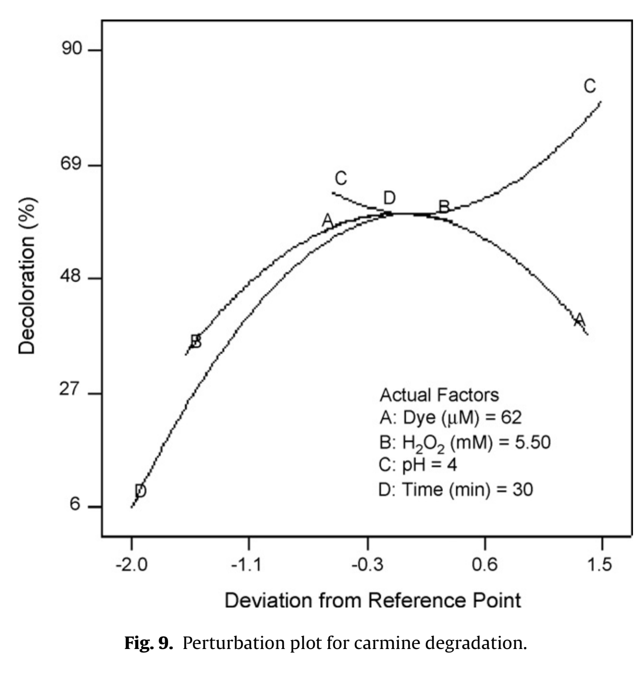

Fig. 9. Perturbation plot for carmine degradation.

5.50 mM H_2O_2, pH 4.0, and 30 min of reaction time. In Fig. 9, the steep curvatures in carmine concentration, H_2O_2 concentration, pH and reaction time factors show that the response of carmine degradation is very sensitive to these factors.

4. Conclusion

Under the optimized conditions of 62 μM dye, 5.5 mM H_2O_2, and pH 4, the experimental values agreed with the predicted ones, indicating suitability of the model and the success of RSM in optimizing the conditions of photo-oxidation of carmine dye. In the optimization, R^2 and R^2_{adj} correlation coefficients for quadratic model was evaluated quite satisfactorily as 0.998 and 0.997, respectively.

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