



Photolytic decolorization of Rose Bengal by UV/H₂O₂ and data optimization using response surface method

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ABSTRACT

Rose Bengal (C.I. name is Acid Red 94) was irradiated with UV light in the presence of hydrogen peroxide. The photoinduced decolorization of the dye was monitored spectrophotometrically. The apparent rate of decolorization was calculated from the observed absorption data and was found to be pseudo first order. A systematic study of the effect of dye concentration and H₂O₂ concentration on the kinetics of dye decolorization was also carried out. Dye decolorization increased with increasing H₂O₂ concentration and decreasing dye concentration. The maximum dye decolorization was determined as 90% with 0.005 mM dye at optimum 0.042 M H₂O₂ and pH 6.6. Additionally, the effect on decolorization of this dye in the presence of some additives (ions) was also investigated. It was seen that sulphite caused a maximum effect on % decolorization of the dye solution. A plausible explanation involving the probable radical initiated mechanism was given to explain the dye decolorization. The experimental data was also optimized using the response surface methodology (RSM). According to ANOVA results, the proposed model can be used to navigate the design space. It was found that the response of Rose Bengal degradation is very sensitive to the independent factors of dye concentration, H₂O₂ 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 0.85 and 0.80, respectively.

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1. Introduction

Treatment of industrial wastewater is more important than treating other colorless organics, because the presence of small amounts of dyes is clearly visible and has detrimental affects on the aquatic species [1–4]. New environmental policies in many countries apply strict regulations concerning wastewater discharge [5]; therefore, decolorization of dye effluents has attracted increased attention.

Many different techniques have been employed for removing pollutants from wastewater. These include adsorption, coagulation, ultrafiltration, sedimentation and the membrane process [6–11]. These are fairly effective in removing pollutants, however these techniques transform dyes in solution into solid forms, such that the secondary waste produced has to be either treated again or dumped as such. Advanced oxidation processes (AOPs) are alternative methods for decolorizing and reducing wastewater effluents generated by industries [12–19]. Most investigations employing the photo-assisted decomposition of dyes have utilized either H₂O₂, Fenton's reagent, ozonation or TiO₂ in their treatment procedures. In our

present study we are reporting the decolorization studies of Rose Bengal using H₂O₂ in the presence of UV light. Rose Bengal (C.I. name is Acid Red 94) is a tetraiodo-substituted dye of the xanthene class of dyes. It exhibits unusual spectroscopic and photochemical properties including a large absorption coefficient in the visible region and a high tendency for intersystem crossing to produce a photochemically active triplet excited state. The dye has been used in photodynamic inactivation of catalase, photoinactivation of olefins via the production of singlet oxygen, as a photosensitizing agent for inactivating biological species such as vaccinia virus, microsomal glucose-6-phosphatase, trypsin, *Escherichia coli*, acetylcholinesterase, and HL-60 cells [20–22]. Despite the numerous applications of Rose Bengal dye in various areas, information on its photolytic decolorization is not available in the literature. We studied the decolorization of this molecule by UV/H₂O₂ because of the reason that in this approach •OH radicals are directly produced from H₂O₂ on irradiation with UV light [23,24]. These radicals can then take part in subsequent reaction to decolorize the dye solution. Another part of the present study was to use response surface methodology (RSM) and find a suitable approximating function in order to predict and determine the future response, and to investigate the optimum operating conditions in a region for which the factors at a certain operating specifications are met. RSM is essentially a particular set of mathematical and statistical methods for

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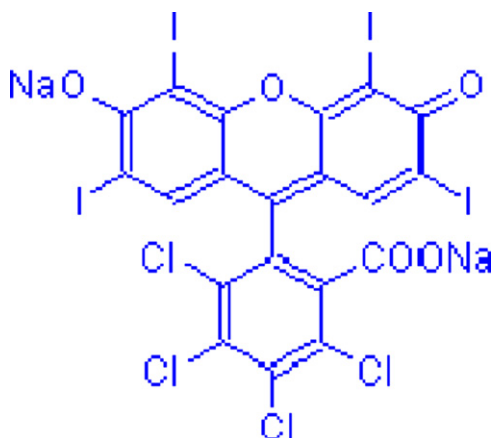


Fig. 1. Molecular structure of Rose Bengal.

designing experiments, building models, evaluating the effects of variables, and searching optimum conditions of variables to predict targeted responses [25–33]. RSM is an important branch of experimental design and a critical tool in developing new processes, optimizing their performance, and improving design and formulation of new products. Its greatest applications have been in industrial research, particularly in situations where a large number of variables influence the system feature. This feature which is termed as response and normally measured on a continuous scale represents the most important function of the system [34]. One is often interested in finding a suitable approximating function for the purpose of predicting and determining the future response. Response surface procedures are not only primarily used for the purpose of allowing the researcher in order to understand the mechanism of the system or process; rather its purpose is to determine the optimum operating conditions or to determine a region for the factors at a certain operating specification.

2. Experimental

2.1. Materials

The dye under investigation was Rose Bengal (M.wt. = 1017.7, C.I. name is Acid Red 94, C.I. number = 45440, λ_{\max} = 500 nm). The dye with a labeled purity of more than 90% was obtained from either Sigma or Aldrich and used as such. The structure of the dye is given in Fig. 1. The decolorization studies were attempted by observing changes in the absorbance value of the dye at 500 nm. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time. Deionized water was used to make the dye solutions of desired concentration. For studying the effect of pH on dye decolorization, the pH of the dye solution was altered by adding incremental amounts of either dilute HCl or diluted NaOH.

2.2. Preparation of samples and decolorization studies

Dye 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, the absorbance of the solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the order of apparent decolorization rate. Photolytic oxidation studies were carried out at $25 \pm 2^\circ\text{C}$.

Table 1

Experimental design of photolytic decolorization of Rose Bengal (C.I. Acid Red 94) dye with H_2O_2

Factor name	Low actual value	High actual value
Dye (mM)	0.005	0.030
H_2O_2 (M)	0.01	0.05
pH	3.75	10.0

For photolytic experiments, the samples were irradiated with a UV lamp (UVGL-58, J-129, Upland make). The instrument operates at 0.12 A with a UV output at 365 and 254 nm, however, the lamp was selectively used in the 254 nm output mode (by using appropriate cut off filters) for these studies. For experiments examining the effects of different ions on the decolorization of Rose Bengal, a final concentration of 500 mg L^{-1} of various salts were added to the dye solution before the addition of H_2O_2 . The solution was then subjected to UV light and change in absorbance value was noted to calculate the apparent decolorization.

2.3. Experimental design and optimization

The experimental results were subsequently analyzed by using the RSM which was used for the experimental design and optimized conditions. In this study, the photolytic decolorization of Rose Bengal (C.I. name is Acid Red 94) via UV radiation in the presence of H_2O_2 was optimized using RSM by 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 [25]. The set of candidate points to use should depend upon the order of the model the experimenter wishes to fit [26]. The independent variables of dye concentration, pH and H_2O_2 concentration was coded with low and high levels in D-optimal design as shown in Table 1, while decolorization of dye was the response (dependent variable).

The D-optimal designed experiments were carried out with six 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 decolorization percent. In the optimization process, the responses can be simply related to chosen factors by linear or quadratic models. A quadratic model, which also includes the linear model, is given as [35]

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

where η is the response, x_i and x_j are variables, β_0 is the constant coefficient, β_j , β_{jj} s and β_{ij} s are interaction coefficients of linear, quadratic and the second-order terms, respectively, and e_i is the error. In the study, decolorization percent data were processed by Eq. (1) including 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 namely R^2 and R_{adj}^2 . The statistical significance was checked with adequate precision ratio and by the F-test.

3. Results and discussion

3.1. Photodecolorization of Rose Bengal

In the present work, the kinetics of H_2O_2 assisted photochemical oxidation of Rose Bengal (RB) was investigated. Initially, experi-

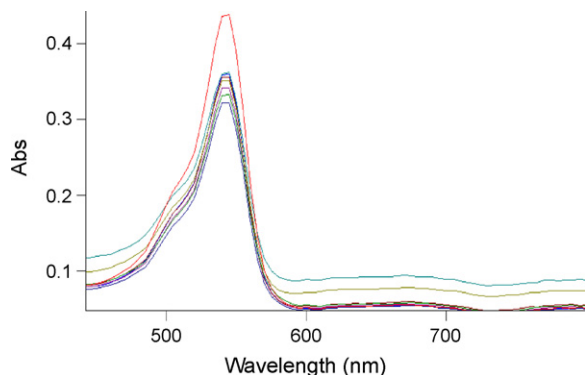


Fig. 2. Decrease in absorbance value of Rose Bengal with time.

ments were carried out with either UV light or H_2O_2 alone. The results showed that mere UV light or H_2O_2 alone did not result in any significant decolorization of this dye. However when the dye solutions of various concentrations were mixed with H_2O_2 and subjected to UV light, the dye started degrading immediately in the presence of H_2O_2 and the UV radiation. Percentage decrease in absorption was calculated as follows [13]

$$\% \text{ decrease in absorption} = \left[\frac{(A_i - A_f)}{A_i} \right] \times 100 \quad (2)$$

where A_i and A_f are the initial and final absorbance values of solution before and after irradiation. The change of absorption value which is a measure of its decolorization, as a function of irradiation time is depicted in Fig. 2. The kinetics of dye decolorization with respect to its change in absorption values fitted well to a pseudo first order rate equation [14]

$$\ln(A_i) - \ln(A_f) = kt \quad (3)$$

where k is the apparent rate constant, t is the irradiation time and A_i and A_f are the initial and the final absorbance values of the dye solution, respectively. A typical form of this kinetic trend is shown in Fig. 3.

The decolorization of the dye solution is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light [16]



Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates which can cause the decolorization of the original solution [13]



Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the decolorization reaction of the dye molecule [24].

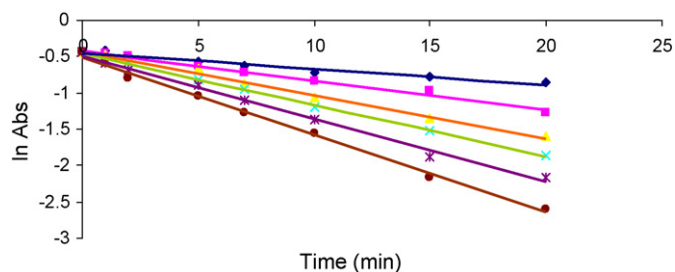


Fig. 3. Kinetics of Rose Bengal decolorization (dye conc = 5×10^{-6} M) with changing concentration of H_2O_2 (\blacklozenge = 0.01, \blacksquare = 0.015, \blacktriangle = 0.02, $*$ = 0.03, \bullet = 0.04 mM).

Table 2

Effect of dye concentration on % decolorization with changing amount of H_2O_2 (irradiation time = 20 min)

Dye (M)	% decolorization ($H_2O_2 = 0.02$ M)	% decolorization ($H_2O_2 = 0.04$ M)
3×10^{-5}	20	56
2.5×10^{-5}	21	58
2×10^{-5}	24	68
1.5×10^{-5}	26	80
1×10^{-5}	28	82
5×10^{-6}	68	88

Table 3

Effect of H_2O_2 on % decolorization with changing amount of dye (irradiation time = 20 min)

H_2O_2 (M)	% decolorization (dye = 1×10^{-5} M)	% decolorization (dye = 3×10^{-5} M)	% decolorization (dye = 3×10^{-5} M)
0.01	13	18	34
0.02	28	20	68
0.03	45	50	82
0.04	82	56	88
0.05	48	50	80

To optimize the decolorization kinetics of the dye, we carried out a systematic study varying the concentration of both H_2O_2 and of Rose Bengal. Tables 2 and 3 show the effect of various variables on % decolorization of the dye solutions. The dye decolorization increased with H_2O_2 concentration (as shown in Table 3), however, at high concentrations of H_2O_2 the increase in dye decolorization started decreasing. This is because of the reason that at high concentrations, the solution undergoes self quenching of $\cdot OH$ radicals by added amounts of H_2O_2 to produce $HO_2\cdot$ radicals [14]



The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/ H_2O_2 . Fig. 4 shows the % change in decolorization of the dye at three different pH values. The photolytic dye decolorization appears to be less in more acidic solution and increases to a maximum value at pH 6.6 and then again starts decreasing in alkaline media. The enhancement in dye decolorization in less acidic conditions is most likely due to the fact that peroxide anions (HO_2^-) are produced in solution by UV radiation, which in turn can generate more OH radicals [16]

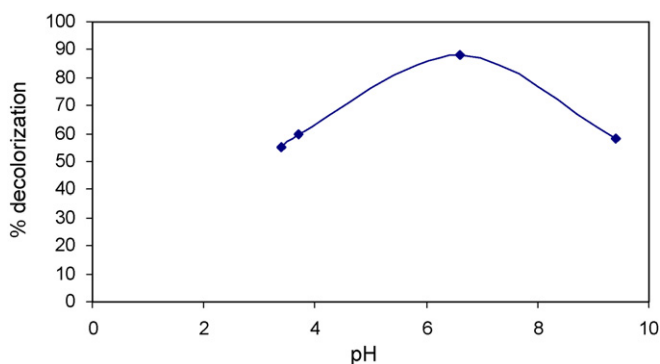


Fig. 4. Effect of pH on % decolorization (dye = 5×10^{-6} M, $H_2O_2 = 0.04$ M, time = 20 min).

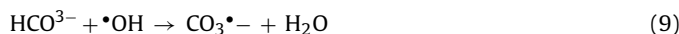
Table 4

Effect of ions on % decolorization (dye = 5×10^{-6} M, $H_2O_2 = 0.04$ M, irradiation time = 20 min, pH 6.6)

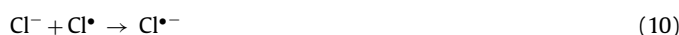
Ions	% decolorization
Pure dye solution	88
Carbonate	74
Bicarbonate	84
Chloride	82
Nitrate (as sodium salt)	76
Phosphate	78
Sulphate	80
Sulphite	68

3.2. Effect of additives

It has been previously shown that ions that are normally present in solution can have dramatic effects on the kinetics of dye decolorization [23]. Therefore, we tested the effects of various anions on the photolytic decolorization of Rose Bengal. None of the salts used had any effect on the dye spectra in the absence of UV light. The results of this study are shown in Table 4. It can be seen from this table that all the anions had some effect on % decolorization. The presence of CO_3^{2-} and HCO_3^- ions also effected the dye decolorization. In the presence of these ions, dye decolorization decreased slightly. This can be explained on the basis that the presence of these ions scavenge the $\bullet OH$ radicals according to the following reactions thus causing a decrease in percentage decolorization [23]



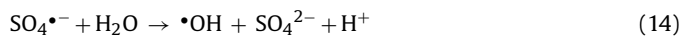
Similarly, the decrease in decolorization value in the presence of Cl^- is due to hydroxyl radical scavenging effect, which occurs as follows [23]



The presence of sulphate ions in solution also caused a slight decrease in percentage decolorization because these ions can react with $\bullet OH$ radicals in solution and result in their depletion as follows [16]



The sulphate radical ions can further react with water molecules to produce more sulphate ions as follows:



Since $SO_4^{\bullet-}$ is less reactive than $\bullet OH$ radicals, therefore SO_4^{2-} concentration increases in solution which leads to less dye decolorization.

Table 5

ANOVA results of the quadratic model of photolytic decolorization of Rose Bengal (C.I. Acid Red 94) dye with H_2O_2

Source	Sum of squares	Degrees of freedom	Mean square	F-value	P-value
Model	18812.09	7	2687.44	19.86	<0.0001
x_1 : dye (mM)	4041.15	1	4041.15	29.86	<0.0001
x_2 : H_2O_2 (M)	8619.69	1	8619.69	63.69	<0.0001
x_3 : pH	52.58	1	52.58	0.39	0.5387
x_1x_2	0.044	1	0.044	3.23×10^{-4}	0.9858
x_1^2	1457.11	1	1457.11	10.77	0.0030
x_2^2	1494.26	1	1494.26	11.04	0.0027
x_3^2	1592.46	1	1592.46	11.77	0.0021
Residual	3383.38	25	135.34		
Lack of fit	3383.38	19	178.07		
Pure error	0	6	0		

$$R^2 = 0.85; R_{adj}^2 = 0.80; \text{adequate precision} = 15.58$$

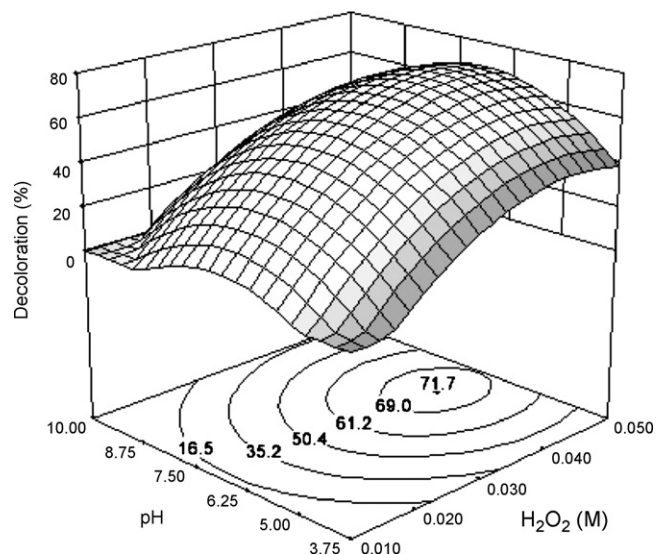
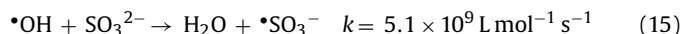


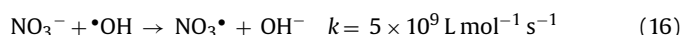
Fig. 5. The effect of initial H_2O_2 concentration and pH on dye decolorization ([Dye] = 0.010 mM).

The maximum change in percent decolorization was observed in the case of sulphite anions, which reduced this to 68%. This can be explained by the fact that sulphite anions can readily react with hydroxyl radicals as shown below [36]



The above reaction causes a depletion of $\bullet OH$ radicals in solution, thereby affecting the overall % decolorization.

Likewise the decrease in decolorization value in the presence of NO_3^- is due to hydroxyl radical scavenging effect, which occurs as follows [37]



Photolysis of phosphate ions also produces phosphate radicals. These radical exists in three acid–base forms, $H_2PO_4^{\bullet}$, $HPO_4^{\bullet-}$ and $PO_4^{\bullet 2-}$.



$H_2PO_4^{\bullet}$ is more reactive as compared to the other two species. Phosphate radicals abstract hydrogen from saturated organic compounds, add to olefins, and oxidize many organic and inorganic compounds with moderate or high rate constants ($k \approx 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$, refs. [38,39]).

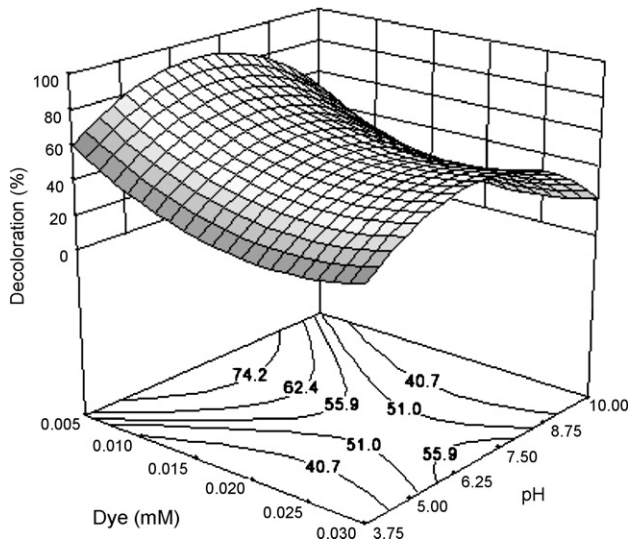


Fig. 6. The effect of initial dye concentration and pH on dye decolorization ($[H_2O_2]_{opt} = 0.042$ M).

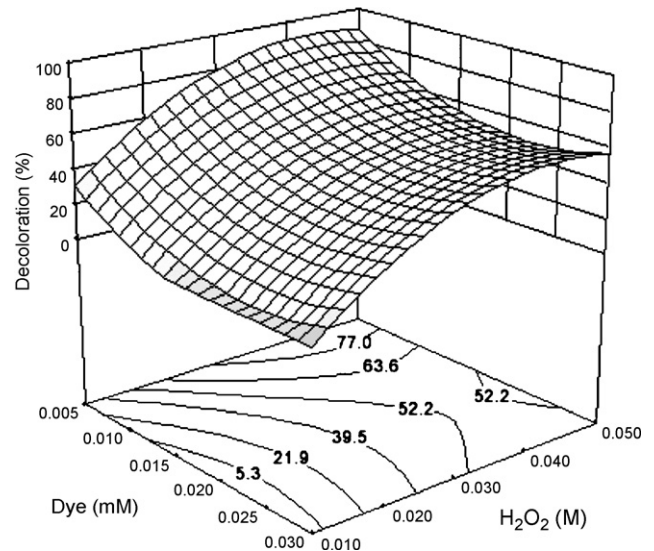


Fig. 7. The effect of dye concentration and H_2O_2 concentration on dye decolorization ($pH_{opt} = 6.60$).

3.3. Analysis by RSM

In the first step of the study, the effect of operating variables of initial dye concentration, H_2O_2 concentration and pH on decolorization of Rose Bengal (C.I. Acid Red 94) dye was investigated using response surface methodology according to D-optimal design. In the second step, the main objective was to select the H_2O_2 concentration and pH in order to achieve optimal decolorization of Rose Bengal (C.I. Acid Red 94) dye.

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 [25]. The experimental results were evaluated and approximating function of dye decolorization percent were obtained in Eq. (16),

$$\hat{y} = -5466.60x_1 + 4748.85x_2 + 46.66x_3 + 304.92x_1x_2 + 1.21 \times 10^5x_1^2 - 5.58 \times 10^4x_2^2 - 3.49x_3^2 - 142.78 \quad (16)$$

where \hat{y} is the dye decolorization percent; x_1 , x_2 and x_3 are corresponding to independent variables of dye concentration (mM), H_2O_2 concentration (M) and pH, respectively. ANOVA results of this quadratic model presented in Table 5 indicate that it can be used to navigate the design space. The model F -value of 19.86 in this table implies that the model is significant for dye decolorization and there is only a 0.01% chance that a model F -value this large could occur due to noise. The adequate precision ratio of 15.58 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 5 shows the results of this model when applied to dye concentration (x_1) and H_2O_2 concentration (x_2). The terms are significant according to P -values.

Eq. (16) has been used to visualize the effects of experimental factors on decolorization percent response in Figs. 5–13. The model adequacy checking was performed to determine the approximating model that would give poor or misleading results if it were an inadequate fit.

The dye decolorization percent response surface graphs are shown in Figs. 5–7. The effect of H_2O_2 concentration and pH on dye decolorization percent is shown in Fig. 5 as a semispherical response surface plot. The dye decolorization percent increased up

to pH 6.60 and above this value decreased with the increase in pH, and increased with the increase in H_2O_2 concentration up to 0.042 M and did not change significantly above this concentration value. The maximum dye decolorization obtained was 72% at the optimum point of 0.042 M H_2O_2 , pH 6.6, 0.010 mM initial dye concentration. Fig. 6 shows the effect of dye concentration and pH on dye decolorization percent at optimum 0.042 M H_2O_2 concentration. The dye decolorization percent increased with the increase in pH at the optimum value of 6.6 and above this value decreased with the increase in pH. The dye decolorization percent decreased with the increase in initial dye concentration at all pH values. In Fig. 7, the effect of dye concentration and H_2O_2 concentration on dye decolorization is shown at optimum pH 6.6. Dye decolorization increased with increasing H_2O_2 concentration and decreasing dye concentration. The maximum dye decolorization was determined as 90.0% with 0.005 mM dye at optimum 0.042 M H_2O_2 and optimum pH 6.6.

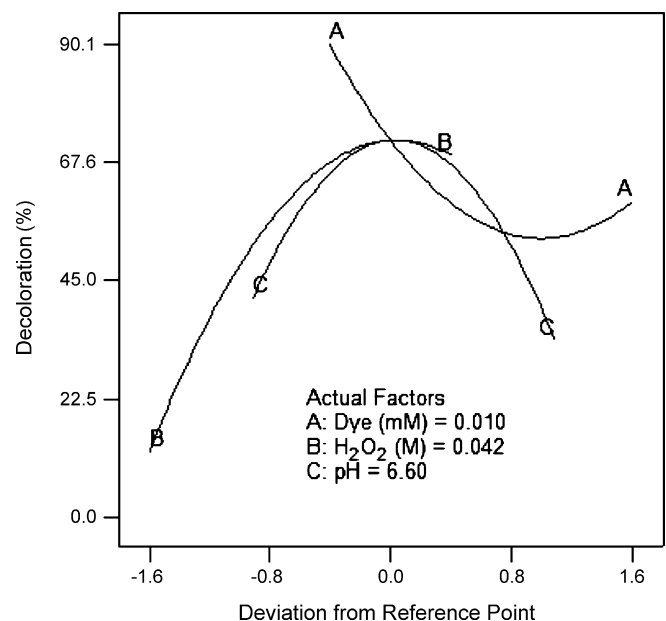


Fig. 8. Perturbation plot for dye decolorization.

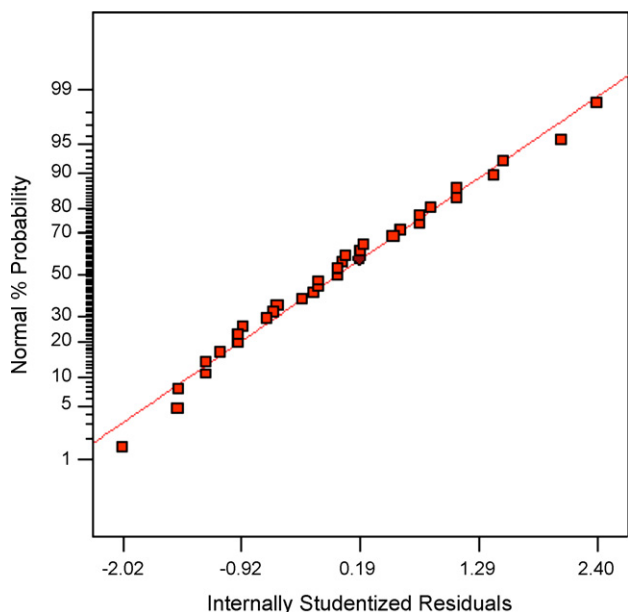


Fig. 9. The internally studentized residuals and normal % probability plot of photolytic decolorization of dye.

In the perturbation plot (Fig. 8) the effects of all the factors at the optimal run conditions in the design space are compared. The plot was obtained at 0.010 mM dye, 0.042 M H₂O₂ and pH 6.6. In Fig. 8, a steep curvature in dye concentration, H₂O₂ concentration and pH factors show that the response of dye decolorization is very sensitive to all of these factors.

The diagnostic plots of this optimization study are shown in Figs. 9–13. The normal probability and internally studentized residuals plot is shown in Fig. 9 for dye decolorization percent. The residuals show how well the model satisfies the assumptions of the analysis of variance (ANOVA) whereas the internally studentized residual is the residual divided by the estimated standard deviation of the residual that measures the number of standard deviations separating the actual and predicted values [33]. The data

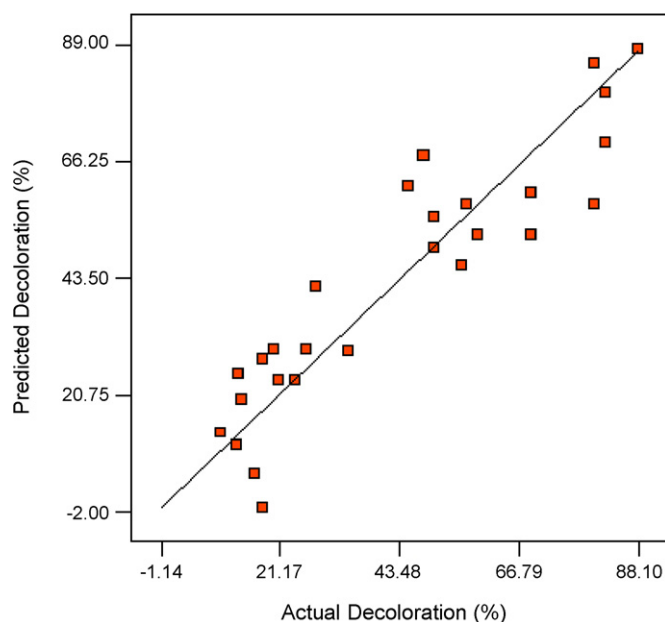


Fig. 11. The actual and predicted plot of dye decolorization ($R^2 = 0.85$, $R^2_{adj} = 0.80$).

points lying on the straight line in Fig. 9 indicate that there was no apparent problem with the normality.

Fig. 10 shows the internally studentized residuals and predicted dye decolorization percent. The general impression is that the plot should be a random scatter rather than a funnel-shaped pattern, suggesting the variance of original observations is constant for all values of the response [34]. This figure is also indicating that there was not any apparent problem with the response variable.

The actual and the predicted dye decolorization percent is shown in Fig. 11. Actual values are the measured response data for a particular run, and the predicted values were evaluated from the model and generated by using the approximating functions. In this figure, the values of R^2 and R^2_{adj} were determined to be 0.85 and 0.80, respectively. The fair correlation coefficients might have

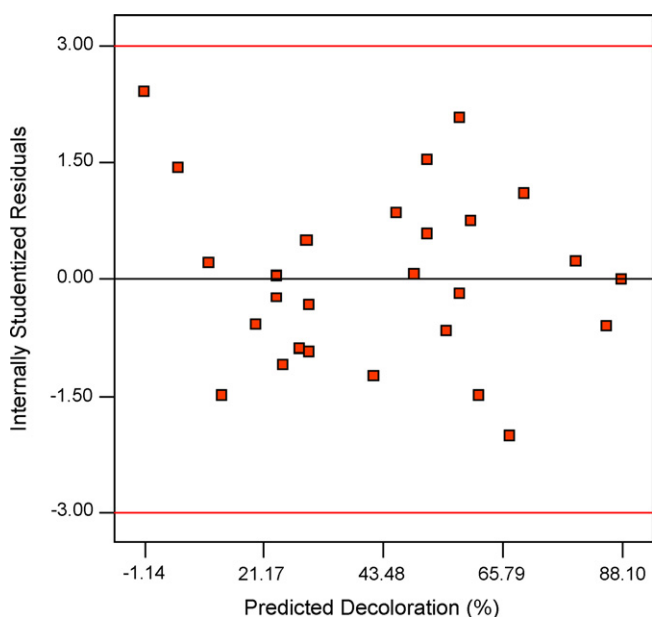


Fig. 10. The predicted decolorization of dye and internally studentized residuals plot.

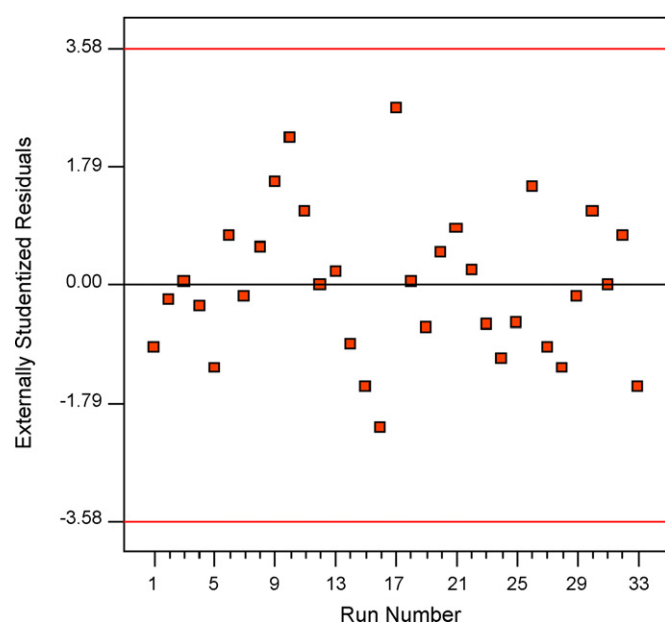


Fig. 12. The externally studentized residuals plot for the batch runs of dye decolorization.

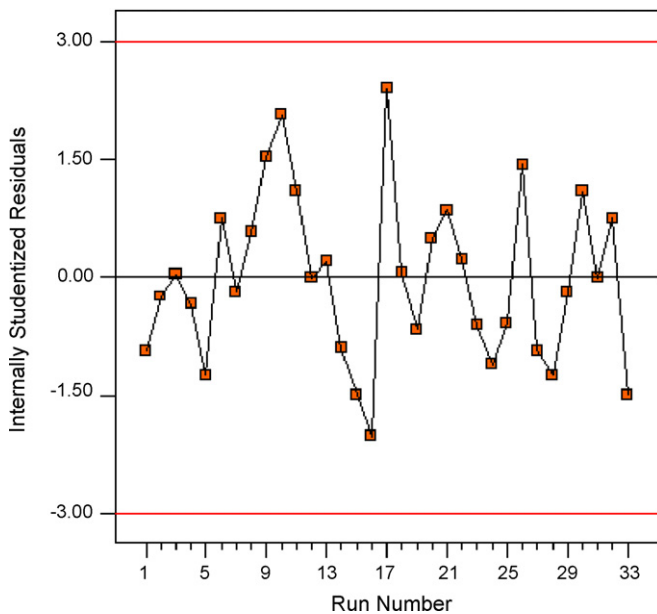


Fig. 13. The internally studentized residuals plot for the batch runs of dye decolorization.

resulted by the insignificant x_3 and x_1x_2 terms in Table 5, and most likely due to three different variables selected in wide ranges with a limited number of experiments as well as the nonlinear influence of the investigated parameters on process response [27].

The externally and internally studentized residuals plots for the batch runs of Rose Bengal (C.I. Acid Red 94) dye decolorization is shown in Figs. 12 and 13. The externally studentized residuals are the 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 [28]. In Figs. 12 and 13, the externally and internally studentized residual values below the interval of ± 3.50 indicate that the approximation of the fitted model to the response surface was fairly good with no data recording error.

4. Conclusion

The photo-oxidation of Rose Bengal was monitored spectrophotometrically. The apparent rate of decolorization was found to fit the pseudo first order kinetics. The dye decolorization was dependent on its concentration, amount of hydrogen peroxide, time of irradiation and pH of the solution. Dye decolorization increased with increasing H_2O_2 concentration and decreasing dye concentration. The maximum dye decolorization was determined as 90% with 0.005 mM dye at optimum 0.042 M H_2O_2 and pH 6.6. It was seen that added amounts of ions caused a changed in % decolorization of the dye; the effect was more pronounced in the case of sulphite ions. This was explained in terms of scavenging of $\bullet OH$ radicals by the additives. The experimental data was also optimized using the RSM and the ANOVA results were evaluated. It was found that the response of Rose Bengal degradation is very sensitive to the independent factors of dye 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 0.85 and 0.80, respectively.

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