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Application of response surface analysis to the photolytic degradation of Basic Red 2 dye

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Abstract

In this study, the photolytic degradation of Basic Red 2 (BR2) via UV radiation in the presence of H_2O_2 was optimized using response surface methodology (RSM). Under the optimized conditions of 20 μM BR2, 1.67 mM H_2O_2, and pH 7.6, the ANOVA results indicated that the proposed model can be used to navigate the design space. It was found that the response of BR2 degradation is very sensitive to the independent factors of BR2 concentration and H_2O_2 concentration. In the optimization, R^2 and R^2_{adj} correlation coefficients for the model were evaluated as 0.89 and 0.80, respectively.

Keywords: Photolysis; Degradation; Basic Red 2; Dye removal; Optimization; Response surface methodology (RSM)

1. Introduction

Industrial effluent discharge poses a big threat to our environment and its safe handling is a challenge for scientists [1,2]. Numerous chemicals such as dyes are extensively employed to impart color to various industrial products. There are many kinds of dyes available in the market such as azo, anthraquinone, triarylmethane, diarylmethane, acridine, quinine, xanthenes, and nitro dyes. Safranin-O (C.I name is Basic Red 2 (BR2)) is a representative example of an organic dye, which belongs to the Quinone–Imine class, and is widely used for counterstaining purposes, for example, as a metachromatic method for cartilages which is stained yellow. Since the dye is known to be carcinogenic in nature, the presence of even trace amounts of this dye in wastewater would have detrimental effects on marine life.

Numerous efforts have been devoted to develop technologies that are able to minimize the hazardous effects caused by industrial activities. The many different traditional treatment techniques applied in industrial wastewaters, such as coagulation/flocculation, membrane separation (ultra filtration, reverse osmosis) or elimination by activated carbon adsorption, only produce a secondary pollutant, whereas biological treatment is not a complete solution to the problem due to biological resistance of some dyes [3–7]. The use of advanced oxidation processes (AOP's), like UV/H_2O_2, photocatalytic, Fenton and photo-Fenton processes, has shown promising results as these processes appear to have the capacity to completely decolorize and partially mineralize the textile industry dyes in short reaction time, as shown by several studies [8–10]. Advance oxidation processes based on the UV/ H_2O_2 system have shown high efficiency in the degradation of several organic compounds of environmental relevance [11–14]. In UV/H_2O_2 process one can produce the oxidizing species such as hydroxyl radical ($^\bullet$OH) which has the oxidation potential of 2.8 eV and can completely destroy the pollutants present in waste water or convert them into simple harmless compounds.

In this study, response surface methodology (RSM) was used for the experimental design and optimization of BR2 decoloration. The experimental conditions for the decoloration of this dye have already been reported [11]. 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 [15,16]. It 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 [17]. RSM has shown promising results in industrial research, particularly in situations where a large

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number of variables influence the system feature. This feature termed as response, and normally measured on a continuous scale, represents the most important function of the systems [18].

2. Materials and methods

2.1. Experimental

The dye under investigation namely Safranin-O (C.I name is BR2, F.wt = 350.84) with a labeled purity of more than 90% was obtained from Sigma and used as such. The structure of this dye is shown in Fig. 1. Deionized water was used to make the dye solutions of desired concentration. Hydrogen peroxide (35% w/w) was obtained from Merck and was diluted in water right before use. UV–vis studies were done on a CARY 50 UV–vis spectrophotometer, using a 1 cm quartz cell. 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 used in the 254 nm output mode for these studies. Experimental details are already reported in our earlier paper [11].

2.1.1. Preparation of samples and decoloration studies

BR2 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 for different periods of time. After irradiation, the absorbance of the solution was monitored instantaneously on a spectrometer. The change in absorbance value obtained in each case was used to obtain the percentage decoloration of the dye solution. Photolytic oxidation studies were carried out at $25 \pm 2\,°C$.

2.2. Experimental design and optimization

In this study, the photolytic degradation of BR2 via UV radiation in the presence of H_2O_2 was optimized by RSM using the Design Expert 6.0 [19]. The runs were designed in accordance with D-optimal design and carried out batchwise. 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. The set of candidate points to be used should depend upon the order of the model the experimenter wishes to fit [19]. The main purpose of 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.

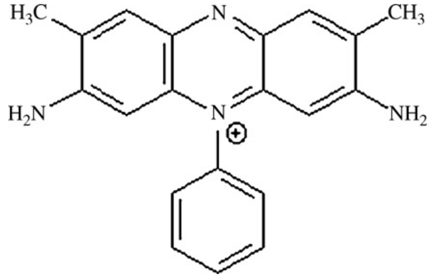

Fig. 1. Structural formula of Safranin-O {C.I name is Basic Red 2}.

Table 1
Application of response surface analysis on photolytic degradation of Basic Red 2 dye

Factor name	Low actual value	High actual value
[BR2] (μM)	5	50
[H_2O_2] (mM)	0.21	1.67
pH	3.0	11.0

The independent variables of BR2 concentration, pH and H_2O_2 concentration was coded with low and high levels in D-optimal design as shown in Table 1, while degradation of BR2 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 a randomized order as required in many design procedures. Performance of the process was evaluated by analyzing the response of degradation percentage.

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;

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

where η is the response, x_i and x_j are variables, β_o is the constant coefficient, β_j's, 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 this study, percent degradation 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 R^2 and R^2_{adj}. The statistical significance was checked with adequate precision ratio and by the F-test.

3. Results and discussion

Dye solutions of various concentrations in the presence of 1.67 mM H_2O_2 were 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 rate of degradation was monitored by measuring the decrease in absorption value of the peak at 520 nm in the visible region. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time. The percentage decoloration was calculated as follows:

$$\text{Percentage decrease in absorption} = [1 - (A_f/A_i)] \times 100 \quad (2)$$

where A_i and A_f are initial and final absorbance values. A systematic study was done to monitor the dye decoloration by altering

Table 2
ANOVA results of the quadratic model of photolytic degradation of Basic Red 2 (BR2) dye with H_2O_2

Source	Sum of squares	Degrees of freedom	Mean square	*F*-value	*P*-value
Model	7225.20	6	1204.20	9.71	0.0042
A: [BR2]	3667.40	1	3667.40	29.56	0.0010
B: [H_2O_2]	2321.66	1	2321.66	18.71	0.0035
C: pH	8.04	1	8.04	0.06	0.8064
A^2	107.60	1	107.59	0.87	0.3827
B^2	95.37	1	95.37	0.77	0.4097
C^2	209.90	1	209.90	1.69	0.2346
Residual	868.51	7	124.07		
Lack of fit	868.51	6	144.75		
Pure error	0	1	0		

$R^2 = 0.89$, $R^2_{adj} = 0.80$, adequate precision = 8.76.

the dye concentration, concentration and pH. The results have already been reported [11]. This paper is an attempt to use our previous experimental findings and put it to test with respect to theoretical analysis (called as RSM analysis) and see the match between the two approaches.

In using the RSM approach, 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. The experimental results were evaluated and approximating function of BR2 degradation percent obtained in Eq. (3).

$$\hat{y} = 68.759 - 0.489x_1 + 73.465x_2 - 11.773x_3 - 0.019x_1^2 - 21.620x_2^2 + 0.809x_3^2 \quad (3)$$

In Eq. (3), $\hat{y}$ is the BR2 degradation percent; x_1, x_2, and x_3 correspond to independent variables of BR2 concentration (μM), H_2O_2 concentration (mM) and pH, respectively.

ANOVA results of this model presented in Table 2 indicate that it can be used to navigate the design space. In Table 2, the model *F*-value of 9.71 implies the model is significant for BR2 degradation and there is only a 0.42% chance that a model *F*-value this large could occur due to noise. In BR2 degradation model, the adequate precision ratio of 8.76 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 nonsignificant. Table 2 shows the results of this model when applied to BR2 concentration and H_2O_2 concentration. The terms are significant according to *P*-values.

Equation (1) has been used to visualize the effects of experimental factors on degradation percentage response in Figs. 2–9. The model adequacy check is an important part of the data analysis procedure as the approximating model would give poor or misleading results if it were an inadequate fit. This is done by looking at the residual plots which are examined for the approximating model [20]. The normal probability and studentized residuals plot is shown in Fig. 2 for BR2 dye degradation percent. In Fig. 2, residuals show how well the model satisfies the assumptions of the analysis of variance (ANOVA) whereas the studentized residuals measure the number of standard deviations separating the actual and predicted values. Fig. 2 shows that neither response transformation was needed nor there was any apparent problem with normality.

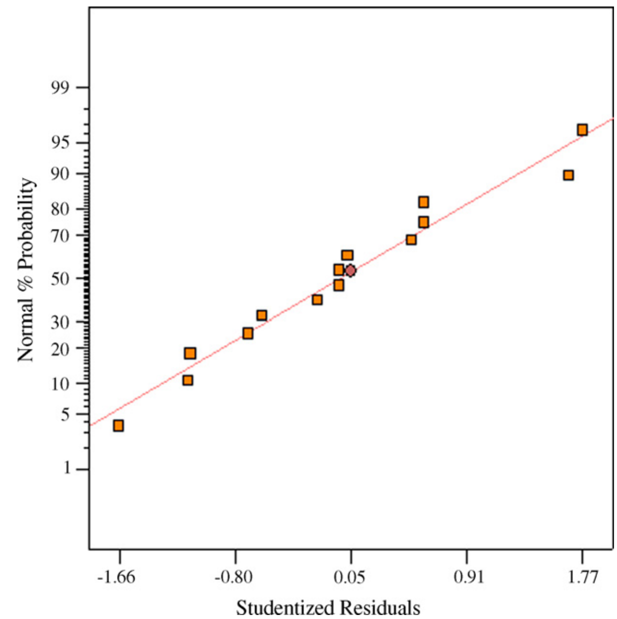

Fig. 2. The studentized residuals and normal percentage probability plot of photolytic degradation of Basic Red 2 dye.

Fig. 3 shows the studentized residuals versus predicted BR2 degradation percent. The general impression is that the plot should be a random scatter, suggesting the variance of original observations is constant for all values of the response. If the variance of the response depends on the mean level of *y*, then this plot often exhibits a funnel-shaped pattern [15]. This is also

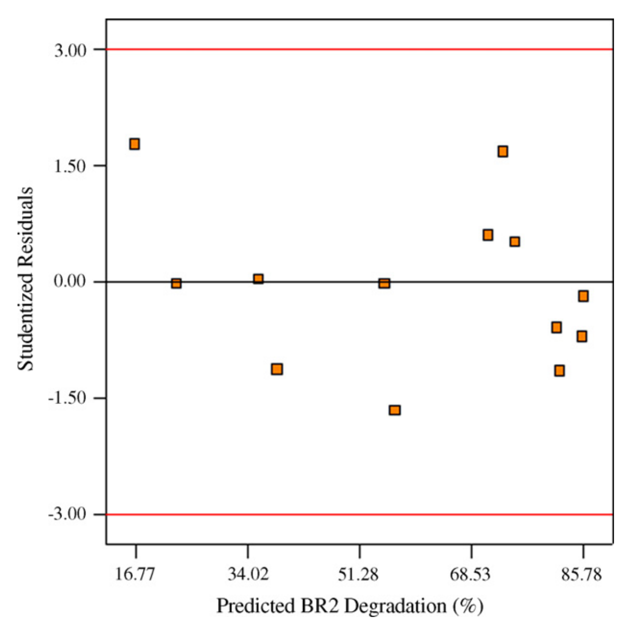

Fig. 3. The predicted degradation of Basic Red 2 dye and studentized residuals plot.

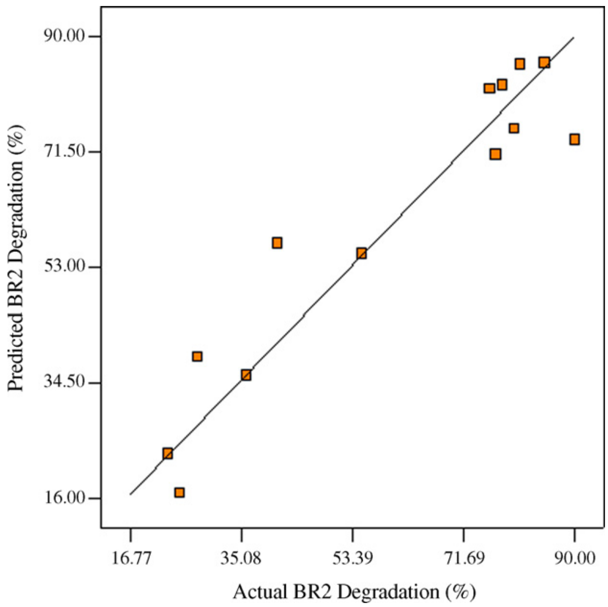

Fig. 4. The actual and predicted plot of Basic Red 2 degradation ($R^2 = 0.89$, $R^2_{adj} = 0.80$).

an indication that there was no need for transformation of the response variable.

The actual and the predicted BR2 degradation percent are shown in Fig. 4. Actual values are the measured response data for a particular run, and the predicted values are evaluated from the model and are generated by using the approximating functions. In Fig. 4, the values of R^2 and R^2_{adj} were found to be 0.89 and 0.80, respectively. The fair correlation coefficients might have resulted by the insignificant terms in Table 2, 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 [19].

The BR2 degradation percent response surface graphs are shown in Figs. 5–7. In Fig. 5, the effect of BR2 concentration and H_2O_2 concentration on BR2 degradation is shown at pH 7.6 (neat dye). BR2 degradation increased with increasing H_2O_2 concentration and decreasing BR2 concentration. A maximum of 85% dye degradation was determined with 5 μM BR2 and 1.67 mM H_2O_2 at pH 7.6 (neat dye). The effect of H_2O_2 concentration and pH on BR2 degradation percent is shown in Fig. 6. In Fig. 6, BR2 degradation percent increased with the decrease in dye concentration at 1.67 mM H_2O_2. Fig. 7 shows the effect of H_2O_2 concentration and pH on BR2 degradation percentage and shows that dye degradation increased with the increase in H_2O_2 concentration at pH 7.6 (neat dye). In Figs. 6 and 7, the degradation percent decreased with increasing the pH value from 3 to 7.2 and increased with the increase in pH above pH 7.2. The highest BR2 degradation was obtained at pH 3 and 11.

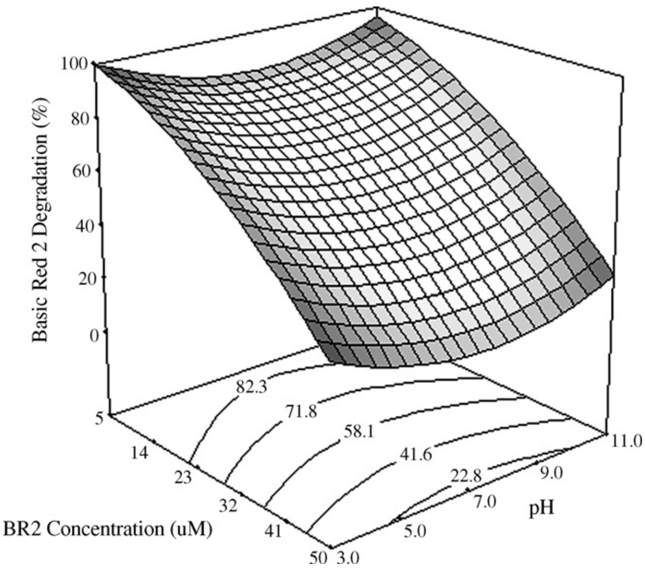

Fig. 6. The effect of initial Basic Red 2 (BR2) concentration and pH on BR2 degradation ($[H_2O_2]$: 1.67 mM).

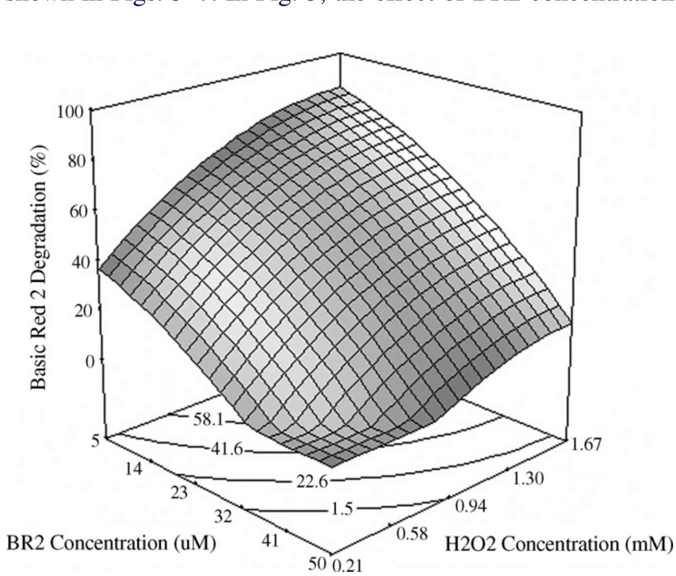

Fig. 5. The effect of Basic Red 2 (BR2) concentration and H_2O_2 concentration on BR2 degradation (neat dye pH 7.6).

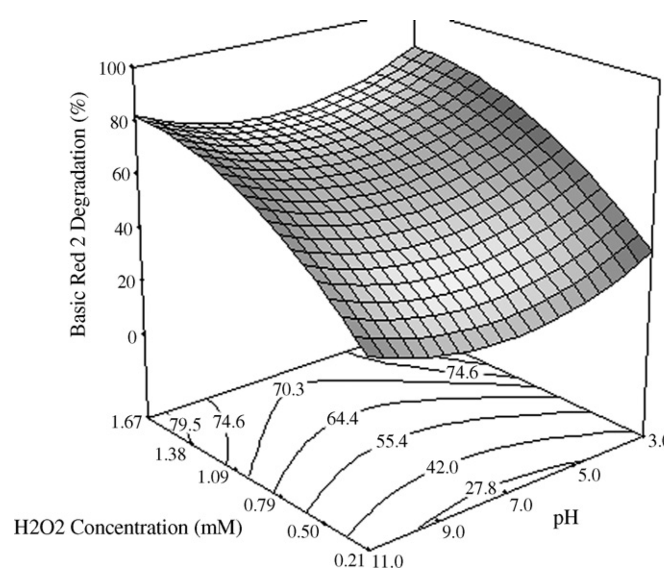

Fig. 7. The effect of initial H_2O_2 concentration and pH on Basic Red 2 (BR2) degradation ([BR2]: 20 μM).

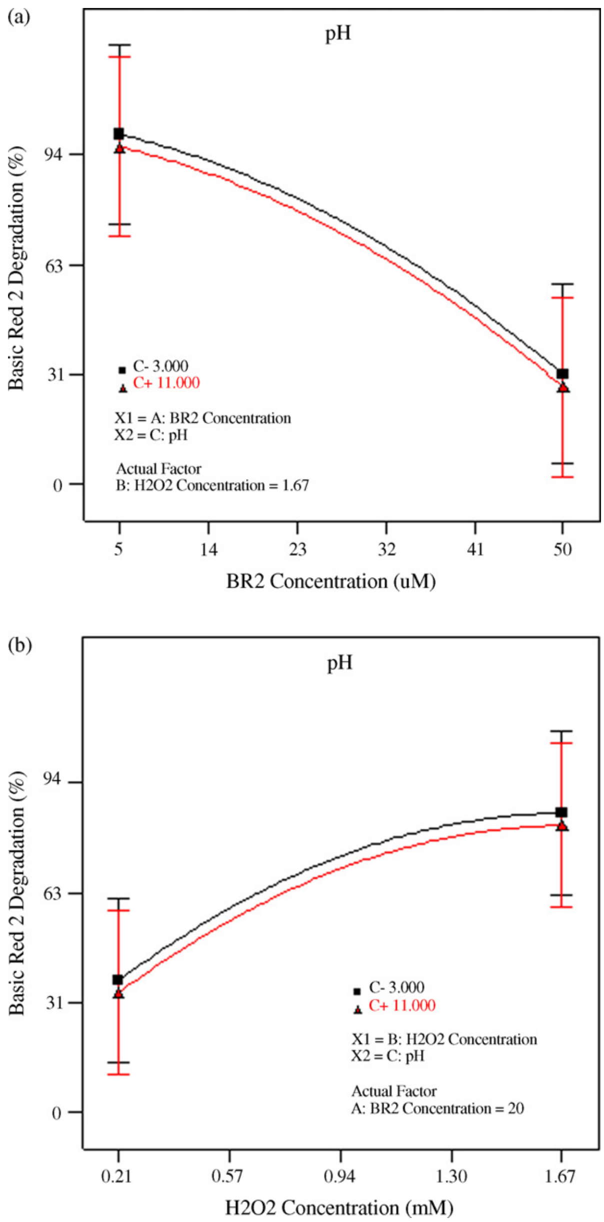

Fig. 8. Two-factor interaction plots of Basic Red 2 (BR2) degradation; (a) pH 3 and 11 at 1.67 mM H_2O_2, (b) pH 3 and 11 at 20 μM BR2 dye.

The two-factor interaction graphs of BR2 dye degradation are shown in Fig. 8. In these graphs one factor was fixed while the other was investigated. BR2 degradation increased with increasing H_2O_2 and decreasing BR2 concentration both at pH 3 and 11. In Fig. 8a, complete BR2 degradation was obtained with 5 μM BR2 and 1.67 mM H_2O_2 while the highest value achieved was 97%. The results in Fig. 8b were obtained with 20 μM BR2, where the highest percentage degradation obtained with 1.67 mM H_2O_2 was 86 and 82% at pH 3 and 11 respectively.

In the perturbation plot (Fig. 9) the effects of all the factors at the selected run conditions in the design space are compared. The plot was obtained at 20 μM BR2, 1.67 mM H_2O_2 and pH 7.6. In Fig. 6, a steep curvature in BR2 concentration and H_2O_2 concentration factors show that the response of BR2 degradation

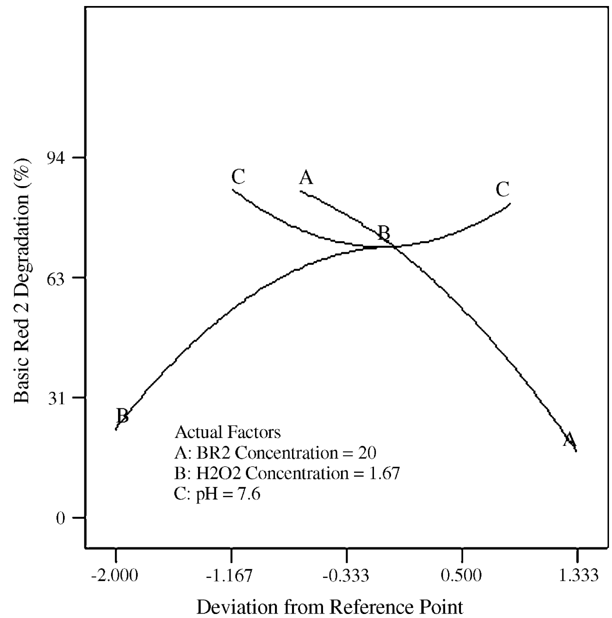

Fig. 9. Perturbation plot for Basic Red 2 degradation.

is very sensitive to these factors. The relatively flat line of pH shows insensitivity to change in this particular factor.

4. Conclusion

Under the optimized conditions of 20 μM BR2, 1.67 mM H_2O_2 and pH 7.6, 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 BR2 dye. In the optimization, R^2 and R^2_{adj} correlation coefficients for quadratic model was evaluated quite satisfactorily as 0.89 and 0.80 respectively.

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