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Response surface methodology (RSM) analysis of photoinduced decoloration of toludine blue

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Abstract

In this study, the decoloration of toludine blue (TB) in the presence of UV radiation and heterogeneous hybrid catalyst, namely titanium oxide impregnated with vanadium oxide was optimized using response surface methodology (RSM). The optimum removal conditions were determined as 26.5 mg/20 mL V_2O_5/TiO_2 catalyst concentration at pH 7.7. At optimized conditions the complete decoloration was obtained at 50 μM TB concentration. In the optimization, R^2 and R^2_{adj} correlation coefficients for quadratic model was evaluated quite satisfactorily as 0.98 and 0.96, respectively.

Keywords: Photocatalysis; Optimization; Response surface methodology (RSM); Vanadium oxide; Titanium oxide; Toludine blue

1. Introduction

Decoloration of reactive dyes in industrial effluents has been a key issue for a long time. This is mainly because of the reason that many of these organic molecules pose a direct or indirect threat to the environment due to their chemical nature [1,2]. Various approaches have been forwarded to handle the clean-up of effluents containing these chemicals; these include biodegradation, adsorption, coagulation and advanced oxidation process (AOP) [3–6]. In this study, we have used the response surface methodology (RSM) for the experimental design and optimized conditions. 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 [7–9]. 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 termed as the response and normally measured on a continuous scale, represents the most important function of the system [10,11].

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. In this work we are presenting the results of RSM analysis of toludine blue decoloration reported earlier in the presence of an impregnated catalyst namely TiO_2/V_2O_5 and UV light [12].

2. Materials and methods

2.1. Experimental materials

Toludine blue dye (F.wt. = 373.97) with a labeled purity of more than 90% was obtained from either Sigma or Aldrich and used as such. The structure of toludine blue (TB) dye is given in Fig. 1. Deionized water was used to make the dye solutions of desired concentration. The λ_{max} value for the dye was 623 nm and for decoloration studies, the λ_{max} of the dye was chosen for further investigations. The primary catalyst namely titanium oxide was Degussa P-25 and it was mainly in the anatase

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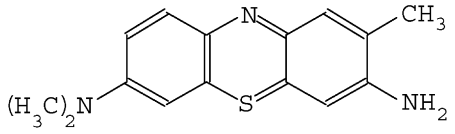

Fig. 1. Chemical structure of toludine blue.

form (approximately 75% anatase and 25% rutile). The Brauner Emmett Teller (BET) surface area of the catalyst was found to be 50 m^2/g by using the nitrogen adsorption method.

The primary catalyst was loaded with 2% vanadium oxide, and used to study the effect on dye decoloration. The V_2O_5/TiO_2 catalyst was prepared by incipient wetness impregnation technique using ammonium meta-vanadate as a precursor [13]. The nominal surface coverage in this case was 33%.

2.2. Preparation of samples and decoloration 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. A 0.01 g of the catalyst (V_2O_5/TiO_2) was added to 20 mL of this diluted solution. The contents of the dye solution were allowed to equilibrate for a given time (usually 15–30 min) at room temperature (25 ± 2 °C) in the dark before irradiating with a UV light of 254 nm. During irradiation, the contents of the solution were agitated continuously so as to maintain a homogeneous environment. After a certain time interval, the cell was drawn away from the UV light and centrifuged and the absorbance of the supernatant solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the rate of decoloration. UV/VIS studies were done on a CARRY 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.

2.3. Experimental design and optimization

In this study, the decoloration of toludine blue (TB) in the presence of UV radiation using a heterogeneous hybrid V_2O_5/TiO_2 catalyst was optimized with response surface methodology (RSM) by Design Expert 6.0 [13]. 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. The set of candidate points to use should depend upon the order of the model the experimenter wishes to fit [7].

In the present study, the independent variables of dye concentration, pH and catalyst concentration was coded with low and high levels in D-optimal design, while decoloration of TB dye was the response (dependent variable). The independent variables were initial TB dye concentration: 50–80 μM, V_2O_5/TiO_2 catalyst concentration: 10–40 mg/20 mL and pH in the range of 5.0–10.5 as shown in Table 1.

Table 1
Experimental design of photoinduced decoloration of toludine blue dye using a hybrid catalyst V_2O_5/TiO_2

Factor name	Low actual value	High actual value
TB concentration (μM)	50	80
V_2O_5/TiO_2 (mg/20 mL)	10	40
pH	5.0	10.5

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 decoloration 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 [14]

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

where η is the predicted response, x_i and x_j the variables, β_0 the constant coefficient, β_j's, β_{jj}'s and β_{ij}'s the interaction coefficients of linear, quadratic and the second-order terms, respectively, and e_i is the error. In the study, decoloration data were processed for 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} in Eqs. (2) and (3), respectively. The statistical significance was checked with adequate precision ratio in Eqs. (4) and (5), and by the F-test in the program [15].

$$R^2 = 1 - \frac{\mathrm{SS}_{\mathrm{residual}}}{\mathrm{SS}_{\mathrm{model}} + \mathrm{SS}_{\mathrm{residual}}} \qquad (2)$$

$$R^2_{\mathrm{adj}} = 1 - \frac{\mathrm{SS}_{\mathrm{residual}}/\mathrm{DF}_{\mathrm{residual}}}{(\mathrm{SS}_{\mathrm{model}} + \mathrm{SS}_{\mathrm{residual}})/(\mathrm{DF}_{\mathrm{model}} + \mathrm{DF}_{\mathrm{residual}})} \qquad (3)$$

$$\text{Adequate precision} = \frac{\max(\hat{Y}) - \min(\hat{Y})}{\sqrt{\bar{V}(\hat{Y})}} \qquad (4)$$

$$\bar{V}(\hat{Y}) = \frac{1}{n}\sum_{1=1}^{n} V(\hat{Y}) = \frac{p\sigma^2}{n} \qquad (5)$$

In Eq. (5), p is the number of model parameters, σ^2 the residual mean square from ANOVA table, and n is the number of experiments. The terms SS and DF corresponds to sum of squares and degrees of freedom, respectively.

3. Results and discussion

In the first step of the study, the effect of operational variables of initial dye concentration, V_2O_5/TiO_2 catalyst concentration and pH on decoloration of toludine blue dye was investigated using response surface methodology according to D-optimal design. In the second step, the main objective was to select the V_2O_5/TiO_2 catalyst concentration and pH in order to achieve optimal decoloration of toludine blue dye.

Table 2
ANOVA results of the quadratic model of photoinduced decoloration of toludine blue dye using a hybrid catalyst V_2O_5/TiO_2

Source	Sum of squares	Degrees of freedom	Mean square	F value	Prob > F	
Quadratic model	2921.74	6	486.96	51.65	<0.0001	Significant
x_1	1205.88	1	1205.88	127.90	<0.0001	Significant
x_2	93.18	1	93.18	9.88	0.0200	Significant
x_3	8.20	1	8.20	0.87	0.3869	
x_1^2	110.19	1	110.19	11.69	0.0142	Significant
x_2^2	751.96	1	751.96	79.76	0.0001	Significant
x_3^2	1130.84	1	1130.84	119.95	<0.0001	Significant
Residual	56.57	6	9.43			
Lack of fit	56.57	4	14.14			

$R^2 = 0.98$; $R^2_{adj} = 0.96$; Adequate precision = 22.69 (>4.0); x_1: TB concentration (μM); x_2: V_2O_5/TiO_2 (mg/20 mL); x_3: pH.

3.1. Decoloration of dye solution

Dye solution of known concentration was prepared in water and subjected to UV light in the presence of a given amount of a catalyst. The change in the absorption spectra of the dye solution was monitored at regular intervals of time. It was noted that the absorption value of dye became minor with irradiation time, thus indicating the decoloration of dye solution. The decrease in absorption value of dye solution can be related in terms of percentage decoloration as follows

$$\%\text{Decrease in absorption} = \left[1 - \frac{A_f}{A_i}\right] \times 100 \qquad (6)$$

where A_i and A_f are the initial and the final absorption values, respectively.

3.2. Mechanism of dye decoloration

The photocatalytic decoloration of dye is believed to take place according to the following mechanism. When a catalyst is exposed to UV radiation, electrons are promoted from the valence band to the conduction band. As a result of this phenomenon, an electron–hole pair is produced [16].

$$\text{Catalyst} + h\upsilon \rightarrow e^-_{cb} + h^+_{vb} \qquad (7)$$

where, e^-_{cb} and h^+_{vb} are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases h^+_{vb} can react easily with surface bound H_2O molecules to produce $^\bullet OH$ radicals, whereas, e^-_{cb} can react with O_2 to produce superoxide radical anion of oxygen.

$$H_2O + h^+_{vb} \rightarrow {}^\bullet OH + H^+ \qquad (8)$$

$$O_2 + e^-_{cb} \rightarrow O_2^{\bullet -} \qquad (9)$$

This reaction prevents the combination of the electron and the hole which are produced in the first step. The $O_2^{\bullet -}$ produced in the above manner can then react with H^+ to produce H_2O_2 which again in turn can produce $^\bullet OH$ and these can react with dye, and is thus responsible for its decoloration [17,18].

$$2H^+ + 2O_2^{\bullet -} \rightarrow H_2O_2 + O_2 \qquad (10)$$

$$H_2O_2 + h\nu \rightarrow 2^\bullet OH \qquad (11)$$

$$^\bullet OH + \text{Dye} \rightarrow \text{Intermediates} \rightarrow \text{Products} \qquad (12)$$

3.3. Evaluation of experimental results

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 decoloration percent obtained in Eq. (13).

$$y = -7.71x_1 + 5.47x_2 + 101.92x_3 + 0.049x_1^2 - 0.102x_2^2 - 6.61x_3^2 - 100.90 \qquad (13)$$

In Eq. (13), y is the response of decoloration percent; x_1, x_2 and x_3 are corresponding to independent variables of dye concentration (μM), hybrid catalyst V_2O_5/TiO_2 (mg/20 mL) concentration and pH, respectively. ANOVA results of these quadratic models presented in Table 2 indicate that these quadratic models can be used to navigate the design space.

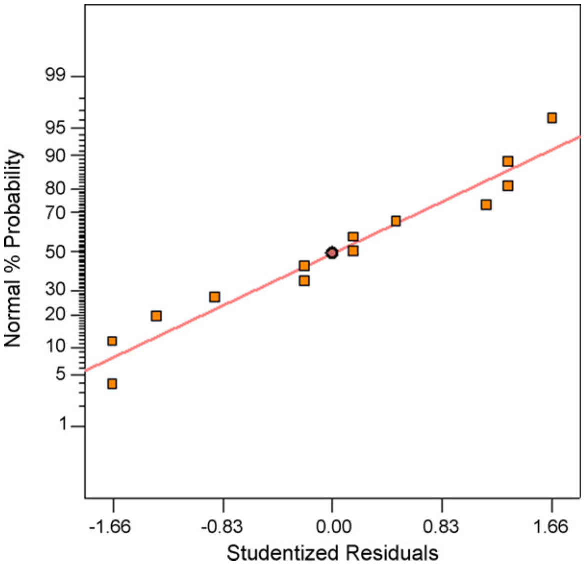

Fig. 2. The studentized residuals and normal %probability plot of decoloration of toludine blue (TB) dye.

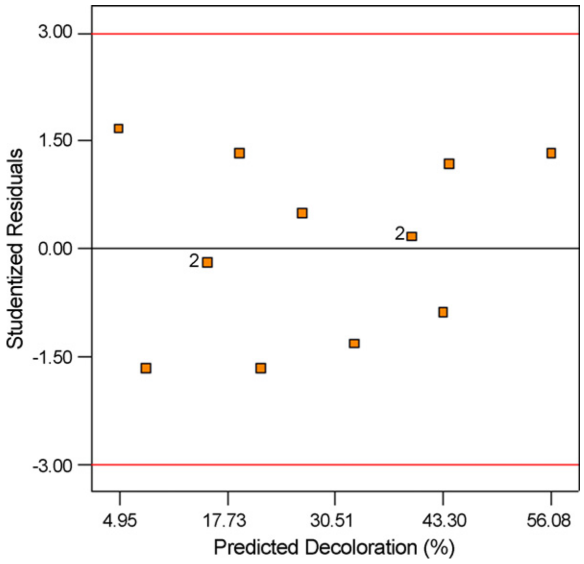

Fig. 3. The predicted decoloration of toludine blue (TB) dye and studentized residuals plot.

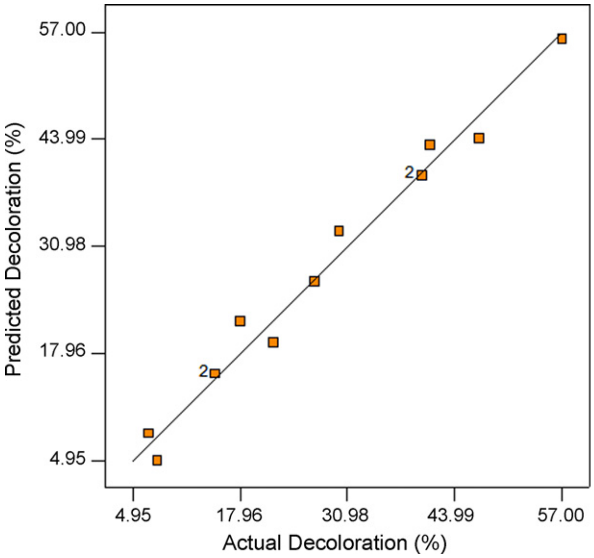

Fig. 5. The actual and predicted plot of decoloration of toludine blue (TB) dye ($R^2 = 0.98$, $R^2_{\text{adj}} = 0.96$).

In Table 2, the quadratic model F-value of 51.65 implies that the model is significant for decoloration. Adequate precision measures the signal to noise ratio and a ratio greater than 4 is generally desirable. Therefore, in the quadratic model of decoloration, the ratio of 22.69 indicates adequate signal for the model to be used to navigate the design space. The values of Prob > F less than 0.0500 indicate that the model terms are significant, whereas, the values greater than 0.1000 are not significant. In Table 2, the terms are significant in all sources except pH (x_3) according to Prob > F values.

Eq. (13) has been used to visualize the effects of experimental factors on decoloration response in Figs. 2–9. The checking of model adequacy is an important part of the data analysis procedure, as it would give poor or misleading results if it were an inadequate fit. The residual plots were examined by the approximating model [7–9], whereas, the normal probability and studentized residuals plots are shown in Fig. 2 for TB dye decoloration. Residuals are the difference between actual and predicted values for each point and show how well the model satisfies the assumptions of the analysis of variance (ANOVA). Studentized residuals in Fig. 2 are the residuals divided by the estimated standard deviation of that residual. It measures the number of standard deviations separating the actual and predicted values. The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. S-shaped curve was not formed according to Fig. 2, indicating that neither response transformation was needed nor there was any apparent problem with normality.

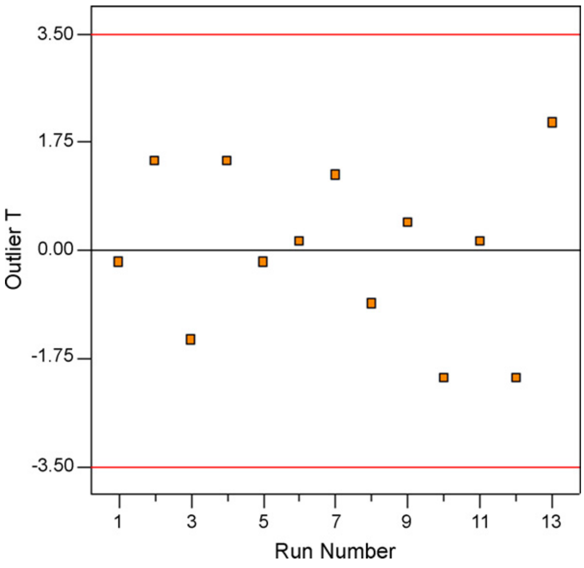

Fig. 4. The outlier t plot of decoloration of toludine blue (TB) dye.

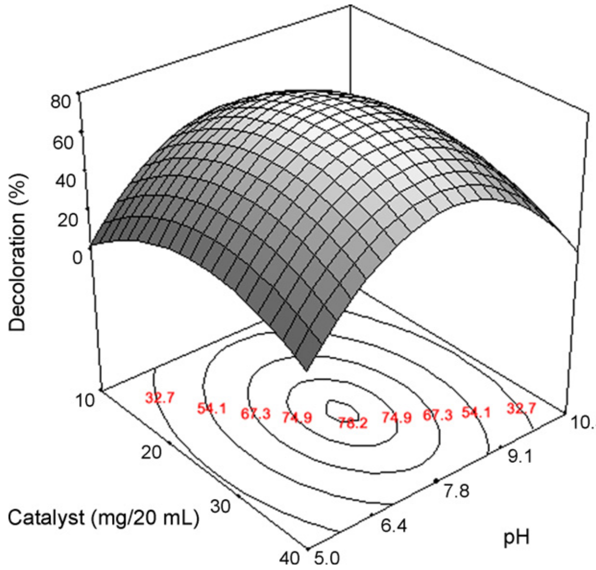

Fig. 6. The effect of V_2O_5/TiO_2 hybrid catalyst concentration and pH on decoloration of toludine blue (TB) dye (TB dye: 60 μM).

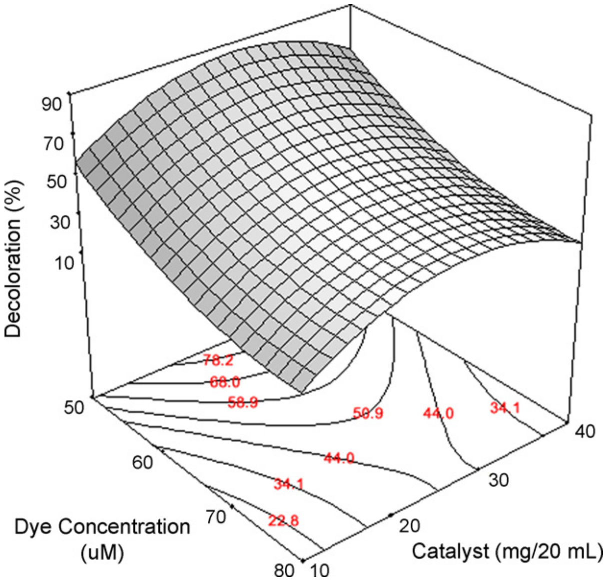

Fig. 7. The effect of initial TB dye concentration and V_2O_5/TiO_2 hybrid catalyst concentration on decoloration of toludine blue (TB) dye (neat dye pH: 6.1).

Fig. 3 shows the studentized residuals versus predicted decoloration plot. The general impression is that the plot should be a random scatter, suggesting that 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 [7–9]. This is also an indication that there was no need for transformation of the response variable. In Fig. 4, outlier *t* for the batch runs of TB dye decoloration is shown. The outlier *t* is a measure of how many standard deviations the actual value deviates from the predicted value [7–9]. 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

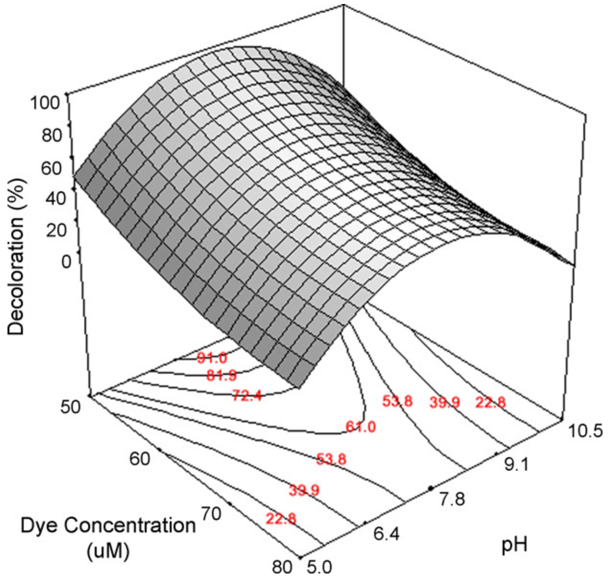

Fig. 8. The effect of initial TB dye concentration and pH on decoloration of toludine blue (TB) dye (V_2O_5/TiO_2 hybrid catalyst: 20 mg/20 mL).

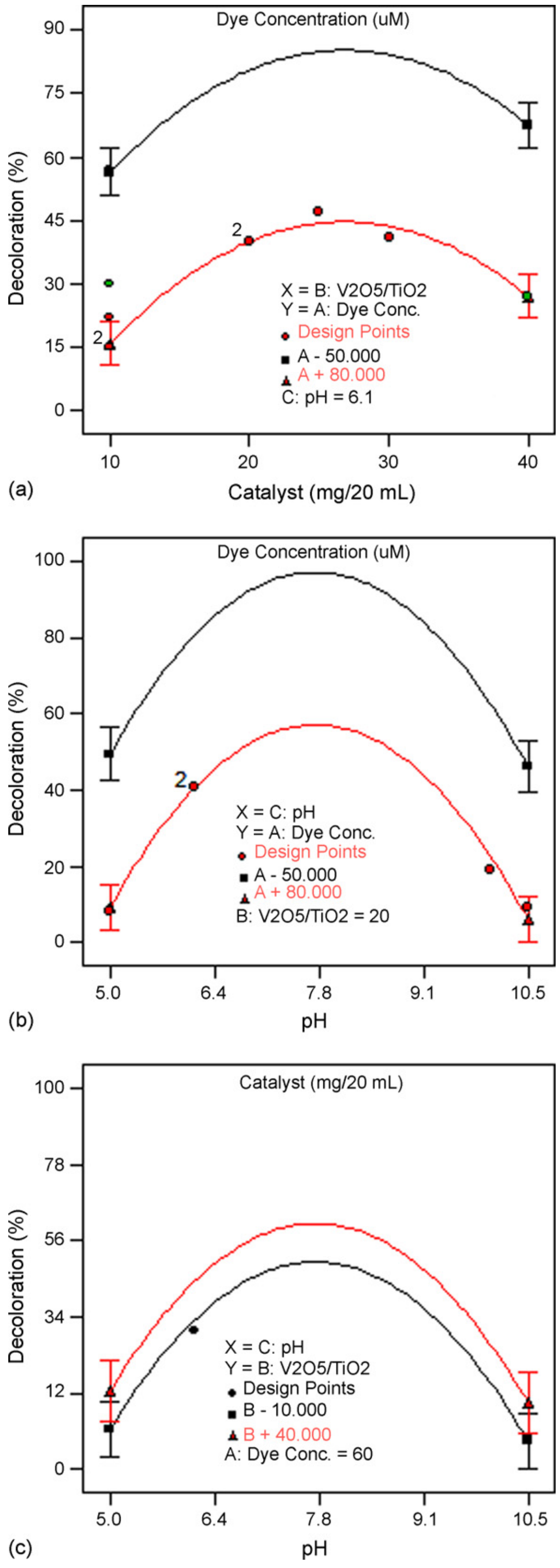

Fig. 9. Two-factor interaction plots of decoloration of toludine blue (TB) dye: (a) TB dye concentrations at 6.1 neat dye pH; (b) TB dye concentrations at 20 mg/20 mL V_2O_5/TiO_2 hybrid catalyst; (c) V_2O_5/TiO_2 hybrid catalyst concentrations at 60 μM toludine blue (TB) dye.

observed response [7–9]. 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 actual and the predicted decoloration plot are shown in Fig. 5. 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 Fig. 5, the values of R^2 and R^2_{adj} were evaluated as 0.98 and 0.96, respectively. The correlation coefficient R^2_{adj} of 0.96 indicates that it might be due to the result of the insignificance of pH (x_3) term in Table 2.

The decoloration response surface graphs of toludine blue (TB) dye are shown in Figs. 6–8. In Fig. 6, the effect of catalyst concentration and pH on decoloration of TB dye is shown at 60 μM dye. The semi-spherical response surface of decoloration gradually increased with increasing pH and from 5.0 to 7.7 at any catalyst concentration, and again gradually decreased above pH 7.7. A similar trend was also observed for catalyst concentration. The maximum value of decoloration determined was 78.6% at pH 7.7 and 26.5 mg/20 mL catalyst. In the scope of operational cost, the optimum pH value and catalyst concentration was determined to be 7.7 and 26.5 mg/20 mL, respectively, for optimum decoloration percentage.

The effect of dye concentration and catalyst concentration on decoloration of TB dye is shown in Fig. 7. In Fig. 7, decoloration decreased with the increase in dye concentration at pH 6.1 (neat dye). Decoloration increased up to 26.5 mg/20 mL catalyst and then decreased with increasing catalyst concentration. The decrease in decoloration can be attributed to the fact that increasing concentrations of catalyst causes the solution to become turbid, thus blocking the penetration of light. Maximum decoloration obtained at 50 μM TB dye was 85%. Fig. 8 shows the effect of dye concentration and pH on decoloration of TB dye. Decoloration of TB dye increased with decreasing dye concentration at 20 mg/20 mL as shown in Fig. 8. The decoloration increased up to pH 7.7 and then decreased above 7.7 with increasing pH. Complete decoloration was obtained at 50 μM TB dye and 20 mg/20 mL V_2O_5/TiO_2 hybrid catalyst.

The two-factor interaction graphs of TB dye decoloration are shown in Fig. 9. In these graphs one factor was fixed while the other was investigated. In Fig. 9a, maximum decoloration was obtained at 26.5 mg/20 mL catalyst for both low and high levels of dye concentration at pH 6.1 (neat dye). The maximum decoloration was determined at pH 7.7 for 50 μM and 80 μM TB dye with 20 mg/20 mL V_2O_5/TiO_2 hybrid catalyst and shown in Fig. 9b. The effect of pH on TB dye decoloration at low and high levels of catalyst concentration of 10 mg/20 mL and 40 mg/20 mL is shown in Fig. 9c. The optimum pH obtained was 7.7 at 60 μM TB dye for both with low and high V_2O_5/TiO_2 catalyst concentrations.

4. Conclusion

Under optimized conditions, the experimental values agreed with the predicted ones, indicating suitability of the model and the success of RSM in optimizing the conditions of photocatalysis. In the optimization, R^2 and R^2_{adj} correlation coefficients for quadratic model was evaluated quite satisfactorily as 0.98 and 0.96, respectively.

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