



# Optimization of photocatalytic degradation of methyl blue using silver ion doped titanium dioxide by combination of experimental design and response surface approach

C. Sahoo, A.K. Gupta\*

Environmental Engineering Division, Department of Civil Engineering, Indian Institute of Technology, Kharagpur, 721302, India

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## ABSTRACT

Photocatalytic degradation of methyl blue (MYB) was studied using Ag<sup>+</sup> doped TiO<sub>2</sub> under UV irradiation in a batch reactor. Catalytic dose, initial concentration of dye and pH of the reaction mixture were found to influence the degradation process most. The degradation was found to be effective in the range catalytic dose (0.5–1.5 g/L), initial dye concentration (25–100 ppm) and pH of reaction mixture (5–9). Using the three factors three levels Box–Behnken design of experiment technique 15 sets of experiments were designed considering the effective ranges of the influential parameters. The results of the experiments were fitted to two quadratic polynomial models developed using response surface methodology (RSM), representing functional relationship between the decolorization and mineralization of MYB and the experimental parameters. Design Expert software version 8.0.6.1 was used to optimize the effects of the experimental parameters on the responses. The optimum values of the parameters were dose of Ag<sup>+</sup> doped TiO<sub>2</sub> 0.99 g/L, initial concentration of MYB 57.68 ppm and pH of reaction mixture 7.76. Under the optimal condition the predicted decolorization and mineralization rate of MYB were 95.97% and 80.33%, respectively. Regression analysis with R<sup>2</sup> values >0.99 showed goodness of fit of the experimental results with predicted values.

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## 1. Introduction

In the era of water scarcity, indiscriminate discharge of pollutants by various industries along with their untreated or partially treated wastewater into the water bodies is a great concern [1]. Many of these pollutants are toxic and recalcitrant in nature and tend to bio accumulate [2]. They enter the human system through food chain and continue to accumulate there and may lead to cancerous growths as many of the pollutants are carcinogenic [3]. Colored wastewater emanating from various color manufacturing and color consuming industry is one among the wastewaters of greatest concern because of its high visibility and recalcitrant nature [4]. The recalcitrant pollutants escape the conventional biological treatment processes as they are not biodegradable. Hence there is a need to develop suitable methods that can be effectively used for their complete degradation before discharge. Many researchers have worked in this regard and have come up with many physical [5–8], chemical [9–12] and biological [13–16] processes. But none of the processes have been successfully employed in the field so far. Advanced oxidation processes (AOP) proposed

in last few decades seem to be the most promising methods investigated [17–19]. Among the AOPs, TiO<sub>2</sub> mediated semiconductor photocatalysis is gaining more importance due to its capacity to produce higher amount of hydroxyl radicals and ability to degrade numerous organic pollutants of varying kinds [20]. TiO<sub>2</sub> is cheap and easily available, non-toxic and photo stable [21]. Recent research interests are focused on the development of modified semiconductor photocatalysts to increase the efficiency of the AOP.

Many researchers have studied the photocatalytic degradation of different dyes using TiO<sub>2</sub> and metal doped TiO<sub>2</sub> either in powder or thin film form [22–25]. However, most of them have followed the classical method of optimizing one parameter at a time keeping others constant, which is more time consuming and laborious. The method does not consider the combined effect of different parameters. Response surface methodology (RSM) combines mathematics and statistics to analyze the relative significance of different operating parameters even in very complicated systems [26]. Hence this method can be used to find out the optimal conditions of various reactions and reduce time, labor and cost.

Methyl blue, MYB (Acid Blue 93, C.I. 42780) is an anionic triphenyl methane dye used for dyeing cotton, cotton based fibers and leather. It is also used as a biological and bacteriological stain. It is harmful if swallowed and causes skin, eye and respiratory tract irritation. As evident from the literature, much research has not been

\* Corresponding author. Tel.: +91 3222 283428; fax: +91 3222 255303.  
E-mail address: [agupta@civil.iitkgp.ernet.in](mailto:agupta@civil.iitkgp.ernet.in) (A.K. Gupta).

done on the degradation of this dye. Hence the dye was selected for the study and it was degraded photocatalytically using Ag<sup>+</sup> doped TiO<sub>2</sub>. Cheap and easily available micro size TiO<sub>2</sub> obtained from Merck India was used for the study. In the present work, the effects of catalytic dose, initial dye concentration and pH on both color removal (decolorization) and COD removal (mineralization) were studied under different designed experimental conditions in a batch reactor. First of all preliminary information regarding the suitable reaction parameters was obtained and then two quadratic models were fitted to optimize the parameters using RSM [27]. The required number of experiments was designed using Box–Behnken design of experiments. Box–Behnken designs are experimental designs for response surface methodology, devised by George E.P. Box and Donald Behnken. It is a combination of two level factorial designs and an incomplete block design. In each block, some factors are kept at the central value and the other factors are put through all combinations of factorial design. A Box–Behnken design for three factors involves three blocks. In each block one factor is kept at its central value and the other two factors are varied through four different combination of high and low value. Adding three central runs the total number of experiments becomes 15. This study presents effective information about the optimized reaction conditions for the decolorization and mineralization of methyl blue.

## 2. Materials and methods

### 2.1. Materials

Methyl blue (99% pure) purchased from Loba Chemie was used without further purification. Titanium dioxide procured from Merck India was used as photo catalyst. Silver nitrate (99.9% pure) from S.D. Fine chem. was used for silver ion doping. NaOH and HNO<sub>3</sub>, obtained from Merck India were used for the adjustment of pH of the reaction medium. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>, HgSO<sub>4</sub> and Ag<sub>2</sub>SO<sub>4</sub> obtained from Merck India were used for COD analysis. The reagents used were of analytical reagent grade and triple distilled water was used to prepare all solutions.

### 2.2. Instruments

The instruments used for the study were Thermo Spectronic's Genesys 20 spectrophotometer, USA, Philips UV fluorescent lamp (15 W, 254 nm), Netherlands, Gallenkamp incubator, UK, Merck Spectroquant TR 320 COD digester, Germany, Remi laboratory centrifuge, India, Mettler Toledo AG 135 digital balance (Fact), Systronics digital pH meter, India, Reico muffle furnace, India, and Remi magnetic stirrer, India.

### 2.3. Preparation of the photocatalyst

Micro sized commercially available TiO<sub>2</sub> from Merck India was doped with silver ion in 1% molar ratio using liquid impregnation technology to prepare 1% Ag<sup>+</sup> doped TiO<sub>2</sub>. First 0.01 mol AgNO<sub>3</sub> was dissolved in 100 mL triple distilled water in a porcelain crucible. Then 0.99 mol TiO<sub>2</sub> was added to the solution and the resulting suspension was stirred well and allowed to stand for 24 h. Water was evaporated out from the suspension by heating it at 100 °C for 12 h in an incubator. The dried solids were ground in an agate mortar and calcined at 400 °C for 6 h in a muffle furnace [28].

### 2.4. Experimental

The experiments were carried out in a batch reactor made up of a 500 mL borosil beaker placed over a magnetic stirrer, which was mounted on a wooden frame. A 15 W lamp from Phillips emitting UV light of wavelength 254 nm served as the UV light source.

The volume of the reaction mixture was 60 mL and the concentrations of MYB degraded were 25 ppm, 62.5 ppm and 100 ppm, respectively. The doses of Ag<sup>+</sup> doped TiO<sub>2</sub> used were 0.5 g/L, 1 g/L and 1.5 g/L. The degradation was tested under the pH of 5, 7 and 9, respectively. Dilute sodium hydroxide and dilute nitric acid were used for pH adjustment. The reaction mixture was stirred in the dark for 30 min to establish the adsorption equilibrium and then UV irradiated for 120 min. Aliquots were then taken and analyzed for dye decolorization and mineralization after centrifugation.

### 2.5. Analysis

Color removal was monitored by Thermo Spectronic's Genesys 20 spectrophotometer at the λ<sub>max</sub> value of 607 nm for MYB. The color removal was determined using Eq. (1).

$$\% \text{Colour removal} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

where C<sub>0</sub> is the initial concentration of dye in ppm and C<sub>t</sub> is dye concentration in ppm at any time t. The degree of mineralization of the dyes was ascertained by measuring the COD removal at different time intervals using closed reflux colorimetric method (5220D) [29]. The COD removal was determined using Eq. (2).

$$\% \text{COD removal} = \left( \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \right) \times 100 \quad (2)$$

where COD<sub>0</sub> is initial COD in ppm and COD<sub>t</sub> is COD in ppm at any time t.

### 2.6. Experimental design and statistical analysis

Initially preliminary experiments were conducted following single factor study method to decide the most influential experimental parameters affecting the photocatalytic degradation of MYB and to find out their ranges. The parameters selected were catalytic dose, initial concentration of dye and pH of reaction mixture. The three experimental parameters were optimized based on the information obtained from the single factor study.

The three selected experimental parameters were optimized using RSM considering them as independent variables and %color removal and %COD removal as response variables. Box–Behnken design of experiments was adopted to evaluate the combined effect of the three independent variables on the two responses using 15 set of experiments. The ranges and levels of independent variables are shown in Table 1. Box–Behnken design was used because it is very efficient and does not contain any point at the vertices of the cubic region formed by the upper and lower limits of the variables. It has been extensively used along with RSM to optimize various physical, chemical and biological processes [30–34]. Using RSM the results were fitted to an empirical quadratic polynomial model for three parameters expressed as shown in Eq. (3).

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{23} BC + \beta_{31} CA \quad (3)$$

where, Y represents the response variable, β<sub>0</sub> the intercept, β<sub>1</sub>, β<sub>2</sub>, β<sub>3</sub> coefficients of the independent variables, β<sub>11</sub>, β<sub>22</sub>, β<sub>33</sub> quadratic coefficients, β<sub>12</sub>, β<sub>23</sub>, β<sub>31</sub> interaction coefficients and A, B, C are the independent variables studied. Multivariate regression analysis and optimization process with the help of RSM were performed using Design Expert software version 8.0.6.1 from Stat Ease Inc., USA. Analysis of variance (ANOVA) of the data was performed and the values were considered significant when p-value <0.05. The optimum values of the independent variables were found out by conducting three-dimensional response surface analysis of the independent and dependent variables. The details of the designed

**Table 1**  
The levels and ranges of variables in Box–Behnken statistical experiment design.

Independent variables	Symbol	Coded variable level		
		Low	Center	High
		–1	0	+1
Catalytic dose (g/L)	A	0.5	1	1.5
Initial concentration of dye (ppm)	B	25	62.5	100
pH	C	5	7	9

**Table 2**  
Box–Behnken experiments along with actual and predicted values of responses.

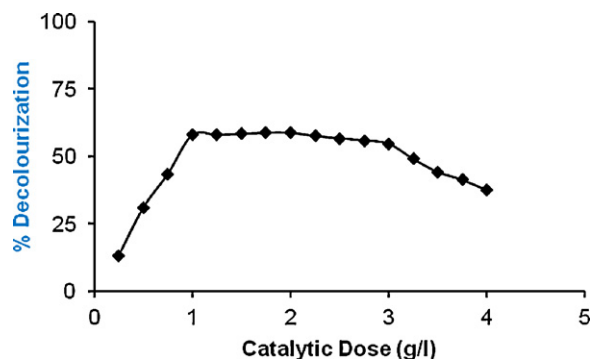
Run	A, catalytic dose (g/L)	B, initial dye concentration (ppm)	C, pH	Y <sub>1</sub> , color removal (%)		Y <sub>2</sub> , COD removal (%)	
				Actual	Predicted	Actual	Predicted
1	0.5	25	7	96.11	96.03	90.11	89.86
2	1.5	25	7	96.23	95.90	90.42	89.66
3	0.5	100	7	51.76	52.09	39.25	40.01
4	1.5	100	7	62.55	62.63	48.01	48.26
5	0.5	62.5	5	85.55	85.39	74.04	73.92
6	1.5	62.5	5	90.76	90.85	78.37	78.76
7	0.5	62.5	9	88.70	88.61	79.17	78.78
8	1.5	62.5	9	93.42	93.58	81.87	81.99
9	1	25	5	94.21	94.45	88.49	88.86
10	1	100	5	55.36	55.19	46.33	45.69
11	1	25	9	96.6	96.77	94.73	95.37
12	1	100	9	59.05	58.81	47.64	47.27
13	1	62.5	7	93.55	93.53	76.59	76.43
14	1	62.5	7	93.42	93.53	76.17	76.43
15	1	62.5	7	93.62	93.53	76.53	76.43

experiments along with experimental and predicted values of the two responses are shown in Table 2.

### 3. Results and discussion

#### 3.1. Preliminary experiments

Preliminary experiments were conducted in the batch reactor to determine the effective ranges of the three parameters catalytic dose, initial dye concentration and pH to be used in the Box–Behnken experimental design. The percentage decolorization of MYB (50 ppm) at different catalytic doses was found out and plotted in Fig. 1. It was observed that the percentage decolorization increased up to a dosage of 1 g/L and remained almost constant up to a dosage of 2 g/L. It gradually decreased at higher doses. The increase in decolorization rate up to certain catalytic dosage may be attributed to the enhancement in number of hydroxyl ions produced in the reaction medium. At higher dosage of Ag<sup>+</sup> doped TiO<sub>2</sub> the reaction mixture becomes turbid. The decolorization rate decreases as the light does not reach the surface of major fraction

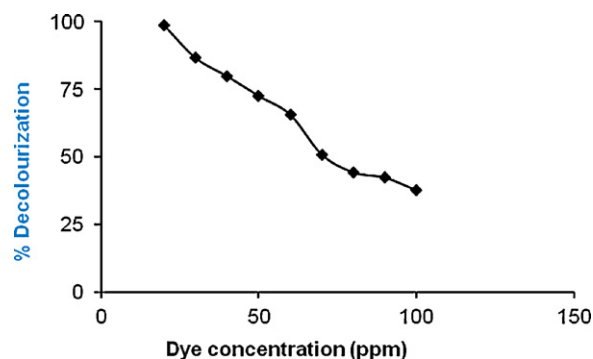


**Fig. 1.** Effect of catalytic dosage on dye decolorization; concentration of MYB: 50 ppm; pH: 7.2; temperature: 32 ± 2 °C; time: 1 h.

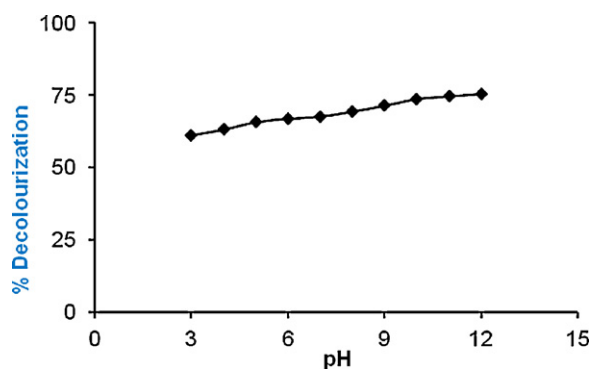
of catalyst. Optimum catalyst dosage should be determined for any photocatalytic degradation reaction in order to avoid excess use of the catalyst and to ensure total absorption of the radiated photons for efficient degradation [30].

The effect of the next important parameter, initial dye concentration, on the percentage decolorization of MYB was then investigated and represented in Fig. 2. The decolorization rate gradually decreased with the increase in initial dye concentration. This is because photocatalytic degradation is a light dependent process. As the concentration of MYB increases the depth of penetration of UV light decreases and it does not reach the surface of large portion of photocatalyst. As the initial concentration of the dye increases, the requirement of catalyst surface needed for the decolorization also increases; since illumination time and amount of catalyst are constant, the hydroxyl radical (primary oxidant) formed on the surface of TiO<sub>2</sub> is also constant. So the relative number of free radicals attacking the dye molecules decreases [35].

The next important parameter affecting the photocatalytic degradation process is the pH of the reaction mixture. The effect of pH of the reaction mixture on the percent decolorization of MYB



**Fig. 2.** Effect of initial dye concentration on dye decolorization; Ag<sup>+</sup> doped TiO<sub>2</sub>: 1 g/L; pH: 7.2; temperature: 32 ± 2 °C; time: 1 h.



**Fig. 3.** Effect of pH of reaction mixture on dye decolorization; Ag<sup>+</sup> doped TiO<sub>2</sub>: 1 g/L; concentration of MYB: 50 ppm; temperature: 32 ± 2 °C; time: 1 h.

was studied in the pH range 3–13 and represented in Fig. 3. The decolorization was less in acidic pH range and slightly higher in the basic pH range. This may be because of the higher color intensity of MYB in the acidic pH range. More over the  $pH_{zpc}$  of Ag<sup>+</sup> doped TiO<sub>2</sub> is around 6.4 and at pH less than  $pH_{zpc}$  the surface of the catalyst is positively charged. Hence at low pH the dye forms multilayer on the catalyst particles preventing the UV light from reaching its surface. Hence less hydroxyl radical will be formed ultimately resulting in lower decolorization rate [30,35].

### 3.2. Statistical analysis

A three variable Box–Behnken design was adopted to optimize the photocatalytic degradation process of MYB using Ag<sup>+</sup> doped

TiO<sub>2</sub>. The design was used because it is very efficient and requires minimum number of experiments. It is a spherical design containing all points lying on a sphere of radius square root of two. It does not contain any point on the vertices of the cubic region formed by the upper and lower limits of each variable [26,36].

Following the experimental design presented in Table 2 empirical second order polynomial equations were developed for the two response variables %color removal and %COD removal in terms of the three independent variables as shown in Eqs. (4) and (5).

$$Y_1 = 95.53 + 2.6A - 19.3B + 1.49C + 2.67AB - 0.12AC + 0.32BC - 1.78A^2 - 15.09B^2 - 2.14C^2 \quad (4)$$

$$Y_2 = 76.43 + 2.01A - 22.82B + 2.02C + 2.11AB - 0.41AC - 1.23BC - 0.21A^2 - 9.27B^2 + 2.14C^2 \quad (5)$$

where  $Y_1$  and  $Y_2$  represent color removal (%) and COD removal (%), respectively.  $A$ ,  $B$  and  $C$  are the coded values of catalytic dose, initial dye concentration and pH of reaction mixture, respectively.

The experimental data for both color and COD removal were statistically analyzed by analysis of variance and the results are shown in Tables 3 and 4. The ANOVA of the second order quadratic polynomial model for both the responses show that the models are highly significant, as the  $F$ -values for the models are 4527.33 and 916.63 and the corresponding  $p$ -values are <0.0001. This means that, there is only a 0.01% chance of occurrence of model  $F$ -value because of noise. The lack of fit  $F$ -values of 14.93 and 17.35 are not significant as the  $p$ -values are >0.05. For a model to be successfully used for prediction the lack of fit should be insignificant. The ANOVA for

**Table 3**  
ANOVA results of the response surface quadratic model for color removal.

Source	Sum of squares	Degree of freedom	Mean square	$F$ -value	$p$ -Value
Model	3926.90	9	436.32	4527.33	<0.0001
Residual	0.48	5	0.096		
Lack of fit	0.46	3	0.15	14.93	0.0634
Pure error	0.021	2	0.010		
Total	3927.38	14			
	$R^2 = 0.9999$	Adj $R^2 = 0.9997$	Ped $R^2 = 0.9981$		

**Table 4**  
ANOVA results of the response surface quadratic model for COD removal.

Source	Sum of squares	Degree of freedom	Mean square	$F$ -value	$p$ -Value
Model	4602.06	9	511.34	916.63	<0.0001
Residual	2.79	5	0.56		
Lack of fit	2.69	3	0.90	17.35	0.0550
Pure error	0.10	2	0.052		
Total	4604.85	14			
	$R^2 = 0.9994$	Adj $R^2 = 0.9983$	Ped $R^2 = 0.9906$		

**Table 5**  
ANOVA results for the coefficients of quadratic model for color removal.

Factor	Coefficient	Degree of freedom	Standard error	$F$ -value	95% confidence interval low	95% confidence interval high	$p$ -Value
Intercept	93.53	1	0.18	–	93.07	93.99	–
$A$	2.60	1	0.11	563.30	2.32	2.89	<0.0001
$B$	–19.30	1	0.11	30932.07	–19.59	–19.02	<0.0001
$C$	1.49	1	0.11	183.36	1.20	1.77	<0.0001
$AB$	2.67	1	0.16	295.33	2.27	3.07	<0.0001
$AC$	–0.12	1	0.16	0.62	–0.52	0.28	0.4658
$BC$	0.32	1	0.16	4.38	–0.074	0.72	0.0905
$A^2$	–1.78	1	0.16	121.73	–2.20	–1.37	0.0001
$B^2$	–15.09	1	0.16	8718.15	–15.50	–14.67	<0.0001
$C^2$	–2.14	1	0.16	175.45	–2.56	–1.72	<0.0001

**Table 6**  
ANOVA results for the coefficients of quadratic model for COD removal.

Factor	Coefficient	Degree of freedom	Standard error	F-value	95% confidence interval low	95% confidence interval high	p-Value
Intercept	76.43	1	0.43	–	75.32	77.54	–
A	2.01	1	0.26	58.08	1.33	2.69	0.0006
B	–22.82	1	0.26	7464.72	–23.49	–22.14	<0.0001
C	2.02	1	0.26	58.66	1.34	2.70	0.0006
AB	2.11	1	0.37	32.00	1.15	3.07	0.0024
AC	–0.41	1	0.37	1.19	–1.37	0.55	0.3250
BC	–1.23	1	0.37	10.89	–2.19	–0.27	0.0215
A <sup>2</sup>	–0.21	1	0.39	0.29	–1.21	0.79	0.6143
B <sup>2</sup>	–9.27	1	0.39	569.23	–10.27	–8.27	<0.0001
C <sup>2</sup>	2.14	1	0.39	30.35	1.14	3.14	0.0027

the coefficients of regression models for color removal and COD removal are shown in Tables 5 and 6.

The coefficient of determination is defined as the ratio of the explained variation to the total variation and is used as a measure of degree of fit of the model. The predicted  $R^2$  value of 0.9981 and 0.9906 for color removal and COD removal are in good agreement with the corresponding adjusted  $R^2$  values of 0.9997 and 0.9983. For the model to fit to the experimental data better the  $R^2$  value should be close to 1. Smaller the value of  $R^2$ , lesser will be the fit of the model to the experimental data. The values of  $R^2$  found out indicate that, the quadratic polynomial equations can be used to predict the decolorization and mineralization of MYB in the experimental range [37,38]. The predicted values of color and COD removal are plotted versus corresponding observed values in Fig. 4a and b.

In case of color removal, the independent variables of the quadratic polynomial model A, B and C, the interaction between catalytic dose (A) and initial dye concentration (B), AB and the quadratic terms A<sup>2</sup>, B<sup>2</sup> and C<sup>2</sup> are highly significant as p-value for them is >0.001. From the values of the coefficients in the regression model, the order in which the independent variables affect the degradation of MYB is, initial dye concentration (B) > catalytic dose (A) > pH (C). The negative effect of B is very high as compared to the positive effects of A and C. In case of COD removal, the independent variables of the quadratic polynomial model A, B and C, the interaction between catalytic dose (A) and initial dye concentration (B), AB, the interaction between initial dye concentration (B) and pH of reaction mixture (C), BC and the quadratic terms A<sup>2</sup>, B<sup>2</sup> and C<sup>2</sup> are significant as p-value for them is >0.05. Out of these, B and B<sup>2</sup> are highly significant as their p-value is >0.001. From the values of the coefficients in the regression model, the order in which the independent variables affect the mineralization of MYB is, initial dye concentration (B) > catalytic dose (A) ≈ pH (C). The negative effect of B is very high as compared to the positive effects of A and C. The initial dye concentration (B) has high negative effect while catalytic dose and pH of reaction mixture have low positive effect both for decolorization and mineralization of MYB. This is in accordance with the results of preliminary experiments. Thus initial dye concentration is the major factor affecting the photocatalytic degradation of MYB using Ag<sup>+</sup> doped TiO<sub>2</sub>. This finding is validated by the fact that, photocatalytic degradation needs UV light to reach the surface of the photocatalyst for the effective production of oxidising species like hydroxyl radicals to cause degradation, which is not possible at higher concentration of dye.

Plots of normal probability of internally studentized residuals for color and COD removal are shown in Fig. 5a and b. The normal probability plot of the residuals is an important diagnostic tool to detect and explain the systematic departures from the assumption that errors are normally distributed and they are independent of each other, and that the error variance is homogeneous. Information regarding the lack of fit of the selected model is contained in the residuals [39]. The normal probability

plot of the residuals shown in Fig. 5 showed that there is almost no serious violation of the assumptions underlying the analyses and it confirmed the normality assumptions and independence of the residuals. Moreover, the comparison of the residuals with the error variance showed that none of the individual residual exceeded the value twice of the square root of the error variance [40].

### 3.3. Response surface analysis

Using RSM, the effects of the independent variables (catalytic dose, initial dye concentration and pH of reaction mixture) and their interaction on the decolorization and mineralization of MYB were graphically represented by three-dimensional response surface plots and two-dimensional contour plots. The responses were predicted and the optimum values for decolorization and mineralization were determined [30,41].

The interaction effect of initial concentration of MYB and the dose of Ag<sup>+</sup> doped TiO<sub>2</sub> on decolorization rate of MYB is shown in Fig. 6a and that on mineralization rate is shown in Fig. 7a. From Fig. 6a, it is evident that the rate of decolorization of MYB decreased with increase in concentration irrespective of the dose of catalyst. The maximum decolorization was found in the concentration range of 25–40 ppm, as evident from the contour plot. The dye decolorization increased with increase in catalytic dose up to a dose of 1 g/L and then remained almost constant irrespective of the initial concentration. From the contour plots the maximum degradation was found out in the range 0.9–1.4 g/L. Fig. 7a showed similar effects of initial dye concentration and catalytic dose on mineralization rate as in case of decolorization. The corresponding maximum regions were dye concentration 25 ppm and catalytic dose 0.9–1.1 g/L. The observations were in accordance with the preliminary test results.

Fig. 6b shows the interaction effects of pH of reaction mixture and catalytic dose on the rate of decolorization of MYB and Fig. 7b shows the interaction effect of the same parameters on the mineralization of the dye. Fig. 6b shows that the decolorization rate slightly increased with the increase in pH up to a pH of 8 and then slightly decreased irrespective of the catalytic dose. The dye decolorization rate increased with the increase in catalytic dose and then remained almost constant irrespective of the pH of the reaction mixture. The maximum region as found from contour plot was in the range 1.1–1.4 g/L. Fig. 7b showed similar trends of effects of pH and catalytic dose on the mineralization of dye as decolorization, the maximum region being pH 8–9 and catalytic dose 1.1–1.4 g/L.

The interaction effects of pH of reaction mixture and the initial concentration of MYB on its decolorization rate are shown in Fig. 6c and the same on the mineralization rate of the dye is shown in Fig. 7c. From Fig. 6c, it is evident that the decolorization increased at a low rate with the increase in pH irrespective of the concentration of the dye, the maximum region being in the pH range 7–8. Similarly it showed a decrease in decolorization rate with the increase in

initial dye concentration and the maximum region was in the range of 35–45 ppm. Fig. 7c showed that the mineralization rate increased slowly with the increase in pH of reaction mixture irrespective of initial concentration of the dye while it decreased with the increase in initial dye concentration and the maximum was at pH 9 and dye concentration 25 ppm. All the observations are in accordance with the preliminary test results.

### 3.4. Optimization of independent variable

Any reaction system is optimized to find out the optimum operating conditions, which will produce best possible result using various design methodology and analytical procedures. But a good optimization practice is to consider the effects of factors like economy, ecological balance and possibility of subsequent treatment in addition to looking at maximizing the result. So, in the present study, efforts have been made to keep the pH as nearer to the natural pH of the reaction mixture as possible, to minimize the use of the catalyst and to maximize the concentration of MYB degraded, during optimization. Based on the design model and the constraints as described, numerical optimization was carried out

using Design Expert software version 8.0.6.1 considering the three independent variables and the two responses. The optimum conditions for the maximum possible decolorization and mineralization of MYB under the described constraints were found out to be dose of  $\text{Ag}^+$  doped  $\text{TiO}_2$  0.99 g/L, concentration of MYB 57.68 ppm and pH of reaction mixture 7.76. Under these conditions the model predicted the decolorization and mineralization rates of MYB to be 95.97% and 80.33%, respectively. The results showed the effective use of RSM to find out the optimum conditions for the photocatalytic degradation and mineralization of MYB using  $\text{Ag}^+$  doped  $\text{TiO}_2$  [30].

### 3.5. Validation experiment

In order to check the accuracy of the optimization, the model was validated by conducting the photocatalytic degradation of MYB in the batch reactor under optimum conditions. The decolorization and mineralization rates were found out from the validation experiment to be 95.43% and 80.05%, respectively and were in good agreement with the predicted results. Hence the optimum point determined by RSM was successfully validated and it was

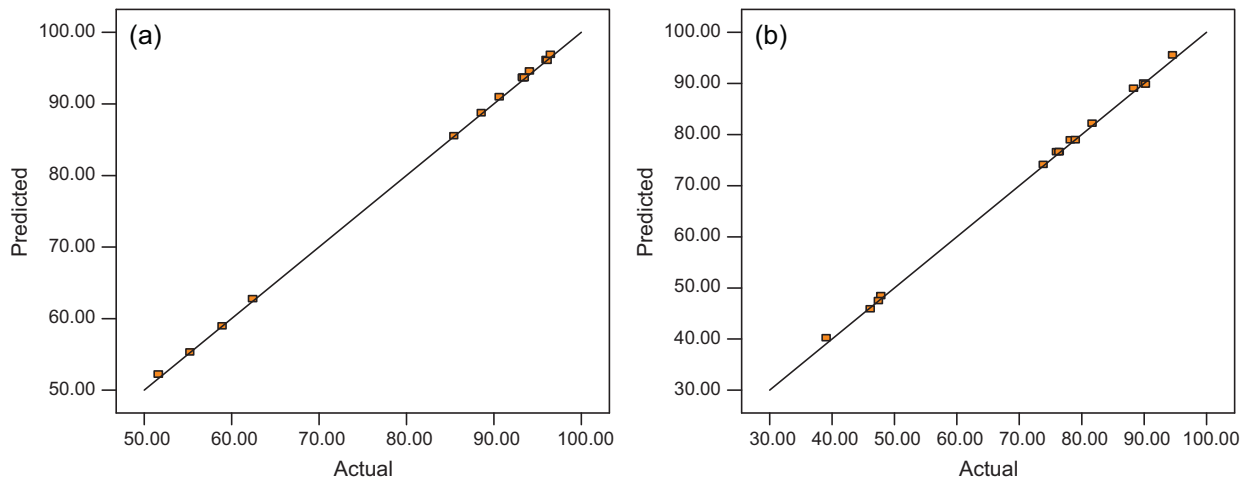


Fig. 4. Plot of the actual and predicted values for (a) color removal (%) (b) COD removal (%).

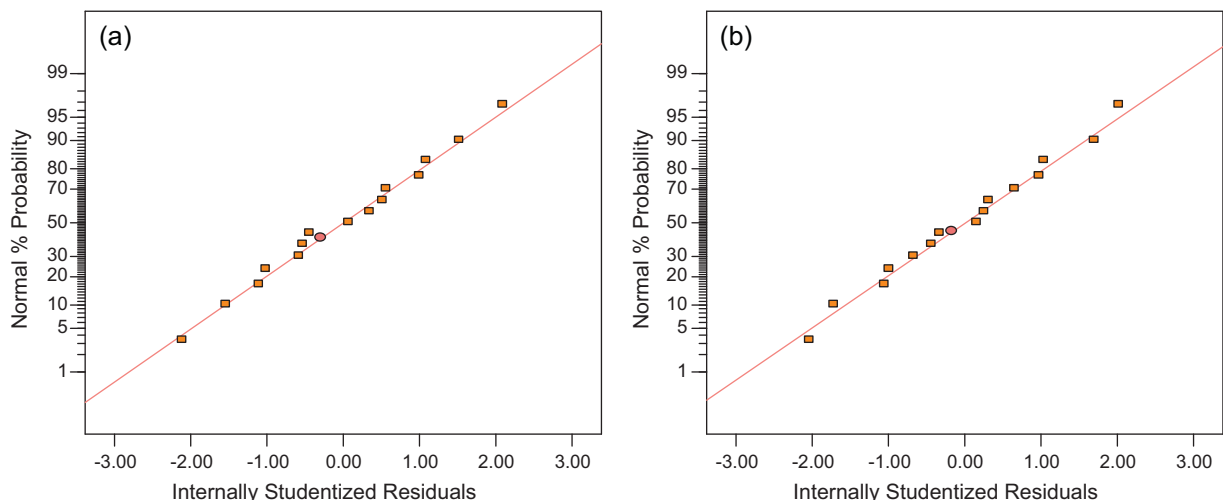
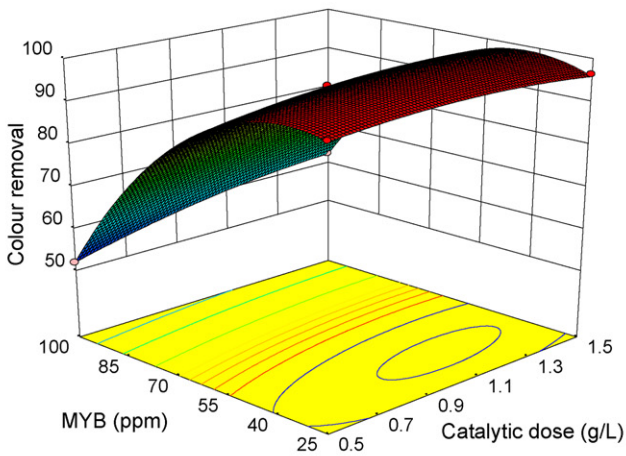
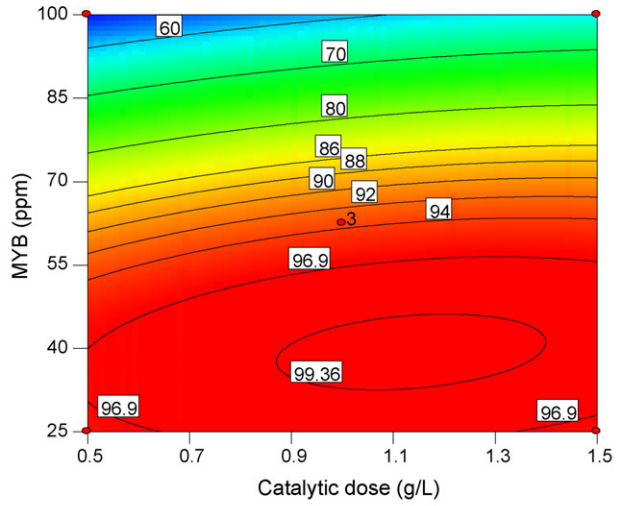


Fig. 5. Plot of the normal probability and internally studentized residuals for (a) color removal (%) (b) COD removal (%).

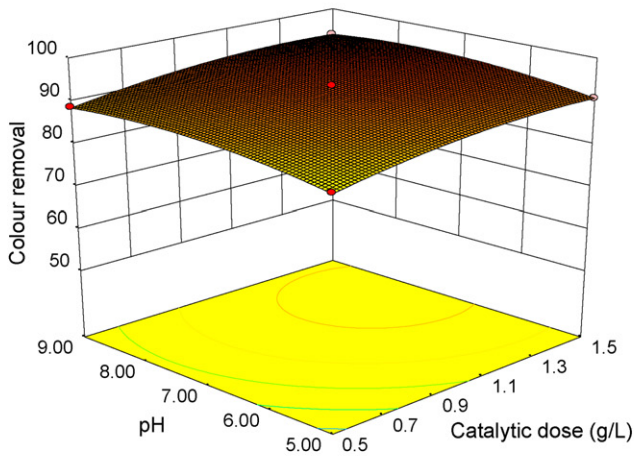
(a1)



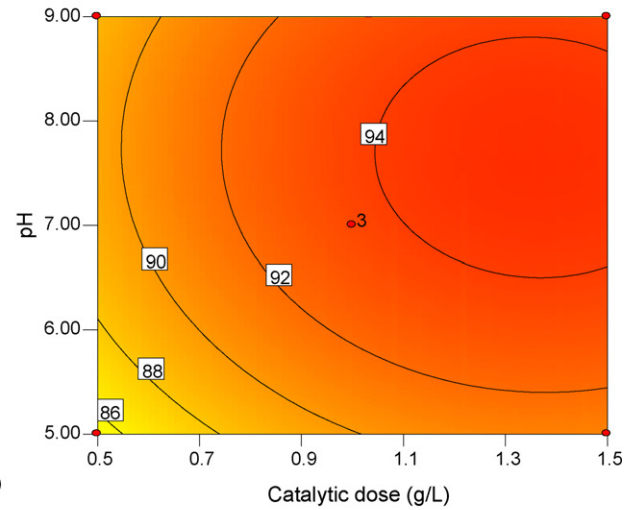
(a2)



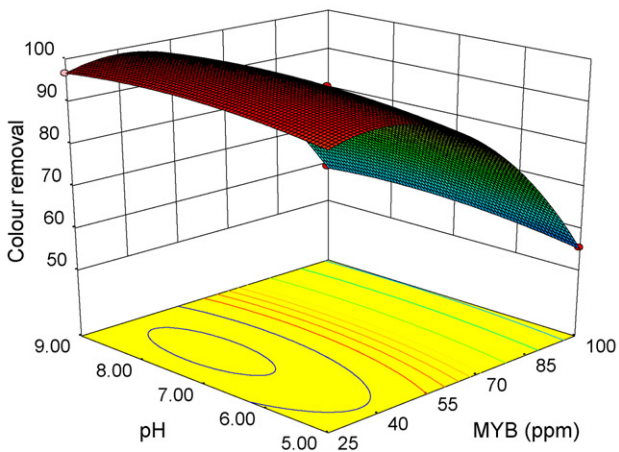
(b1)



(b2)



(c1)



(c2)

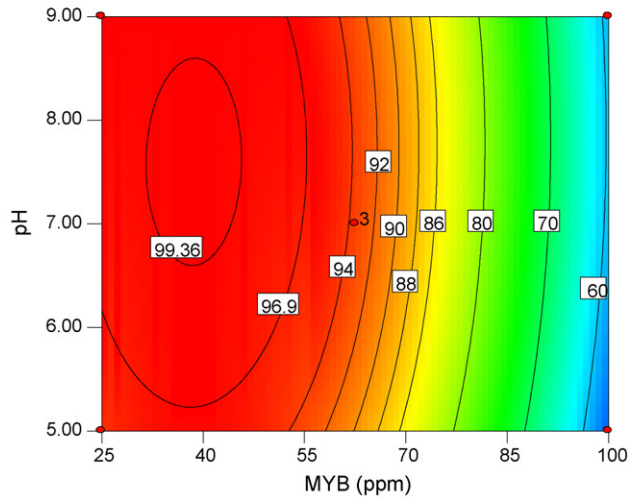
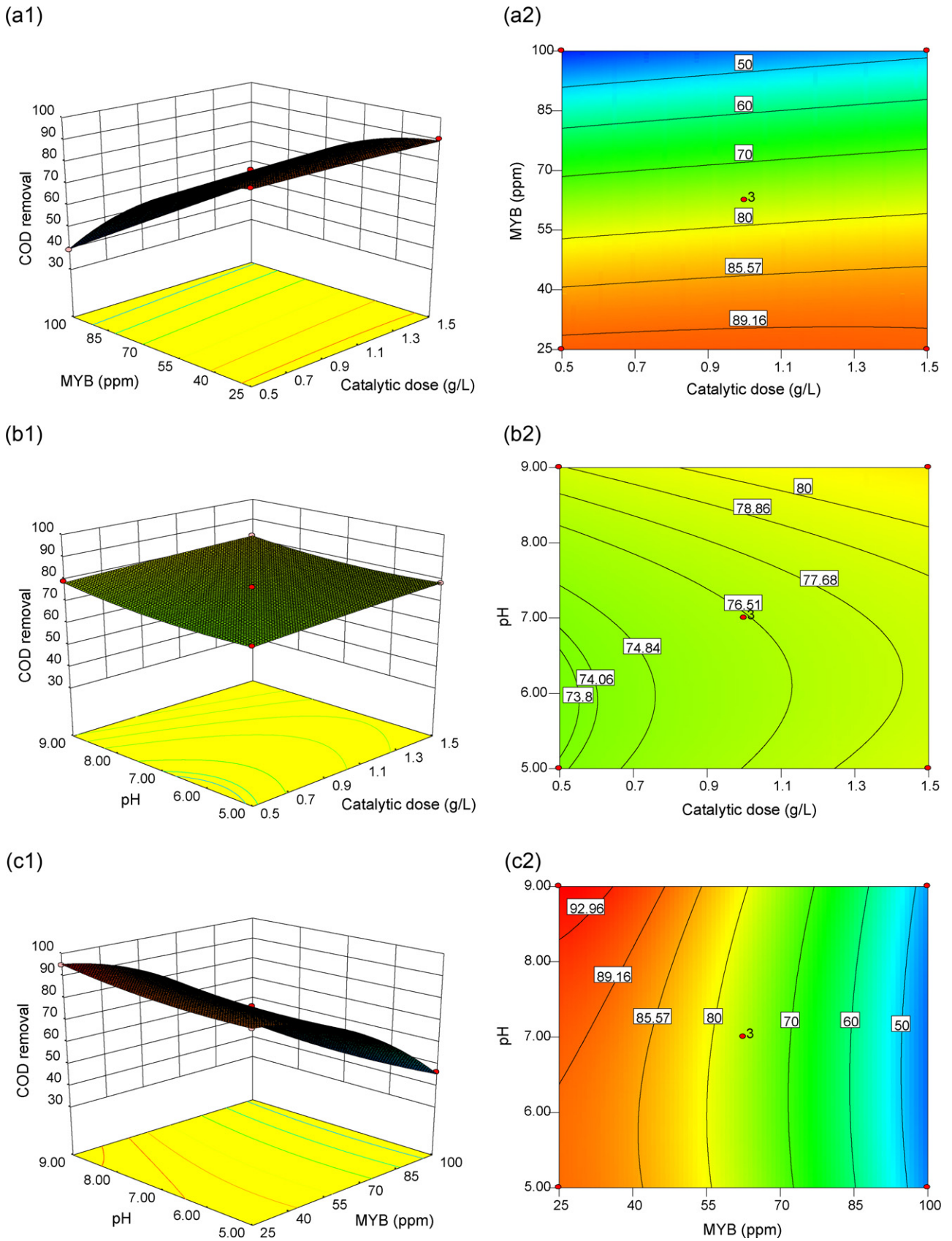


Fig. 6. Effects of catalytic dose, initial dye concentration and pH on decolorization of MYB (a) pH kept constant at 7 (b) MYB concentration kept constant at 62.5 ppm (c) catalytic dose kept constant at 1 g/L.



**Fig. 7.** Effects of catalytic dose, initial dye concentration and pH on mineralization of MYB (a) pH kept constant at 7 (b) MYB concentration kept constant at 62.5 ppm (c) catalytic dose kept constant at 1 g/L.



confirmed that RSM can be used to optimize the photocatalytic degradation process of MYB using Ag<sup>+</sup> doped TiO<sub>2</sub>.

#### 4. Conclusions

A combination of three factors, three levels Box–Behnken design of experiment and response surface methodology was successfully employed in the study to optimize the individual and interaction effects of the parameters catalytic dose, initial dye concentration and pH of reaction mixture on the photocatalytic degradation of MYB using Ag<sup>+</sup> doped TiO<sub>2</sub>. From the quadratic models developed for decolorization and mineralization and subsequent ANOVA test using Design Expert software version 8.0.6.1, the initial concentration of dye was found to be the most influential factor, while all the other factors were also significant. The models fitted very well to the experimental data as confirmed by the high R<sup>2</sup>, adjusted R<sup>2</sup> and predicted R<sup>2</sup> values. The process was optimized under three applied constraints of minimum use of catalyst, degradation of maximum possible dye concentration under the constraints and pH of the reaction mixture as near to the natural pH of the dye solution as possible. The optimum values of the three independent variables were found out as dose of Ag<sup>+</sup> doped TiO<sub>2</sub> 0.99 g/L, initial concentration of MYB 57.68 ppm and pH of reaction mixture 7.76 under the applied constraints. Under the optimum condition the dye decolorization and mineralization were predicted to be 95.97% and 80.33%, respectively and the corresponding experimental values fitted well to the predicted values.

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