Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1030705

57 (2016) 9296–9306
April

Taylor & Francis
Taylor & Francis Group

Optimization of photocatalytic degradation of neutral red dye using TiO_2 nanocatalyst via Box-Behnken design

Naz Chaibakhsh*, Neda Ahmadi, Mohammad Ali Zanjanchi

Faculty of Science, Department of Chemistry, University of Guilan, Rasht, Iran, Tel. +98 1333333262; emails: nchaibakhsh@guilan.ac.ir (N. Chaibakhsh), ahmadi.n666@yahoo.com (N. Ahmadi), zanjanchi@guilan.ac.ir (M.A. Zanjanchi)

Received 5 August 2014; Accepted 11 March 2015

ABSTRACT

In this study, the TiO_2/UV photodegradation of neutral red (NR) dye has been investigated in aqueous heterogeneous suspension. Response surface methodology based on a three-variable, three-level Box-Behnken design was employed to study and optimize the photocatalytic process. The interactive effects of three operational parameters including irradiation time, pH, and the catalyst amount on the dye degradation and chemical oxygen demand (COD) reduction were analyzed. The dye degradation efficiency was accurately modeled by a partial cubic equation with an R^2 of 0.99. A high color (90.0%) and COD (85.6%) reduction was obtained using minimum amount of TiO_2 nanocatalyst (68.0 mg) at the optimal conditions of 28.7 min and pH 6.47. The results also showed that the kinetics of adsorption of NR on TiO_2 nanoparticles can be described by the pseudo-second-order and parabolic diffusion models.

Keywords: Photocatalysis; Dye degradation; TiO_2; Neutral red; Box-Behnken design

1. Introduction

The large volumes of wastewater generated by dye-manufacturing and dye-consuming industries pose serious environmental problems. The total world production of dyes and pigments is estimated to be 800,000 tons per year and at least 10% of them enter the environment [1]. Low amount of dye in water (<1 ppm) may cause severe damages to the environment such as reduction in sunlight penetration, decrease in the photosynthetic activity and dissolved oxygen concentration, and having acute toxic effects on aquatic ecosystem [2]. Many techniques have been developed for the treatment of dye-containing wastewaters including physical, chemical, and biological methods and their combinations [3]. However, these conventional methods are not able to completely destruct the dye molecules. Furthermore, the post-treatment of generated sludge is required in these methods. In recent years, there has been extensive interest in the use of photocatalysts for wastewater decolorization [4]. In the photocatalytic advanced oxidation technology, UV light is usually used to stimulate a semiconductor surface to generate photo-induced holes or reactive oxygen species (ROS), such as hydroxyl and superoxide radicals. The ROS then interacts with organic compounds and leads to their oxidation and overall degradation [5].

Titanium dioxide (TiO_2) is found to be one of the most efficient semiconductor catalysts for photocatalytic degradation of organic pollutant molecules since it is photoactive, available, insoluble, photostable,

---

*Corresponding author.

inexpensive, and non-toxic [6]. Many investigations have reported that TiO_2 photocatalysis is an efficient method for decolorization and oxidation of organic dyes in wastewater [7–9]. TiO_2 nanoparticles, which are a few nanometers in size, are of particular interest for the photocatalytic processes due to their high catalytic activity and special optical and mechanical properties [10].

Neutral red (NR), C.I. 50040, is a basic dye of the azine series and belongs to quinone-imine class of dyes (Fig. 1). NR was selected in this study due to its wide application range and recalcitrant nature. Several studies have been done on the photocatalytic degradation and toxicity reduction of NR using various catalysts such as Fe_3O_4–TiO_2 with core–shell structure [11], Bismuthoxichloride [12], sulfur and copper co-doped TiO_2 (S,Cu-TiO_2) [13], and Copper hexacyanoferrate(II) [14].

In the present study, for the first time, the intrinsic anatase TiO_2 nanoparticles with no modification were used for decolorization of the NR solution. To increase and optimize the color removal efficiency of the photocatalyst, response surface methodology (RSM) with Box-Behnken design (BBD) was used. RSM is an efficient and economical statistical technique in evaluating the effect of various parameters on treatment results. Optimization by RSM has several advantages over one-variable-at-a-time (OVAT) conventional optimization method such as requiring less time and experiments, and considering the interaction of the independent parameters [15]. The two most common RSM designs are central composite design (CCD) and BBD. The BBD is more efficient than CCD. It requires fewer experimental runs and is rotatable with uniform precision.

RSM has been successfully applied for optimization of photocatalytic decolorization of various dyes [16,17]. However, so far, there is no report on the application of RSM in the photocatalytic decolorization of NR. Furthermore, neither specific study on the interactive effect of the main parameters nor any optimal conditions have been reported for the photodegradation of NR in the presence of intrinsic TiO_2.

The aim of the present work was to investigate the possibility of degradation of NR dye in the presence of intrinsic nano-sized TiO_2 particles under UV irradiation. RSM and BBD were used to optimize and analyze the effect of three operational parameters including contact time, pH, and the catalyst amount on the dye degradation efficiency. In this study, chemical oxygen demand (COD) reduction was also monitored in order to explain the degradation of NR in the UV/TiO_2 process, and the optimal conditions were obtained.

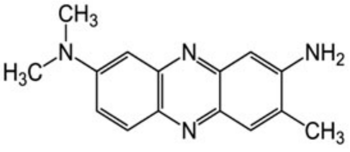

Fig. 1. The chemical structure of NR dye.

2. Experimental

2.1. Photocatalysis experiments

The photocatalyst used in this study was the commercially available TiO_2 nano-sized (<25 nm) powder in anatase crystalline form with purity of >99% and purchased from Sigma-Aldrich. The photochemical reactor was a beaker containing suspension of TiO_2 and NR dye placed in a continuously ventilated chamber [18]. The suspension was magnetically stirred during irradiation. Artificial irradiation was provided by a 400 W Kr UV lamp (Osram). About 90% of the radiated power was in the UV-A region (400–315 nm) and about 10% in the UV-B region (315–280 nm). The distance between the lamp and the reactor was 30 cm. Before irradiation, the sample was stirred for 5 min to establish an adsorption–desorption equilibrium between the catalyst surface and the dye molecules [18].

2.2. Dye removal assay

NR, as a model for the commercial textile dyes, was purchased from Merck (Darmstadt, Germany). A dye solution of 25 mg/L was prepared by dissolving NR in distilled water. The pH of the solution was adjusted to be in the range of 2.5–6.5 by addition of diluted HCl and NaOH using a pH meter (WinLab® Data Line pH meter; Windaus, Clausthal-Zellerfeld, Germany). The range of pH was selected based on the fact that NR could act as a pH indicator, changing from red to yellow between the pH 6.8–8.0 [14,19]. In the selected range of pH 2.5–6.5, the color of NR is red with a maximum absorbency wavelength of 523 nm. Two-hundred milliliter of this initial solution was put into 250 mL-flask, and various doses of catalyst according to the experimental design were added. After irradiation for a certain period of time, removal of the photocatalyst particles was performed by centrifugation.

The reduction in color concentration was measured using a spectrophotometer (Model UV 2100, Shimadzu

Co., Kyoto, Japan). The dye degradation percentage was calculated using the following equation:

$$\text{Dye degradation } (\%) = \frac{A_0 - A}{A_0} \times 100 \tag{1}$$

where A is the average of absorbance values at maximum absorbency visible wavelength of NR solution (523 nm), A_0 the value before treatment, and A the value after treatment process. The readings were done in triplicate.

2.3. COD reduction analysis

Permanganate oxidation method was utilized for measuring COD (COD_{Mn}) [20] before and after each run of the experimental design. The percentage of COD reduction was calculated using the following equation:

$$\text{COD reduction } (\%) = \frac{\text{COD}_0 - \text{COD}}{\text{COD}_0} \times 100 \tag{2}$$

where COD_0 is the value before treatment, and COD the value after treatment process. Each experiment was performed in triplicate.

2.4. Design of experiments, statistical analysis, and optimization

A three-variable, three-level RSM-BBD was employed with 17 experiments. The variables and their levels selected for the photocatalytic degradation of NR were reaction time (1–30 min), pH (2.5–6.5), and catalyst amount (20–100 mg) (Table 1). Color removal and COD reduction were analyzed as the responses. The BBD employed is presented in Table 1. For statistical analysis, the variables were coded according to the following equation:

$$\alpha = \frac{x_i - x_0}{\Delta x} \tag{3}$$

where α is the coded value of the independent variable; x_i is its real value; x_0 is its real value at the center point; and Δx is the step change in the variable x_i.

A software package of Design Expert Version 6.0.6 (Stat-Ease, Statistics Made Easy, Minneapolis, MN, USA) was employed in this study. After testing increasingly complex models from linear to partial cubic, a partial cubic polynomial model was developed to study the effects of the variables on the dye degradation. The final equation of the model is as follows:

Table 1
Composition of various experiments of the BBD, and color and COD reduction responses for the photocatalytic degradation of NR

	Variable				
Exp. No.	pH	Catalyst amount (mg)	Time (min)	Color removal (%)	COD reduction (%)
1	4.5	20.0	1.0	61.6	13.3
2	2.5	20.0	15.5	0.0	53.3
3	6.5	20.0	15.5	6.8	33.3
4	4.5	20.0	30.0	19.4	40.0
5	2.5	60.0	1.0	0.0	28.9
6	6.5	60.0	1.0	4.0	11.0
7	4.5	60.0	15.5	83.8	10.7
8	4.5	60.0	15.5	83.5	1.1
9	4.5	60.0	15.5	83.0	8.9
10	4.5	60.0	15.5	84.3	0.0
11	4.5	60.0	15.5	80.2	5.3
12	2.5	60.0	30.0	0.0	33.3
13	6.5	60.0	30.0	83.8	82.4
14	4.5	100.0	1.0	82.9	45.4
15	6.5	100.0	15.5	92.7	92.4
16	2.5	100.0	15.5	0.0	13.3
17	4.5	100.0	30.0	86.5	69.2

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{112} x_1^2 x_2 + \beta_{113} x_1^2 x_3 \quad (4)$$

where y is the response variable of decolorization efficiency. The β_i is regression coefficients for linear effects; β_{ij} the regression coefficients for quadratic effects, β_{iij} the regression coefficients for cubic effects, and x_i represents coded experimental levels of the variables.

The percentage of COD reduction could be simply related to the independent parameters by a quadratic model as given in Eq. (5).

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \left(\sum_{i=}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j \right)_{i<j} \quad (5)$$

where y is the response; x_i and x_j are the independent variables; β_0 is the constant coefficient; and β_i, β_{ii}, and β_{ij} are the interaction coefficients of linear, quadratic, and second-order terms, respectively.

An analysis of variance (ANOVA) was used to determine whether the generated models were adequate to describe the experimental data. Optimization was performed by the software using a desirability function (Eq. (6)). The experiment with desirability value of 1 was selected as the optimum condition.

$$D = (d_1 \times d_2 \times \ldots \times d_n)^{1/n} = \left(\prod_{i=1}^{n} d_i \right)^{1/n} \quad (6)$$

where n is the number of responses in the measure and d_i is the desirable ranges for each response.

2.5. Photocatalytic kinetic models

The photocatalytic processes can be described by the kinetic models known as the decay models. Kinetic modeling of the photocatalytic reaction is necessary for any practical applications [21]. In this study, six kinetic models were used to analyze the kinetic data of the photocatalytic degradation of NR on TiO_2 [10,22,23]:

(1) First-order model which can be generally written as:

$$\ln (C/C_0) = -k t \quad (7)$$

(2) Second-order model according to the following equation:

$$\frac{1}{C} - \frac{1}{C_0} = k t \quad (8)$$

(3) Pseudo-first-order (Lagergren) model expressed as:

$$\ln (C - C_0) = \ln (C) - k t \quad (9)$$

(4) Pseudo-second-order model using the following equation:

$$\frac{t}{C} = \frac{t}{C_0} - \frac{1}{k C^2} \quad (10)$$

(5) Modified Freundlich model explains that the system is adsorption–desorption controlled by the following equation:

$$\frac{C_0 - C_t}{C_0} - = k t^b \quad (11)$$

(6) Parabolic diffusion model presents the diffusion-controlled degradation of NR on the photocatalyst surface. The equation is expressed as:

$$\frac{(1 - C_t/C_0)}{t} = k t^{-\frac{1}{2}} + \alpha \quad (12)$$

3. Results and discussion

3.1. Dye degradation

Design matrix of the variables along with the obtained dye degradation percentage is presented in Table 1. Fitting of the data to various models and their subsequent ANOVA indicated that the photocatalytic process was most suitably described with a partial cubic model. The equation of the model in terms of coded factors is as follows:

$$\text{Dye degradation } (\%) = +82.96 + 23.41A + 21.79B - 9.65C - 49.37A^2 - 8.72B^2 - 11.64C^2 + 1.47AB + 19.95AC + 11.45BC + 29.60A^2C \quad (13)$$

where *A* is the pH, *B* the catalyst amount, and *C* the reaction time.

The ANOVA for the model is shown in Table 2. Using an *F*-test, the lack of fit (variation of data around the fitted model) was evaluated. The model showed no lack of fit at a 95% level of significance. The *F*-value of the model (547.91) with a *p*-value less than 0.0001 implied that the model was statistically significant at the 95% confidence level. A very high coefficient of determination ($R^2 = 0.9989$) also showed the suitability of the model for representing the actual relationship among the parameters [24].

The predicted R^2 shows the prediction ability of a regression model for new observations. The predicted R^2 of the model (0.9717) is in reasonable agreement with the Adjusted R^2 of 0.9971. Adequate precision measures the signal-to-noise (S/N) ratio. The adequate precision for the generated model (53.237) has been greater than 4, indicating that the model could be used to precisely navigate the design space.

The significance of each term in the model was examined by testing the null hypothesis. In this case, A, B, C, A^2, B^2, C^2, AB, AC, BC, and A^2C were the significant model terms.

The developed model was then used to study the effect of operational parameters on the dye degradation efficiency of the nano-sized TiO_2.

Fig. 2(a) depicts the three-dimensional (3D) response surface plot regarding the effect of catalyst amount, pH, and their interactions on the dye degradation at 15.5 min (center point of the experimental design). At pH below 4, increasing the catalyst dose did not have a significant effect on the dye degradation. A low amount of catalyst also resulted in lower dye degradation percentage. Minimum color removal was observed at low pH and low catalyst dose. At pH 2.5, no color removal was observed using 100 mg catalyst. As TiO_2 dosage increased, the percentage of degradation increased. The highest dye degradation was obtained at a pH range of 4.7–6.2 with TiO_2 amount of 85 mg. At this range of pH, increasing the catalyst amount up to 100 mg did not have a significant effect on the color removal. Concentration of TiO_2 in the photocatalytic water treatment system affects the reaction rate [25]. Increase in the catalyst loading causes increase in the active sites on catalyst surface which in turn increases the generation rate of electron/hole pairs, and hence dye degradation [26,27]. At a certain amount of catalyst, the number of available dye molecules is not sufficient for adsorption by the increased number of TiO_2 particles. Hence, above a certain catalyst amount, additional catalyst particles are not involved in the reaction and the rate tends to level off [28]. Finding the optimum catalyst loading is necessary for efficient removal of the dye. An over optimum amount of photocatalyst would make the solution more turbid and decrease UV light penetration [26]. Higher doses of catalyst, above a saturation level, lead to aggregation of the particles as well as reduced irradiation field due to increase in light scattering by the TiO_2 particles and the opacity [25].

According to ANOVA, pH of the solution had the greatest effect on the degradation of NR, with the highest *F*-value of 929.57. In heterogeneous photocatalysis, pH of the solution is an important factor that affects the surface charge of the catalyst particles, the positions of conductance and valence bands of the catalyst, and the ionization state of the dye molecules [25]. However, the interpretation of pH effect is a very difficult task due to the different dye degradation

Table 2
ANOVA for the partial cubic model used for the analysis of NR dye degradation

Source	Sum of squares	Degree of freedom	Mean square	*F*-value	*p*-value
Model	25,847.10	10	2,584.71	547.91	<0.0001
A, pH	4,385.16	1	4,385.16	929.57	<0.0001
B, catalyst amount	3,797.56	1	3,797.56	805.01	<0.0001
C, time	372.49	1	372.49	78.96	0.0001
A^2	10,261.68	1	1,0261.68	2175.28	<0.0001
B^2	319.98	1	319.98	67.83	0.0002
C^2	570.73	1	570.73	120.98	<0.0001
AB	1,844.70	1	1,844.70	391.04	<0.0001
AC	1,592.01	1	1,592.01	337.47	<0.0001
BC	524.41	1	524.41	111.16	<0.0001
A^2C	1,752.32	1	1,752.32	371.46	<0.0001
Residual	28.30	6	4.72		
Lack of fit	17.89	2	8.95	3.44	0.1353
Pure error	10.41	4	2.60		
Corrected total	25,875.40	16			

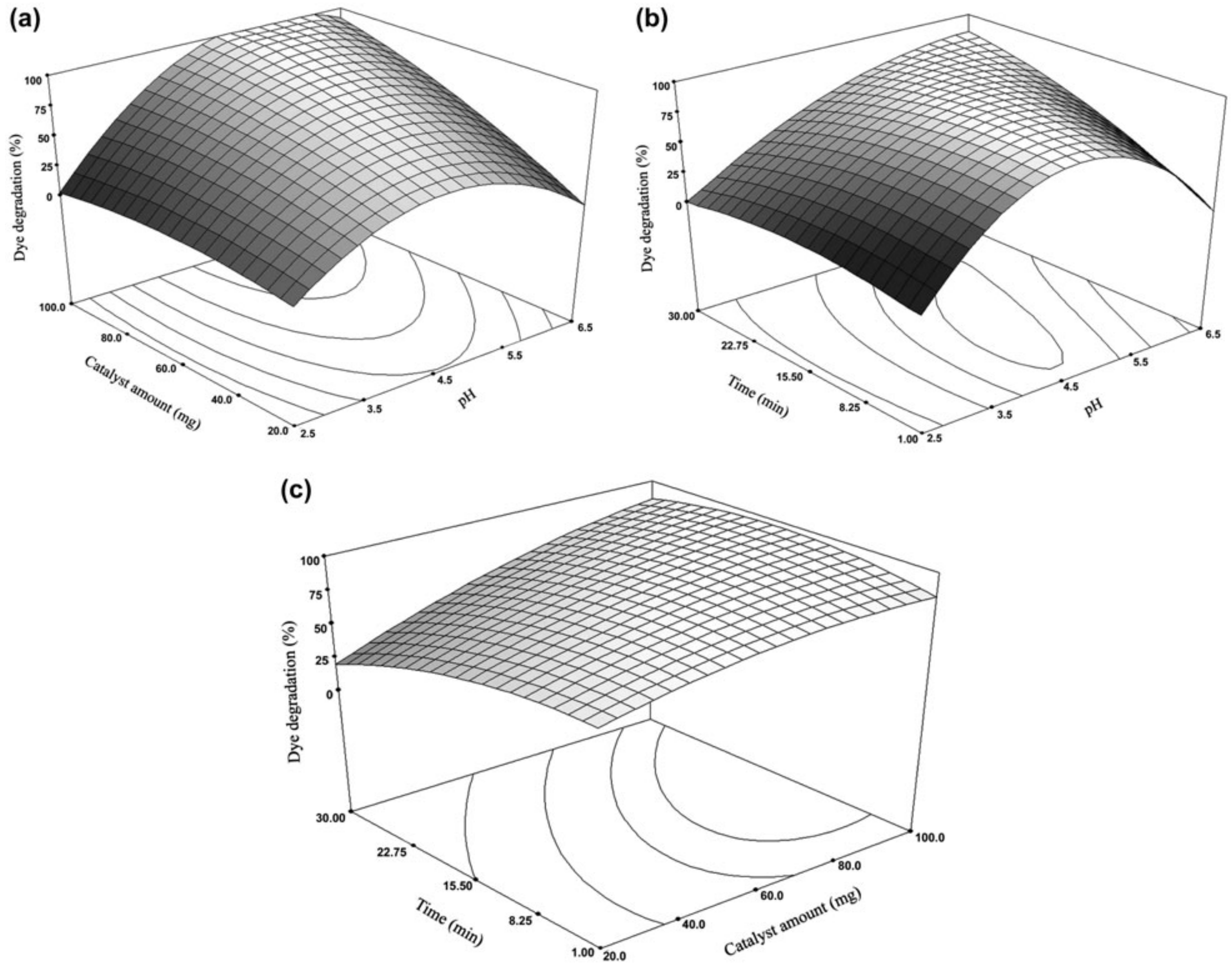

Fig. 2. Response surface plots showing the interaction between two parameters, pH and catalyst amount (a), pH and irradiation time (b), and irradiation time and catalyst amount (c) on the NR dye degradation percentage. Other variables are constant at their center points.

mechanisms such as hydroxyl radical attack, direct oxidation by positive hole, and direct reduction by the electron in the conducting band [29].

The results showed that the degradation of NR was very low in highly acidic pH range lower than pH 3.5. The TiO_2 particles tend to agglomerate under highly acidic condition which reduces the surface area available for dye degradation [28]. Agglomeration of the TiO_2 particles also leads to turbidity of the solution. The significant turbidity would cause shielding effect, which decreases light transmission through the solution. As a result, although there is a low color removal which results in COD reduction (Exp. No. 2, 5, 12, and 16 in Table 1), but it is not detectable. As pH increased, the percentage of photocatalytic degradation also increased. Maximum dye degradation was observed at pH 5. TiO_2 surface is positively charged in acidic media. NR is a cationic dye; therefore, the neutralizing of positively charged NR molecules at higher pH leads to better adsorption of NR dye on the catalyst surface. In addition, at this low pH, $HO_2^{\bullet}$ radicals are also able to form and can be responsible for the oxidation of dye molecules [5]. After optimum pH value, the degradation percentage started to decrease gradually. This can be because at higher pH values, the oxidizing radicals are rapidly scavenged and they do not have the opportunity to react with the dye molecules [26].

Fig. 2(b) shows the effect of varying pH and UV light irradiation time on the decolorization of NR solution using 60 mg of catalyst. Prolonging the time did not have a significant effect on the decolorization at pH below 4.0. A high degradation of NR (85%) was observed at a pH range of 4.5–5.0 and 8–18 min. At pH 6.5, maximum decolorization was obtained at 30 min. At this pH, the effect of time was highly significant, so that by increasing the time from 1 to

30 min, the percentage of dye degradation drastically increased by 70%. Fig. 2(c) depicts the response surface plot as a function of catalyst amount vs. irradiation time at pH 4.5. The effect of catalyst dosage on the decolorization is more significant than the effect of time. By increasing the catalyst amount, the dye degradation increased at any given irradiation time. Maximum dye degradation percentage was obtained using maximum catalyst amount (100 mg) at 15 min.

3.1.1. COD reduction

As the COD indicates the extent of degradation of organic species, the percentage change in COD was investigated in this study. The COD reduction represents the degree of mineralization at the end of the photocatalytic process [30]. Experimental data along with obtained percentage reduction of COD are presented in Table 1. According to ANOVA, a quadratic polynomial model was statistically significant to represent the actual relationship between the response (COD reduction) and the variables, with a small p-value (0.0003), insignificant lack of fit, and a high coefficient of determination ($R^2 = 0.9628$). The ANOVA for the model is shown in Table 3. The equation of the model in terms of coded factors is given below:

$$\begin{aligned}\text{COD reduction} = {} & +5.20 + 11.29\,A + 10.05\,B + 15.79\,C \\ & + 19.90\,A^2 + 22.97\,B^2 + 13.80\,C^2 \\ & + 24.78\,AB + 16.75\,AC - 0.72\,BC\end{aligned} \tag{14}$$

where A is the pH, B the catalyst amount, and C the irradiation time.

The reaction time was found to have the greatest effect on the COD reduction, with the highest F-value of 28.62. The effects of pH and catalyst amount on the response were significant. In this case, A^2, B^2, C^2, AB, and BC were also significant model terms.

Fig. 3(a) shows the 3D response surface generated to show the effect of pH and catalyst amount on the COD reduction. By raising pH of the solution, COD reduction increased and maximum response was observed at pH 6.5 using 100 mg of catalyst. There was a drastic increase in COD reduction as pH increased from 6 to 6.5, whereas at this condition, maximum decolorization was observed at pH 5. It seems that the ROS formed at lower pH can attack the chromophore of dye in the photocatalytic reaction and cause the breakage of molecular bonds or functional groups responsible for the color. However, the dye molecule breaks into smaller pieces and decomposes completely at higher pH by hydroxyl radicals, which results in COD decrease in the latter period [31]. Maximum COD reduction was obtained using maximum catalyst dose. This is because the amount of dye adsorbed on the TiO_2 surface, and hence photodecomposition rate increases with increasing catalyst dosage. Adequate loading of the catalyst increases the photogeneration rate of electron–hole pairs for promoting the degradation of dye molecules [32].

The effect of varying pH and contact time using 60 mg of catalyst is shown in Fig. 3(b). Maximum COD reduction was observed at pH 6.5 and 30 min. As mentioned previously, maximum dye degradation could be obtained at 15 min. However, longer irradiation time is required for complete mineralization of the dye molecules to obtain maximum COD reduction [33]. Fig. 3(c) represents the effect of varying time and photocatalyst

Table 3
ANOVA for the quadratic model used for the analysis of COD reduction

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	12,613.78	9	1,401.53	20.12	0.0003
A, pH	1,019.26	1	1,019.26	14.63	0.0065
B, catalyst amount	808.02	1	808.02	11.60	0.0114
C, time	1,993.96	1	1,993.96	28.62	0.0011
A^2	1,667.41	1	1,667.41	23.93	0.0018
B^2	2,222.53	1	2,222.53	31.90	0.0008
C^2	801.85	1	801.85	11.51	0.0116
AB	2,455.20	1	2,455.20	35.24	0.0006
AC	1,122.25	1	1,122.25	16.11	0.0051
BC	2.10	1	2.10	0.030	0.8670
Residual	487.72	7	69.67		
Lack of fit	399.92	3	133.31	6.07	0.0570
Pure error	87.80	4	21.95		
Corrected total	13,101.50	16			

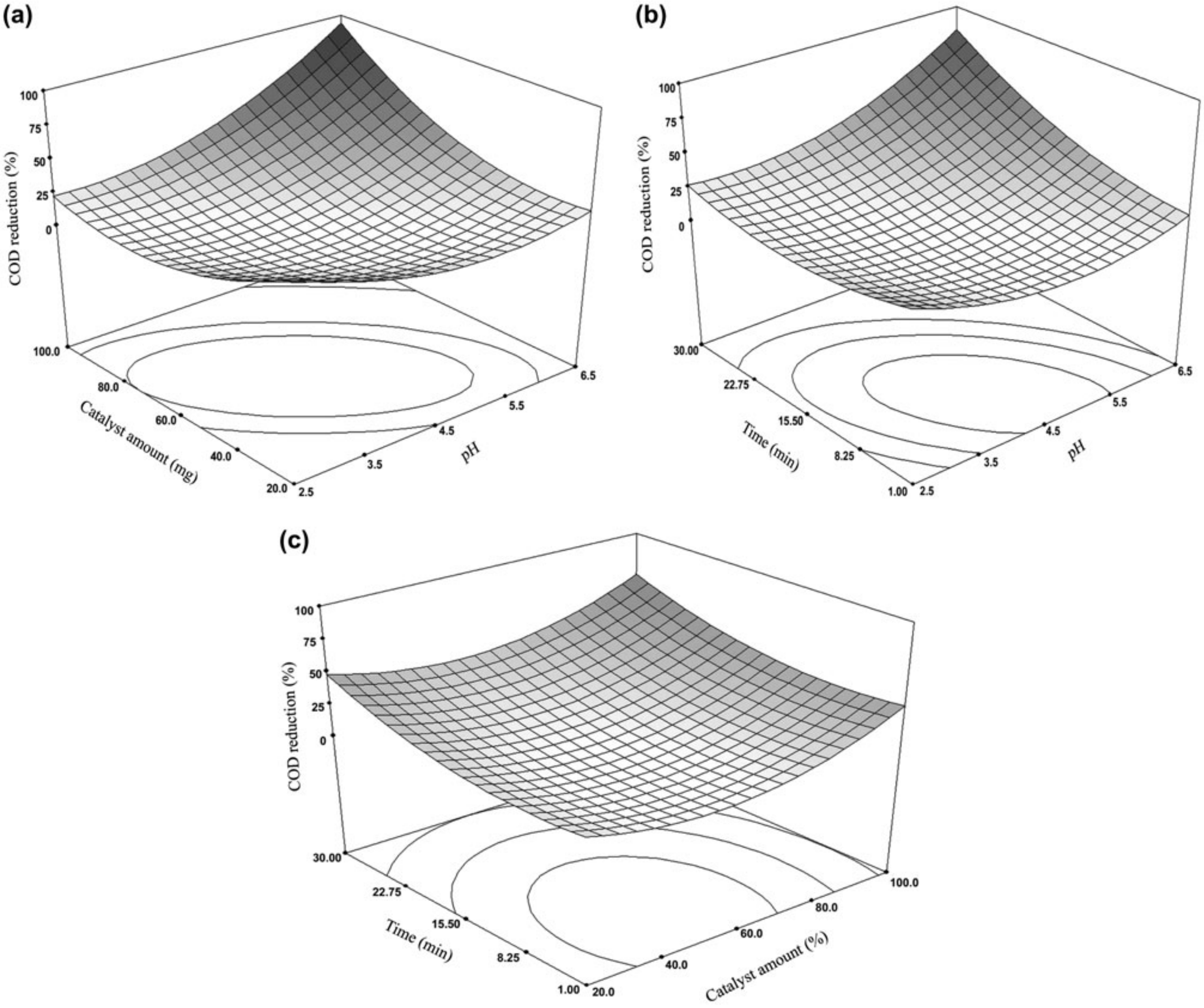

Fig. 3. Response surface plots showing the interaction between two parameters, catalyst amount and pH (a), pH and time (b), and time and catalyst amount (c) on the COD reduction percentage of the NR dye solution. Other variables are constant at their center points.

amount on the COD reduction. According to ANOVA, the interaction effect of time and catalyst amount was not significant; however to obtain an insignificant lack of fit, the BC term was not eliminated from the model. Maximum COD reduction was observed at 30 min by adding 100 mg TiO_2. Longer contact time and availability of more active sites on the catalyst surface leads to high photomineralization of the NR molecules.

3.2. Optimum conditions

RSM can estimate the optimum combination of parameters, on the basis of the ridge maximum analysis and the canonical analysis, to obtain the highest percentage of dye photodegradation. For each parameter, the upper and lower limits of the operating ranges were used as constraints to obtain the optimal values. As can be seen in the experimental design, in a short reaction time of 15.5 min, pH 6.5, and using 100 mg of catalyst, a high decolorization efficiency and COD reduction (92.7 and 92.4%, respectively) were obtained.

Using the optimization function of the Design Expert Software, the maximum color and COD reduction (90.9 and 83.1%, respectively) were predicted under treatment conditions of 28.7 min, pH 6.47 using minimum amount of TiO_2 nanocatalyst 68.0 mg. The actual experimental values obtained were 90.0% with 0.9% deviation for decolorization and 85.6% with 2.5% deviation for COD reduction.

3.3. Kinetic modeling of the photocatalytic process

The photocatalytic kinetic models can be used as a tool to assist the design of pilot-scale or full-scale photocatalytic reactors to treat dye-containing wastewater [34]. To study the mechanism of the decolorization process, including successive adsorption and photocatalytic degradation, six types of kinetic models were applied (first-order, second-order, pseudo-first-order, pseudo-second-order, modified Freundlich, and parabolic diffusion models; Fig. 4). The corresponding coefficients of determination (R^2) are also presented in the figure. From Fig. 4, it can be speculated that the kinetics of degradation of NR on the TiO_2 nanoparticles can be described more accurately by the pseudo-second-order and parabolic diffusion models. Calculated R^2 is closer to unity for these models. The pseudo–second-order mechanism indicates that the rate-limiting step is monolayer chemical sorption through photoinduced electron transfer between dye molecules and the photocatalyst [35]. The dye molecules follow successive degradation under the UV light irradiation. The parabolic diffusion model

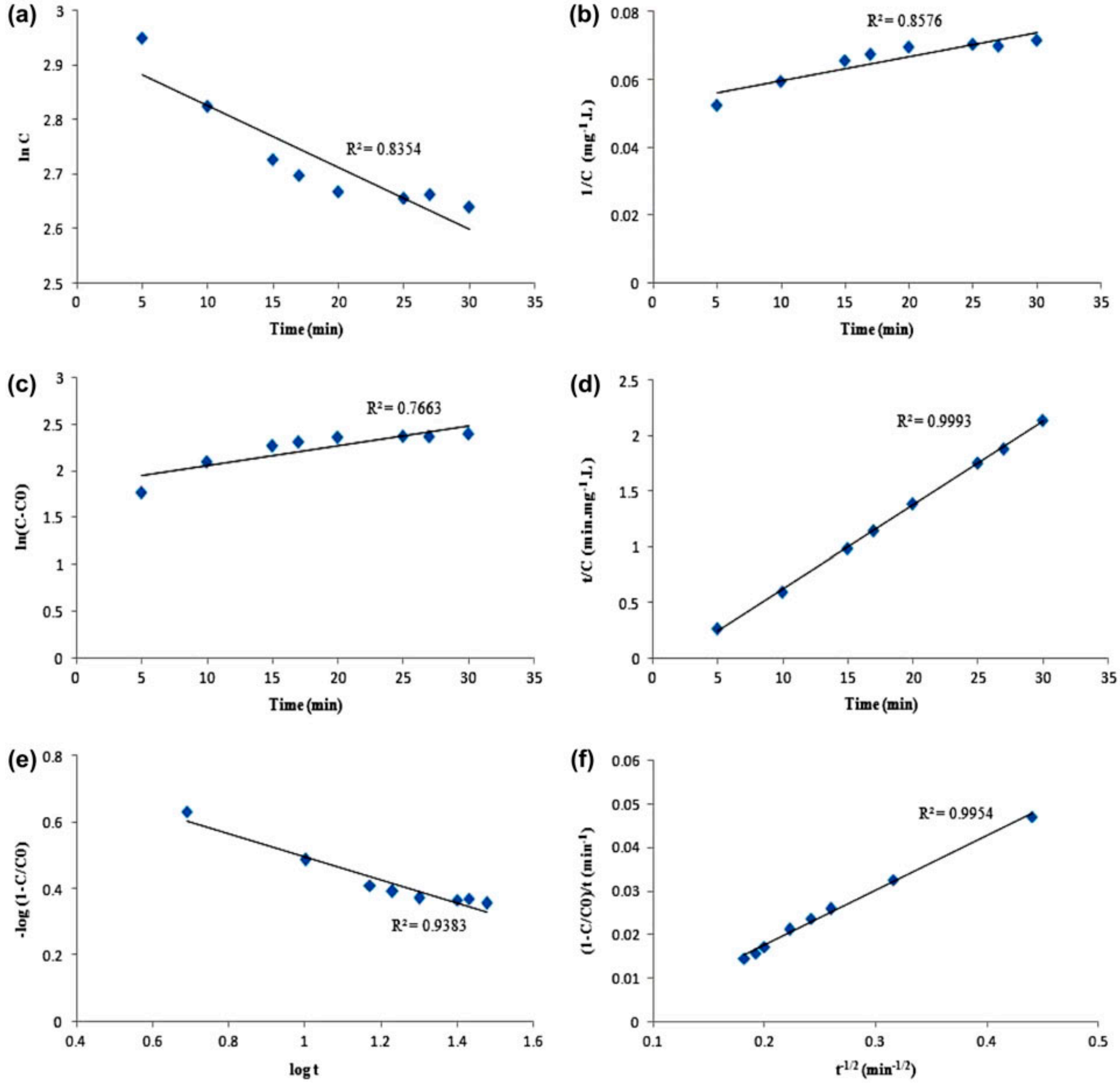

Fig. 4. Kinetic model of the photocatalytic degradation of NR on TiO_2 (a) first-order, (b) second-order, (c) pseudo-first-order, (d) pseudo-second-order, (e) modified Freundlich, and (f) parabolic diffusion models. The solid lines show linear fitting of the corresponding models.

indicates that the rate-limiting step (electron transfer) is controlled by diffusion of the dye molecules from solution to the active sites of the TiO_2 surface.

4. Conclusions

NR dye was successfully removed from solution by photocatalytic degradation over nano-sized TiO_2 suspension in the presence of UV light irradiation. RSM and BBD were effectively applied to the modeling and optimization of the operational parameters. The mineralization of the dye was also studied by measuring the COD reduction percentage. Up to 90.0% dye removal and 85.6% COD reduction were achieved at the optimal conditions, which matched well with the predicted values. The process was highly pH-dependent, and maximum decolorization was obtained at pH 6.5.

Since the pH is within the range of treated effluent discharge standard, there would be no requirement of pH adjustment for wastewater discharge. Degradation of the dye exhibited pseudo-second-order and parabolic diffusion kinetics. Therefore, the mechanism of the process includes diffusion, adsorption, and photocatalytic degradation. The method is eco-friendly and cost–effective, and the obtained results can be used for further upscaling of the treatment process.

List of symbols

NR — neutral red
RSM — response surface methodology
BBD — Box-Behnken design
COD — chemical oxygen demand
AOT — advanced oxidation technology
ROS — reactive oxygen species
CCD — central composite design
OVAT — one variable at a time
ANOVA — analysis of variance
PSOM — pseudo second order model
A — the absorbance value
α — coded value of independent variable
x_i, x_j — independent variable value
x_0 — independent variable value at the center point
Δx — the step change in the variable
y — the response
β_0 — constant regression coefficient
β_i — regression coefficients for linear effects
β_j — regression coefficients for quadratic effects
β_{ij} — regression coefficients for cubic effects
n — number of responses in the measure
d_i — desirable ranges for each response
D — Desirability value
C, C_t — equilibrium concentration
C_0 — initial concentration

References

[1] K. Kalaiarasi, A. Lavanya, S. Amsamani, G. Bagyalakshmi, Decolourization of textile dye effluent by non-viable biomass of *Aspergillus fumigatus*, Braz. Arch. Biol. Technol. 55 (2012) 471–476.

[2] K.P. Singh, D. Mohan, S. Sinha, G.S. Tondon, D. Gosh, Color removal from wastewater using low-cost activated carbon derived from agricultural waste material, Ind. Eng. Chem. Res. 42 (2003) 1965–1976.

[3] V.D. Gosavi, S. Sharma, A general review on various treatment methods for textile wastewater, J. Environ. Sci. Comput. Sci. Eng. Tech. 3 (2014) 29–39.

[4] H.H. Tseng, W.W. Lee, M.C. Wei, B.S. Huang, M.C. Hsieh, P.Y. Cheng, Synthesis of TiO_2/SBA-15 photocatalyst for the azo dye decolorization through the polyol method, Chem. Eng. J. 210 (2012) 529–538.

[5] P. Jantawasu, T. Sreethawong, S. Chavadej, Photocatalytic activity of nanocrystalline mesoporous-assembled TiO_2 photocatalyst for degradation of methyl orange monoazo dye in aqueous wastewater, Chem. Eng. J. 155 (2009) 223–233.

[6] P. Bansal, D. Sud, Photodegradation of commercial dye, Procion Blue HERD from real textile wastewater using nanocatalysts, Desalination 267 (2011) 244–249.

[7] J. Sima, P. Hasal, Photocatalytic degradation of textile dyes in a TiO_2/UV system, Chem. Eng. Technol. 32 (2013) 79–84.

[8] M. Qamar, M. Saquib, M. Muneer, Semiconductor-mediated photocatalytic degradation of anazo dye, chrysoidine Y in aqueous suspensions, Desalination 171 (2005) 185–193.

[9] V.S. Shrivastava, Photocatalytic degradation of Methylene blue dye and Chromium metal from wastewater using nanocrystalline TiO_2 semiconductor, Arch. Appl. Sci. Res. 4 (2012) 1244–1254.

[10] M.J. Uddin, M.A. Islam, S.A. Haque, S. Hasan, M.S.A. Amin, M.M. Rahman, Preparation of nanostructured TiO_2-based photocatalyst by controlling the calcining temperature and pH, Int. Nano Lett. 2 (2012) 19–29.

[11] H. Niu, Q. Wang, H. Liang, M. Chen, C. Mao, J. Song, S. Zhang, Y. Gao, C. Chen, Visible-light active and magnetically recyclable nanocomposites for the degradation of organic dye, Materials 7 (2014) 4034–4044.

[12] B. Sarwan, B. Pare, A.D. Acharya, S.B. Jonnalagadda, Mineralization and toxicity reduction of textile dye neutral red in aqueous phase using BiOCl photocatalysis, J. Photochem. Photobiol., B 116 (2012) 48–55.

[13] C. Yan, W. Yi, H. Yuan, X. Wu, F. Li, A highly photoactive S, Cu-codoped nano-TiO_2 photocatalyst: Synthesis and characterization for enhanced photocatalytic degradation of neutral red, Environ. Prog. Sustainable Energy 33 (2014) 419–429.

[14] O. Sharma, M.K. Sharma, Use of cobalt hexacyanoferrate(ii) semiconductor in photocatalytic degradation of neutral red dye, Int. J. ChemTech Res. 5 (2013) 1615–1622.

[15] T.A. Wani, A. Ahmad, S. Zargar, N.Y. Khalil, I.A. Darwish, Use of response surface methodology for development of new microwell-based spectrophotometric method for determination of atrovastatin calcium in tablets, Chem. Cent. J. 6 (2012) 134–143.

[16] J.F. Fu, Y.Q. Zhao, X.D. Xue, W.C. Li, A.O. Babatunde, Multivariate-parameter optimization of acid blue-7 wastewater treatment by Ti/TiO_2 photoelectrocatalysis via the Box-Behnken design, Desalination 243 (2009) 42–51.

[17] J. Dostanić, D. Lončarević, L. Rožić, S. Petrović, D. Mijin, D.M. Jovanović, Photocatalytic degradation of azo pyridone dye: Optimization using response surface methodology, Desalin. Water Treat. 51 (2013) 2802–2812.

[18] M.A. Zanjanchi, H. Golmojdeh, M. Arvand, Enhanced adsorptive and photocatalytic achievements in removal of methylene blue by incorporating tungstophosphoric acid–TiO_2 into MCM-41, J. Hazard. Mater. 169 (2009) 233–239.

[19] N. Chaibakhsh, N. Ahmadi, M.A. Zanjanchi, Use of *Plantago major* L. as a natural coagulant for optimized decolorization of dye-containing wastewater, Ind. Crops Prod. 61 (2014) 169–175.

[20] J.W. Choi, H.K. Song, W. Lee, K.K. Koo, C. Han, B.K. Na, Reduction of COD and color of acid and reactive dyestuff wastewater using ozone, Korean J. Chem. Eng. 21 (2004) 398–403.

[21] D. Chen, A.K. Ray, Photocatalytic kinetics of phenol and its derivatives over UV irradiated TiO_2, Appl. Catal., B 23 (1999) 143–157.

[22] C. Sarici-Ozdemir, Adsorption and desorption kinetics behaviour of methylene blue onto activated carbon, Physicochem. Prob. Miner. Process. 48 (2012) 441–454.

[23] M.Z.B. Mukhlish, F. Najnin, M.M. Rahman, M.J. Uddin, Photocatalytic degradation of different dyes using TiO_2 with high surface area: A kinetic study, J. Sci. Res. 5 (2013) 301–314.

[24] N. Chaibakhsh, M.B. Abdul Rahman, M. Basri, A.B. Salleh, S. Abd-Aziz, Lipase-catalyzed dimethyl adipate synthesis: Response surface modeling and kinetics, Biotechnol. J. 5 (2010) 848–855.

[25] A. Giwa, P.O. Nkeonye, K.A. Bello, K.A. Kolawole, Photocatalytic decolourization and degradation of C.I. Basic Blue 41 using TiO_2 nanoparticles, J. Environ. Prot. 3 (2012) 1063–1069.

[26] B. Pare, D. Swami, P. More, T. Qureshi, T.R. Thapak, Mineralization of methylene violet dye using titanium dioxide in presence of visible light, Int. J. Chem. Sci. 9 (2011) 1685–1697.

[27] C. Ram, R.K. Pareek, V. Singh, Photocatalytic degradation of textile dye by using titanium dioxide nanocatalyst, Int. J. Theor. Appl. Sci. 4 (2012) 82–88.

[28] M.Y. Ghaly, J.Y. Farah, A.M. Fathy, Enhancement of decolorization rate and COD removal from dyes containing wastewater by the addition of hydrogen peroxide under solar photocatalytic oxidation, Desalination 217 (2007) 74–84.

[29] N.M. Mahmoodi, M. Arami, N.Y. Limaee, N.S. Tabrizi, Decolorization and aromatic ring degradation kinetics of Direct Red 80 by UV oxidation in the presence of hydrogen peroxide utilizing TiO_2 as a photocatalyst, Chem. Eng. J. 112 (2005) 191–196.

[30] M. Rastegar, K.R. Shadbad, A.R. Khataee, R. Pourrajab, Optimization of photocatalytic degradation of sulphonated diazo dye C.I. Reactive Green 19 using ceramic-coated TiO_2 nanoparticles, Environ. Technol. 33 (2012) 995–1003.

[31] C.C. Liu, Y.H. Hsieh, P.F. Lai, C.H. Li, C.L. Kao, Photodegradation treatment of azo dye wastewater by UV/TiO process, Dyes Pigm. 68 (2006) 191–195.

[32] M.A. Barakat, Adsorption and photodegradation of Procion yellow H-EXL dye in textile wastewater over TiO_2 suspension, J. Hydro-environ. Res. 5 (2011) 137–142.

[33] M. Montazerozohori, M. Nasr-Esfahani, S. Joohari, Photocatalytic degradation of an organic dye in some aqueous buffer solutions using nano titanium dioxide: A kinetic study, Environ. Prot. Eng. 38 (2012) 45–55.

[34] Y.H. Lin, Kinetics of photocatalytic degradation of 2-chlorophenol in a TiO_2 catalyst, Res. J. Model. Simul. 1 (2014) 1–7.

[35] A. Hu, R. Liang, X. Zhang, S. Kurdi, D. Luong, H. Huang, P. Peng, E. Marzbanrad, K.D. Oakes, Y. Zhou, M.R. Servos, Enhanced photocatalytic degradation of dyes by TiO_2 nanobelts with hierarchical structures, J. Photochem. Photobiol., A 256 (2013) 7–15.