Chapter 12
Photocatalytic Degradation of Reactive Orange M2R Using Green Route Synthesized Copper Oxide Nanoparticles and Its Optimization Studies

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Abstract The photocatalytic degradation approach for industrial dyes in the presence of appropriate nanocatalyst offers a possible way for the complete removal of various pollutants from the aqueous environment. Therefore, in this study, we have made an attempt on use of bio-synthesized copper oxide (CuO) nanoparticles harnessed by neem extract for the degradation of reactive orange M2R (RO-M2R). The significant catalytic degradation of dye was found to be pH10, catalytic dosage at 10 ppm, and dye concentration at 3 gL^{-1} and irradiation time at 5 h through one factor at a time (OFAT). Further, Box Behnken design was applied to optimize and investigate the interaction between these four variables for the degradation of dye. It was predicted that maximum degradation was 84.04% under optimum conditions of pH at 11.84, catalytic dosage at 2.20 gL^{-1}, dye concentration at 7.49 ppm and irradiation time of 4 h. The validity of the optimal level predicted under the RSM was established by an independent experiment.

Keywords CuO nanoparticles · RSM · Box Behnken design · Photocatalytic degradation

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12.1 Introduction

Water pollution has become a very sensitive issue in the world due to inorganic and organic pollutants. The primary source of contamination of water is the organic dyes discharged by textile industries. There are more than 10,0000 commercially available dyes with over 7×10^5tons of dyestuff produced. In which, concerning 36,000 dye/year are consumed by textile industries across the world. 20% of the dyes in the world production are lost during the dyeing process and is discharged in the textile wastewater (Reza et al. 2017; Esplugas et al. 2002; Houas et al. 2001). In particular, the principal and most adaptable classes of azo dyes are presently utilized in the dyeing of different materials such as textiles, leather, plastics, and cosmetics. The azo dyes containing effluents are released into rivers, lakes, and ground waters for the period of dying process that contains mutagenic and carcinogenic health hazards. As a result, it leads to severe environmental problems due to their good stability under ambient conditions (Mathur et al. 2012).

Organic pollutants are challenging to biological degradation; also, conventional treatment processes are not succeeded to attain their complete elimination of dye molecules. Even though, for a decade, researchers have attempted various methodologies such as membrane filtration, chemical coagulation/flocculation, ion exchange, precipitation, adsorption, biological degradation, and ozonation, etc. Still, these methods are not capable enough and have more limitations. UV light is generally applied to excite a semiconductor surface to produce photoinduced holes or reactive oxygen species (ROS), such as hydroxyl and superoxide radicals in the photocatalytic advanced oxidation technology. Then, the ROS interrelate with organic compounds and guides to their oxidation and overall degradation (Jantawasu et al. 2009). Moreover, for a decade nanocatalyst development has highly attracted researchers to work towards the degradation of industrial wastewater pollutants. Apart from dye degradation studies by nanoparticles, Magnetic Moringa Oleifera (MMO) have also been used as a coagulant for palm oil waste water treatment (Noor et al. 2022).

There are various studies reported on dye degradation by metallic nanoparticles. Chaibakhsh et al. (2016) have reported on photocatalytic degradation of neutral red dye using titanium oxide (TiO_2) nanocatalyst and its optimization by Box-Behnken design. Recently, Uddin and Baig (2019) have studied on the removal of methyl orange dye using cobalt oxide (Co_3O_4) nanoparticles and Dawoud et al. (2020) have also reported on photocatalytic degradation of organic dye of Rhodamine B by using silver (Ag) doped Zirconium oxide (ZrO_2) nanoparticles. Recently, CuO NP‘s have been prepared from various sources such as *Canthium coromandelicum* leaves extract (Selvam et al. 2022), *Punica granatum* (Kaur et al. 2022), *Pistacia vera L.* hull (Ltaief et al. 2021), *Dictyota dichotoma* endophytic fungi (Kumar et al. 2022), *Elaeagnus indica* (Indhira et al. 2022), *Solanum tuberosum* (Hamami and Javanbakht 2021) were used as a catalyst for textile dye degradation.

Most of the reports on dye removal by magnetic nanoparticles have been performed by ‘one variable at a time’ (OFAT) approach that perfectly presumed that all variables are independent and do not represent the combined effect of all the variables involved. Moreover, this method is a prolonged one and also requires a higher number of experiments to determine optimum levels, which may or may not be trustworthy (Farooq et al. 2017). These limitations of the conventional methods can be reduced by response surface methodology (RSM), using this statistical design of experiment.

Thus, herein, biological route synthesized CuO nanoparticles assisted photocatalytic degradation of RO-M2R dye, and their optimization studies were performed using Box-Behnken design to maximize the percentage of dye degradation.

12.2 Materials and Methods

12.2.1 Photocatalytic Degradation Confirmation

RO-M2R was obtained from Precision Scientific Co. Coimbatore, India. The photocatalytic degradation experiment of RO-M2R was performed under sunlight irradiation. The photocatalyst CuO NP's 2 $gL^{-1}$was added to 50 ppm of RO-M2R dye solution at neutral pH to establish the adsorption equilibrium between the dye molecule and CuO NP's. The resulting solution was exposed to sunlight for 4 h, and control was maintained without addition of nanoparticles. These suspensions were measured against absorbance at 495 nm. The percentage of degradation was calculated from the following equation;

$$\% \text{ of Degradation} = (\text{Co} - \text{C}/\text{Co})\ \text{X}\ 100$$

where, Co = Initial concentration of dye, C = Final concentration of dye.

12.2.2 Preliminary Experiment

Preliminary experiments were conducted by one factor at a time (OFAT) approach to identify the ranges of four parameters such as pH, dye concentration, catalytic dosage and irradiation time for the degradation of RO-M2R. Statistical design of experiment consists of a variation of several trials at a time when compared to one factor at a time approach in which only one factor is changed and keeping all other factors constant.

12.2.2.1 Evaluation of Process Parameters by OFAT

The dye solution was taken out in reaction vessel, and the pH (3, 4, 5, 6, 7, 8, 9, 10, 11 and 12) was adjusted by using a pH meter (Elico LI 120, India). Similarly, the different concentrations of RO-M2R working solutions (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 ppm) were prepared and kept the irradiation time for 4 h to study the effect of dye concentration on dye degradation. Likewise, the different concentrations of CuO nanoparticles (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 g/L) were varied and the reaction vessel was kept under sunlight for 4 h. Similarly, the different reaction periods (0, 50, 100, 150, 200, 250, 300, 350, 400 and 450 min) were chosen to check the percentage of degradation. Finally, 2 g/L of CuO nanoparticles was added to various ranges of pH and concentration of RO-M2R dye solution to establish the adsorption equilibrium between the dye molecule and CuO nanoparticles.

12.2.3 Response Surface Methodology for Optimization

Response surface methodology (RSM) was utilized to optimize the four parameters were catalytic dosage, pH, dye concentration and irradiation time. The four parameters were selected as independent variables, and the degradation percentage of RO-M2R was the response variable. Box-Behnken model was preferred to study the combined effect of four independent variables, and Design-expert 11 version was used to explain the response surface. The model was statistically examined. Analysis of variance (ANOVA) employed Fischer's *F*- test to evaluate the overall significance of the model, correlated probability values, and coefficient of determination to estimate the goodness of fit of the regression model. The apt polynomial equation was further conveyed the three-dimensional plots (3D) form, which depicted the interactions graphically. Finally, the central and interaction effects, the 3D plots were analyzed to check the accuracy of the model (Kanmani et al. 2013).

The following second-order polynomial equation explains the connection between the dependent and independent variables:

$$\begin{aligned} \mathrm{Y} = {} & \beta_0 + \beta_1\mathrm{A} + \beta_2\mathrm{B} + \beta_3\mathrm{C} + \beta_{11}\mathrm{A}^2 + \beta_{22}\mathrm{B}^2 + \beta_{22}\mathrm{C}^2 \\ & + \beta_{12}\mathrm{AB} + \beta_{13}\mathrm{AC} + \beta_{23}\mathrm{BC} \end{aligned} \tag{12.1}$$

Here the Y is the predicted response, β0 is the intercept, β_1, β_2, β_3, are the linear coefficients, β_{11}, β_{22}, β_{33}, are the squared coefficients, and β_{12}, β_{13}, β_{23} are the interaction coefficients.

12.3 Results and Discussion

12.3.1 Confirmation of Photocatalytic Degradation

The previously synthesized CuO nanoparticles (Thirumurugan et al. 2017) were used for the photocatalytic degradation of RO-M2R under sunlight. These

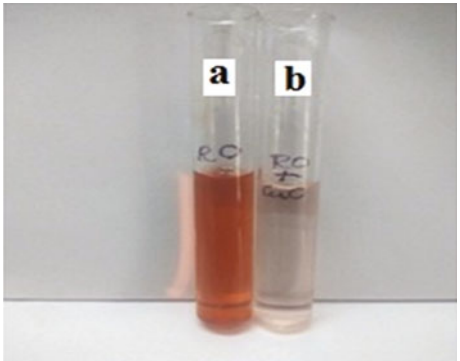


Fig. 12.1 Confirmation of photocatalytic degradation of RO-M2R using CuO NP‘s under sunlight

nanoparticles were already proved its photocatalytic degradation of 4-nitrophenol as a model (Ramya et al. 2019) and photocatalytic degradation of reactive red 120 (Thirumurugan et al. 2017). Thus, in this study, the photocatalytic degradation of RO-M2R was studied by using green synthesized CuO NP‘s under sunlight, as shown in Fig. 12.1. After the addition of nanoparticles, the orange color of the solution decreased significantly, become colorless with 74% degradation, and no changes were observed in control. The dye degradation efficiency of nanoparticles may be due to differences in size, shape and catalytic activity (Moon et al. 2015). Kumar et al. (2013), has also reported that metal nanoparticle synthesized by green approach was effectively degraded the dye with periodically increase in time. There are various parameters affecting the photocatalytic degradation, such as pH, dye concentration, catalytic dosage, irradiation time, reaction temperature, light intensity and the presence of electron acceptors. In particular, we investigated the effect of pH, dye concentration, catalytic dosage, and irradiation time through one factor at a time (OFAT) approach to study the impact of each factor ranges for the photocatalytic degradation of RO-M2R.

12.3.2 Evaluation of Process Parameters by OFAT

Effect of pH is one of the main factors for the degradation of industrial dye. To investigate the effect of pH, the experiments were carried out at different pH ranges from 3 to 12 at 2 gL^{-1} of CuO NP‘s, 50 ppm of RO-M2R and irradiation time of 4 h. The result showed that by increasing the pH of the dye solution, the dye degradation was getting increased, as shown in Fig. 12.2. It was observed that degradation rate increases, with an increase in pH and the maximum photocatalytic degradation, was found to be at pH 10. The cause can be due to efficient formation of hydroxyl radicals in alkaline medium. Excess of hydroxyl anions increases the formation of hydroxyl radicals as the main oxidizing function responsible for dye degradation (Gopalapp et al. 2012). Similarly, Devadi et al. (2014) has observed the maximum degradation

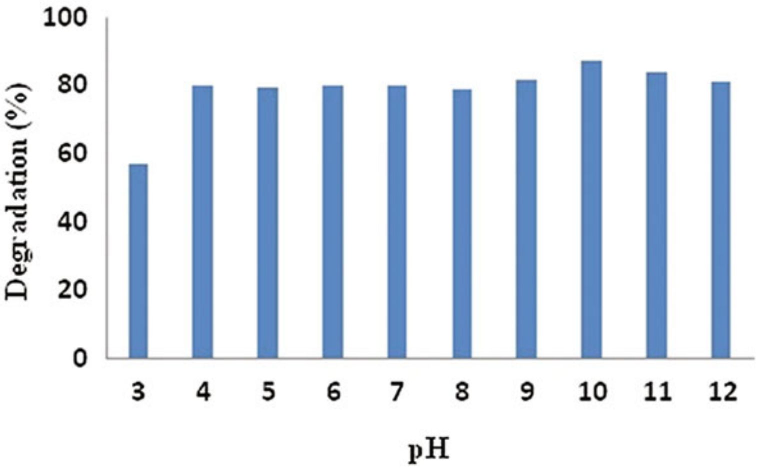


Fig. 12.2 Degradation of RO-M2R at different pH

of methyl blue at pH 11 and at under acidic condition the degradation efficiency get decreased due to the columbic repulsion. Also, Daneshvar et al. (2003) reported that in the presence of ZnO NP‘s, the photodegradation was considerably improved at high pH (pH = 11), While the lower at low pH is due to the photodecomposition of ZnO to Zn^{2+} takes place in acidic and neutral solutions and that efficient formation of hydroxyl radicals occurs in alkaline solution.

The effect of dye concentration for degradation of RO-M2R was varied between 10 to 100 ppm where pH was kept at 10, catalytic dosage at 2 gL^{-1} and irradiation time for 4 h. The degradation of RO-M2R at different concentration of dye is shown in Fig. 12.3. The result showed that up to 40 ppm the percentage of degradation was approximately the same and after 40 ppm the degradation rate was reduced. While maintaining a constant catalyst dose, it caused the fixed number of catalysis sites to be saturated rapidly, which is due to increasing dye concentration in the solution (Mohan and Pittman 2006). In addition, the light transmittance in the solution may be decreased due to the increased dye concentration; decreased light infiltration can diminish the activation rate of nanoparticles and delay the formation of OH radicals, results in decreased photocatalytic degradation.

Figure 12.4 shows the effects of different concentrations of nanoparticles as catalysts on degradation. The increase in concentration up to 3 gL^{-1} contains a high amount of active site and thus producing more free radicals which uninterruptedly increase the degradation of RO-M2R, and beyond 3 gL^{-1} there was a decrease in degradation rate. According to Akpan and Hameed (2009), this was due to the formation of turbid in the solution, which reduces the penetration of sunlight. Hence, it blocks the radiation to enter into the RO-M2R solution. Recently, Mortazavian et al. (2019) has reported in a study that the amounts of catalyst particles might aggregate leading to a reduced number of active sites because the increase of TiO_2 particles in the solution might supply more active sites for the molecules of dye to be adsorbed

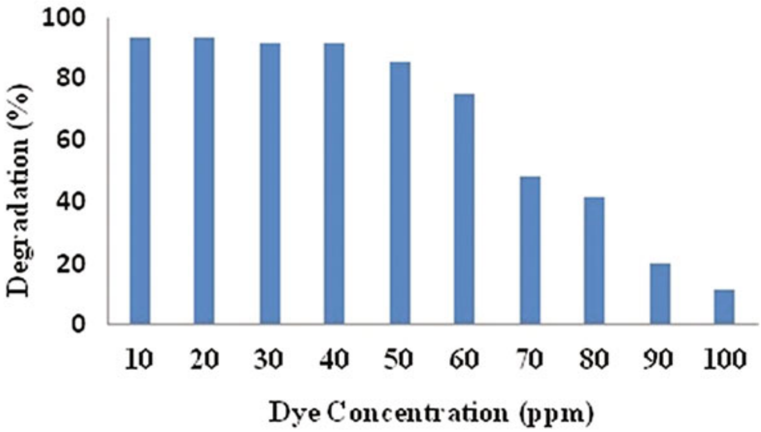


Fig. 12.3 Degradation of RO-M2R at different dye concentration

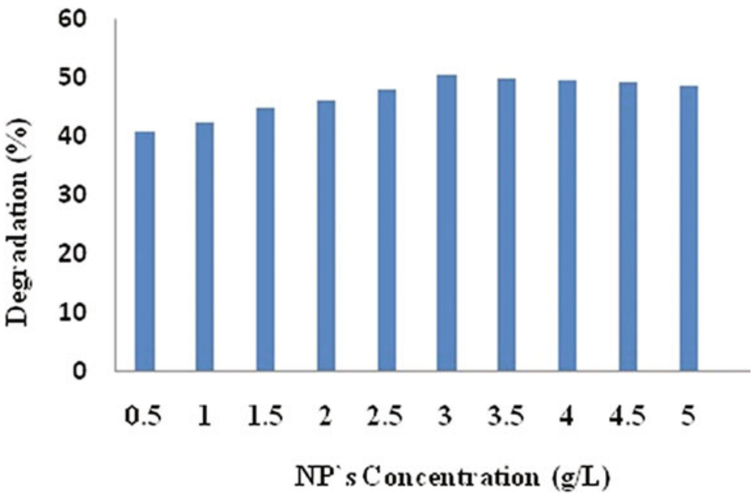


Fig. 12.4 Degradation of RO-M2R at different concentrations of CuO NP's

and degraded. This phenomenon might be one of the reasons for decreasing the degradation rate beyond 3 gL^{-1} of CuO NP's as a catalyst. Very recently, Hashemi et al. (2022) reported the optimization and assessment of photocatalytic degradation of methyl orange using silver nanoparticles synthesized through green route. As a result, observed that the methyl orange pollutant degradation was increased while increasing the concentration of nanocatalyst.

The effect of irradiation time on degradation was investigated by keeping catalyst amount at 3 gL^{-1}, pH at 10, and dye concentration at 40 ppm and varying the irradiation time of the dye solution under sunlight. Figure 12.5 shows that degradation rate

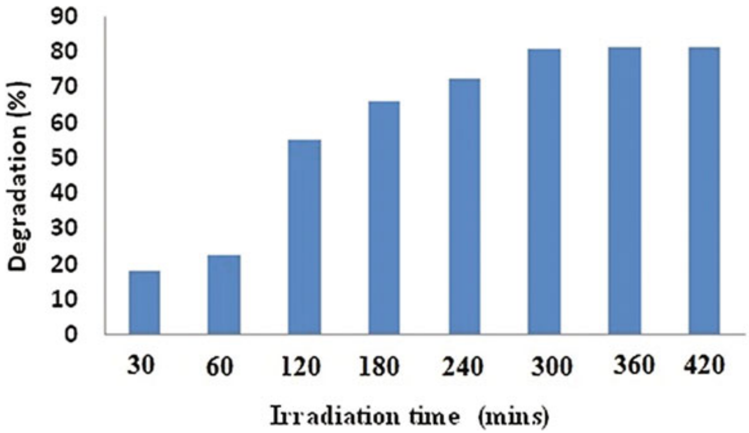


Fig. 12.5 Degradation of RO-M2R at different time intervals

increased as time increased, and this is due to the increased number of photons. The maximum degradation efficiency was observed at 5th h, and after that the degradation remains the same.

12.3.3 Optimization Using Response Surface Methodology

Box Behnken Design (BBD) was employed to evaluate the effect of variables on the degradation of RO-M2R in the presence of sunlight. The influence of operating parameters on the photocatalytic degradation efficiency of RO-M2R were assessed, four main factors were chosen: pH, dye concentration (ppm), catalytic dosage (gL^{-1}), irradiation time (hrs). A total of 29 experiments were used using Design expert software. The experimental outcomes of degradation of dye by nanoparticles were analyzed through RSM as tabulated in Table 12.1 to obtain an empirical model.

Based on the outcomes, an empirical relationship between the responses and independent variables were attained for the dye degradation expressed by the quadratic polynomial equation, as shown below.

$$\begin{aligned}\text{\% of Degradation} &= 59.19 + 14.14 * A - 4.52 * B + 0.19 * C - 2.13 * D \\ &+ 0.38 * AB - 0.74 * AC + 0.80 * AD - 0.71 * BC \\ &- 1.27 * BD + 1.74 * CD + 4.08A^2 + 0.048B^2 + 1.94C^2 + 1.80D^2\end{aligned}$$

Response surface methodology integrated the interaction effects of variables and helps us in simultaneously optimizing many process parameters within a minimum number of trial runs. Such statistically aided experimental designs can guide to considerably better performance of the nanoparticles. The *P* value acts as a tool

Table 12.1 Box-Behnken design of response surface methodology with real values and their responses

S.NO	A: pH	B: Nanoparticles concentration (g/l)	C: Dye concentration (ppm)	D: Irradiation time (hr)	Degradation (%)
1	8	2	22.5	5.5	54.5
2	12	2	22.5	5.5	80.09
3	8	4	22.5	5.5	47.1
4	12	4	22.5	5.5	74.2
5	10	3	5	4	66.85
6	10	3	40	4	65.18
7	10	3	5	7	58.51
8	10	3	40	7	63.8
9	8	3	22.5	4	53.82
10	12	3	22.5	4	80.22
11	8	3	22.5	7	49.25
12	12	3	22.5	7	78.84
13	10	2	5	5.5	67.3
14	10	4	5	5.5	55.51
15	10	2	40	5.5	69.2
16	10	4	40	5.5	54.57
17	8	3	5	5.5	48.65
18	12	3	5	5.5	80.65
19	8	3	40	5.5	49
20	12	3	40	5.5	78.04
21	10	2	22.5	4	64.73
22	10	4	22.5	4	60
23	10	2	22.5	7	62.35
24	10	4	22.5	7	52.55
25	10	3	22.5	5.5	60.85
26	10	3	22.5	5.5	58.02
27	10	3	22.5	5.5	57.83
28	10	3	22.5	5.5	61.34
29	10	3	22.5	5.5	57.89

for assessing the significance of each coefficient and is indicative of the interaction strength of all independent variable. Low values of P at ($P < 0.05$) indicate the high significance of the corresponding coefficients. In general, larger t, F and smaller P values indicate that the corresponding coefficient terms are significant.

From the ANOVA Table 12.2, the model F-value of the model (41.08) and values of $P > F$(<0.0500) implied that the model was significant statistically. The predicted

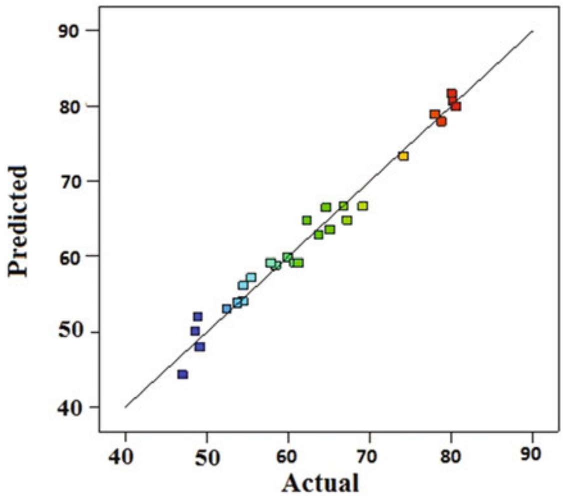
Table 12.2 Analysis of variance (ANOVA) and regression analysis for selected model

Source	Sum of squares	Degree of freedom	Mean squares	F value	P value	
Model	2855.57	14	203.97	41.08	<0.0001	Significant
Residual	69.51	14	4.97			
Lack of fit	57.23	10	5.72	1.86	0.2877	Not significant
Pure error	12.29	4	3.07			
Cor total	2925.09					

$R^2 = 0.9762$; Adj.$R^2 = 0.9525$; Predicted $R^2 = 0.8808$

R^2 of the 0.8808 is in reasonable agreement with the adjusted R^2 of 0.9525. Adequate precision measures signal-to-noise ratio (S/N ratio) and detect which experimental parameters generate signals that are large in comparison to the noise. The observed adequate precision ratio was 23.29, greater than 4, which indicated the selected model could be employed to precisely navigate the design space as reported by Chaibakhsh et al. (2016). The accuracy of the model is shown in Fig. 12.6, which evaluates the measured values against the predicted responses of the model for the degradation of RO-M2R. It can be observed that correlation between the experimental data and predicted values ($R^2 = 0.9762$) showed the data fit well with the model in the range studied.

Fig. 12.6 Predicted plotted against the actual experimental values for photocatalytic degradation of RO-M2R



12.3.3.1 Analysis of Response Surface Plots

Three-dimensional surface can be used as a graphical representation of the regression equation to find the optimum levels of the variables studied and widely used to achieve a better understanding of the interactions between variables within the ranges.

Figure 12.7 represents the interaction effect of pH, nanoparticles concentration and dye concentration and irradiation time on the degradation of dye from aqueous solution. There was a significant degradation observed by increasing pH till 12. Similarly, nanoparticles concentrations also influencing the degradation rate of dye molecules up to 2.20 gL^{-1} then degradation rate declines. Whereas, dye concentration and irradiation time were not influencing the degradation rate as pH and nanoparticles concentration. Recently, Chaker et al. (2021), has studied a statistical modelling optimization approach for efficient photocatalytic degradation of azo dye using cerium-doped mesoporous ZnO by central composite design. Their results indicated that all the variable chosen had an impact on the photocatalytic process and pH was the least factor against the effect of catalyst concentration.

The three-dimensional plots based on the interactions between the variables showed an increase in RO-M2R dye degradation as each variable increased to an optimum level, beyond the optimum level; decline rate could be observed (Fig. 12.7a–f). The optimal values obtained from the three-dimensional were also almost equal to the results obtained by the regression analysis (Eq. 12.1). From the model, a maximum dye degradation of 84% under the optimum condition of pH 11.8, nanoparticle concentration of 2.20 gL^{-1}, dye concentration of 7.49 ppm and irradiation time of 4 h were predicted. The experiment was conducted in triplicate to validate the prediction of the model, and the maximum degradation of RO-M2R was found to be 83.41% which was close to the predicted maximum dye degradation of the model.

12.3.4 Mechanism of Photocatalytic Degradation by CuO NP‘s

For the above observed results, a possible mechanism for the degradation of RO-M2R dye by CuO nanoparticles in aqueous solution can be proposed. A possible photocatalytic mechanism of CuO nanoparticles for the degradation of aqueous RO-M2R is shown in Fig. 12.8. Photocatalytic degradation of organic dyes through the utilization of CuO nanoparticles arises when the photocatalyst absorbs light of a suitable wavelength from sunlight. The light energy from the sun is exciting and promotes electrons in the valence band to conduction band of photocatalyst. As results, creation of positive charges (holes) and negative charges (electrons) on the valence and conduction bands respectively, leads to the formation of electron–hole pairs. This hole oxidizes the water molecule into hydrogen gas and hydroxyl radicals ($OH^{\bullet}$), whereas electron reduces the oxygen molecules to form superoxide radicals ($O_2^{\bullet}$–). Thus radicals formed radicals, attack the dye molecule over the surface of

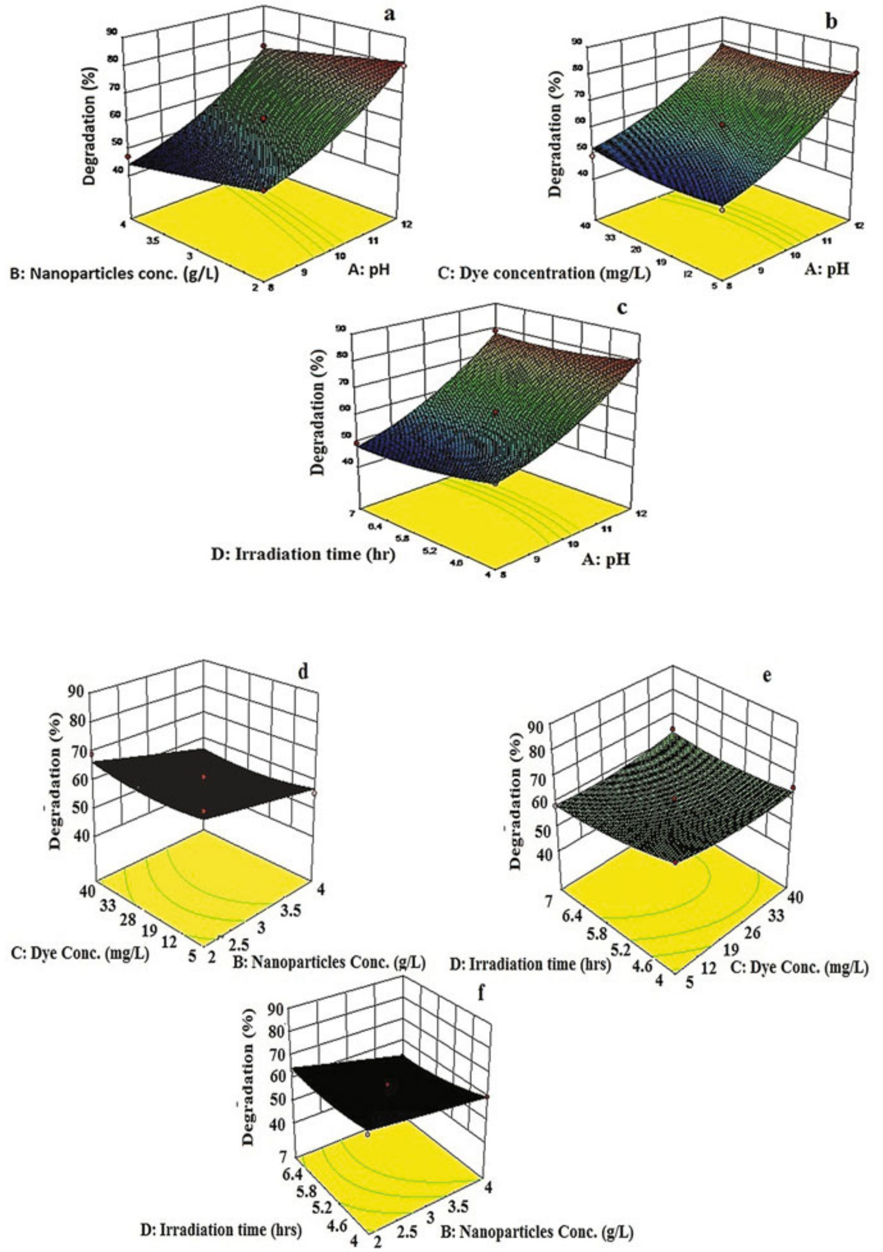


Fig. 12.7 Three dimensional surface plot showing the effect of **a** nanoparticles concentration (gL^{-1}) versus pH **b** dye concentration (mgL^{-1}) versus pH **c** Irradiation time (h) versus pH **d** Dye concentration (mgL^{-1}) versus nanoparticles concentration (gL^{-1}) **e** Irradiation time (h) versus dye concentration (mgL^{-1}) **f** Irradiation time (hrs) versus nanoparticles concentration (gL^{-1}) on degradation of RO-M2R

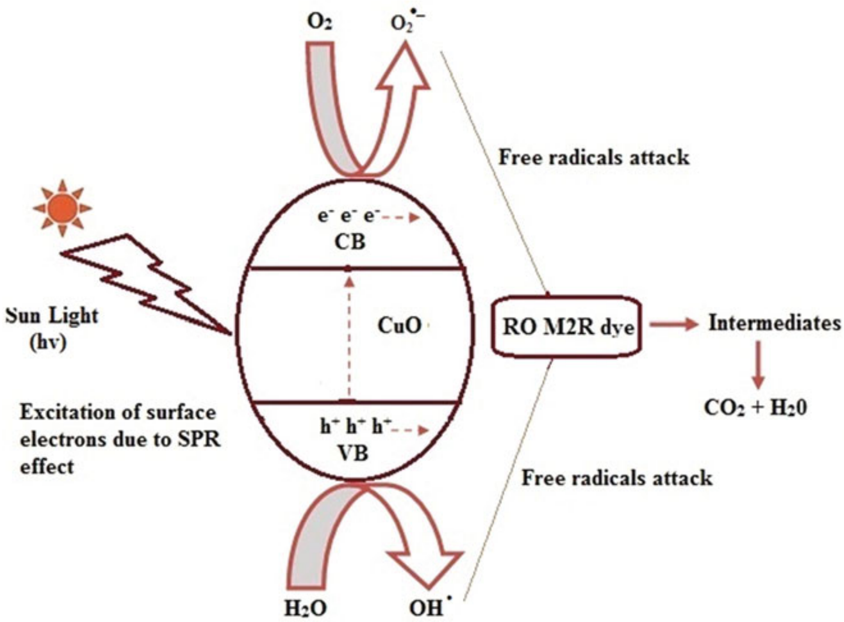


Fig. 12.8 A possible mechanism of photocatalytic degradation by CuO NP's

the CuO NP's and accomplish the dye degradation, and these formed radicals are also responsible for inactivation of bacteria through their cell walls degradation (Dalrymple et al. 2010).

12.4 Conclusions

We conclude that the photocatalytic degradation of RO-M2R by CuO NP's as a catalyst in the aqueous medium was developed a quadratic model using Response Surface Methodology as a functional relationship between catalytic dosage, pH, dye concentration and irradiation time to determine the optimum condition for the degradation of RO-M2R. The optimized degradation of RO-M2R was achieved with 83.41% by Box-Behnken design. Therefore, CuO NP's could be utilized as an efficient photocatalyst for the degradation of dye-containing waste water from textile industries.

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