

Optimization and Modeling of Photooxidative Process for the Degradation of Reactive Red223

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Summary: The optimization of the photooxidative process was carried out with the application of Response Surface Methodology (RSM) to degrade Reactive Red 223 (RR223) dye. Operational parameters of U.V/H₂O₂ process such as irradiation time, initial [dye], initial [H₂O₂] and distance between U.V lamp and the solution were optimized with Central Composite Design (CCD). Correlation coefficient value of the CCD was obtained to be 79 %, showing the correctness of the model and the successful utilization of CCD in getting desired levels of the factors of the process. Moreover, the optimum points were located with the graphical surface and contour plots. At the optimal conditions, the photooxidative removal of the color and COD were observed to be 68%, 81%, respectively. Furthermore, the pseudo-second order kinetic was guiding the removal of the dye in the process. Subsequently, the electrical energy consumption was estimated in term of the merit electrical energy per order (E_{EO}). The figure of merit of the process was found to be 252 kWhm⁻³ order⁻¹. The cost of the treatment was also calculated to be US\$ 25/m³.

Keywords: Central Composite Design; U.V/H₂O₂; Color; COD; Optimization; Modeling; Kinetics; Electrical Energy per Order; Cost Analysis.

Introduction

Textile industrial sector utilizes large fraction of water. The sector also discharges large volume of effluent (1000-3000 m³ per day) into water streams containing various toxic substances viz, dyes, metals etc [1]. Moreover, the wastewater containing colors have adverse effect on ecosystem specifically to aquatic lives [2]. Therefore, the effluents are being purified by various methods. Advanced Oxidation Processes (AOPs) are also being utilized to treat dye-containing effluents [3]. Advanced oxidation processes include combination of UV and H₂O₂ oxidation. In this process photolysis of H₂O₂ is carried out to generate strong hydroxyl radicals in high concentration. These chemical species effectively decompose and even completely mineralize organic pollutants. Furthermore, this process does not need additional disposal problems [4, 5, 10-12]. Hydroxyl ([•]OH) radicals attack an organic molecule (RH) and convert it into radical R[•]. In the solution, R[•] radicals react with hydrogen peroxide and generate more [•]OH radicals. Furthermore, R[•] radicals bond with an oxygen molecule to form peroxy radicals (ROO[•]). The peroxy radicals (ROO[•]) react further with an organic molecule to generate R[•] radicals as given below [13]:



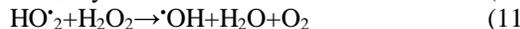
The UV radiation impacts and H₂O₂ decomposition pathway have been given as follow [14-16].

Initiation

In case of direct photo degradation of hydrogen peroxide, the values of the typical molar extinction coefficient and primary quantum yield are 18.6 dm³ mol⁻¹ cm⁻¹ and 0.5 mol E⁻¹ at 254 nm, respectively:



Hydroxyl radical breeding and termination



General reaction



In the presence of UV light, the generation of hydroxyl radicals takes place from hydrogen peroxide, water and oxygen. Furthermore, perhydroxyl radicals are also formed. The hydroxyl

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radicals degrade dye molecules into small fragments [17].

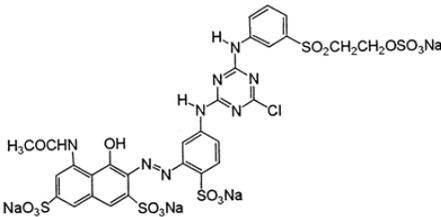
The statistical methodologies are useful solution to attempt fewer number of experiments to evaluate the effects of independent factors on response [6, 7]. RSM is an experimental design technique in which the influence of process variables (input) is analyzed on a specific dependent variable (response). In RSM, analysis of data was carried out by using mathematical and statistical techniques. Consequently, linear, interaction and quadratic effects of the operational variable are estimated and a mathematical model is established to predict the response [8]. Central Composite or Box-Behnken Designs are selected to get experimental data. Experimental runs and the combinations of factors levels are different in these designs. The central composite design can adequately analyze results. Modeling and optimization of different water treatment processes have been done by RSM [9, 18]. However, RSM has not been used to optimize and model the photooxidative process for the removal of RR223 dye from simulated wastewater.

Experimental

Reagents

Hydrogen peroxide (H₂O₂) (30%, d =1.11 g/mL), sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were of laboratory reagent grade. The structure and characteristics of RR223 are presented in Table-1.

Table-1: Structure and characteristics of Reactive red 223.

Molecular formula	C ₂₉ H ₂₁ ClN ₈ Na ₄ O ₁₇ S ₅
Molecular mass	1041.26 (g mol ⁻¹)
Other name	Reactive brilliant Red M-GE
Chemical Class	Vinyl sulphone dyes
Chemical structure	

Experimental

A UV lamp 160W (UV-C) mercury lamp (Philips, the Netherland) was utilized for irradiation. A 250 mL in volume of the solution was kept in a

batch photoreactor. The lamp was put above the reactor. The concentration of the dye, H₂O₂ and other factors level were maintained into the Pyrex Jacketed beaker (Diameter external 110mm, internal 80mm, Height internal 215mm, Height total 235mm) according to the given in the treatments of the experimental design. Afterwards, the reaction was initiated by switched on UV lamp. During the process, the mixture of the reactor was kept uniform by magnetic stirrer (78HW-1 serial constant-temperature magnetic pug mill). A 2mL sample of the solution was taken at different intervals designed by the CCD. Moreover, the residual H₂O₂ was decomposed with MnO₂ powder. The samples were analyzed using a spectrophotometer (T80 UV/VIS spectrometer) to determine the percentage removal of color and COD. A photoreactor diagram is shown in Fig. 1

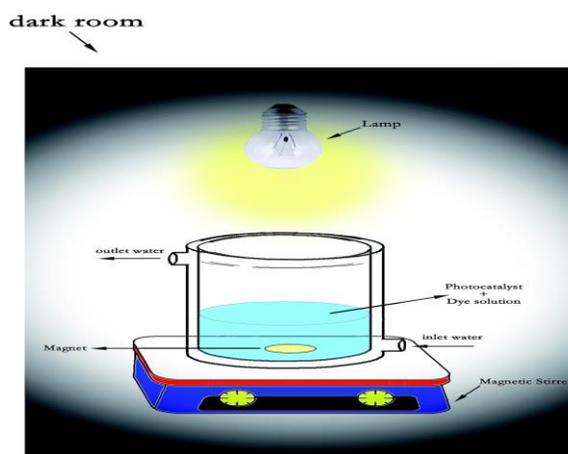


Fig. 1: Photoreactor.

COD determination

COD values were measured by an open reflux colorimetric method using Standard Method of APHA standards. The removal of color was determined accordance to Method 2120C [5].

$$\text{Removal(\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (13)$$

Experimental design

Experimental design, data analysis and process optimization

In the optimization of UV/H₂O₂ process, CCD was adopted, a commonly used feature of RSM. Moreover, in the work, four influential parameters such as irradiation time, distance from UV lamp, dye

and H₂O₂ concentrations were optimized to check the influence on the photooxidative structure-degradability of RR223. Furthermore, in this work, 31 experiments were performed. Analysis of the data was performed by using Minitab 17 software. Response surface plots, contour plots and Pareto chart were plotted using Sigma plot 12 and Statistica 8 software [19-23].

Results and Discussion

Central Composite Design Model

In CCD, factors levels were selected, experimental runs were designed and performed accordingly. Furthermore, data were analyzed to determine the coefficients of the mathematical model to estimate the response and its adequacy. The following second order polynomial equation is as follows [18, 24]:

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i x_i + \sum_{i=1}^4 \sum_{j=1}^4 \beta_{ij} x_i x_j + \sum_{i=1}^4 \beta_{ii} x_i^2 \quad (14)$$

where Y is a specific response. The X_iX_j show the independent variables. While β₀ is the constant coefficient, and β_i, β_{ij} and β_{ii} are coefficients of linear, interaction and quadratic terms, respectively. The following second-order polynomial equations were obtained for the percent color and COD removal as follows:

$$\% \text{ Color Removal} = -108.3 + 5.09 A + 6.52 B + 10.79 C + 1.36 D - 0.3660 A^2 - 0.2722 B^2 - 0.2342 C^2 + 0.002 D^2 + 0.160 AB + 0.0344 AC - 0.005 AD - 0.1031 BC + 0.016 BD - 0.196 CD \quad (15)$$

$$\% \text{ COD Removal} = 65.1 + 4.41 A + 0.98 B + 0.78 C + 3.32 D + 0.1749 AA + 0.0517 BB + 0.0331 CC + 0.092 DD - 0.023 AB - 0.0187 AC + 0.031 AD - 0.0187 BC + 0.031 BD + 0.025 CD \quad (16)$$

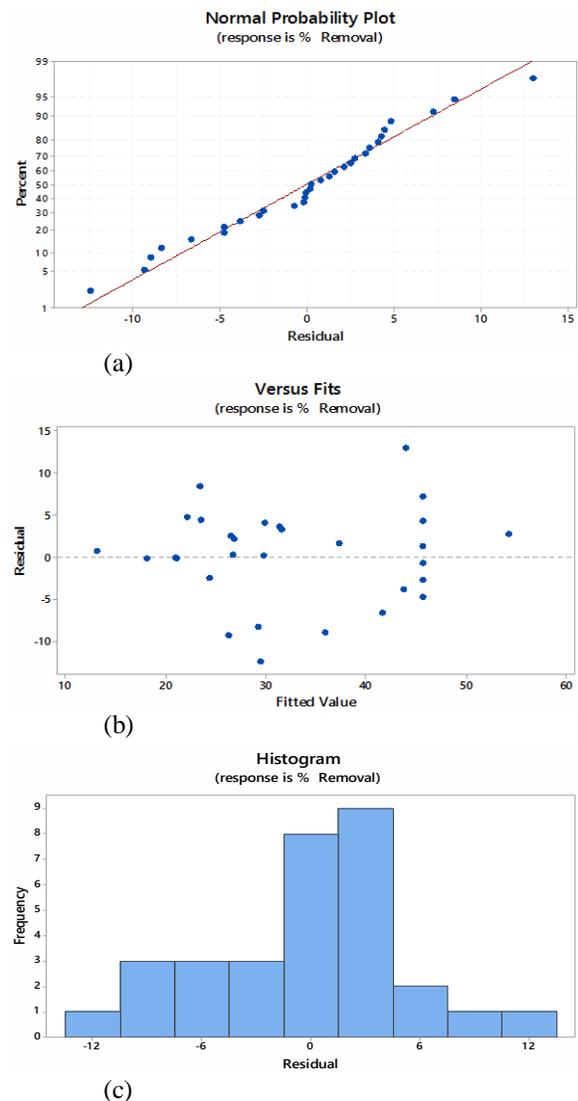
CCD model validation and residual analysis

The regression coefficient R² helps to find the relation between observed and predicted responses. The correlation coefficient R² value was found to be 0.7854, representing the close relation with the predicted responses as given in Table-2. Moreover, It also indicates that about 79% variations in the responses are due to the effect of operational parameters. Adjusted R² (Adj-R²) measures the goodness of a fit. Adjusted R² value is smaller than R² in case when sample size is small and many terms are present in the model [25, 26].

Table-2: Model Summary of the Responses.

Statistical parameters	% color removal potency	% COD removal potency
S _(square mean of error)	7.622	7.900
R ²	78.54%	35.16%
R ² (adj)	59.75%	0.000%
R ² (pred)	0.000%	0.000%

Residual plots help to check the adequacy of the models. The residuals are the differences between observed and predicted responses. The normal probability plots predict the normality of the residuals. The residuals must follow the normal distribution. However, in balanced design or data of large number of observations, moderate deviation in the normal probability plot does not affect the response. The residual plots are given in Figs. 2(a-d), 3(a-d). In Figs. 2a and 3a, the residuals are normal behaving. In Figs. 2b and 3b, data are showing random trend about zero. In Fig. 2d and 3d, it is clear that the residuals data are giving the fluctuation pattern around the central line.



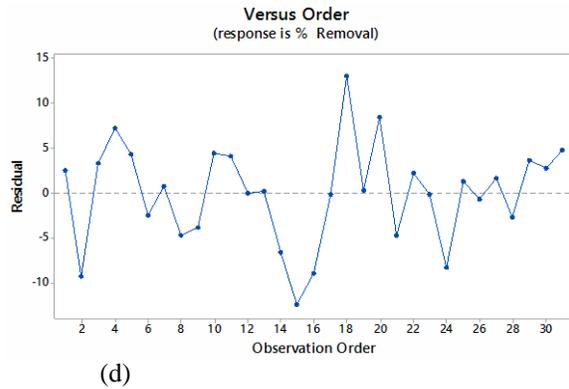


Fig. 2: (a-d): Residual plots for % color removal potency (a) Normal probability plot (b) Residual versus Fitted values (c)Histogram (d)Residual versus Observation order.

Analysis of variance

ANOVA data of the quadratic response surface model are given in Table-2-5. The significance and adequacy of the model is tested by ANOVA. The total variation of the data obtained is subdivided into two components in ANOVA: variation due to the model and the experimental error, showing that the variation due to the model is significant or not against the residual error. The F-values are used to compare the variation of the results due to the model and the residual error. An F-value is the ratio between the mean square of the model and the residual error. The greater value of F- test than that of the tabulated value at a level of significance α . It

represents that the model is predicting the experimental data well [27]. The p-value of the model for the removal of RR223 is found to be 0.004, showing the significance of the CCD model.

Table-3: Analysis of variance (ANOVA) for RR223 Photo catalytic degradation.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	3400	242.9	4.180	0.004
C	1	495.0	495.0	8.520	0.010
D	1	425.0	425.0	7.320	0.016
AA	1	980.5	980.5	16.88	0.001
BB	1	542.5	542.5	9.340	0.008
CC	1	980.5	980.5	16.88	0.001
Error	16	929.5	58.09	*	*
Lack-of-Fit	10	804.1	80.41	3.850	0.056
Pure Error	6	125.4	20.91	*	*
Total	30	4330.4	*	*	*

Table-4: Analysis of Variance for % COD removal potency.

Source	DF	Adj SS	AdjMS	F-Value	P-Value
Model	14	541.0	38.61	0.620	0.813
A ²	1	224.0	223.8	3.590	0.076
Error	16	997.0	62.29		
Lack-of-Fit	10	966.0	96.59	18.78	0.001
Pure Error	6	30.90	5.143		
Total	30	154.0			

Table-5: Estimated regression coefficients and corresponding student-t and P-values for % color removal potency.

Term	Effect	Coef	SECoef	T-Value	P-Value	VIF
Constant		45.71	2.88	15.87	0.000	
C	9.08	4.54	1.56	2.92	0.010	1.00
D	-8.42	-4.21	1.56	-2.70	0.016	1.00
B ²	-8.71	-4.36	1.43	-3.06	0.008	1.03
C ²	-11.71	-5.86	1.43	-4.11	0.001	1.03

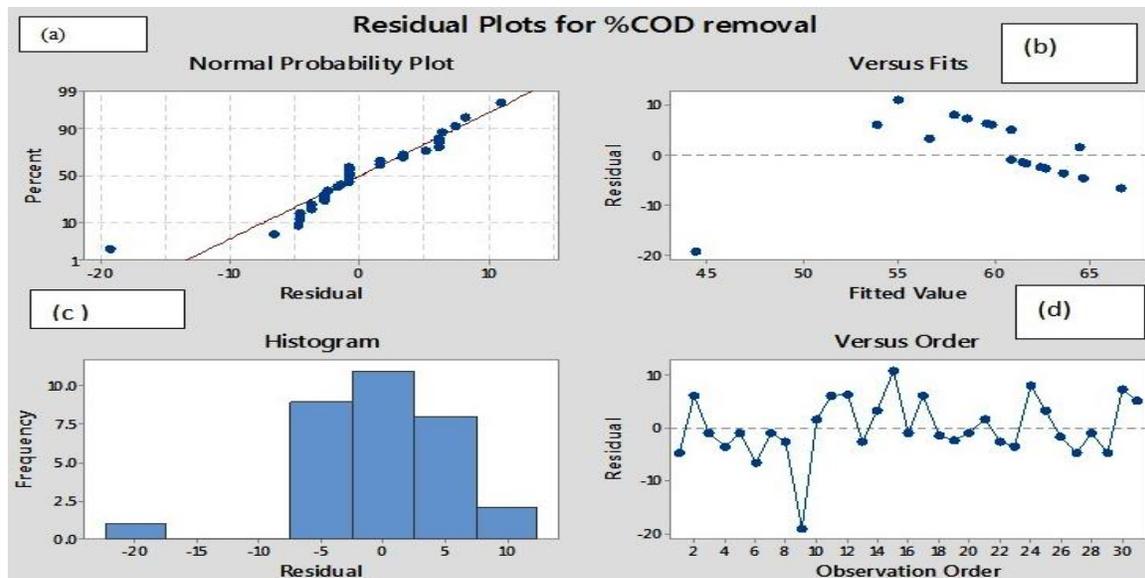


Fig. 3: (a-d): Residual plots for % COD (a) Normal probability plot (b) Residual versus Fitted values (c) Histogram (d) Residual versus Observation order.

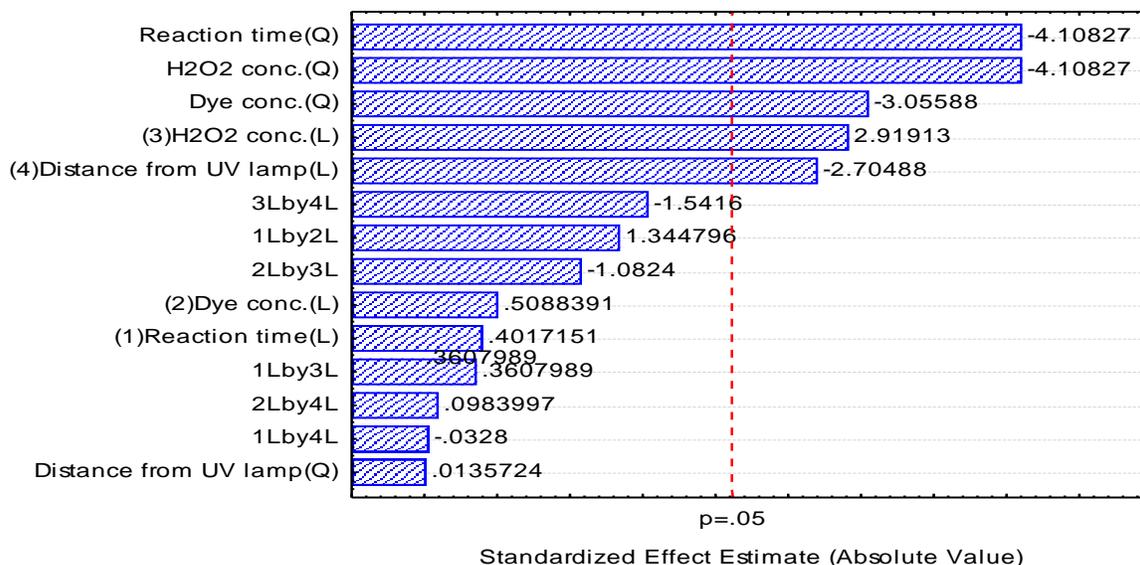


Fig. 4: The Pareto chart of standardized effects and Color Removal efficiency.

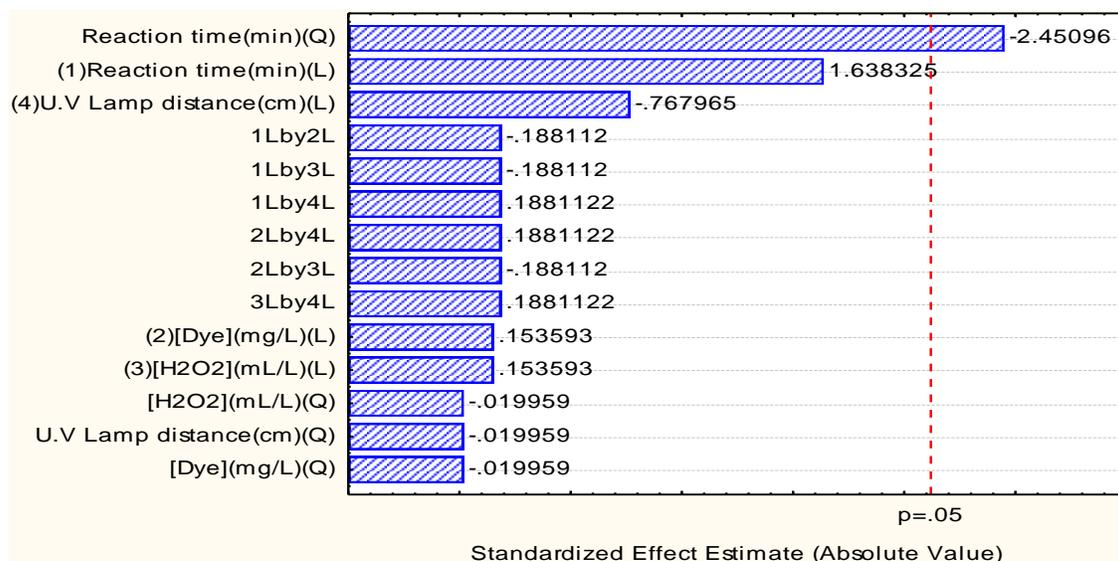


Fig. 5: The Pareto chart of standardized effects and % COD removal potency.

Pareto Chart analysis for Responses

Pareto Charts are shown in Figs. 4 and 5. The values for factors, higher than absolute value are considered significant. The Fig.4 showing that reaction time, [H₂O₂], [Dye], and U.V lamp distance (L) are the significantly affecting the % color removal potency. The Fig. 5 represents Pareto chart for COD removal potency. Furthermore, it was observed that reaction time was the most significant factor for the COD removal potency.

The study of effect of variables

The effect of operational parameters on the resulted responses is shown by plotting the three

dimensional (3D) and contour (2D) plots. The change in the response data is analyzed by the surface plots and contour plots. The surface and contour plots are formed with two factors kept at their zero levels and the other factors levels are changed from lowest to the highest level.

Response surface plots are helpful in finding out the relation between the color removal efficiency and the tested levels of independent variables. Moreover, the type of interaction between the operational parameters is identified by the contour plots [28]. The plots are shown in Figs. 6 and 7.

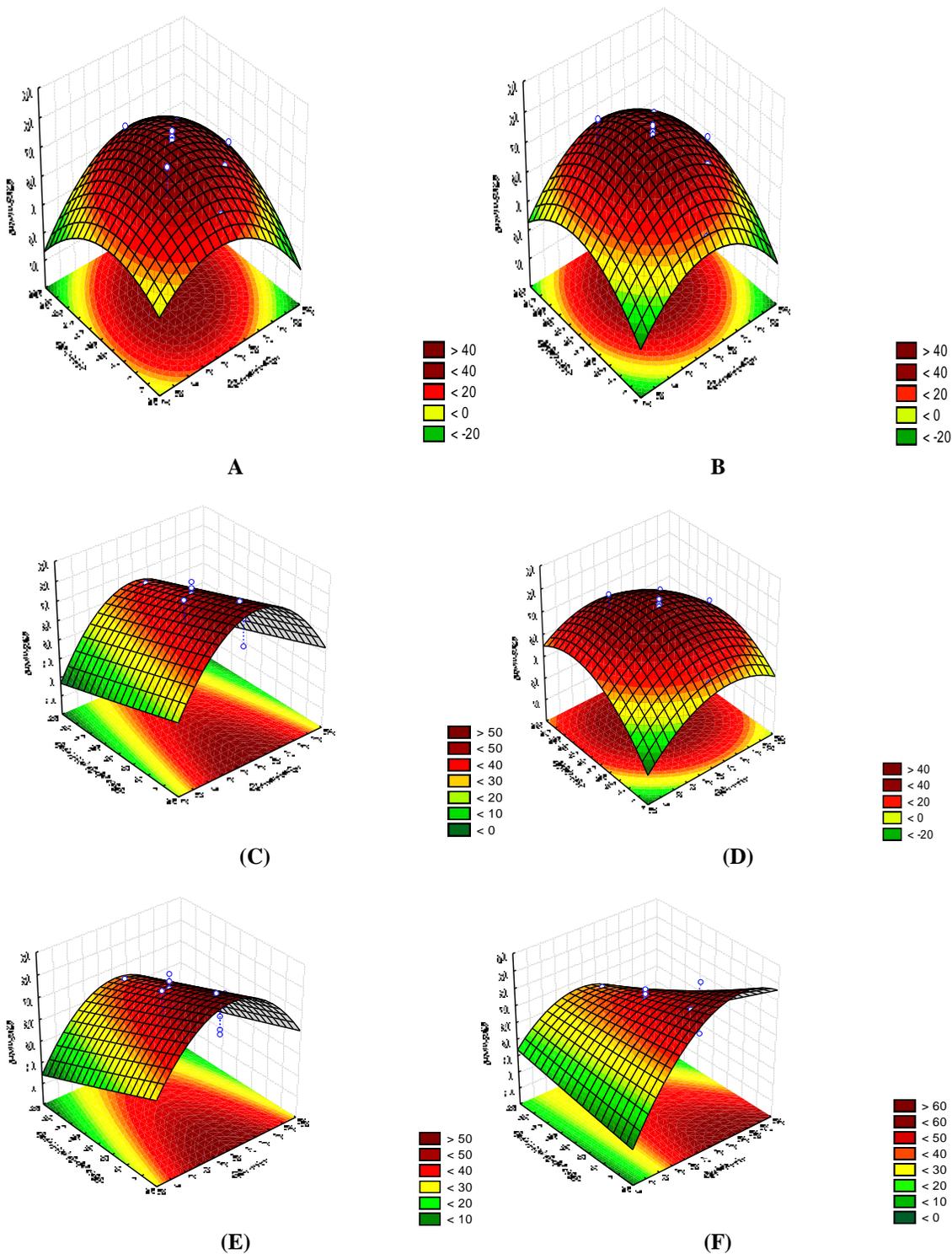


Fig. 6: (a-f): The response surface and contour plots of the (%) color removal efficacy as the function of (a) Reaction time (min) and [dye] (mg/L)(b) Reaction time (min) and [H₂O₂](mg/L) (c) Reaction time (min) and UV lamp distance(d)[dye] (mg/L) and [H₂O₂] (mg/L)(e) [dye] (mg/L) and UV lamp distance (f)[H₂O₂] (mg/L) and UV lamp distance.

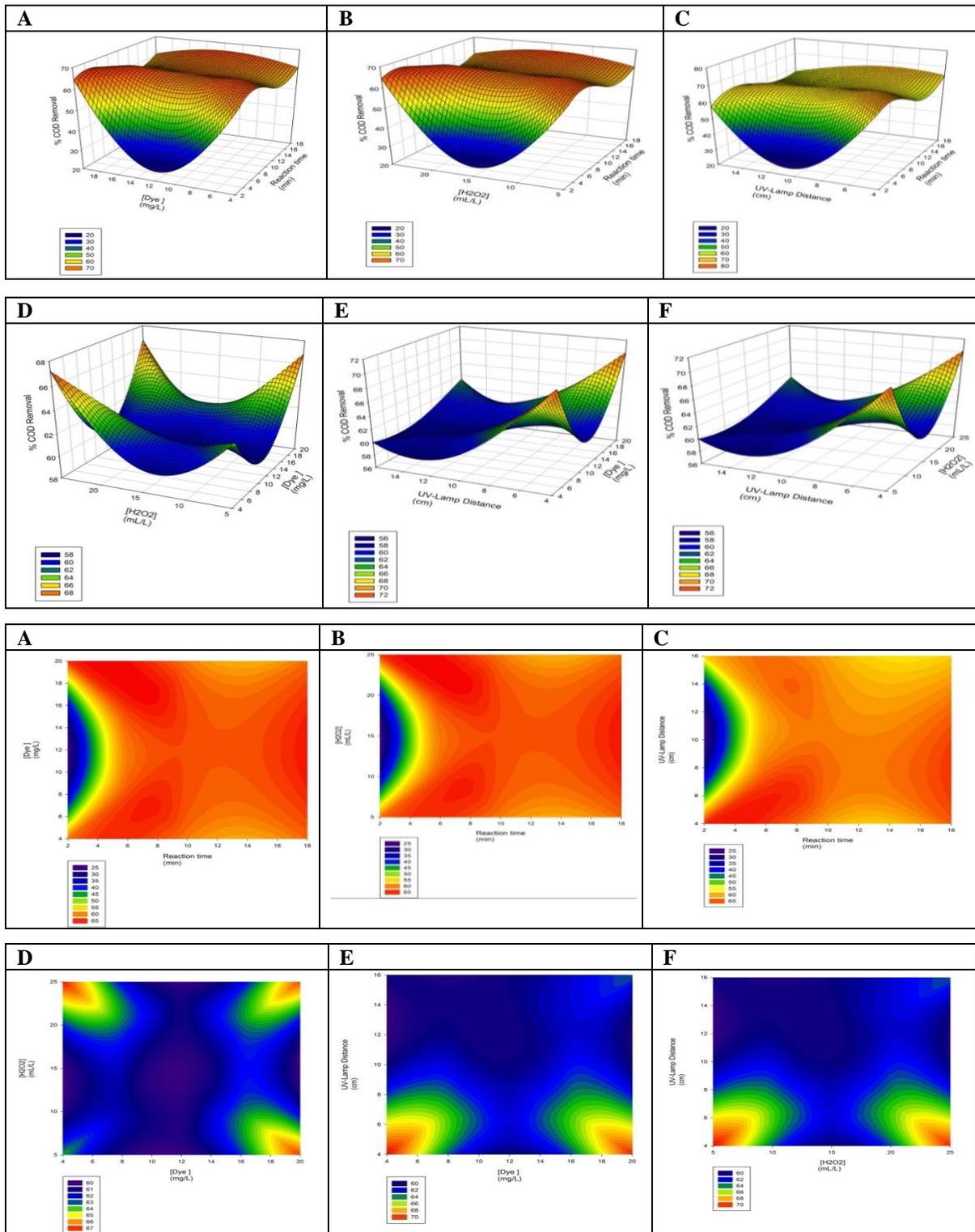


Fig. 7: (a-f) Response Surface and Contour plots for % COD removal potency (a) Reaction time (min) and [Dye] (mg/L) (b) Reaction time (min) and [H₂O₂] (mL/L) (c) Reaction time (min) and U.V lamp distance (cm) (d) [Dye] (mg/L) and [H₂O₂] (mL/L) (e) [Dye] (mg/L) and U.V lamp distance (cm) (f) [H₂O₂] (mL/L) and U.V lamp distance (cm)

Effect of initial H₂O₂ concentrations

The results shown in Figs.6, representing that the degradation of the dye increases with the increase in the concentration of H₂O₂. Because, high concentration of H₂O₂ forms high concentration of OH• radicals. Indeed, it had increased the percent color removal due to increased attack of hydroxyl radicals at the chromophore group of the dye. [29]. The H₂O₂ concentration significantly affected the dye removal potency which was agreed from Pareto chart too. When H₂O₂ concentration was varied 5 to 15mL/L, the response improved upto 74 % at reaction time= 10min, [dye] = 12 mg/L, U.V lamp distance=10 cm as shown in Table-6 and 7. In addition, excess H₂O₂ dosage lead to the formation of less powerful •O₂H (hydroperoxy) radicals. In the UV/H₂O₂ oxidation, rate of color removal is totally depend on dye characteristics and H₂O₂ dose [30-32].

Table-6: Experimental ranges and levels of the independent test variables.

Variables	Ranges and levels				
	-2	-1	0	+1	+2
(A) Reaction time (min) (X1)	2	6	10	14	18
(B) Initial dye concentration (mg/L) (X2)	4	8	12	16	20
(C) Initial H ₂ O ₂ concentration (mL/L) (X3)	5	10	15	20	25
(D) Distance from UV lamp (cm) (X4)	4	7	10	13	16

Table-7: The Central Composite design matrix and responses.

Reaction time (min)	[Dye] (mg/L)	[H ₂ O ₂] (mL/L)	UV-Lamp Distance (cm)	% Removal	% COD Removal
6	16	10	7	29	66
6	8	10	7	17	66
14	16	10	7	35	66
10	12	15	10	53	66
10	12	15	10	50	66
6	16	10	13	22	60
10	12	5	10	14	60
10	12	15	10	41	66
14	16	20	7	40	60
18	12	15	10	28	66
10	20	15	10	34	60
2	12	15	10	21	25
14	16	20	13	30	60
14	8	20	7	35	66
6	8	20	13	17	60
6	16	20	7	27	66
14	8	10	13	18	60
6	8	20	7	57	66
10	4	15	10	27	60
6	8	10	13	32	60
10	12	15	10	41	60
14	8	20	13	29	60
14	8	10	7	21	60
14	16	10	13	21	60
10	12	15	10	47	60
10	12	15	10	45	66
10	12	15	16	39	60
10	12	15	10	43	66
10	12	25	10	35	60
10	12	15	4	57	60
6	16	20	13	27	66

Effect of initial dye concentrations:

The percent color removal increased to 21% when concentration was varied from 4 to 20 mg/L at reaction time of 10 min, [H₂O₂] 15mL/L and U.V lamp distance of 10 cm as shown in Table-7. It is the result of increased collision between hydroxyl radicals and the dye particles. However, light penetration through the solution is inhibited at high dye concentration.

Effect of Irradiation time

Figs.6, 7 show that reaction time is the most vital factor among other respective factors. The color removal increases with time particularly for lower initial dye concentrations. It is observed that at initial irradiation stage of the process, the hydroxyl radicals fastly degrade the dye molecules and increase the color removal efficiency. Moreover, the formation of intermediates owing to the reactions of •OH and •O₂H with dye molecules resulted in decreasing the concentration of •OH radicals. Furthermore, it causes the decrease in color removal potency. Additionally, it was observed that when reaction time was changed from 2 to 18 min at [dye] 12mg/L, [H₂O₂] 15 mL/L, U.V lamp distance 10 cm about 7% color removal was increased .

Effect of U.V lamp distance

It was cleared from the observation as shown in Table-7 that the % decolourization was increased from 39 to 57%, when the reaction time about 10 min, [dye] 12 mg/L and [H₂O₂] 15mL/L by decreasing U.V lamp distance varying from 16 to 4 cm. Moreover, it is agreed from Pareto chart too.

Effect of Reaction time on %COD removal

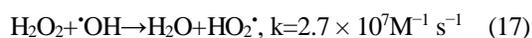
The reaction time is significantly changing the removal of COD as shown in Fig. 7. Moreover, it was also agreed by Pareto chart too. It was determined that when reaction time was increased from 2 to 10 min , about 62 % removal was achieved at same conditions.

Effect of dye concentrations

The effect of initial dye concentration was observed range from 4–20 mg/L of RR223. The results demonstrated that, by increasing the dye concentration from 4 to 12 mg/L, the 10% removal of COD was inflated under same conditions. This behavior was observed due to the higher concentration of dye and another effect is to prevent U.V light interaction with the H₂O₂. It resulted lowering the rate of photo- degradation as shown in Fig. 7.

Effect of H₂O₂ concentrations

H₂O₂ has not shown a significant effect on % COD removal of the system it is agreed from Pareto chart too .When H₂O₂ concentration was increased from 10 to 20 mL/L, negligible increased in % COD removal was observed at same conditions. U.V decomposition of H₂O₂ into hydroxyl radical is totally depend on pH of the system so high % COD removal was not observed .The effect of [H₂O₂] on % COD removal is shown in Fig. 7. The negligible effect on % COD removal potency with increasing H₂O₂ concentration is owing to the free radical scavenging effect as given in the following reaction [26];



Effect of U.V lamp distance

U.V lamp distance affects the degradation of pollutants as U.V lamp distance was increased from 7 to 13 cm, 10 % decreased in % COD removal was calculated at reaction time 6 min, [dye] 16 mg/L, [H₂O₂] 10 mL/L.

Main interaction plots

Main Effects Plot is helpful in understanding the statistical importance of data. The values of independent variables are taken on x-axis and response of the process on y-axis. If the response does not change with respect to change in the levels of factors its mean no correlation is present between them. In the graphs Fig.8a, the factors levels are significantly changing the response mean value. In Fig.8b reaction time is more considerably affecting the response mean (% COD removal).

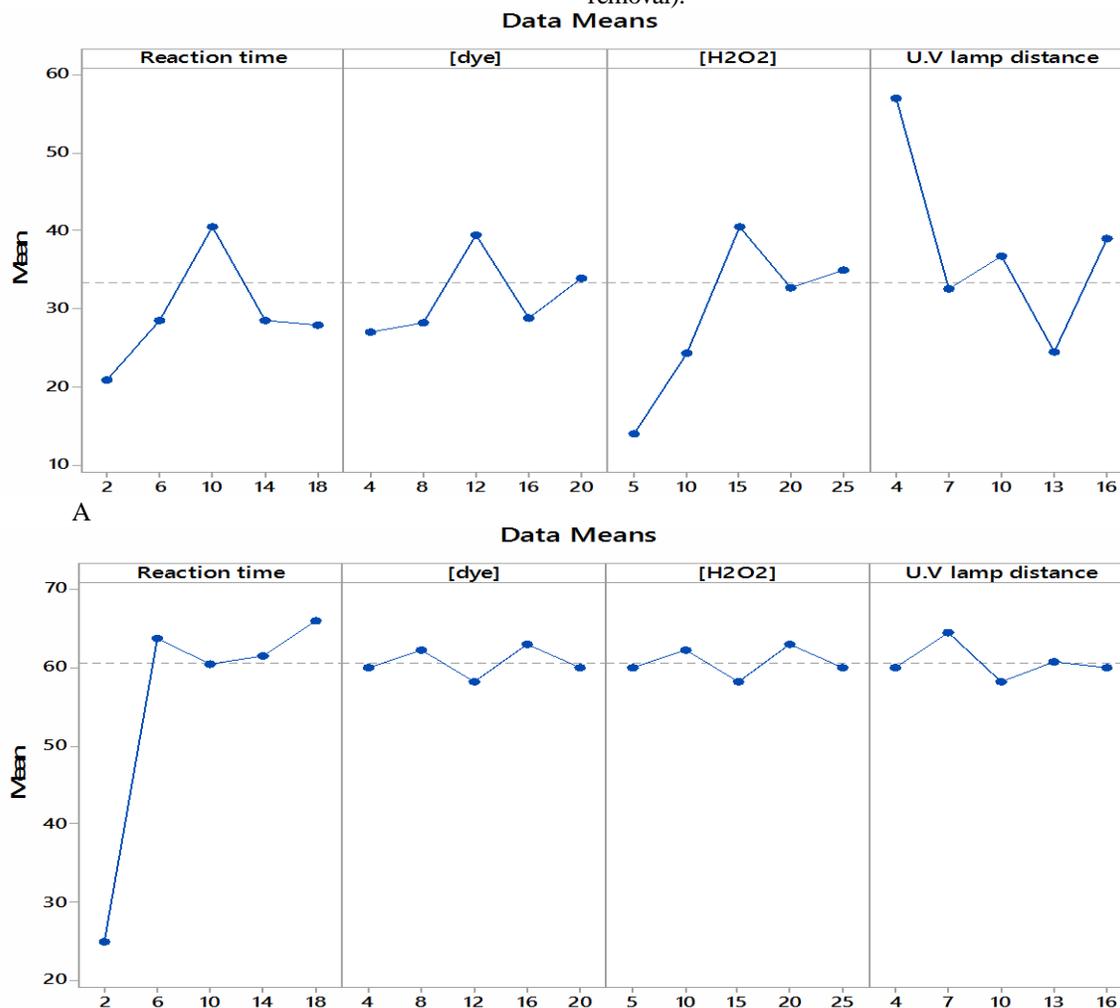


Fig. 8: Main interaction plot for (a)%color removal potency (b)% COD removal potency.

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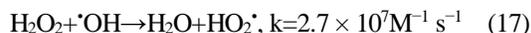
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Effect of H₂O₂ concentrations

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*Effect of U.V lamp distance*

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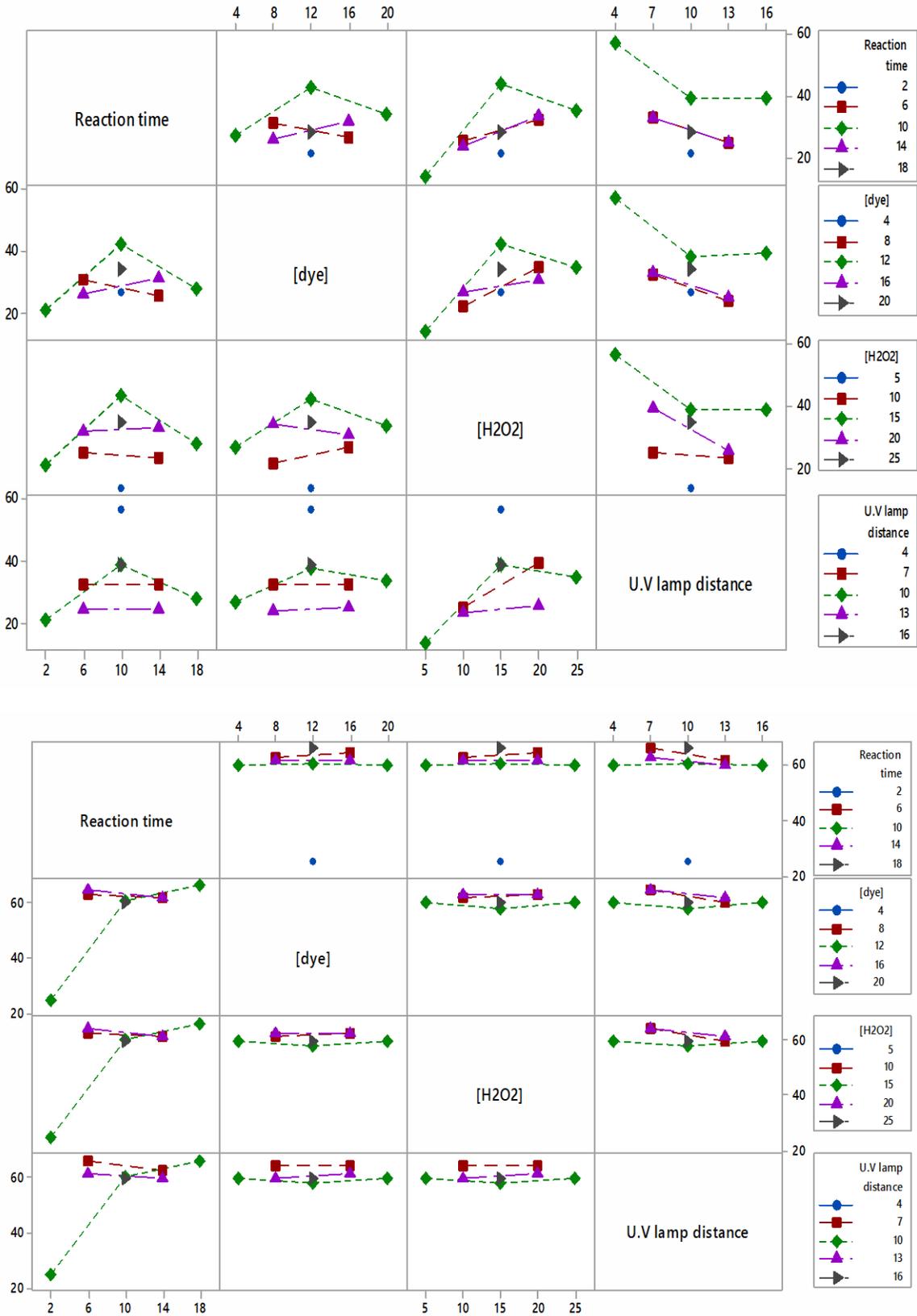


Fig. 9: Full interaction plots for (a)% color removal potency (b)% COD removal potency.

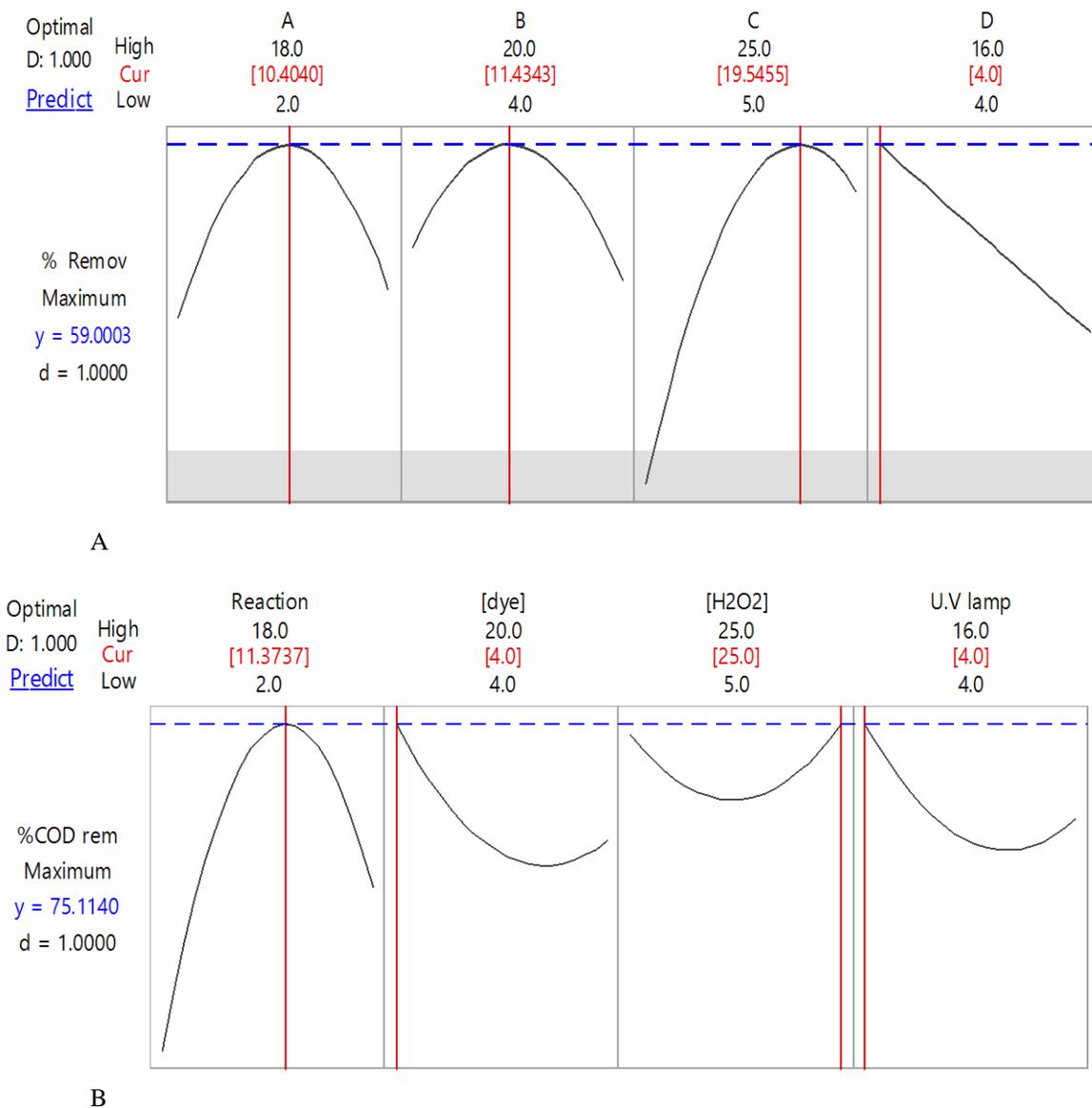


Fig. 10: Optimum values for % color and COD removal potency.

FTIR Spectrum

The characterization of dye and its chemical characteristics were determined by Fourier transform infrared (FTIR) spectroscopy by NICOLET 67000 spectrometer. It was observed that the intense bands appeared at 3420 cm^{-1} are owing to the stretching vibration of O–H and/or N–H. Moreover, the absorption bands appeared at 1031 cm^{-1} showing the C–O stretching. The peak appeared in the spectrum at 1600 cm^{-1} indicating that an azo dye is present. The Table-8 and Fig.11 show the characteristic peaks in FTIR spectrum of RR223.

Table-8: FTIR Spectrum of RR223 and its Characteristics peaks.

Functional groups	Wave number (cm^{-1})
OH, NH	3450.41
CH, Arom	3095.54
C=C-	1481.23
N=N	1434.94
-C=N-	1587.31
C-N	1220.86
Sulfonates	1365–1340/1200–1100
Disulfides (CS stretch)	705–570
Sulfate ion	1130–1080/680–610

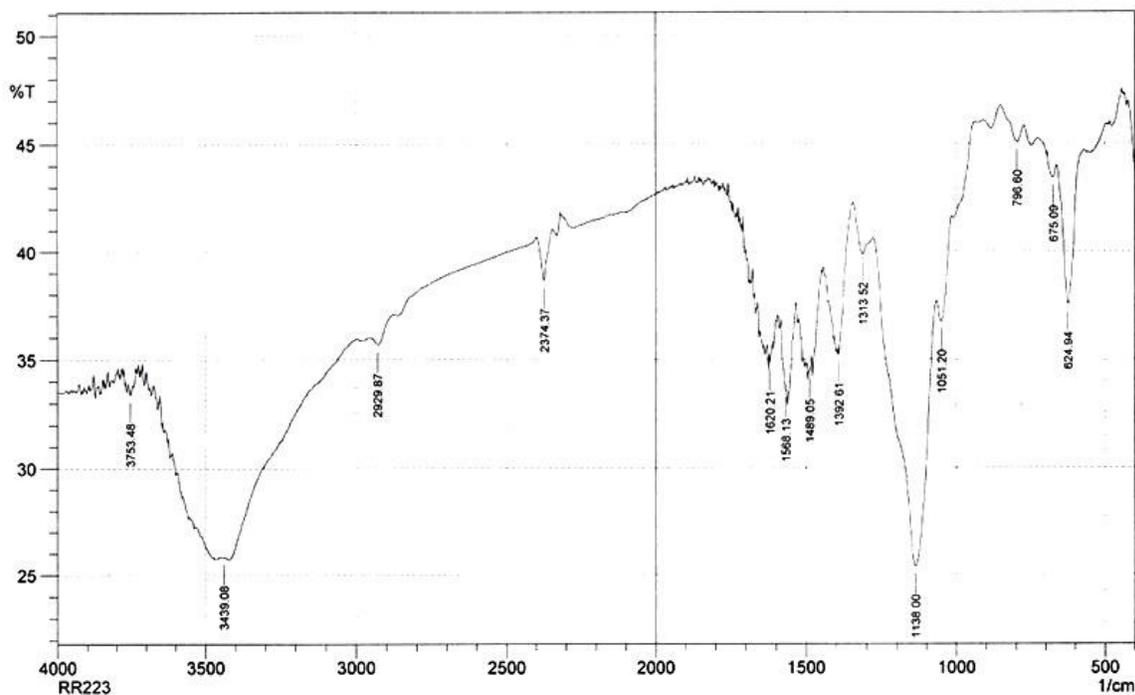


Fig.11: FTIR spectrum of Reactive red 223.

Kinetics study

The kinetic study proved that UV/H₂O₂ process could be effectively applied to remove the color of simulated dye system. Moreover, the Pseudo-second order kinetics was applied for the dye removal by UV/H₂O₂ process as shown below:

$$\frac{1}{At} = kt + \frac{1}{Ao} \quad (18)$$

where k (M⁻¹min⁻¹) denotes the observed Pseudo-second order reaction rate constant, t (min) represents the reaction time, A_0 (the initial absorbance and A_t is the absorbance at any time t [33-36]. The values of kinetics parameters are given in Table-9.

Table-9: Kinetics study.

Kinetic order	k(M ⁻¹ min ⁻¹)	t _{1/2} (min)	R ²
Pseudo-second order	0.032	134	0.989

Electrical energy per order

The International Union of Pure and Applied Chemistry (IUPAC) have proposed two figures-of-merit for advance oxidation processes for electrical energy consumption. The Photochemical process efficiency is evaluated by electrical energy consumption in kWh. It requires removing the concentration of a pollutant by 1 order of magnitude

in 1 m³ of pollutant water. Moreover, it is calculated as follow:

$$EE/O(\text{KWh.m}^{-3}) = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_i}{C_f}\right)} \quad (19)$$

where P is the power in kW. (V) is volume in litre, C_i and C_f (mg/L) is [COD]_{Initial} and [COD]_t at time "t". $\ln(C_i/C_t)$ is the multiplication product of rate constant (k) for the dye degradation at time (t) in min [37]. The value of EE_o is 25.165\$/m³ as given in Table-10 which is indicating that the UV-photolysis in the presence of H₂O₂ is effectively degrading RR 223 dye.

Table-10: Electrical energy per order of photo catalytic process.

Optimum parameters	Values
Reaction time(min)	12
[Dye] mg/L	4
[H ₂ O ₂] mL/L	25
U.V lamp distance(cm)	4
Electrical energy per order (kWhm ⁻³ order ⁻¹)	252
Cost Analysis(\$/m ³)	25.165\$/m ³

Conclusions

The present study was successfully carried out for the color and COD removal of simulated dye effluent by U.V/H₂O₂. It was determined that CCD methodology was effectively optimized the process

variables for the treatment of the simulated effluent at laboratory scale. The desired levels of the reaction time, initial[dye], initial[H₂O₂] and distance of UV lamp from the solution were found to be 11 min, 12 mg/L, 20 mL/L and 4 cm, respectively. Moreover, the color removal 62% was obtained at the optimum levels of the studied factors. Furthermore, ANOVA calculated a high value of correlation coefficient viz, R² 79% and Adj-R² 60% for percent color removal potency, thus ensuring a satisfactory regulation of the second-order regression model with the experimental data. In the residual plots, the data are following a normal distribution patterns. The study proved that photo catalytic degradation of dye using UV-lamp source can be an economically effective and feasible treatment process for the treatment of textile effluent.

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