Photocatalytic degradation of Reactive Black 8 in UV/TiO_2/H_2O_2 system: Optimization and modeling using a response surface methodology (RSM)

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Degradación fotocatalítica de Reactivo Negro 8 en el sistema UV/TiO_2/H_2O_2 : optimización y modelización utilizando una metodología de superficie de respuesta (RSM)

Degradació fotocatalítica de Reactiu Negre 8 en el sistema UV/TiO_2/H_2O_2: optimització i modelització utilitzant una metodologia de superfície de resposta (RSM)

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RESUMEN

Los colorantes reactivos azo son de los más utilizados en la industria textil. Sin embargo, estos compuestos son ambientalmente peligrosos y difíciles de tratar por métodos clásicos. En el presente estudio un fotoreactor discontinuo agitado y con un nuevo sistema de irradiación se utilizó para la decoloración de un colorante reactivo azo. Se investigaron los efectos de ciertos parámetros sobre la decoloración y la degradación de Reactivo Negro 8 C.I., incluyendo el colorante inicial, concentración de H2O2, cantidad de fotocatalizador y pH inicial en un sistema constituido por UV/TiO2/H2O2. El método Box-Behnken de diseño experimental estadístico, se utilizó para optimizar el proceso de decoloración. La eficiencia en la decoloración aumenta con la disminución de la concentración inicial de colorante, con la adición de H2O2 hasta un valor óptimo, con el aumento de la cantidad de fotocatalizador y con los valores de pH originales (sin adición de productos de ajuste de pH).
Los parámetros óptimos obtenidos para la decoloración de Reactivo Negros 8 son los siguientes: TiO2 1.59 g L-1, concentración de Reactivo Negro 8 = 34.65 ppm, pH = 5.5, concentración de H2O2 = 1.82 (relación estequiométrica). Utilizando estos parámetros óptimos se observó el 96.1% de decoloración y el 78.6% de degradación del colorante en solución en los 60 minutos de irradiación.

Palabras clave: Fotocatalizador, TiO2, LED-UV, Box-Behnken.

SUMMARY

Reactive azo dyes are among the most applicable dyes in textile industries. However, these compounds are environmentally hazardous and difficult to treat by classical methods. In the present study a batch stirred photoreactor with a novel irradiating setup was utilized for decolorization of a reactive azo dye. The effects of certain parameters including initial dye, H_2O_2 concentration, photocatalyst loading and initial pH in a system consisting of UV/TiO_2/H_2O_2 on the decolorization and degradation of C.I. Reactive Black 8 were investigated. Box-Behnken method, a statistical experimental design method, has been used to optimize the decolorization process. Decolorization efficiency increases with decreasing initial dye concentration, addition of H_2O_2 up to an optimum value, increasing photocatalyst loading and at original pH values (containing no pH adjusting chemicals).
The optimum parameters for decolorization of Reactive Black 8 are obtained as follows: TiO_2 = 1.59 g L^{-1}, Reactive Black 8 concentration =34.65 ppm, pH = 5.5, H_2O_2 concentration = 1.82 (stoichiometric ratio). By use of these optimum parameters 96.1% decolorization and 78.6% degradation of the dye in the solution was observed within 60 minutes irradiation.

Keywords: Photocatalyst, TiO_2, UV-LED, Box-Behnken.

RESUM

Els colorants reactius azo són dels més utilitzats en la indústria tèxtil. No obstant això, aquests compostos són ambientalment perillosos i difícils de tractar per mètodes clàssics. En el present estudi un fotoreactor discontinu agitat i amb un nou sistema d'irradiació es va utilitzar per la decoloració d'un colorant reactiu azo. Es van investigar els efectes de certs paràmetres sobre la decoloració i la degradació de Reactiu Negre 8 C.I., incloent el colorant inicial, la concentració d'H2O2, la quantitat de fotocatalitzador i el pH inicial en un sistema constituït per UV/TiO2/H2O2. El mètode Box-Behnken de disseny experimental

estadístic, es va utilitzar per optimitzar el procés de decoloració. L'eficiència en la decoloració augmenta amb la disminució de la concentració inicial de colorant, amb l'addició d'H2O2 fins a un valor òptim, amb l'augment de la quantitat de fotocatalitzador i amb els valors de pH originals (sense addició de productes d'ajustament de pH).
Els paràmetres òptims obtinguts per a la decoloració de Reactiu Negre 8 són els següents: TiO2 =1.59 g L-1, concentració de Reactiu Negre 8 = 34.65 ppm, pH = 5.5, concentració d'H2O2 = 1.82 (relació estequiomètrica). Utilitzant aquests paràmetres òptims es va observar el 96.1% de decoloració i el 78.6% de degradació del colorant en solució en els 60 minuts d'irradiació.

Paraules clau: Fotocatalitzador, TiO2, LED-UV, Box-Behnken.

1. INTRODUCTION

Textile industry dye pollutants are an important source of environmental contamination. A high percent of the dye is released in wastewaters during dyeing processes (Sauer et al., 2002).
Azo dyes, containing one or more azo bonds, are the most widely used synthetic dyes and are major dye wastewater pollutants. Removing color from wastewater is more important than treating other colorless organics, because, presence of only minute amounts of dyes is clearly visible and affects the water environment (Wu, 2008).
Physical, chemical and biological methods are presently available for treatment of textile wastewater. Biological treatment is a cost effective technology. However, in several studies, the majority of dyes are only adsorbed on the sludge without any degradation (Pagga & Taeger, 1994). From another point of view, conventional biological methods are ineffective for degradation due to the aromatic structure and stability of these dyes (Dai et al., 1995). Physical methods including ion-exchange, adsorption and air stripping are also ineffective as they only transfer the pollutants to another phase rather than degrading them (Sauer et al., 2002). The advanced oxidation processes (AOPs) are more efficient methods as they are capable of mineralizing a wide range of organic pollutants (Muruganandham & Swaminathan, 2006). AOPs are related to the generation of hydroxyl radical which is a very powerful and non-selective oxidizing agent. Heterogeneous photocatalysis by irradiation of UV on photocatalyst surface is a more applicable advanced oxidation process.
In the present study, a heterogeneous photocatalytic process UV/TiO_2/H_2O_2 was applied for the decolorization of Youhaoreactive Black KBR commercial reactive azo dye solution. In addition, the effect of pertinent system parameters (catalyst loading, initial concentrations of both dye and H_2O_2 and solution pH) on the dye decolorization was examined and decolorization rate was calculated.

2. EXPERIMENTAL

2.1. Materials

C.I. Reactive Black 8 with commercial name of Youhaoreactive Black KBR was supplied by Youhao Co. (China) and used without further purification. Fig. 1 shows the chemical structure of Reactive Black 8 and Fig. 2 shows it absorbance spectrum. The chemical formula, molecular weight and $\lambda_{max1,2}$ of this dye were $C_{19}H_{11}ClN_8Na_2O_{10}S_2$, 656.9 g/mol and 334, 578 nm, respectively. A gift sample of TiO_2 P25 catalyst was received from Degussa (Frankfurt, Germany). TiO_2 P25 consists of anatase 80% and rutile 20% with the mean particle size of 20 nm and a BET surface area of 50 m^2/g. All other chemicals used in this study were of analytical grades and obtained from Merck Company. De-ionized water was used to prepare necessary solutions.

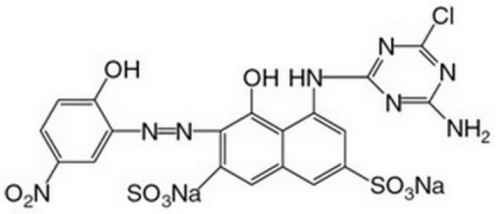


Fig. 1. Chemical structure of Reactive Black 8

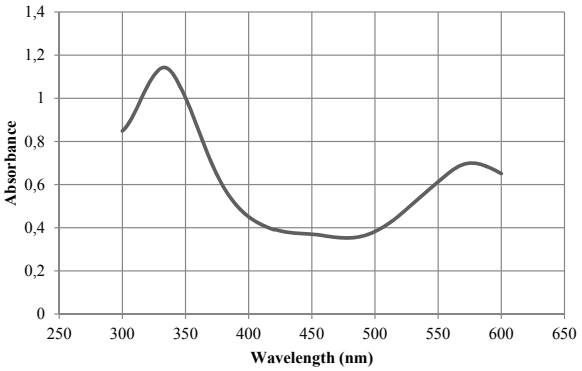


Fig. 2. Absorbance spectrum of Reactive Black 8 (Initial dye concentration: 50 ppm, pH 5.5)

2.2 Analytical procedure

Throughout the experiments, the dye concentration was determined at 578 nm wavelength applying a UV-Vis spectrophotometer (DR 2800 Hach) after calibrating the device with the dye. The TOC of the solutions was measured using Merck TOC Cell Test Method (Spectroquant®).

2.3 Device

All photocatalytic experiments were conducted in a stirred 500 mL batch Pyrex cylindrical reactor. 250 mL of dye solution was added to the reactor. The reactor content was stirred with a mechanical stirrer. Six UV-A LED lamps (Edison Co.) were mounted on the stirrer blade so it simultaneously mixed and irradiated the solution. Since by applying the photocatalyst, the solution becomes blurred and light cannot be distributed well throughout the solution, this new design would provide simultaneous mixing and irradiation to the reaction mixture. The experimental apparatus is shown in Fig. 3. No heat effect was observed due to the UV LED lamps during the photoreaction.

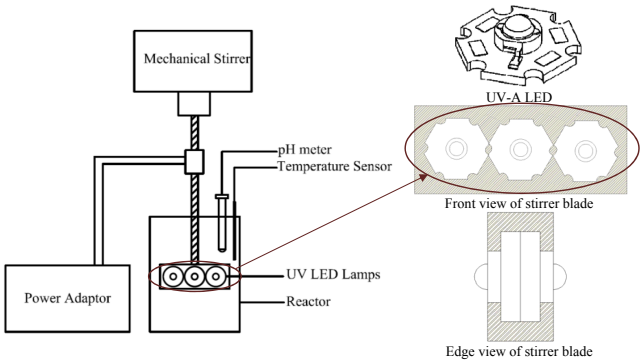


Fig. 3. Photo-Reactor scheme

For pH adjustment of the photocatalytic experiments (UV/TiO_2/H_2O_2), dilute sulfuric acid and sodium hydroxide solutions were used.
At regular time intervals, samples of about 3 mL in volume were withdrawn from the reactor, and filtered, using a 0.22 µm membrane filter.

2.4 Experimental design

In order to find the optimum conditions for the decolorization process, to avoid unnecessary experiments and also regarding economical issues, it is needed to perform an experimental design as a function of the main factors. Within this study, the Box-Behnken method, a branch of response surface methodology (RSM), was used to do the design of experiments (DOE) table by the Design Expert software.

3. RESULTS AND DISCUSSION

3.1 Box-Behnken design

Four factors (variables) including catalyst loading (A), initial dye concentration (B), pH (initial pH) (C) and H_2O_2 concentration (D) in three levels were used in the Box-Behnken method for designing the DOE. The designed table in coded form consists of 29 experiments shown in Table 2. It also should be noted that throughout this paper, the pH stated is the initial pH of the solution.

Table 1. The original and coded levels of the input variables

Original factors	Coded levels		
	-1	0	1
TiO_2 concentration (g L^{-1}): A	0.50	1.25	2.00
Initial dye concentration (mg L^{-1}): B	30.00	50.00	70.00
pH: C	4.00	5.50	7.00
H_2O_2 stoichiometric ratio: D	0.50	1.25	2.00

Table 2. Design of experiments table (coded parameters)

Run	Parameters in coded levels			
	A	B	C	D
	TiO_2 concentration	Initial dye concentration	pH	H_2O_2 stochiometric ratio
1	1	0	0	1
2	0	-1	1	0
3	0	0	1	-1
4	0	-1	0	-1
5	0	0	0	0
6	1	-1	0	0
7	0	0	0	0
8	-1	1	0	0
9	0	0	-1	-1
10	-1	0	0	1
11	-1	0	1	0
12	0	1	1	0
13	0	-1	0	1
14	-1	-1	0	0
15	0	1	-1	0
16	0	0	1	1
17	1	0	-1	0
18	0	0	0	0
19	0	-1	-1	0
20	0	1	0	-1
21	0	0	-1	1
22	1	1	0	0
23	0	0	0	0
24	-1	0	-1	0
25	0	1	0	1
26	1	0	0	-1
27	0	0	0	0
28	-1	0	0	-1
29	1	0	1	0

3.2 The quadratic model and analysis of variances (ANOVA)

All 29 experimental runs designed by the software were performed according to Table 2 and the response was set as percentage of decolorization after 60 minutes.

$$\%\ \text{Decolorization} = \frac{C_0 - C}{C_0} \times 100$$

The regression equations given in Table 3 were derived from the analysis of variances.

Table 3. Regression equations derived for decolorization of Reactive Black 8

Regression equations
Analysis in un-coded parameter (A, B, C, D)
$Y\,(\%) = -390.06 - 16.75 \times A - 0.04 \times B + 136.21 \times C + 187.59 \times D + 23.79 \times A \times D - 0.89 \times B \times D - 17.95 \times C \times D - 11.14 \times C^2 - 21.96 \times D^2$

Table 4 shows the designed table with the actual and predicted values of the response according to the model.

Table 4. Actual and predicted values for decolorization of Reactive Black 8 after 60 minutes

Run	Parameters in uncoded levels				Response	
	A	B	C	D	% Decolorization	
	TiO_2 concentration	Initial dye concentration	pH	H_2O_2 stochiometric ratio	Actual Value	Predicted Value
1	2	50	5.5	2	84.72	83.09
2	1.25	30	7	1.25	33.26	42.68
3	1.25	50	7	0.5	28.71	23.15
4	1.25	30	5.5	0.5	29.7	30.69
5	1.25	50	5.5	1.25	54.26	57.88
6	2	30	5.5	1.25	89.05	90.56
7	1.25	50	5.5	1.25	59.9	57.88
8	0.5	70	5.5	1.25	13.25	15.19
9	1.25	50	4	0.5	1.92	1.08
10	0.5	50	5.5	2	35.25	36.84
11	0.5	50	7	1.25	0.001	7.00
12	1.25	70	7	1.25	8.81	3.19
13	1.25	30	5.5	2	93.91	96.24
14	0.5	30	5.5	1.25	88.58	81.08
15	1.25	70	4	1.25	22.29	22.97
16	1.25	50	7	2	3.93	1.64
17	2	50	4	1.25	64.26	65.65
18	1.25	50	5.5	1.25	62.87	57.88
19	1.25	30	4	1.25	73.74	68.85
20	1.25	70	5.5	0.5	23.08	21.49
21	1.25	50	4	2	57.93	68.19
22	2	70	5.5	1.25	31.58	34.69
23	1.25	50	5.5	1.25	64.64	67.88
24	0.5	50	4	1.25	30.61	36.16
25	1.25	70	5.5	2	33.96	33.69
26	2	50	5.5	0.5	24.49	27.45
27	1.25	50	5.5	1.25	67.39	67.88
28	0.5	50	5.5	0.5	28.55	34.73
29	2	50	7	1.25	19.07	19.49

Actual (observed) value versus predicted value plot is shown in Fig. 4. It helps one detect a value, or group of values, that are not easily predicted by the model. It is observed that the fitted regression equation shows a good fit of the model.

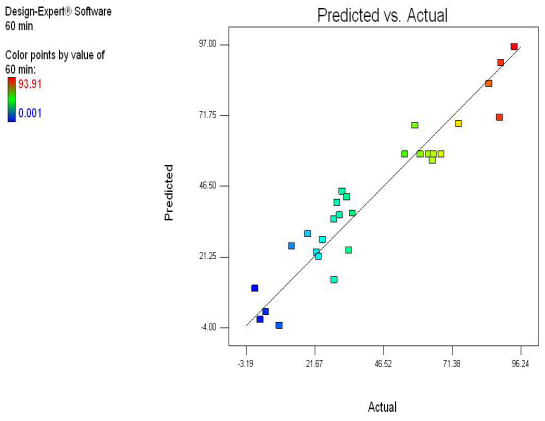


Fig. 4. The actual values plotted against the predicted values obtained from the model

The long line is the regression line with regression coefficient R^2=0.9081. Each point refers to the experimental number listed in Table 4.

A model is considered significant if the p-value is less than 0.1, 0.05 and 0.001, on 10, 5 and 1% significance levels, respectively. From Table 5 it can be concluded that linear and quadratic contribution of the model were significant, whereas for the cubic contribution of the model was insignificant.

Table 5. Analysis of variance for response surface model

Source of variation	Response	
	F value	p-value
Linear	19.56	0.0053
Quadratic	5.55	0.0566
Cubic	0.58	0.6010

In order to estimate the quantitative effect of each factor, Table 6 presents the F value and associated p-values for the response.

In general, a term that has a p-value less than 0.05 would be considered significant. A probability value greater than 0.10 is generally regarded as not significant. So, it can be seen in Table 6 that parameters A, B, C, D, C^2, D^2, AD, BD, CD have significant effects on the model. By eliminating the not significant parameters, we can have our model and the new F value and p-values are also shown in Table 6.

3.3 Effect of the significant parameters and optimal conditions

The main effect plots (Fig. 5) show the linear effect of changing the level of a single factor. It is constructed by predicting the responses for the low (-1) and high (+1) levels of a factor.

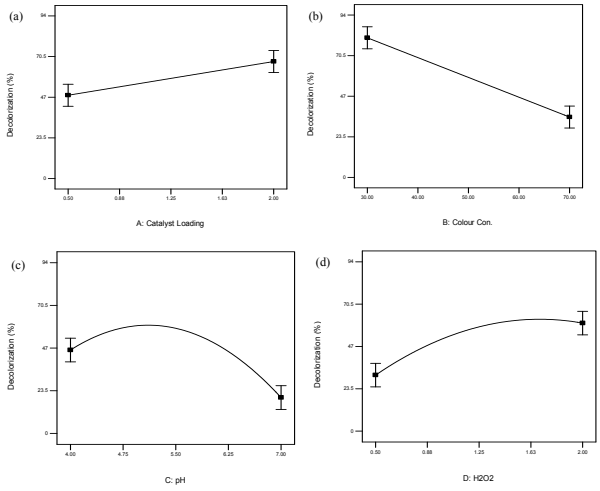


Fig. 5. Main effect plots for decolorization in uncoded value for t=60 min at center design points

Data from Fig. 5 (a) reveal that the decolorization efficiency is promoted by increasing TiO_2 loading. It may be caused by increased both active sites for dye adsorption and free hydroxyl radical generation.

In many studies, increasing catalyst loading more than 1 g/l leads to lower decolorization efficiency. Reasons such as, increased light scattering, decreased radiation penetration and even possible photocatalyst particle agglomeration decreasing the active catalytic surface, may cause this observed behavior (Sauer et al., 2002; Muruganandham & Swaminathan, 2006; Kaur & Singh, 2007). However, with the novel structure of the reactor, decolorization ef-

Table 6. F value and p-values for total and model parameters

Relationship		Factor	Response (Total parameters)		Response (Model parameters)	
			F value	p-value	F value	p-value
Main effects	Linear	A	10.63	0.0057	10.72	0.0040
	Linear	B	58.92	<0.0001	59.39	<0.0001
	Linear	C	19.16	0.0006	19.31	0.0003
	Linear	D	23.34	0.0003	23.52	0.0001
Interactions	Pure quadratic	A^2	1.89	0.1906	-	-
	Pure quadratic	B^2	0.16	0.6971	-	-
	Pure quadratic	C^2	41.55	<0.0001	40.75	<0.0001
	Pure quadratic	D^2	11.03	0.0050	9.90	0.0053
	Cross product	AB	0.74	0.4029	-	-
	Cross product	AC	0.50	0.4928	-	-
	Cross product	AD	6.68	0.0216	6.74	0.0177
	Cross product	BC	1.70	0.2132	-	-
	Cross product	BD	6.63	0.0220	6.69	0.0181
	Cross product	CD	15.23	0.0016	15.35	0.0009

ficiency increases due to penetration of light to all points of the solutions because of its simultaneous mixing and radiating structure, causing the renewal of the solution film near the lights.

From Fig. 5 (b) it can be observed that the decolorization efficiency decreases with increasing the concentration of dye solutions. At higher initial dye concentrations the UV photons are absorbed by the dye molecules instead of photocatalyst particles, resulting in lower decolorization efficiency (Tang & An, 1995; Arslan & Balcioglu, 2001; Muruganandham & Swaminathan, 2004, 2006; Velegraki et al., 2006). By increasing the initial dye concentration, the photocatalyst surfaces adsorbed additional dye molecules, inhibiting direct contact between the dye molecules and photogenerated holes. This could also suppress the generation of hydroxyl radicals at the photocatalyst surface due to the shielding of the catalyst's active sites by dye molecules sites (Sauer et al., 2002). In addition, the intermediates formed during photocatalytic process may compete with the dye molecules for the available active sites on the photocatalyst particles (Velegraki et al., 2006).

pH affects degradation efficiency in many ways such as influencing the surface properties of TiO_2, dissociation of dye and formation of hydroxyl radicals. In particular, pH affects the adsorption of dye molecules on TiO_2 surface, which is an important step in photodegradation process of dye molecules on TiO_2 surface.

Adsorption of dye on TiO_2 at the initial pH of 5.5 is rather high, but it is lower at acidic pH and very weak at alkaline medium. This fact is due to the electrostatic interaction between the negative charged dye while the catalyst surface is positively charged in acidic conditions and the catalyst surface's zero point charge is at pH=6.6 (Galindo & Jacques, 2000; Arslan et al., 2002; Konstantinou & Albanis, 2004; Muruganandham & Swaminathan, 2004,2006; Habibi et al., 2005).

The effect of H_2O_2 shown in Fig. 5 (d) may be explained by the fact that hydrogen peroxide is an electron acceptor having a much greater efficiency than that of oxygen and thus, may improve the generation of hydroxyl ion according to the following reactions (Sauer et al., 2002; Daneshvar et al., 2004):

$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \quad (1)$$

$$H_2O_2 + h\nu \rightarrow 2\,\cdot OH \quad (2)$$

$$H_2O_2 + O_2^- \rightarrow \cdot OH + OH^- + O_2 \quad (3)$$

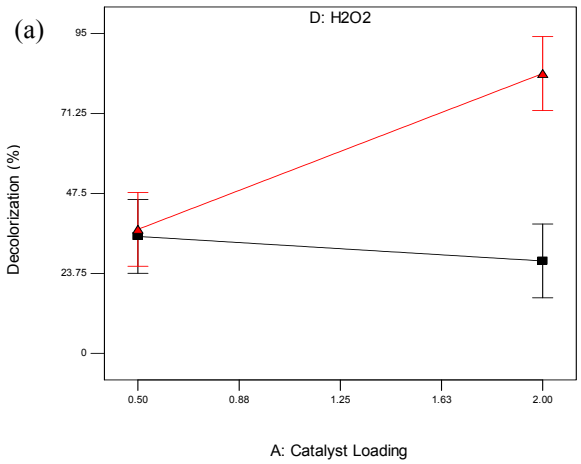
Addition of hydrogen peroxide to the heterogeneous system can increase the concentration of OH radical and inhibit the electron-hole recombination (Lin & Hua, 2010). As it can be seen in the plot, the degradation rate increased with H_2O_2 dosage up to a critical value. Beyond this value, degradation efficiency declines, since H_2O_2 scavenges hydroxyl radicals when present at high concentrations, yielding hydroperoxyl radicals having lower oxidation capacity compared to that of hydroxyl radicals (Eq. (4)) (Tang & An, 1995; Daneshvar et al., 2003; Konstantinou & Albanis, 2004; Muruganandham & Swaminathan, 2004,2006; Velegraki et al., 2006).

$$H_2O_2 + 2h^+_{vb} \rightarrow O_2 + 2H^+ \quad (4)$$

$$H_2O_2 + \cdot OH \rightarrow H_2O + \cdot OOH \quad (5)$$

$$\cdot OOH + \cdot OH \rightarrow H_2O + O_2 \quad (6)$$

In addition to the effect of each of the parameters on the decolorization individually, it is also important to check the interaction effect. According to Fig. 6, H_2O_2 had interaction with 3 other parameters. Hydrogen peroxide dissociates in water and produces hydroxyl radical and ion. Hydroxyl radical is by far the most aggressive reactive oxygen radical known. As soon as it is formed it reacts with almost any molecule found in its vicinity with equally high rate.



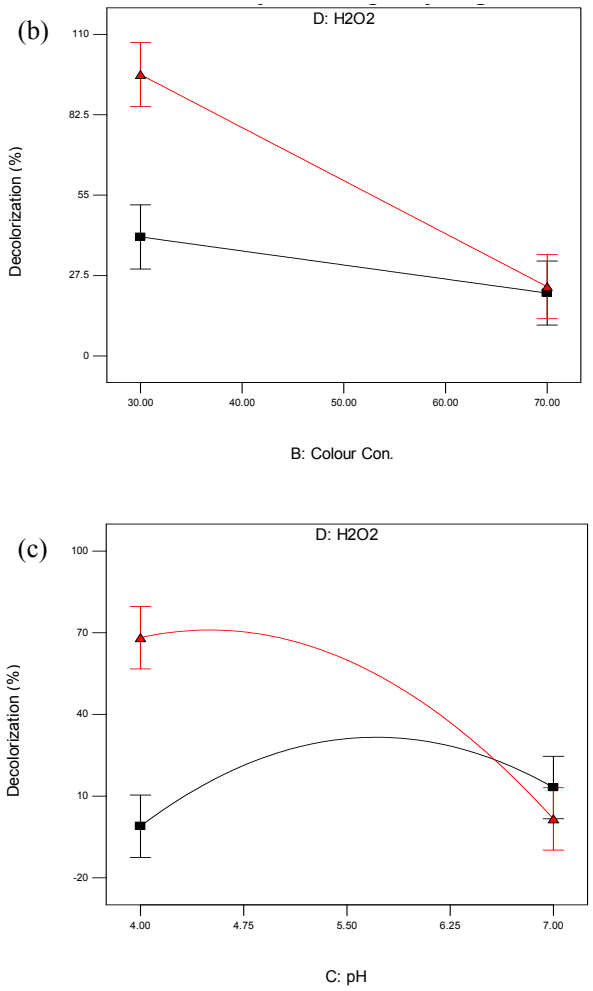


Fig. 6. Interaction plots for decolorization in uncoded values for t=60 min (a) A (TiO_2) and D (H_2O_2) in fixed B (dye) at 50 ppm and C (pH) at 5.5, (b) B (dye) and D (H_2O_2) in fixed A (TiO_2) at 1.25 g/lit and C (pH) at 5.5, (c) C (pH) and D (H_2O_2) in fixed A (TiO_2) at 1.25 g/lit and B (dye) at 50 ppm.

Canonical analysis is a mathematical approach to examine the overall shape of the curve, to locate the stationary point of the response surface, and to decide whether it describes a maximum, minimum or saddle point. The relationship between the dependent and independent variables can be also understood by these plots. The interaction parameters were used to plot the graphs and since the model has more than two factors, two factors were held constant for each diagram.
Fig. 7 (a), (b) and (c) all describe a maximum point for % decolorization in graphical 3D and 2D representation of the polynomial obtained.

The optimization and the modeling of photocatalytic degradation of Reactive Black 8 were performed by using an experimental design. The ensuring mathematical model could predict the photocatalytic degradation at any point in the experimental domain as well as the determination of the optimal degradation conditions. The high correlation in the model indicates that the second-order polynomial model could be used to optimize the photocatalytic degradation of dye. The conditions to get 100% decolorization (optimum condition) and the experimental values are shown in Table 7.

Table 7. Comparison of experimental and predicted values of the response at the optimal levels predicted by RSM

Optimal conditions	Stationary point	Predicted value (%)[a]	Observed value (%)
A = 1.59 g L^{-1}	Maximum	96.1	93.1
B =34.65 ppm			
C = 5.5			
D = 1.82			

[a] *Predicted using analysis of response surface quadratic model.*

These results implicate that the optimization using a response surface methodology based on the Box-Behnken design can save the time and effort by estimation of the optimum conditions of the maximum removal of dye.
By measuring the TOC of the solution before and after decolorization, it was seen that 78.6% of the dye was degraded. Also, the absorption spectrum during the decolorization process is shown in Fig. 8. The peak in wavelength of 334 nm has been decreased which shows that the hydroxyl radicals have attacked and the aromatic rings of the dye have been broken and they has been degraded. In addition, with regards to the decrease in the height of the peak at 578 nm it can be concluded that the chromophore of the dye has been broken.

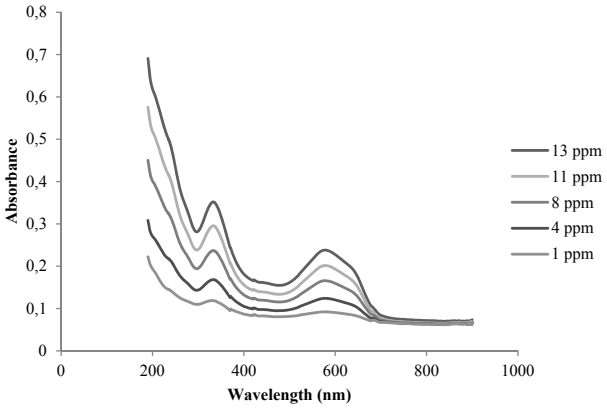


Fig. 8. UV-vis absorption spectrum of Reactive Black 8 at different time intervals (optimal conditions)

The power of the UV-A LED lamps have been measured by Digital Lux Light Meter, Lutron, LX – 107 (Taiwan). The power of each one of the LEDs was equal to 84 μW/cm^2. The number of photons entering the reactor per second per cm^2 of the surface emitted by the UV LEDs is equal to 1.89 × 10^{14} photons/s.cm^2 ($N_{photons} = E_{pulse}/E_{photon}$, $E_{photon} = hc/\lambda$).

CONCLUSION

In the present study, decolorization of Reactive Black 8 by use of a novel reactor setup was studied. Effective parameters including dye & H_2O_2 concentration, catalyst loading and pH were determined and a table of design of experiments was designed based on Box-Behnken method in order to be able to obtain the optimum conditions for decolorization. Some major points derived from this study are as follows,
Decolorization efficiency declines with increasing initial dye concentration.
Addition of H_2O_2 up to an optimum value promotes the decolorization rate.

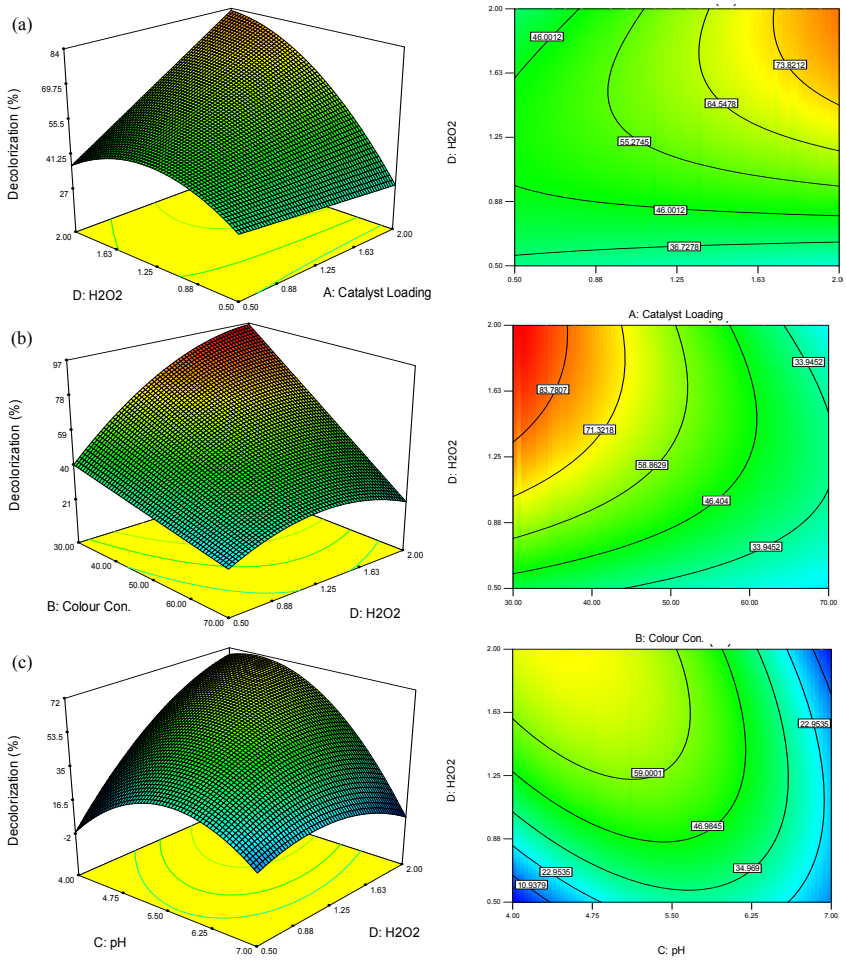


Fig. 7. 3D surface and contour plots of decolorization in uncoded values for t=60 min. (a) A (TiO_2) and D (H_2O_2) in fixed B (dye) at 50 ppm and C (pH) at 5.5, (b) B (dye) and D (H_2O_2) in fixed A (TiO_2) at 1.25 g/lit and C (pH) at 5.5, (c) C (pH) and D (H_2O_2) in fixed A (TiO_2) at 1.25 g/lit and B (dye) at 50 ppm.

Decolorization efficiency increases with increasing photocatalyst loading. It should be noted that in comparison to same works, the decolorization efficiency increases due to the novel structure of the reactor, because the renewal of the solution film near the UV-LEDs.

The optimum parameters for decolorization of Reactive Black 8 obtained from the software used is as follow,

A = 1.59 g L^{-1}, B =34.65 ppm, C = 5.5, D = 1.82

With use of these optimum parameters 96.1% decolorization occurred. For observing the degradation of the dye, the TOC of the solution before and after irradiation with use of optimum conditions was tested and was observed that 78.6% of the dye molecule was degraded with 60 minutes irradiation.

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