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Optimization of Photocatalytic Decolourization of Cationic Azo Dye in Thin Film Fixed Bed Photoreactor

Mohammed Berkani*[a], Mohamed Bouhelassa[a], Abdelkrim Bouzaza[b], Mohammed K. Bouchareb[a] , Yassine Kadmi[b], Isabel Soutrelle[b]

[a]Université de Constantine 3, Génie des procédés pharmaceutique, génie chimique, 25000 Route Ain el bey Constantine, Algérie
[b]Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France
chem.engd@gmail.com

The photocatalytic decolourization of C.I. Basic Red (BR46) was carried out in a thin film fixed bed photoreactor with external UV light irradiation. The optimization of UV/TiO_2 process was carried out using full factorial experimental design (2^4) approach in order to assess individual and interactive effects of the four main independent parameters (initial dye concentration (mg/L), Intensity I ($w.m^{-2}$), flow rate ($L.min^{-1}$) and reaction time (min) on the decolourization efficiency Y (%), Experimental findings were in close agreement with the prediction model (R = 99.57 %, Adj-R^2 = 0.987) and the photocatalytic degradation efficiency Y (%). The effects of individual variables and their interaction were determined using ANOVA analysis. The results indicate that the reaction time and the light Intensity exhibit a significant positive effect on the efficiency of decolourization, whereas the initial dye concentration and the flow rate show a significant negative effect. Moreover, the interaction between light Intensity and reaction time was the most influence one, the experimental values agreed with the predicted ones, indicating suitability of the model employed. The maximal decolourization efficiency of 99.95 % was achieved at initial dye concentration 20 mg/L, UV light intensity 38.1 W/m^2, flow rate 0.3 L/min and reaction time 150 min. Thus, under this condition the highest TOC removal efficiency of 61 % mineralization was obtained.

1. Introduction

The dyes in waste water are part of organic pollutants and often require specific treatment. A progress in chemical wastewater treatment has driven the development of some number of chemical technologies, called advanced oxidation processes (AOPs) (Salari et al., 2009) Hydroxyl radicals (•OH) are the main oxidizing species produced by AOP'S, because of their non-selectivity and their high reactivity (Andreozzi et al., 1999). AOP'S can be classified by the way in which they generate OH radicals to: chemical and catalytic, photochemical and photocatalytic, mechanical and electrical processes (Koprivanac and Kusic, 2009). Heterogeneous photocatalysis methods have been used in the recent years for complete mineralization to CO_2, H_2O and mineral acids of toxic organic and inorganic contaminants from industrial waste water of textile (Gupta et al., 2006) , pharmaceutical (Nan et al., 2011) and aquaculture industry (Emomotimi et al., 2011), photocatalytic process is a set of reduction and oxidation photocatalytic reactions occurring in the presence of very efficient catalysts, illumination sources, a strong oxidizing agent in the most cases oxygen and adapted reactors at the process (Orozco et al., 2009). The organic compounds degradation by photocatalysis is highly dependent on a number of the operation parameters (pH, temperature, amount of catalyst, UV irradiation time, light intensity, and initial pollutants concentration) and reactor technology (implementation of photocatalyst, oxygen transfer, agitation, flow of gas and liquid...).The high number of influential variables makes the use of suitable experimental design attractive, in order to optimize the influence of this parameters, factorial experiments are experiments that investigate the effects of two or more factors or input parameters on the

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output response of a process. By the way, it has been successfully applied to a different process for achieving its optimization using experimental designs, which include TiO_2-coated/UV oxidation (Danion et al., 2004), TiO_2 slurry/UV oxidation (Bouchareb et al., 2014), O_3 oxidation and electrochemical oxidation (Chen, 2000). A factorial experimental design is a powerful technique that can be used for realizing a set of the factors that are most important to the process and then determine at what levels these factors must be kept to optimize the process performance. To evaluate the performance of our photoreactor, we studied the photocatalytic degradation in a thin film fixed bed photoreactor with immobilized catalysts of an azo dye known as Basic Red 46 (BR46), by TiO_2/UV process. Also we developed a simulation model using factorial design methodology based on the full factorial design in order to examine the main effects and the interactions between the concentration of TiO_2 initial dye concentration, Intensity, flow rate and reaction time in the photocatalytic degradation process of an aqueous solution containing an azo dye Basic Red 46 (BR46).

2. Experimental

2.1 Chemicals and materials

Experiments were carried out in a thin film fixed bed photoreactor Figure1 (a) and (b) with immobilized catalyst in the form of AHLSTROM paper containing 20 $g.m^{-2}$ of TiO_2 Millennium PC500. The irradiation was performed using a three 24W UV fluorescent lamps (PL-L 24W/10/4P PHILIPS) having the radiation peak at 365 nm, which were fixed on the stainless steel lid Figure1 (a), that was placed against the inclined steps of the photoreactor and externally irradiated the solution Figure1 (b), UV intensity was measured with a VLX-3W radiometer (Cole Parmer), which measures UV radiation at 365 nm. The range of UV intensity was varied by changing the number of irradiated UV lamps. The effective volume of photoreactor was 2L. The flow rate is controlled by a peristaltic pump and can be varied between 0.1 and 0.9 $L.min^{-1}$. The agitation was assured by means of a magnetic stirrer placed at the tank. The textile dye, Basic Red 46 (BR 46, commercial name Astrazon Red FBL) was provided by Aurassienne Spinning and Blankets (SAFILCO) Company, Algeria. (molecular formula = $C_{18}N_6H_{21}$, colour index number = 110,825, λ_{max} = 531 nm, Mw = 357.5 g/mol, azo group one, type cationic).

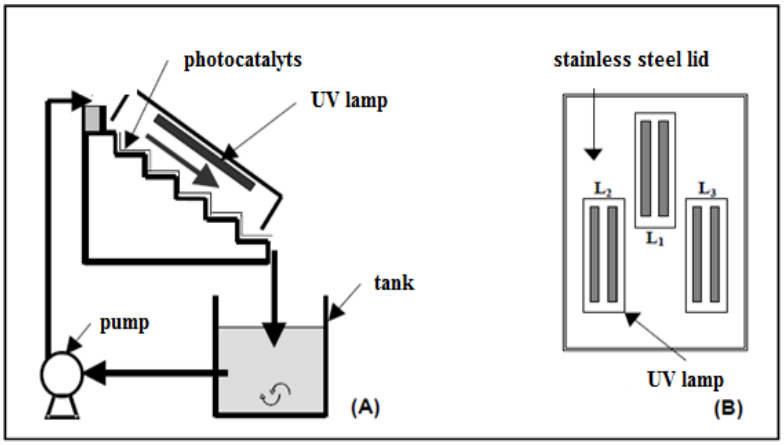

Figure1: Schematic representation of the experimental device

2.2 Analysis

All the collected samples of Basic Red 46 in water was performed using a spectrophotometer by UV–VIS spectra using a Shimadzu UV-1603 spectrophotometer, the yield of decolourization Y (%) was expressed as the percentage ratio of decolorized dye concentration to that of the initial one.

The photocatalytic efficiency was determined by using the following equation: Eq (1) $Y = \frac{C_0 - C_i}{C_0} \times 100$ (1)

Where Y is the Decolourization efficiency (%), C_0 and Ci both in ($mg.L^{-1}$), respectively, the initial and residual concentrations of Basic Red 46 in solution. The extent of mineralization was determined by monitoring the total organic carbon (TOC) of the samples using a TOC analyser (V-CPH SHIMADZU).

2.3 Experimental design

The experiments in which the effects of more than one factor on response are investigated are known as full factorial experiments. In a full factorial experiment, both of the (-1) and (+1) levels of every factor are

compared with each other and the effects of each of the factor levels on the response are investigated according to the levels of other factors. The main objective is to determine the optimum operating conditions for a given system that satisfies the specific operating conditions. The experimental plan was carried out as a full factorial design (2^4) consisting of 16 experiments for four variables (initial dye concentration (X_1), Intensity (X_2), I ($w.m^{-2}$), flow rate (X_3) and reaction time (X_4)).

Table 1: Range and levels of experimental parameters

Variables		Ranges and levels -1	+1
[BR46] ($mg.L^{-1}$)	(X_1)	20	50
Intensity I ($w.m^{-2}$)	(X_2)	14,5	38,1
Flow rate ($L.min^{-1}$)	(X_3)	0,3	0,9
Time of reaction (min)	(X_4)	60	150

Table1 Shows the values of the factors selected in this study at two levels low (-) and high (+),The statistical software MINITAB (16 Minitab Institute, USA) was used to fit the experimental data to the first-order model with all possible interactions which related the response Y to factors X_1, X_2, X_3, X_4. Eq(2):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 + b_{134}X_1X_3X_4 + b234X_2X_3X_4 + b_{1234}X_1X_2X_3X_4. \quad (2)$$

3. Results and discussions

3.1 Experimental design methodology

Based on the obtained results, an empirical relationship between the response Y and selected variables was attained and expressed by the following first–order polynomial equation therefore insignificant terms were eliminated since they did not have any statistical effect Eq(3):

$$Y = 94.30 - 1.26X_1 + 3.69X_2 - 2.08X_3 + 4.43X_4 + 1.81X_2X_3 - 2.83X_2X_3 + 1.28X_3X_4 - 1.27X_2X_3X_4 \quad (3)$$

Experimental value versus predicted value displays the real responses data against the predicted responses shown in the design matrix (Table 2), which shows the statistical combinations of independent variables: initial dye concentration (X_1), Intensity (X_2), I ($w.m^{-2}$), flow rate (X_3) and reaction time (X_4) with the yield Y (%) (Measured) and predicted. Thus, the model explains the experimental range studied adequately. The fitted regression equation showed a good fit of the model. (Barka et al., 2014)

Table 2: experimental design matrix, experimental results and predicted photocatalytic degradation efficiency

Exp	[BR46] ($mg.L^{-1}$)	Intensity ($w.m^{-2}$)	Flow rate ($L.min^{-1}$)	Time (min)	Decolourization efficiency (%)	
					Experimental	Predicted
1	- 1	- 1	- 1	- 1	90.55	91.07
2	+1	- 1	- 1	- 1	89.07	88.54
3	- 1	+1	- 1	- 1	98.88	97.93
4	+1	+1	- 1	- 1	94.47	95.41
5	- 1	- 1	+1	- 1	78.55	78.14
6	+1	- 1	+1	- 1	75.22	75.62
7	- 1	+1	+1	- 1	98.91	97.37
8	+1	+1	+1	- 1	93.31	94.84
9	- 1	- 1	- 1	+1	99.67	100.4
10	+1	- 1	- 1	+1	98.76	97.95
11	- 1	+1	- 1	+1	99.95	101.1
12	+1	+1	- 1	+1	99.77	98.59
13	- 1	- 1	+1	+1	98.32	97.81
14	+1	- 1	+1	+1	94.78	95.28
15	- 1	+1	+1	+1	99.72	100.6
16	+1	+1	+1	+1	98.98	98.08

3.2 Analysis of variance (ANOVA)

The predicted values are very close to the observed ones in all set of experiments, the value R^2 was evaluated as 0.984, the model may explain 98.4 % of the variability in the response and the variations for percent color removal are explained by the independent variables. Adjusted R^2 (Adj–R^2) is also a measure of the goodness of a fit and corrects the determination coefficient R^2-value for the sample size and the number of terms in the model. In this study, the value of Adj-R^2 is very close to the corresponding R^2 value.

The analysis of variance (ANOVA) (Table 3) study was performed to determine the significant main and interaction effects of factors affecting Basic Red 46 photocatalytic decolourization efficiency. The high significant of the model is performed by (F–value = 55.68). The *P*-values were used as a tool to check the significance of each of the coefficients, the P-value less than 0.0500 indicate model terms are significant; moreover the larger magnitude of the student's t– test and smaller P–value (Liu and Chiou, 2005).

Table 3: Estimated regression coefficients and Analysis of variance ANOVA.

Source	Sum of Squares	DF	Mean Square	F-value	P-Value
Model	861.46	8	107.68	55.68	0.00001
X1	25.47	1	25.47	13.17	0.00840
X2	218.07	1	218.07	112.77	0.00001
X3	69.43	1	69.43	35.90	0.00054
X4	314.97	1	314.97	162.88	0.00000
X2X3	52.67	1	52.67	27.23	0.00122
X2X4	128.19	1	128.19	66.29	0.00008
X3X4	26,6	1	26.60	13.75	0.00756
X2X3X4	26.03	8	26.03	13.46	0.00797
Total	2203.49	15	1.93		

R^2= 0.964, Adj- R^2= 0.933, Pred-R^2= 0.857, DF: Degree of Freedom

Shown in Figure 2, the Pareto chart of effects on photocatalytic decolorization efficiency, the student's t-test was employed in order to determine the significant effects whether calculated effects were significantly different from zero (Liu and Chiou, 2005). For a 95 % confidence level and 15 degrees of freedom, the t-value is equal to 2.36.

The Pareto analysis gives more significant information to interpret the results. In fact, this analysis calculates the percentage effect (P_i) of each factor on the response, according to the following relation. (Kesraoui et al., 2008)

$$P_i = \frac{b_i^2}{\sum b_i^2} \times 100 \qquad i \neq 100 \tag{4}$$

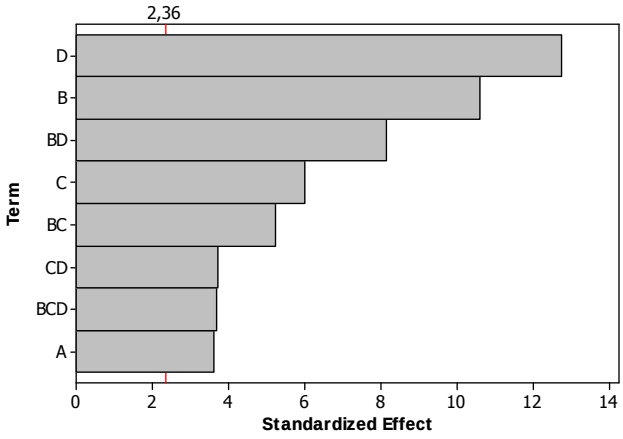

Figure 2: Pareto graphic analysis

It is clear from the Pareto graphic analysis (Figure3), that the main significant reaction parameters were (most to least significant): reaction time> UV intensity > interaction between reaction time and intensity > flow rate.

3.2 Main and interaction effect plots

The contours of the plots facilitate the identification of the type of interactions between the variables values of the decolourization efficiency Y (%), an elliptical or saddle nature of the contour plots indicates the significance of the interaction between the corresponding variables (Liu and Chiou, 2005). Contour plots shown in Figure 3 (a) and (b) provide the results of the interaction between factors which are more significant, as can be seen in the figure, intensity had a strong effect on the response. The contour plot (a) indicates a wide range of colour removal Y (%) combinations resulting in a low flow rate. The decrease in flow rate (X3) and the increase in UV intensity (X2) increased in Y (%) of colour removal at the ranges of dye concentration (20 mg.L^{-1}) and while keeping reaction time at 60 min. shown in Figure 3(b) the UV intensity (X2) and reaction time (X4) were considerably higher in the photocatalytic decolourization Y (%), increases in UV intensity would have an important additional effect on the rate of production of OH° radicals which are the critical species in the decolourization process. The finding was in agreement with literature reports where higher light intensities would result in higher photodecolorization efficiency. (Behnajady and Modirshahla, 2006)

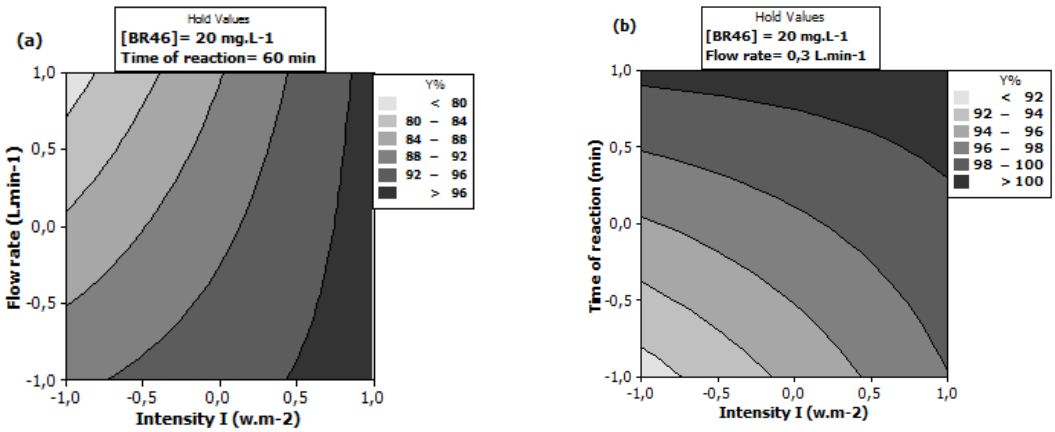

Figure 3: Contour plots of photocatalytic decolourization efficiency Y (%) for *(a) X2* (Intensity I) *and X3 (Flow rate) in fixed X1 (dye concentration) at 20 mg.L^{-1} and X4 (time) at 60min, (b) X2* (Intensity I) and *X4 (time) in fixed X1 (dye concentration) at 20 mg.L^{-1} and X3 (Flow rate) at 0.3 L.min^{-1}.*

The result indicated that the maximal decolourization efficiency for >99 % was obtained when the values of each parameter were set as the optimum values, which was in good agreement with the value predicted from the model.

4. Total organic carbon

Total organic carbon removal efficiencies were measured for all experiments set in the factorial design (Figure3). TOC removal efficiency was determined as 61 % at initial dye concentration 20 mg/L, UV intensity 38,1W/m^2, flow rate 0.3 L/min and reaction time 150 min. TOC removal indicating the ultimate oxidation of BR46 was much slower than decolourization. The complete decolourization of BR46 occurred in 60 min, thus it requires more than 150 min to reach the complete mineralization. This might be due to the formation of intermediates and its competiveness with parent dye molecules in the process. In fact, in the present work, the intermediates did not identify and this is one of our future works.

5. Conclusions

This study has demonstrated the applicability of this experimental design to develop the first-order polynomial response equation, based on analysis of variance (ANOVA) indicating a high coefficient of determination (R^2 = 98.4 %, Adj- R^2 = 0.966). The light intensity and time have a synergetic effect. However, the BR46 concentration and flow rate have an antagonist effect on the photodecolourization efficiency. The obtained results demonstrated that the experimental values were reasonably close to the predicted values, indicating

the validity and adequacy of the predicted models. Moreover, the verification experiments also proved that the predicted values of the 100 % of decolourization could be achieved within 95 % confidence interval of the experimental values. These results implicate that the optimization using factorial experimental design approach is an excellent tool to estimate the optimum conditions of the maximum removal of dye by saving both time and effort.

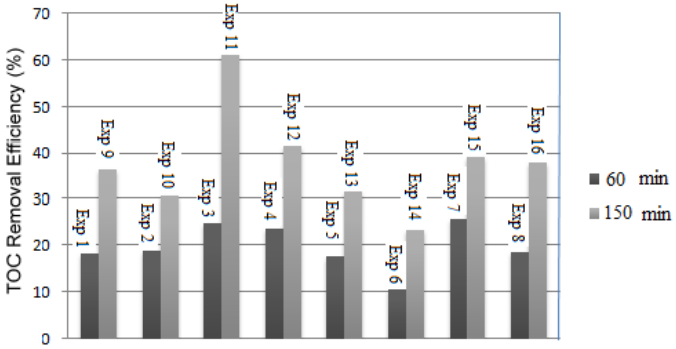

Figure 4: TOC removal efficiency of BR46

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