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Full Factorial Experimental Design Applied to Photocatalytic Decolorization of a Cationic Azo Dye in Solar Photo-reactor

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***Abstract*—**Full factorial experimental design was developed to assess individual and interactive effects of the four main independent parameters, namely catalyst concentration (X1), initial dye concentration (X2), flow rate (X3) and initial pH (X4) on the decolorization efficiency of an Cationic Azo Dye, C.I. Basic blue (BB41), using TiO2 aqueous suspension in a semi-pilot scale solar photo-reactor with compound parabolic collectors (CPCs). The parameters were investigated at two levels (−1 and +1) for 60 KJ L-1 of visible energy accumulated. From the statistical analysis, the main significant reaction parameters were (most to least significant): interaction between the catalyst concentration and initial pH, catalyst concentration, initial dye concentration and flow rate. The variance analysis (ANOVA) was applied and the statistic data showed adequate model.

Keywords—Photocatalysis, decolorization, solar photoreactor, response surface methodology (RSM), TiO2, Full factorial experimental design.

I. Introduction

HETEROGENEOUS photocatalysis represents a promising alternative technology for the degradation of organic pollutants [1]. It offers a unique advantage over other alternative treatment methods because it presents a 'green' treatment approach; since, toxic organic pollutants are converted into carbon dioxide (CO2), water and mineral acids [2]. Photocatalytic degradation efficiency is dependent on a number of parameters such as the reactor configuration, initial dye concentration, catalyst concentration, flow rate, reaction time and pH. In the conventional methods used to determine the influence of operational parameters, experiments were carried out varying systematically the studied parameter and keeping constant the others. This should be repeated for all the influencing parameters, resulting in an unreliable number of experiments. Design of experiments is a powerful technique used for discovering a set of process variables (or factors) which are most important to the process. Statistical design of experiments is a quick and cost-effective method to understand any manufacturing processes.

In the present work we developed a simulation model using full factorial design in order to examine individual and interactive effects of the four main independent parameters, namely catalyst concentration (X1), initial dye concentration (X2), flow rate (X3) and initial pH (X4) on the decolorization efficiency of an Cationic Azo Dye, C.I. Basic blue (BB41), using TiO2 aqueous suspension in a solar photo-reactor and under solar radiation.

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II. Material And Methods

A. Chemicals and materials

The textile dye, C.I. Basic Blue 41 (BB41) was obtained from Aurassienne Spinning and Blankets (SAFILCO) Company, Algeria (molecular formula = C20H26N4O6S2, color index number = 11105, λmax = 608 nm, Mw = 610 g/mol, Single azo class). Titanium dioxide powder used is TiO2 Degussa P-25. Initial pH of the aqueous solutions was adjusted by both sulfuric acid and sodium hydroxide.

B. Solar photo-reactor

Photocatalysis experiments were carried out on a semi-pilot scale solar photo-reactor based on compound parabolic collectors (CPCs). The apparatus operating in batch mode is composed by a plastic tank (40 liter capacity) with an integrated stirrer, centrifugal recirculation pump, flowmeter, thermocouple, five borosilicate glass tubes (length: 1 m, external diameter: 30 mm, thickness: 1.4 mm). These tubes are connected in series to the tank by plastic joints and mounted on CPC-type aluminium reflectors (concentration factor = 1). The volume effectively irradiated was 3.2 L and the volume of colored water to be treated was 10 L. A stirrer inside the tank ensures a homogeneous suspension. The reactor was oriented southward and inclined at an angle of 36° (latitude at Constantine. Algeria) with respect to the horizontal, with this position the annual collection of solar energy is maximized. Solar visible radiation (400–700 nm) was measured by lightmeter Lutron, LX-107 fixed next to the CPCs. which provide data in term of incident solar power, $W.m^{-2}$.

C. Procedure and analysis

All the collected samples from the experiments were centrifuged at 4000 rpm for 25 min using a centrifuge (sigma 2-16) to remove the TiO2 and color removal of the dye BB41 was determined by UV absorption at λmax = 608 nm using a UV–vis spectrophotometer (Shimadzu UV-160A) and calibration curve. The percent decolorization rate (Y (%)) was expressed as the percentage ratio of decolorized dye concentration (Cr) to that of the initial one (C_0):

$$Y(\%) = \frac{C_0 - C_r}{C_0} \times 100 \quad (1)$$

The data obtained from experiments using sunlight which is a discontinuous source whose radiation varies in intensity (cloud cover) and composition (direct or diffuse). To eliminate such intermittences, the results are expressed as a function of accumulated Visible energy Q_V (KJL^{-1}) received by the reactor per unit volume of solution to be treated (2).

$$Q_{V,n} = Q_{V,n-1} + \Delta t_n \bar{V}_{G,n} \frac{A_r}{V_t} \quad (2)$$

$$\Delta t_n = t_n - t_{n-1},$$

This expression was developed by S. Malato et al. [3] and used for UV radiation intensity, we have adapted it for our case, where $Q_{V,n}$ is the accumulated Visible (V) energy incident on the reactor (KJ L^{-1}), t_n is the experimental time of each sample, $\bar{V}_{G,n}$: the V radiation intensity (W m^{-2}) measured by the lightmeter, A_r : the collector surface (m^2) and V_t : volume of solution to be treated (L).

This dimension makes possible the comparison of degradation kinetics for different operating conditions independent of the weather and the conditions of solar irradiation.

D. Experimental Design

If we call n the number of variables to be tested, in order to measure the effect of all the variables combinations when each variable is tested at a high and a low level, 2n experiments will be needed. In order to study the variables that define the process, 24 factorial experimentations were carried out, in two levels (i.e. high and low). The higher level of variable was designed as '+1' and the lower level was designed as '−1'. For ease of notation, the effects were designed as in Table 1, which shows the values of the factors selected in this study. This factorial design results in sixteen tests with all possible combinations of X1, X2, X3 and X4. Photocatalytic decolorization efficiency (Y (%)) was measured for each of these tests for 60 KJ L^{-1} of visible energy accumulated. A first-order polynomial response equation (See (3)) was used to correlate the dependent and independent variables.

TABLE I
FACTORS AND LEVELS USED IN THE 2^4 FACTORIAL DESIGN STUDY

Variables	Code	Ranges and levels	
		-1	**+1**
$[TiO_2]$(g/L)	X_1	0.35	0.85
$[BR41]_0$(mg/L)	X_2	20	40
Flow rate(L/h)	X_3	600	1200
Initial pH	X_4	4.5	9.5

III. RESULTS AND DISCUSSION

The statistical calculations and multiple regressions were performed using Minitab 16 software. Regression analysis was performed to fit the response function (photocatalytic decolorization efficiency) with the experimental data. Table II indicates the results of the response surface quadratic model fitting in the form of analysis of variance (ANOVA). According to ANOVA the best fitted model with the significant terms is:

$$Y= 85,5294 + 5,15812 X_1 - 3,74312 X_2 + 2,95563 X_3 - 1,64562 X_1 X_3 + 7,43562 X_1 X_4 + 2,85563 X_2 X_3 + 2,84437 X_2 X_4 \quad (3)$$

Equation (3) shows the effect of individual variables and interactional effects for BB41 photocatalytic decolorization. According to this equation, the TiO_2 dosage and flow rate have a positive effect, while the initial dye concentration has a negative effect in the range of variation of each variable selected for the present study. It is known that the larger the coefficient, the larger is the effect of related parameter. The most effective parameters in this study were : interaction between catalyst concentration and initial pH, catalyst concentration, initial dye concentration and flow rate.

TABLE II
ANALYSIS OF VARIANCE ANOVA

Source	F-value	P-Value	Status
Model	32.78	0.0001	Significant
X_1	49.41	0.0001	Significant
X_2	26.01	0.0009	Significant
X_3	16.22	0.0037	Significant
X_1X_4	102.67	0.0001	Significant
X_2X_4	15.02	0.0047	Significant
X_2X_3	15.14	0.0045	Significant
X_1X_3	5.029	0.05	Significant

R^2= 0.966, Adjusted R^2=0.936

Table II Shows the results generated by the software For a 95% confidence level, The model F-value (Fisher variation ratio) of 32.78 implies this model is significant. P-value (probability value) less than 0.05 indicate model terms are significant.

A. Response surface plots

Fig. 1(a) represents the photocatalytic decolorization efficiency as a function (Y (%)) of flow rate and catalyst concentration at initial dye concentration of 20 mg L^{-1} and initial pH of 4,5. The figure shows that the increase in decolorization efficiency of BB41 was caused by an increase in flow rate at the lower values of the catalyst concentration. The presumed reason is that when the the recirculated liquid flow is increased, the turbulence in the system is enhanced which ensure better dispersion of particles in the solution inside the reactor. It may lead to decompose more and more adsorbed dye molecules on the surface of TiO_2 thus photocatalytic decolorization efficiency increases. Also it could be seen from the figure that decolorization efficiency of the dye decreases as the catalyst concentration increases, in this case when catalyst concentration is very high, after travelling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor [4].

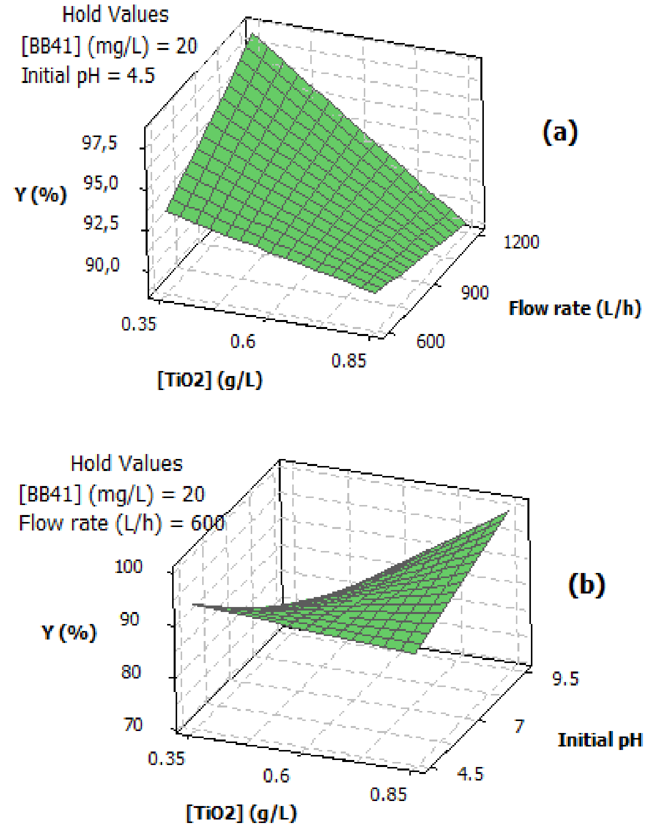

Fig. 7 The response surface plots of photocatalytic decolorization efficiency (Y(%)) as the function of, (a) catalyst concentration (g/L) and flow rate (mg/L) and (b) catalyst concentration (g/L) and Initial pH.

Fig. 1(b) illustrates the effects of initial pH and catalyst concentration on photocatalytic decolorization efficiency (Y (%)) for initial dye concentration of 20 mg L^{-1} and flow rate of 600 L h^{-1}. As can be seen in the figure, the decrease in decolorization efficiency was caused by an increase in pH at the lower values of the catalyst concentration and by an decrease in pH at the higher values of the catalyst concentration . According to the literature reports [5,6], the pH of the solution significantly affects TiO_2 activity, including the charge on the particles, the size of the aggregates it forms and the positions of the conductance and valence bands, Thus pH changes can influence the adsorption of dye molecules onto the TiO_2 surfaces. Since C.I. Basic Blue 41 is a cationic dye, in acidic medium the repulse force inhibiting the adsorption of dye molecule in the catalyst surface, but the formation of hydroxyl radicals remains possible which react with dye molecule. High pH favors adsorption on the catalyst surface which results in high decolorization efficiency.

IV. Conclusion

This study showed that factorial experimental design approach is an excellent tool and could successfully be used to develop empirical equation for the prediction and understanding the photocatalytic decolorization efficiency of BB41 using aqueous suspension of TiO_2-P25 and under solar irradiation. The analysis of variance (ANOVA) showed a high coefficient of determination (R^2=0,966, adj- R^2=0.936), thus confirming adequacy of adjustment of the first-order regression model with the experimental data.

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