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Optimizing operating parameters using experimental design in photocatalytic degradation of a model pollutant paracetamol by TiO_2

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ABSTRACT

The main objective of this study was to demonstrate the efficiency and to optimize the operating conditions of photodegradation of paracetamol in the presence of suspended titanium dioxide catalyst in a photoreactor. An experimental design study was carried out using central composite design modelling. Optimization was applied to the tubular reactor under fixed photonic flux with radiation from two 24-watt UV-A lamps. The optimal values of the operating parameters were found to be pH of 7.288, TiO_2 concentration of 0.9932 g·L^{-1} and paracetamol initial concentration of 15 mg·L^{-1}. The paracetamol degradation rate approached 98.46% under optimal conditions. Modelling of the system led to a second-degree polynomial. Regression analysis gave an R^2 value of 0.977 which meant good agreement between the experimental results and the predicted values. An interaction was demonstrated between the catalyst and the operating parameters (pH, C_{Para} and C_{TiO2}) as well as between the model pollutant concentration and the pH had an insignificant effect on the yield compared to that of the quantity of the catalyst and the initial pollutant concentration.

Keywords: Experimental design; Wastewater treatment; Paracetamol; MOD-6

1. Introduction

The demand for water is rising as a result of population growth, human progress, and industrial activity. The reuse of treated wastewater is a promising solution. The use of this effluent in agriculture, however, necessitates adherence to regulations and standards. Large amounts of organic chemicals, including textile colours, aromatic compounds, chlorinated hydrocarbons, and pharmaceutical products, have been found in the wastewater originating from sectors like textile, pharmaceutical, pesticides, and petrochemical processing [1,2]. Persistent pollutants are not completely eliminated by wastewater treatment plants [3,4], and they are not entirely degraded by traditional procedures [5]. Applying sophisticated treatments to the water and performing high-performance tertiary treatments are required to remove these pollutants. Furthermore, advanced oxidation processes (AOPs) are being used as promising techniques for removing persistent pollutants from wastewater effluents [6,7]. They can breakdown the pollutant as well as intermediate by-products, reaching a complete mineralization if necessary [8].

The existence of highly reactive HO radicals, which are appropriate for a swift and indiscriminate interaction with an organic component and leading to its practically entire mineralization, is what distinguishes the AOPs [9]. Heterogeneous photocatalysis, a flexible, affordable, and

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environmentally friendly treatment method for a variety of contaminants, is one of the more advanced oxidation processes [10].

Photocatalysis effectiveness as a wastewater treatment technique depends on several factors which influence the kinetics. Among the parameters that need to be optimized are the amount and type of catalyst, the pollutant initial concentration, the pH, the luminous flux, and particle structure and size. In most previous studies, only a one factor at a time was tested for evaluating the influence of the operating parameters on the photocatalytic process efficiency. The major disadvantage of this method was that it failed to consider possible interactions between the different factors [11]. It may be useful to know their effect and to be able to model it. This limitation of the classical method can be addressed by optimizing all the influencing parameters through statistical experimental design [12,13].

Parametric optimization is the first step in any study. It is a question of the variation of a single parameter – the others being fixed – and evaluating the influence of its variations on the whole system. This method ignores the consequences of the interactions of various parameters on the experience. It also requires the performance of a considerable number of tests.

An efficient method that maximizes precision and minimizes the number of experiments without compromising the quality of the data is the experimental design method. This technique may be used to explore the influence of a parameter on a response [14]. It consists of a series of tests based on a systematic program which makes it possible to arrive at a mathematical model with a minimum number of tests [15,16]. One of the most used is the central composite design (CCD) which includes a factorial plan or a fractional factorial plan with central points, to which is added a group of axial points (or stars) which allows for estimating the curvature.

In the present work, the photocatalytic degradation of paracetamol was investigated using a TiO_2 aqueous suspension. This drug, also known as acetaminophen, is classified as an anti-inflammatory and non-steroidal analgesic. Paracetamol has been found in wastewater treatment plants [17,18]. Although it is degraded quite effectively by biological processes, appreciable concentrations of this drug can be also found in effluents of these plants which reach the natural environment [19]. Chekir et al. [20] showed that the photocatalytic process using solar radiation/TiO_2 seemed to be more efficient than the removal of paracetamol by conventional techniques. The degradation of paracetamol in aqueous solutions in the presence of hydrogen peroxide was carried out by photochemistry, electrolysis and photo-electrolysis. The degradation was carried out in the presence of UV reaching 95% degradation with TiO_2/RVC/UV and 99% with $CuO/TiO_2/Al_2O_3$/RVC/UV in 1 h [7].

The primary objective of this research was to investigate the major impacts and interactions between catalyst concentration, initial pollutant concentration, and pH of the solution, an experimental study was conducted using design plan. The, interaction between the parameters that affected the paracetamol photodegradation ratio was investigated. The goal was to identify the ideal operating circumstances for à tubular photoreactor.

2. Materials and methods

2.1. Reagents

Paracetamol was used as a model organic pollutant to evaluate the parameters influencing the photodegradation kinetics by TiO_2/UV heterogenous photocatalysis. Paracetamol $C_8H_9NO_2$ (p-acetamidophenol, N-acetyl-p-aminophenol, 4′-hydroxyacetanilide, PA) which has been extensively utilized as an analgesic and antipyretic drug was provided by the Saidal Pharmaceutical Company in Algeria. The maximum optical density of the drug was detected at a wavelength of 243 nm. The chemical structure and the UV absorption spectrum are given in Fig. 1.

Commercial titanium dioxide used as powdered photocatalyst was PC-500 Titania Millennium Inorganic Chemicals (anatase > 99%) with a BET specific surface area of 320 $m^2 \cdot g^{-1}$.

2.2. Experimental system

Photocatalytic experiments were carried out in the photoreactor, which was composed of 19 parallel quartz tubes, with a total mirror area for solar irradiation caption-reflection of 0.128 m^2. Pollutant solution with suspended TiO_2 was continuously re-circulated through the photoreactor and the reservoir tank (1 L) by employing a peristaltic pump (Ecoline VC-280, ISMATEC).

The photoreactor was placed into a lamp box and irradiated by 2 Phillips PL-L 24W/10/4P lamps (l_{max} = 365 nm). Samples were taken from the reservoir tank and filtered through a Millipore disk with a porosity of 0.45 μm. The temperature was not controlled, varying from 20°C to 30°C and the pH of the reaction mixture was not adjusted (natural solution pH).

2.3. Experimental design

The photocatalytic degradation of paracetamol via UV irradiation in the presence of TiO_2 was optimized using MODDE 6.0 software. The central composite design (CCD) with three independent variables was used for the

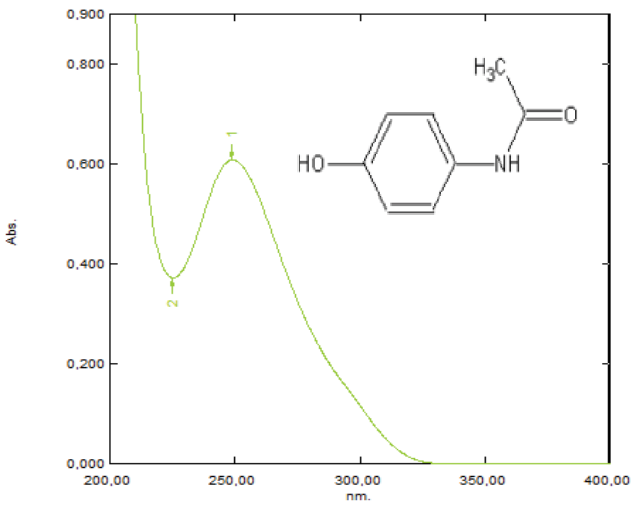

Fig. 1. UV spectra and chemical structure of paracetamol.

optimization of the photocatalytic degradation process: initial pollutant concentration (mg·L^{-1}), photocatalyst loading (g·L^{-1}) and pH. The response factor was the paracetamol degradation rate (%yield) after 300 min of irradiation. A total of 20 experiments was considered to calculate the coefficients of the second-order polynomial regression model for the three variables. Each variable was studied at five levels: –α, –1, 0, +1 and + α where alpha (α) was the distance of each axial point (also called a star) from the central composite design. Table 1 presents the ranges and experimental levels of the independent test variables.

α = 1.68 (The axial point for the orthogonal CCD in the case of three independent variables).

For statistical calculations, the X_i variables were coded as x_i according to Eq. (1):

$$x_i = \frac{X_i - X_0}{\delta X} \tag{1}$$

where X_0 is the X_i value at the center point and δX presents the step change.

3. Results and discussion

The 3-factor CCD matrix and the experimental results obtained in the photocatalytic degradation tests are presented in Table 2. The second-order polynomial response Eq. (2) was used to correlate the dependent and independent variables:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 \tag{2}$$

where Y was the response (degradation yield), x_i values (i = 1, 2, 3) indicated the corresponding parameter in their coded form and b was the regression coefficient. x_1: reduced catalyst concentration (g·L^{-1}); x_2: reduced concentration of paracetamol (mg·L^{-1}); x_3: reduced pH value.

The data in Table 2 show that the empirical relation between the response and the independent variables were reached and could be expressed by the following second-order polynomial [Eq. (3)]:

$$Y_{\text{Predicted}} = 86.3532 + 19.2433x_1 + (-3.86789)x_2 + (-2.71124)x_3 + (-9.21185)x_1^2 + (2.78656)x_2^2 + (-1.68655)x_3^2 + 3.135x_1x_2 + 0.87999x_1x_3 + 1.045x_2x_3 \tag{3}$$

Table 1
Ranges and experimental levels of independent test variables

	Range and level				
	–α	–1	0	+1	+α
Catalyst loading (g·L^{-1})	–0.0728	0.2	0.6	1	1.2728
Initial pollutant concentration (mg·L^{-1})	1.59	5	10	15	18.410
pH	2.954	5	8	11	13.046

These results indicated a good agreement between the experimental and predicted values. The correlation coefficient R^2 evaluated quantitatively the correlation between the experimental and predicted responses. By comparing the experimental results and the predicted values obtained from the model, we found that the predicted values corresponded reasonably well to the experimental values with R^2 = 0.977 (Fig. 2).

Adjusted R^2 (R^2_{adj}) was also a measure of the quality of an adjustment. It corrected the value of R^2 for the size of the sample and the number of terms in the model using the degrees of freedom on the calculations. If there were many terms in the model and the sample size was not very large, R^2_{adj} may be visibly smaller than R^2 [21,22]. Here, the adjusted R^2 value (0.948) was very close to the corresponding R^2 value (Table 3).

In addition to the correlation coefficient, the fit of the models was also assessed by the residuals (difference between observed and predicted value of response). Residuals are considered as unexplained elements of variation by the fitted model and therefore are expected to occur in a normal distribution. Normal probability plots present a convenient graphical method for judging normalized residuals. The observed residuals are plotted against the expected values, given by a normal distribution (Fig. 2). The trends observed in Fig. 3 reveal reasonably well-behaved residuals. The graph presented in Fig. 3 showed us that the observed experimental points were randomly dispersed around the zero line, which meant that the difference between the predicted values and the observed values was negligible [Eq. (4)].

$$\text{Residual} = \text{Value}_{\text{Predicted}} - \text{Value}_{\text{observed}} \tag{4}$$

Table 2
Experimental design matrix, experimental results and predicted degradation

Experiment	x_1 (TiO_2)	x_2 (Para)	x_3 (pH)	Y (%)	
				Observed	Predicted
1	0.2	5	5	75.34	70.64
2	1	5	5	100	101.09
3	0.2	15	5	58.84	54.54
4	1	15	5	98.26	97.54
5	0.2	5	11	62.88	61.36
6	1	5	11	93.28	95.34
7	0.2	15	11	52.78	49.45
8	1	15	11	93.5	95.97
9	0	10	8	20.77	27.92
10	1.2728	10	8	96.65	92.66
11	0.6	1.59	8	100	100.74
12	0.6	18.41	8	85.31	87.73
13	0.6	10	2.954	82.09	86.14
14	0.6	10	13.046	77.91	77.02
15	0.6	10	8	86.5	86.35
16	0.6	10	8	86.7	86.35
17	0.6	10	8	86.4	86.35

Positive values of the residuals meant that the prediction was too low while negative values revealed a prediction that was too high, points on the zero-line meant that the prediction was correct.

3.1. Statistical analysis of analysis of variance

The analysis of variance consisted of comparing, using a Fisher test, the sum of the squares of the deviations due solely to the regression of the model with the sum of the squares of the residuals. Table 3 shows the results of the quadratic response surface model in the form of analysis of variance (ANOVA). ANOVA is required to examine the significance and adequacy of the model [23,24].

ANOVA subdivided the variation of the results into two components: a variation associated with the model and a variation associated with the experimental error, showing whether the variation of the model was significant or not compared to those associated with the residual error [5,7,25]. This comparison was made by the value of *F*, which corresponded to the ratio between the mean square of the model and the residual error. If the model was a good predictor of the experimental results, the value of *F* must be greater than that tabulated for a certain number of degrees of freedom in the model at a level of significance α. The *F*-value obtained (33.62), was clearly higher than the tabulated *F*-value (2.352 at 95% significance) confirming the relevance of the model adjustments.

As seen in Table 3, it can be concluded that the catalyst concentration (x_1) was a very important parameter because the probability p was less than 0.001. In addition, the value of the initial concentration of the pollutant (x_2) was significant ($p < 0.05$). Parameters with a probability $p > 0.05$ were insignificant as in the case of pH (x_3) and interactions between the three factors.

3.2. Effects and interactions analysis

The effects of different factors and their interactions are shown in Fig. 4 based on the graphical analysis of the effects; it was found that the catalyst loading had a significant positive effect on the photocatalytic degradation yield. This increased with the amount of titanium dioxide, unlike the initial paracetamol concentration which had a negative effect on the yield. When the concentration

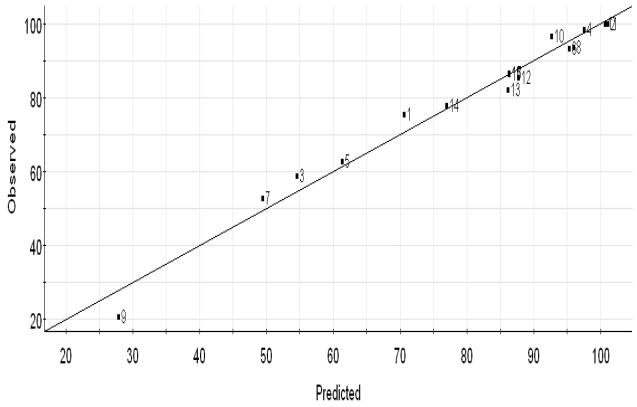

Fig. 2. Predicted values by the model according to the observed values.

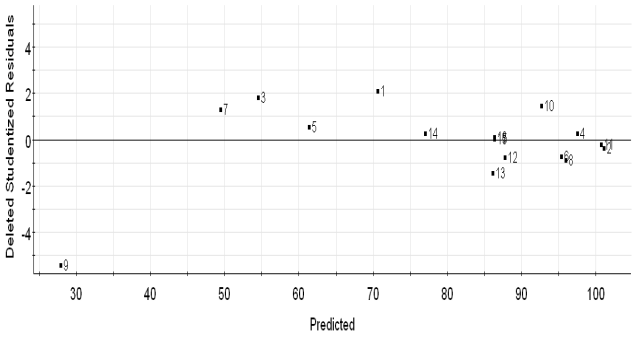

Fig. 3. Observed residuals vs. predicted values.

Table 3
ANOVA for the response surface quadratic model

Source	Sum of squares	Degrees of freedom	Mean squares	Ratio *F*	Prob. > *F*	Remark
Model	6,788.47	9	754.27	33.62	<0.001	Significant
A_1	5,057.63	1	5,057.63	225.45	<0.001	Significant
A_2	204.33	1	204.33	9.108	0.0194	Significant
A_3	100.40	1	100.40	4.47	0.07	–
A_{12}	78.62	1	78.62	3.50	0.10	–
A_{13}	6.19	1	6.19	0.27	0.6155	–
A_{23}	8.73	1	8.73	0.39	0.55	–
A_{11}	956.95	1	956.95	42.65	0.0003	Significant
A_{22}	87.62	1	87.62	3.90	0.0887	–
A_{33}	32.05	1	32.05	1.42	0.27	–
Residual	157.98	7	22.43	–	–	–
Pure error	0.04	2	0.02	–	–	–
Total	6,945.51	16	434.1	–	–	–
–	$R^2 = 0.977$	$R^2_{adj} = 0.948$	–	–	–	–

was lower, the better was the yield. But it remained low compared to the catalyst effect. As for the pH of the solution, it had a negligible negative effect on the degradation yield. The interactions between the parameters were also negligible and insignificant.

To determine the contribution of each effect and their interactions on the response, the Pareto diagram was employed [26]. Pareto analysis provided more significant information to interpret the results. This analysis gave the percentage effect of each factor on the response, according to the following relationship [Eq. (5)]:

$$P_i = \left(\frac{b_i^2}{\sum b_i^2} \right) \times 100 \quad (i \neq 0) \tag{5}$$

The Pareto diagram in Fig. 5 shows that among all the variables studied, the catalyst concentration (b_2, 74.09%) had the main effect on the photocatalytic degradation efficiency. Nevertheless, the paracetamol concentration had a fairly significant effect with 3% efficiency.

3.3. Optimization of photodegradation parameters

MODDE 6.0 software was used to produce three-dimensional (3D) and two-dimensional (2D) response surfaces of contour plots. These surfaces were graphical representations of the regression equation to optimize reaction conditions and were the most effective approach for revealing the reaction system conditions. The response function were presented by varying two factors and fixing the third. The results of the interactions between the three independent variables and the dependent variable are shown in Figs. 6–8.

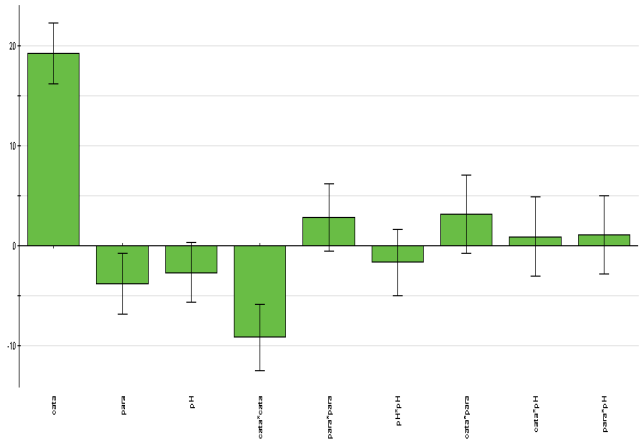

Fig. 4. Graphical analysis of effects.

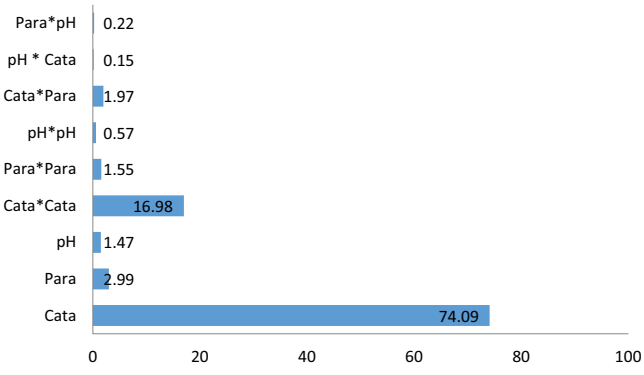

Fig. 5. Pareto diagram.

3.3.1. Catalyst concentration constant

Fig. 6 illustrates the contours and response surfaces of the paracetamol photodegradation yield for catalyst concentrations set at 0.2, 0.6 and 1 g·L^{-1}. It represented the interaction effect between the paracetamol concentration and the pH on the photodegradation rate for the different titanium dioxide concentrations.

Fig. 6 showed that by varying the pH between 5 and 11, the degradation yield did not exceed 54% in the case of solutions with a high paracetamol concentration (15 mg·L^{-1}) and 0.2 g·L^{-1} of catalyst concentration. Decreasing the paracetamol concentration at low pH, resulted in yield that was greater (70%) using 5 mg·L^{-1}.

At a fixed catalyst concentration of 0.6 g·L^{-1}, a minimum yield of 82.6% was found at pH 11 and a paracetamol concentration of 15 mg·L^{-1}. Overall, the yield increased by decreasing the paracetamol concentration and changed slightly with pH variation. For a catalyst concentration maintained at 1 g·L^{-1}, the optimum was reached for very low paracetamol concentrations of the order of 5 mg·L^{-1} and a pH of approximately 6.

The photodegradation efficiency decreased with an increase in the paracetamol concentration and pH. This could be explained by the saturation of the catalyst active sites by the pollutant molecules absorbed. This meant that as the pollutant concentration increased, molecules would be absorbed, consequently the reactive species ($OH^{\bullet}$ and $O_2^{-\bullet}$) necessary for the paracetamol degradation also increased and became insufficient for the pollutant degradation at high concentrations [27,28].

3.3.2. Pollutant concentration is constant

Fig. 7 shows the interaction effect between catalyst concentration and pH on the rate of photodegradation at fixed paracetamol concentrations.

The contours and response surfaces shown in Fig. 7 indicated a slight influence of pH on the paracetamol photodegradation. This was in contrast to the catalyst concentration which generated a significant yield increase exceeding 98%. The contours and response surfaces had the same appearance for the three concentrations employed which showed that the initial pollutant concentration did not have a significant influence.

The yield variation was better with increasing catalyst loading whatever the pH of the solution, reaching 97%, 97% to 98% while maintaining the initial pollutant concentrations at 5, 10 and 15 mg·L^{-1}, respectively. The photodegradation yield increased considerably by increasing the catalyst concentration from 0.2 to 1.2 g·L^{-1}.

According to this Table 4 at a greater concentration (from 0.2 to 1.2 g·L^{-1}), the paracetamol degradation yield was 44% greater. This behavior is explained by the fact that

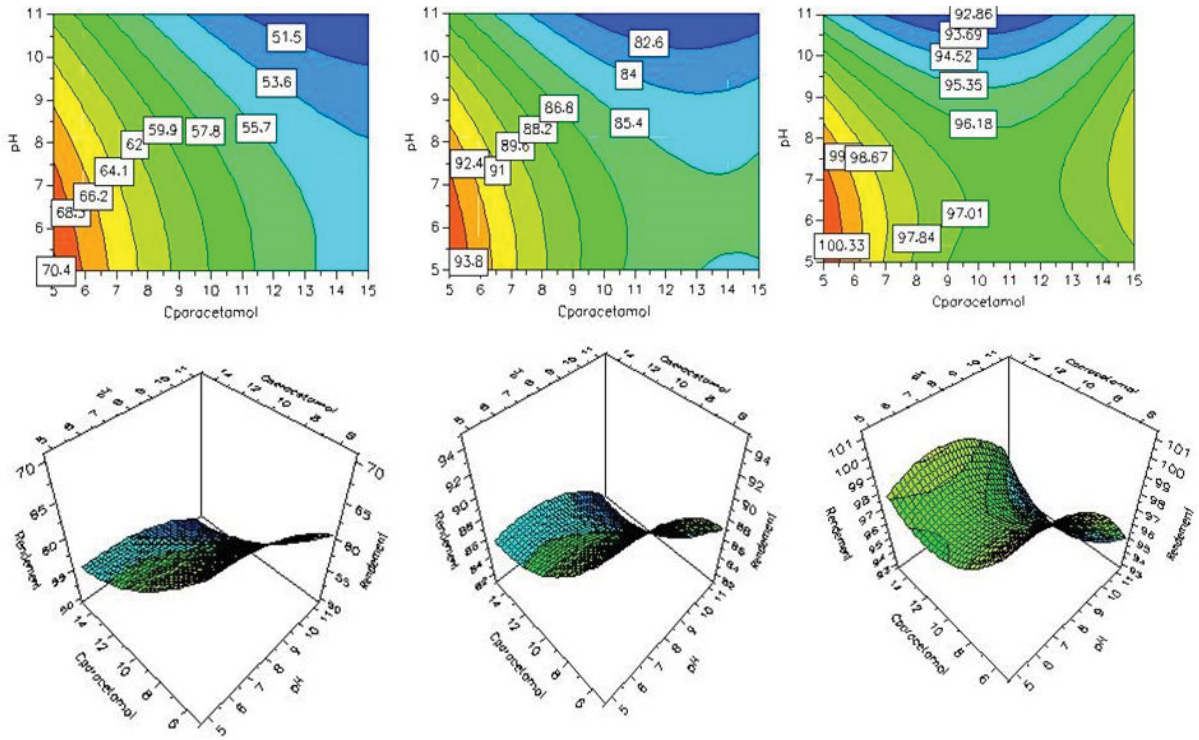

Fig. 6. Interaction effect between the paracetamol concentration and the pH on the photodegradation rate for a titanium dioxide concentration kept constant at 0.2, 0.6 and 1 g·L^{-1}.

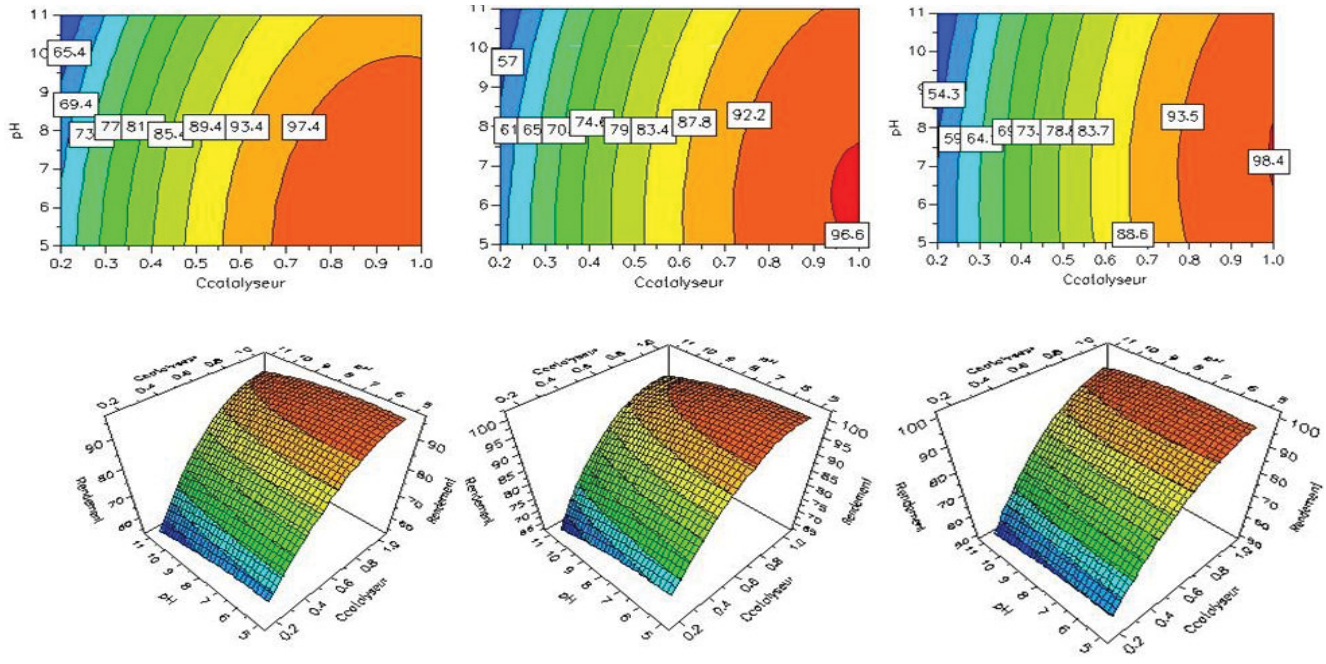

Fig. 7. Interaction effect between catalyst concentration and pH on the photodegradation rate for an initial paracetamol concentration kept constant.

above the optimal concentration, the TiO_2 particles cause a screen effect with respect to sunlight and thus reduce the formation of hydroxyl radicals responsible for the pollutant oxidation reaction.

3.3.3. pH of the solution constant

The interaction effect between the paracetamol concentration and catalyst concentration on the photodegradation rate for different pH set at 5; 8 and 11 is shown in Fig. 8.

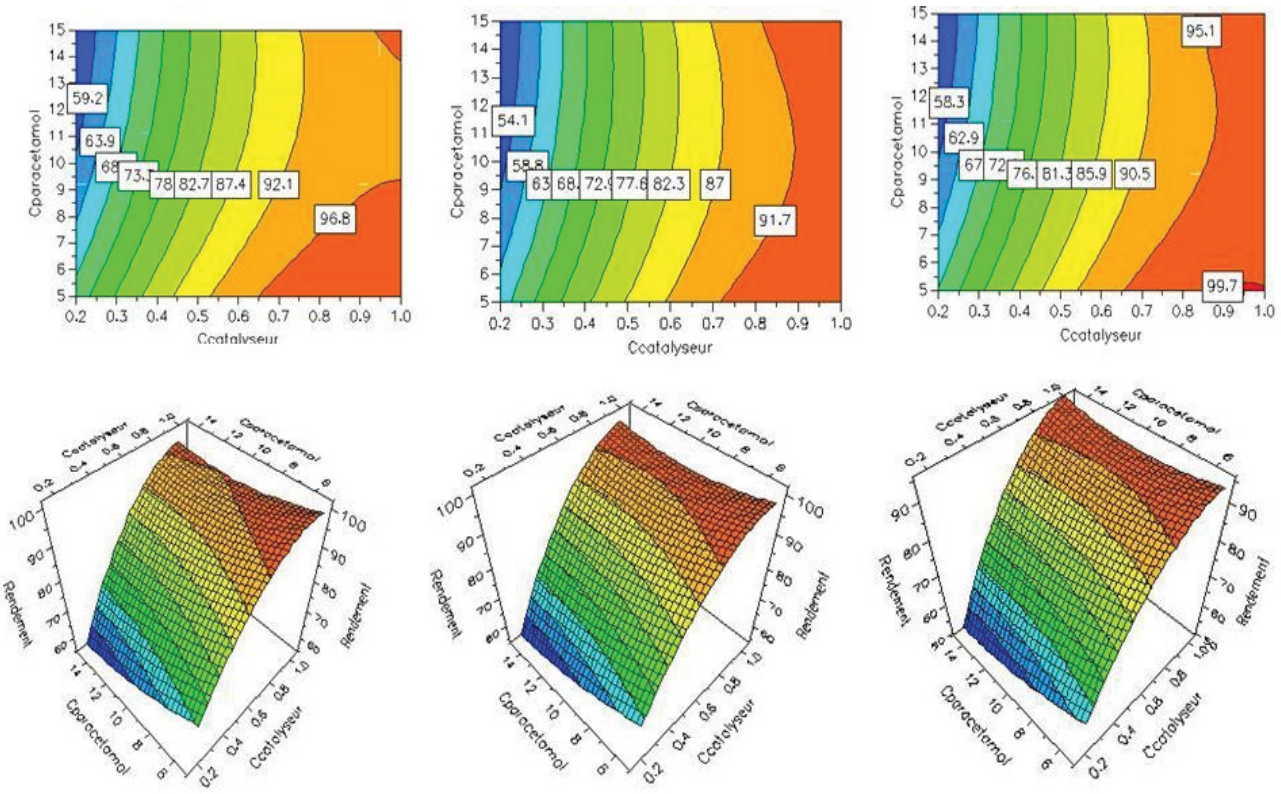

Fig. 8. Interaction effect between catalyst concentration and pollutant concentrations photodegradation rate with fixed pH at 5, 8 and 11.

Table 4
Photodegradation yield evolution for different initial pollutant concentrations

$C_{Pollutant}$ (mg·L^{-1})	R_{min} (%)	R_{max} (%)
5	65	97
10	57	97
15	54	98

Table 5
Evolution of the photodegradation yield for different pH

pH	R_{min} (%)	R_{max} (%)
5	59	97
8	54	92
11	58	99

The degradation yield increases with the increase in the catalyst amount used and decreases with the increase in the initial pollutant concentration. In the case of low paracetamol concentrations, the yield increases linearly with the catalyst concentration until reaching a value of 80%. For high catalyst concentrations, by increasing the paracetamol concentration, the yield does not exceed 59%. From Table 5 it was noted that photodegradation is favored by increasing the catalyst amount from a minimum rate of 50% to more than 92%. On the other hand, the pH variation between 5 and 11 causes a very slight increase in yield. These results are in harmony with those obtained by Yang et al. [29] and Jallouli et al. [30], which confirm that the degradation rate slowly increased between pH 3.5 and 9.5.

3.3.4. Optimization of factors influencing degradation performance

The objective of the design-based optimization was to determine the optimal value of variables from the model. Therefore, in this work, the highest degradation rate of paracetamol was obtained not only from optimization, but also from the conditions of pH, TiO_2 concentration and initial concentration of paracetamol at the same time. There were aspects for consideration. Firstly, the maximum degradation of paracetamol which was the main objective of the optimization. Secondly, the optimal level of the pH value was to be kept close to neutral as far as possible, so that the solution could be discharged directly into the aquatic environment after removal of the catalyst or it could be reused for irrigation. Thirdly, a small amount of catalyst was to be employed.

Based on the relative stress models and conditions, the numerical optimization was performed with the help of design expert MODDE 6.0 considering each response value. The optimal conditions for the maximum rate of paracetamol degradation under relative stress conditions were found to be a pH value of 7.3, a TiO_2 concentration

Table 6
Optimum values of the process parameter

C catalyst	0.9932
C paracetamol	15
pH	7.288
Yield	98.46

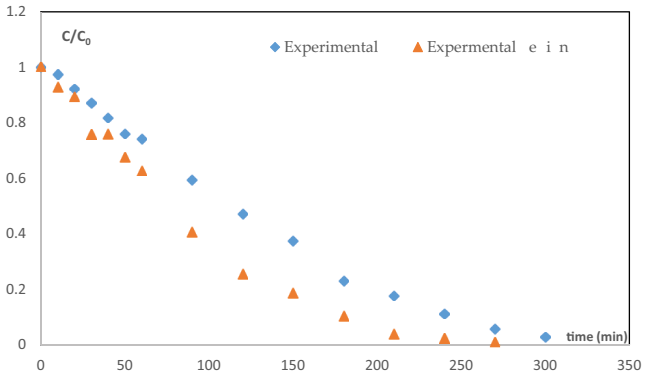

Fig. 9. Temporal evolution of the reduced paracetamol concentration with the optimal conditions of the parametric study and the experimental design.

equal to 1 g·L^{-1}, and an initial paracetamol concentration of 15 mg·L^{-1} (Table 6). Under optimal conditions, the model predicted a maximum paracetamol degradation rate of 98.46%. These results implied that there were optimal reaction conditions for the rate of degradation of paracetamol by photocatalysis in the presence of TiO_2.

3.3.5. Verification of results

To confirm the relevance of the model for predicting the rate of maximum degradation of paracetamol, the model was validated by carrying out experiments in the R1 tubular reactor using optimal conditions. The experiment resulted in a maximum degradation rate of 97.3%. The good agreement between the predicted results and the experimental results verified the validity of the optimal point, which confirmed that it was possible to optimize the rate of paracetamol degradation with the response surface methodology.

On the other hand, it was noticed that the optimization by design of experiment was better than that obtained by the traditional method using a simple parametric study as shown in Fig. 9.

4. Conclusions

To assess the interactions between the different parameters, an investigation was successfully carried out by modeling by central composite design (CCD). This optimization was applied to a tubular reactor by maintaining a fixed photonic flux with radiation with two UVA lamps of 24 W each. The modeling of the system led to a polynomial of the second degree. The results showed that the most influential factor in photodegradation was the amount of catalyst used, followed by the initial concentration of paracetamol which was inversely proportional to the degradation rate, followed by the effect of pH which was negligible. The existence of interaction between the type of catalyst used and the different parameters studied (pH, C_{Para} and C_{TiO2}) as well as the interaction between the concentration of the pollutant and the pH had a negligible effect on the yield compared to that of the quantity of the catalyst and the initial concentration of the pollutant. The model allowed for the prediction of the degradation yields of paracetamol without resorting to experimentation. This was a considerable economic gain. It can be concluded that solar photocatalysis was very effective for the degradation of paracetamol and was thus a useful technique for reducing the toxicity of polluted waters with minimal energy costs due to the use of free solar renewable energy.

Acknowledgments

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