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ORIGINAL ARTICLE

# Full factorial experimental design applied to oxalic acid photocatalytic degradation in $TiO_2$ aqueous suspension

**N. Barka [a,*], M. Abdennouri [b,c], A. Boussaoud [d], A. Galadi [b], M. Baâlala [c], M. Bensitel [c], A. Sahibed-Dine [c], K. Nohair [c], M. Sadiq [c]**

[a] *Faculté Polydisciplinaire de Khouribga, Université Hassan 1er, B.P. 145, Khouribga, Morocco*
[b] *Equipe de Recherche Analyse Contrôle et Environnement (ERACE), Ecole Supérieure de Technologie de Safi, B.P. 89, Route Dar Si Aissa, Safi, Morocco*
[c] *Laboratoire de Catalyse et Corrosion des Matériaux, Faculté des Sciences, Université Chouaib Doukkali, B.P. 20, El Jadida, Morocco*
[d] *Laboratoire Matière, Matériaux: Applications et Modélisation, Faculté Polydisciplinaire de Safi, B.P. 416, Route Sidi Bouzid, Safi, Morocco*

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**Abstract** Full factorial experimental design technique was used to study the main effects and the interaction effects between operational parameters in the photocatalytic degradation of oxalic acid in a batch photo-reactor using $TiO_2$ aqueous suspension. The important parameters which affect the removal efficiency of oxalic acid such as agitation, initial concentration, volume of the solution and $TiO_2$ dosage were investigated. The parameters were coded as $X_1$, $X_2$, $X_3$ and $X_4$, consecutively, and were investigated at two levels (−1 and +1). The effects of individual variables and their interaction effects for dependent variables, namely, photocatalytic degradation efficiency (%) were determined. From the statistical analysis, the most effective parameters in the photocatalytic degradation efficiency were initial concentration and volume of solution. The interaction between initial concentration, volume of solution and $TiO_2$ dosage was the most influencing interaction.

* Corresponding author. Tel.: +212 661 66 66 22; fax: +212 523 49 03 54.
E-mail address: barkanoureddine@yahoo.fr (N. Barka).
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However, the interaction between agitation, initial concentration and volume of solution was the least influencing parameter.



## 1. Introduction

Heterogeneous photocatalysis, a new technique belonging to the class of advanced oxidation processes (AOPs), is emerging as an attractive alternative treatment method for the removal of toxic pollutants from wastewaters owing to its ability to convert them into innocuous end products such as $CO_2$, $H_2O$ and mineral acids (Herrmann et al., 1993; Hoffmann et al., 1995; Mills and Le Hunte, 1997; Ollis and Turchi, 1990; Wei and Wan, 1992). The process involves the generation of conduction band electrons and valence band holes by the illumination of a semiconductor, usually $TiO_2$, with light energy greater than the band gap energy. The electrons and holes form hydroxyl radicals which are assumed to be the main reactants in the degradation of the most recalcitrant molecules such as chlorocarboxylic acids (Mas et al., 2005), chloroanilines (Chu et al., 2007), chlorophenols (Bayarri et al., 2005; Guillard et al., 1999; Ku et al., 2006; Abdennouri et al., 2010), dyes (Barka et al., 2010; Qamar et al., 2004; Zainal et al., 2005; Essam et al., 2007), fungicides (Danion et al., 2006), herbicides (Haque and Muneer, 2003), ketones (Vorontsov et al., 2000), phenolics (Pelizzetti and Minero, 1993; Qourzal et al., 2008) and bacteria (Rincón and Pulgarin, 2003).

The rate and efficiency of a photocatalytic reaction depend on a number of factors which govern the kinetics of photocatalysis. Among these parameters that could be cited were initial concentration of pollutant, mass of catalyst, pH, volume of solution, radiant flux and agitation. In most previous studies, only traditional one-factor-at-a-time experiments were tested for evaluating the influence of operating factors on photocatalytic process.

Design of experiments is a powerful technique used for discovering a set of process variables (or factors) which are most important to the process and then determine at what levels these factors must be kept to optimize the process performance. Statistical design of experiments is a quick and cost-effective method to understand and optimize any manufacturing processes (Antony and Roy, 1999). 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. Doing so with the factorial planning of the experiments, it was possible to investigate simultaneously the effect of all the variables (Montgomery, 1997).

In the present work, the photocatalytic degradation of oxalic acid was investigated in batch photo-reactor using $TiO_2$ aqueous suspension. The experimental work is carried out using a $2^4$ factorial design in order to examine the main effects and the interactions between agitation speed, volume of solution, initial concentration and $TiO_2$ dosage.

## 2. Materials and methods

### 2.1. Materials

$TiO_2$ "Degussa P-25" was used for the degradation process. It consists of 80% anatase and 20% rutile with a specific BET-surface area of 50 $m^2/g$ and primary particle size of 20 nm (Bickley et al., 1992). All other chemicals used in the experiments were of laboratory reagent grade and used as received without further purification. Oxalic acid (Scharlau, 99.5%), sodium hydroxide (Fluka, 99%) and bromothymol blue (Acros Organics).

### 2.2. Photo-reactor and light source

Photocatalytic experiments were performed in batch cylindrical photo-reactor with 10 cm in diameter and 20 cm in height (Fig. 1). The reactor was made from quartz glass, which made possible the transfer of the irradiation. The reactor was exposed to a luminous source composed of a medium pressure mercury-lamp (400 W), placed in axial position inside a cooling water jacket system positioned inside the inner part of the photo-reactor containing the aqueous solution of oxalic acid. The agitation was assured by means of a magnetic stirrer placed at the reactor base.

### 2.3. Procedure and analysis

Sixteen experiments were carried out by varying the volume of solution 400 mL or 800 mL, initial concentration 0.001 M or 0.01 M, $TiO_2$ dosage 0.01 g $L^{-1}$ or 0.2 g $L^{-1}$ and agitation speed (400 rpm or 800 rpm). After 1 h of preliminary adsorption in the dark and 1 h of UV irradiation, the residual concentration of oxalic acid was determined by titration of the solution with NaOH using bromothymol blue as colour indicator.

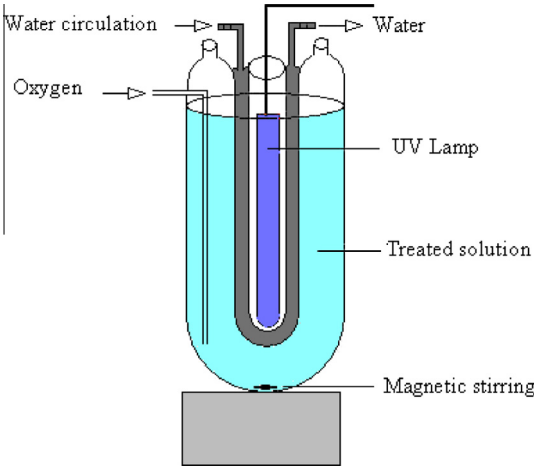


**Figure 1** Schematic diagram of the photocatalytic reactor.

The photocatalytic efficiency was determined by using the following equation:

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

where $Y$ *is* the photocatalytic efficiency (%), $C_o$ and $C_r$ both in (mol $L^{-1}$) are, respectively, the initial and residual concentrations of oxalic acid in solution.

## 3. Results and discussion

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, $2^n$ experiments will be needed (Morais et al., 1999). In order to study the variables that define the process, $2^4$ factorial experimentations were carried out, in two levels (i.e. high and low). The higher level of variable was designed as '+' and the lower level was designed as '−'. 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 $X_1$, $X_2$, $X_3$ and $X_4$. Photocatalytic degradation efficiency ($Y$) was measured for each of these tests as shown in Table 2.

A first-order model with all possible interactions was chosen to fit the experimental:

$$\begin{aligned} Y = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 \\ & + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 \\ & + b_{34}X_3X_4 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 \\ & + b_{134}X_1X_3X_4 + b_{234}X_2X_3X_4 + b_{1234}X_1X_2X_3X_4 \end{aligned} \quad (2)$$

**Table 1** Factors and levels used in the $2^4$ factorial design study.

| Parameter name | Code | Low (−1) | High (+1) |
|---|---|---|---|
| Agitation speed (rpm) | $X_1$ | 400 | 800 |
| Initial concentration (mol $L^{-1}$) | $X_2$ | 0.001 | 0.01 |
| Volume of solution (mL) | $X_3$ | 400 | 800 |
| $TiO_2$ dosage (g $L^{-1}$) | $X_4$ | 0.01 | 0.2 |

where $Y$ is the response (photocatalytic degradation efficiency), $X_i$ values ($i$ = 1, 2, 3, 4) indicate the corresponding parameter in their coded forms.

The statistical calculations and multiple regressions were performed using Nemrodw software. Regression analysis was performed to fit the response function (photocatalytic degradation efficiency) with the experimental data. The values of regression coefficients obtained are given in Table 3. The final regression equation, after putting values of all coefficients, is as follows:

$$\begin{aligned} Y = {} & 65.98 + 1.83X_1 - 7.83X_2 - 8.64X_3 + 2.64X_4 \\ & + 0.33X_1X_2 - 0.11X_1X_3 + 0.36X_1X_4 + 0.29X_2X_3 \\ & + 0.21X_2X_4 - 0.23X_3X_4 + 0.21X_1X_2X_3 \\ & + 0.04X_1X_2X_4 + 0.23X_1X_3X_4 + 0.58X_2X_3X_4 \\ & + 0.17X_1X_2X_3X_4 \end{aligned} \quad (3)$$

The seventh column in Table 2 presents the calculated values by way of the modelling procedure. The values obtained by the model ($Y$ predicted) are compared with those of experimental data ($Y$ experimental). These values are very close

**Table 3** Values of model coefficients.

| Main and interaction coefficients | Values | Error |
|---|---|---|
| $b_0$ | 65.98 | 0.037 |
| $b_1$ | 1.83 | 0.37 |
| $b_2$ | −7.83 | 1.616 |
| $b_3$ | −8.64 | 1.764 |
| $b_4$ | 2.64 | 0.536 |
| $b_{12}$ | 0.33 | 0.06 |
| $b_{13}$ | −0.11 | 0.014 |
| $b_{14}$ | 0.36 | 0.053 |
| $b_{23}$ | 0.29 | 0.065 |
| $b_{24}$ | 0.21 | 0.051 |
| $b_{34}$ | −0.23 | 0.058 |
| $b_{123}$ | 0.21 | 0.035 |
| $b_{124}$ | 0.04 | 0.017 |
| $b_{134}$ | 0.23 | 0.04 |
| $b_{234}$ | 0.58 | 0.127 |
| $b_{1234}$ | 0.17 | 0.042 |

**Table 2** Experimental design matrix, experimental results and predicted photocatalytic degradation efficiency for oxalic acid (%).

| Experiment | $X_1$ | $X_2$ | $X_3$ | $X_4$ | $Y$ (Experimental) | $Y$ (Predicted) | Residue |
|---|---|---|---|---|---|---|---|
| 1 | −1 | −1 | −1 | −1 | 78 | 77.94 | −0.06 |
| 2 | +1 | −1 | −1 | −1 | 81 | 81.06 | 0.06 |
| 3 | −1 | +1 | −1 | −1 | 62 | 61.94 | −0.06 |
| 4 | +1 | +1 | −1 | −1 | 66 | 66.06 | 0.06 |
| 5 | −1 | −1 | +1 | −1 | 62.5 | 62.46 | −0.04 |
| 6 | +1 | −1 | +1 | −1 | 64.6 | 64.06 | −0.54 |
| 7 | −1 | +1 | +1 | −1 | 45.2 | 45.14 | −0.06 |
| 8 | +1 | +1 | +1 | −1 | 48 | 48.06 | 0.06 |
| 9 | −1 | −1 | −1 | +1 | 84 | 83.9 | −0.1 |
| 10 | +1 | −1 | −1 | +1 | 88 | 88.06 | 0.06 |
| 11 | −1 | +1 | −1 | +1 | 67 | 66.94 | −0.06 |
| 12 | +1 | +1 | −1 | +1 | 71 | 71.06 | 0.06 |
| 13 | −1 | −1 | +1 | +1 | 65 | 64.94 | −0.06 |
| 14 | +1 | −1 | +1 | +1 | 68 | 68.06 | 0.06 |
| 15 | −1 | +1 | +1 | +1 | 50 | 49.94 | −0.06 |
| 16 | +1 | +1 | +1 | +1 | 56 | 56.06 | 0.06 |

indicating a correspondence between the mathematical model and the experiment. The statistically significant variables at 95% level of confidence were tested using analysis of variance (ANOVA) and were: $r^2 = 0.994$, $\chi^2 = 156.98$ and $F = 7.658 \times 10^{-5}$; where $r^2$ is the correlation coefficient, $\chi^2$ is the sum of quadratic residuals and $F$ is the $F$-value. The coefficient of multiple determinations, $r^2$, representing the fit of the models to the experimental data was 0.994 which means that 99.4% of the data about their mean was accounted for by the factor effects in the model.

Eq. (3) shows the effect of individual variables and interactional effects for oxalic acid photocatalytic degradation. According to this equation, the agitation speed and $TiO_2$ dosage have a positive effect, while the initial concentration and solution volume have a negative effect on the photocatalytic degradation of oxalic acid in aqueous solution in the range of variation of each variable selected for the present study.

The positive sign shows that there is a direct relation between the parameter and the dependent variable. Heterogeneous photocatalysis is governed by two steps in series, the mass-transfer and the chemical reaction. The mass transfer is influenced by the agitation speed. So the increase of the agitation speed leads to high mass transfer and then to high degradation rate. On the other hand, the increase of the agitation speed can promote the oxygen transfer on the liquid phase (Merabet et al., 2009). And thereby increase the degradation kinetics. The increase in $TiO_2$ dosage increases the surface area available by more photocatalyst particles. The number of active sites on the photocatalyst surface increases, which in turn increase the number of hydroxyl radicals. The increase of hydroxyl radicals leads to the increase of the photocatalytic degradation efficiency.

The negative signs in the case of solution volume and initial concentration are due to the fact that the numbers of molecules of oxalic acid were very important with the increase of these two parameters. Since irradiation time and the amount of catalyst are constant, the $OH^{\cdot}$ (primary oxidant) concentration remains practically same. Thus, although bulk liquid concentration increases, the rate of photocatalytic degradation decreases due to a lower $OH^{\cdot}$/oxalic acid ratio. On the other hand, the penetration of light decreases when the pollutant concentration increases, this leads to less active sites creation.

It is known that the larger the coefficient, the larger is the effect of related parameter. The most effective parameters in

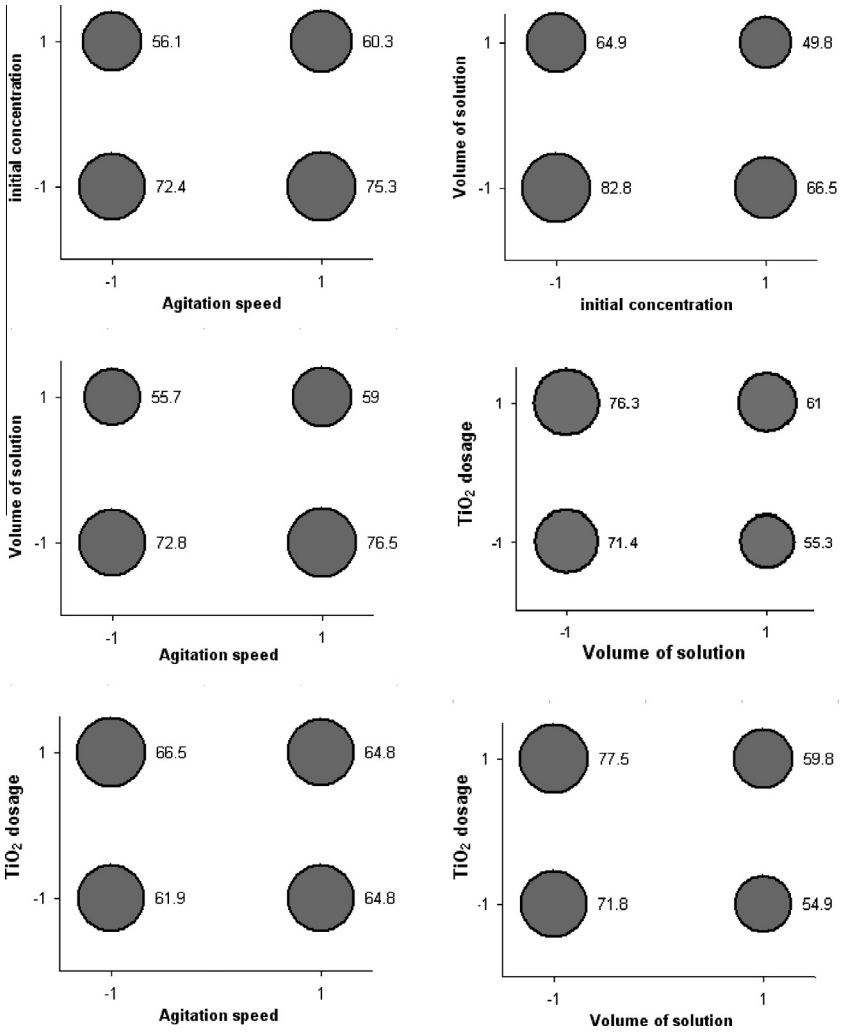


**Figure 2** Interaction effects of two-variables among the four variables for photocatalytic degradation efficiency. The balls represent the weight for the response variable and the values are the average of the response variables.

the photocatalytic degradation efficiency were initial concentration and volume of solution, which are followed by $TiO_2$ dosage and agitation speed. From Eq. (2) it is also seen that two-variable or three-variable interactions are significant. The interaction between initial concentration, volume of solution and $TiO_2$ dosage was the most influencing interaction. However, the interaction between agitation speed, initial concentration and volume of solution was the least influencing parameter.

The maximum photocatalytic degradation efficiency of oxalic acid obtained in this study was found to be 88%, corresponding to the operating conditions of 800 rpm, 0.001 M, 400 mL and 0.2 g $L^{-1}$, respectively, for the agitation speed, initial concentration, volume of solution and $TiO_2$ dosage.

Fig. 2 illustrates the possible positive and negative two-variable interactions among the four variables for photocatalytic degradation efficiency. These results support the previous findings related to the effect of each factor on photocatalytic degradation. Because it has been found that the higher is the agitation speed or $TiO_2$ dosage, the higher is the photocatalytic degradation efficiency; and lower is the initial concentration or volume of solution, and higher is the photocatalytic degradation efficiency.

From the figure, it can be seen that the interaction between initial concentration and volume of solution was the most important interaction. Because photocatalytic degradation efficiency decreases significantly from 82.8% to 49.8% with an increase in initial concentration from 0.001 to 0.01 M and an increase in volume of solution from 400 to 800 mL. However, the interaction between agitation speed and $TiO_2$ was least influencing because photocatalytic degradation efficiency does not change significantly.

## 4. Conclusions

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 of oxalic acid photocatalytic degradation efficiency. As observed, the most effective parameters in the photocatalytic degradation efficiency were initial concentration and volume of solution. The agitation speed and $TiO_2$ dosage have a positive effect, while the initial concentration and solution volume have a negative effect on the photocatalytic degradation. The interaction between initial concentration, volume of solution and $TiO_2$ dosage was the most influencing interaction. However, the interaction between agitation speed, initial concentration and volume of solution was the least influencing parameter.

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