Effect and interaction study of acetamiprid photodegradation using experimental design

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ABSTRACT

The methodology of experimental research was carried out using the MODDE 6.0 software to study the acetamiprid photodegradation depending on the operating parameters, such as the initial concentration of acetamiprid, concentration and type of the used catalyst and the initial pH of the medium. The results showed the importance of the pollutant concentration effect on the acetamiprid degradation rate. On the other hand, the amount and type of the used catalyst have a considerable influence on the elimination kinetics of this pollutant. The degradation of acetamiprid as an environmental pesticide pollutant via UV irradiation in the presence of titanium dioxide was assessed and optimized using response surface methodology with a D-optimal design. The acetamiprid degradation ratio was found to be sensitive to the different studied factors. The maximum value of discoloration under the optimum operating conditions was determined to be 99% after 300 min of UV irradiation.

Key words | acetamiprid, D-optimal design, experimental design, wastewater treatment

INTRODUCTION

Recalcitrant organic pollutants like pharmaceuticals, pesticides and dyes in municipal and industrial waste water are a threat to the environment and human and animal health, because of their high toxicity and resistivity to the biodegradation processes. The detection of a weak amount of these products in water shows clearly that some of them cannot be removed during the wastewater treatment in the wastewater treatment plants (WWTPs) by using the classical treatment processes because they were not initially designed for this purpose. Conventional WWTPs can eliminate part of the micropollutants by adsorption on sludge, biodegradation and/or volatilization. However, some micropollutants are still found in treated wastewater. One of the major challenges of wastewater treatment is to reliably remove these micropollutants and the related toxicity from treated water. However, this has led to the development of new water treatment technologies for the elimination of the recalcitrant compounds in water.

Neonicotinoid pesticides comprise a fairly new and widely used category of organic compounds, which covers the 17% of global pesticide market and therefore could pose a threat to the aquatic and terrestrial environment. The acetamiprid is a widely applied third generation insecticide. It can be used in a variety of crops, for example vegetables, melons, fruit trees, wheat, tobacco, cotton. It is soluble in most organic solvents and shows increased solubility in water (25 g.L\(^{-1}\)) (Kagabu 1997). It absorbs to less than \(\lambda_{\text{max}} = 290\) nm and therefore is stable to the influence of solar radiation. Efficient degradative microbial strains for acetamiprid were very hard to get; the pesticide has been reported as a resistant chemical for environmental microbes (Dai et al. 2013). The study conducted by Elena et al. (2013) was to evaluate the degradation of acetamiprid with the use of Fenton reaction to investigate the effect of different concentrations of H\(_2\)O\(_2\) and Fe\(^{2+}\), initial pH and various iron salts, on the degradation of acetamiprid and to apply
response surface methodology for the evaluation of degradation kinetics. The photo-assisted oxidative degradation of acetamiprid in the presence of titanium dioxide (TiO$_2$) was studied by Valéria et al. (2009). The quantitative analysis showed that the reaction is of a pseudo-first-order and the advanced oxidation process (AOP) based on O$_2$/TiO$_2$ and UV light appeared to be a simple and rapid procedure for the removal of acetamiprid.

The AOP was defined as a water treatment process under atmospheric pressure condition and ambient temperature by generating hydroxyl radicals in sufficient quantity to influence the purification rate of wastewater. The AOP is intended for the total mineralization of the organic pollutants which can be transformed to CO$_2$, H$_2$O and inorganic materials (Andreozzi et al. 1999; Horáková et al. 2014).

AOPs have been introduced to eliminate different potentially harmful compounds that could not be effectively removed by conventional treatment processes. These AOPs include O$_3$/UV, H$_2$O$_2$/UV, O$_3$/H$_2$O$_2$/UV and TiO$_2$/UV. Among the AOPs, TiO$_2$/UV based photocatalytic oxidation processes have been of great interest in recent years as an alternative for water detoxification (Hoffmann et al. 1995; Crini & Badot 2007). The processes offer many advantages: simple to perform, rapid elimination of pollutants, *in situ* reactive radicals production, do not produce secondary wastes, they are effective in the treatment of recalcitrant compounds, toxic and non-biodegradable.

These techniques have one drawback as they engender inappropriate discharges with large polluting masses; their use is most suitable for decreasing chemical oxygen demand values below 5 g/L and for the greater values, it is preferred to opt for the wet oxidation or even incineration which proved to be more effective and suitable for the treatment of water heavily loaded with pollutants (Crini & Badot 2007).

The rate and the degradation yield of the photocatalytic reaction depend on a number of factors which influence the photocatalysis kinetics. Among these parameters that could be cited are the initial concentration of the pollutant, the catalyst amount and type and the pH of the medium. In the most previous studies cited in the literature, only a one-factor-at-a-time experiment was tested for evaluating the influence of the operating parameters on the photocatalytic process efficiency. The major disadvantage of this method is that it fails to consider possible interactions between these different factors (Montgomery 1997). This limitation of the classical method can be addressed by optimizing all the influencing parameters through statistical experimental design.

The experimental design is a powerful technique used for discovering the most important factors that influence the process and at what levels these factors must be kept to optimize the photodegradation process performances. Statistical design of experiments is a quick and cost-effective method to understand and optimize any manufacturing processes (Antony & Roy 1999). The principal advantage of this mathematical tool is the reduced number of experiments that are carried out in order to get the optimum conditions. The obtained results of the studies that involve the application of factorial design in the photocatalytic degradation of organic compounds are satisfactory. 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 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 acetamiprid, a pesticide widely used in agriculture in Algeria, was investigated in a hexagonal photoreactor using TiO$_2$ aqueous suspension. The experimental work is carried out using a 24 factorial design in order to examine the main effects and the interactions between catalyst concentration, initial concentration of the pollutant, TiO$_2$ type and pH of the solution. The effect of the interaction between these parameters influencing the photodegradation ratio will be studied by using Experience Plan design. The main objective is to determine the optimum operating conditions for a given system that satisfies the specific operating conditions.

**MATERIALS AND METHODS**

**Experimental system**

Photocatalytic experiments for the degradation of organic pollutant (acetamiprid) were performed in a closed circulation system (Figure 1) using a new photoreactor design. It is a hexagonal photoreactor composed of double walled glass that works under artificial ultraviolet light. The reactor has 20 cm in external diameter, 15 cm in internal diameter and 30 cm in height (Figure 1). The photocatalytic reactor is transparent to UV radiation. It is made from quartz glass, which made possible the transfer of the irradiation using Philips ATLD A/24 W fluorescent tube of 365 nm wavelength maximum irradiation peak and placed in vertical axial position inside a cooling water jacket of 8 L volume capacity. Peristaltic pump was used for the agitation...
of the solution to obtain good dispersion of the catalyst. The used flow rate of the peristaltic pump is 3.7 L/min. A synthetic solution of the pollutant was introduced into the space between inner and outer walls of the reactor; different amounts of TiO₂ were introduced inside the reactor.

Reagents

In this study, the acetamiprid is used as an organic pollutant model to study the parameters influencing the photocatalytic degradation kinetics of this pollutant by heterogeneous photocatalysis process in the presence of two catalysts under UV radiation.

The acetamiprid molecule, presented in Figure 2, is an organochlorine compound and an odorless insecticide from the neonicotinoid family. It is intended to eliminate sucking insects in crops of leafy vegetables, citrus, piridions into the vineyard, in the cultivation of cotton, brassica and ornamental plants. It is also a key pesticide for the cultivation of cherry because of its effectiveness against the larvae of the cherry fruit fly.

To study the pH solution influence on the photocatalyst, the pH was adjusted using 0.1 mol.L⁻¹ HCl (Fluka, 99%) and/or 0.1 mol.L⁻¹ NaOH (Fluka, 99%). The distilled water, used to prepare the aqueous solutions, was obtained from the distillation system of the laboratory. Two types of commercial TiO₂ are used in powder form: TiO₂ ‘Degussa P25’ which consists of 80% anatase and 20% rutile with a specific Brunauer–Emmett–Teller (BET)-surface area of 50 m²/g (Bickley et al. 1992); titanium dioxide T42 (BIOCHEM) composed of 90% anatase and 10% Rutile and have a specific surface equal to 4.61 m²/g. All other chemicals used without further purification in the experiments were of laboratory reagent grade.

Experimental procedure

The experimental work was carried out using a D-optimal design to study the main factors and their interactions influencing the photocatalytic degradation of the aqueous pollutant solution.

The D-optimality concept can be applied to select a design when the classical symmetrical designs cannot be used, such as when the experimental region is not regular in shape, when the number of experiments chosen by a classical design is too large or when one wants to apply models that deviate from the usual first or second order ones. The D-optimal algorithm works as follows. First, specify an approximate mathematical model which defines the functional form of the relationship between the response (Y) and the independent variables (the factors). Next, generate a set of possible candidate points based on this model. Finally, from these candidates, select the subset that maximizes the determinant of the XX matrix. This is the D-optimal design. In other words, the candidate set is a collection of treatment combinations from which the D-optimal algorithm chooses the treatment combinations to include in the design.

The experimental conditions for the photocatalytic degradation are conducted depending on studied parameter and the combinations proposed by the D-optimal algorithm and presented in the Table 2. The extreme levels are denoted by minus one (lower level) and plus one (higher level). Total number of 20 experiments was employed for the response surface modeling (Table 2). The order of experiments was arranged randomly. The acetamiprid samples were collected directly from the photoreactor and analyzed using Shimadzu UV-1603 UV–Vis spectra spectrophotometer (Laoufi et al. 2008; Tassalit et al. 2011), after filtration with a Millipore membrane (0.45 μm) to remove catalyst. The acetamiprid spectrum shows absorption maxima at 245 nm as shown in the Figure 3. The degradation yield Y (%) was expressed as the percentage ratio of the degraded pollutant concentration to that of the initial one. The degradation yield was determined by the following equation:

\[ Y(\%) = \frac{C_0 - C}{C_0} \times 100 \] (1)
where $Y$ is the degradation yield (%), $C_0$ and $C$ both in (mol.L$^{-1}$) are, respectively, the initial and residual concentrations of acetamiprid in the solution.

**RESULTS AND DISCUSSION**

In this study, the photocatalytic degradation of acetamiprid via UV irradiation in the presence of TiO$_2$ was optimized using MODDE 6.0 software. The runs were designed in accordance with D-optimal design. The D-optimal criterion can be used to select points for a mixture design in a constrained region. This criterion selects design points from a list of candidate points, so that the variances of the regression coefficients model are minimized (Myers et al. 2009). One of the objectives of this work is to find a suitable approximating function in order to determine the pollutant removal efficiency and investigate the operating conditions in the region for the factors at certain operating specifications.

The methodology typically used to study the influence of operating parameters is to change the value of a one parameter while holding the others fixed. The exploitation of results and the experimental study can be greatly simplified by the methodology of experimental design. This technique creates a statistically significant model that incorporates the interactions between variables while maximizing the number of tests for this purpose; we used the experimental design to model the photo-degradation of acetamiprid in water.

The proposed strategy is dependent on the objectives, studied factors and on the possibility of interaction between these factors. The methodology of experimental research is particularly appropriate when the objectives are as follows (Hoffmann et al. 1996):

- Isolate the most influential factors (factors’ weight) from a large number of factors that could have influence on the studied phenomenon (screening).
- Study the influence of various factors, taking into account the possible existence of interaction effects between these factors.
- Develop a descriptive or predictive model, relating to the phenomenon studied (modeling).
- Search the optimum of one or more responses (process optimization).

This methodology uses a specific vocabulary:

- **Factor**: it is a parameter assumed to influence the studied phenomenon, also called parameter.
- **Response**: this is a parameter characterizing the result of the phenomenon.
- **Variable code**: it corresponds to a natural variable data in a dimensionless space. In order to measure the effect of all the variable combinations, each variable is tested at a high (+1) and a low level (−1).
- **Experimental plan**: all experimental conditions are determined by the chosen experimental strategy and the successful experimental field. This plan, specific to the studied problem, is expressed in real variables.
- **Experience matrix**: a table expressed in coded variable form and weight) from many rows and columns as the experimental plan. Each point of the matrix is a point of the experimental plan.

**Experimental response and selected factors**

The effects of the three operational variables on the acetamiprid degradation yield $Y(\%)$ were studied: Initial concentration of acetamiprid; initial pH; catalyst concentration and a qualitative factor (type of catalyst (TiO$_2$-T42 or P25-TiO$_2$)). To estimate the response outputs of $Y(\%)$ for the completion point, the ratio was calculated according to Equation (1). The most appropriate experimental design for this study is D-optimal (it was suggested by the MODDE 6.0 software).

The Table 1 shows the values of the selected factors in this study. This factorial design results using 24 tests with all possible combinations of X1, X2 and X3 for each catalyst. Degradation yield ($Y(\%)$) was measured for each test as shown in Table 1.

D-optimal design model with all possible interactions was chosen to fit the experimental:

$$Y = b_0 - b_1X_1 + b_2X_2 - b_3X_3 - b_{11}X_1^2 - b_{22}X_2^2 - b_{33}X_3^2 - b_{12}X_1X_2 - b_{23}X_2X_3 + b_{13}X_1X_3$$

(2)

where $Y$ is the response (degradation yield), $X_i$ values ($i = 1, 2, 3$) indicate the corresponding parameter in their coded form and $b$ is the regression coefficient.

The experimental results of the D-optimal design after 300 min of the photodegradation reaction are represented

<table>
<thead>
<tr>
<th>Parameter name</th>
<th>Code</th>
<th>Low (−1)</th>
<th>High (+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetamiprid initial concentration (mg/L)</td>
<td>$X_1$</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>Catalyst dosage (g/L)</td>
<td>$X_2$</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>pH of the solution</td>
<td>$X_3$</td>
<td>3</td>
<td>9</td>
</tr>
</tbody>
</table>

**Table 1** | Ranges and experimental levels of the independent variables tested in the presence of TiO$_2$-T42 and TiO$_2$-P25 as catalysts
in Table 2 which shows the combinations of statistical studied variables (initial concentration of acetamiprid, catalyst concentration, initial pH of the medium and the type of catalyst).

The statistical calculations and multiple regressions were performed using MODDE 6.0 software. Regression analysis was performed to fit the response function (degradation yield) with the experimental data. The values of regression coefficients obtained are given in the Equations (3) and (4). The final regression equations describing the photo-degradation of acetamiprid after putting values of 10 statistically significant coefficients expressed as follows:

1. TiO₂-Degussa P25

\[ Y = 72.55 - 13.61X_1 + 3.38X_2 - 3.72X_3 - 8.26X_1^2 \\
- 1.15X_2^2 - 1.20X_3^2 - 1.64X_1X_2 - 0.63X_2X_3 \\
+ 2.83X_1X_3 \]  

\text{(3)}

2. TiO₂-T42

\[ Y = 58.71 - 7.90X_1 + 9.84X_2 - 2.54X_3 - 8.26X_1^2 \\
- 1.15X_2^2 - 1.20X_3^2 - 1.64X_1X_2 - 0.63X_2X_3 \\
+ 2.83X_1X_3 \]  

\text{(4)}

Effects and interactions analysis

The effects of different factors and their interactions are shown in Figure 4 based on the graphical analysis of the effects; it is found that the concentration of acetamiprid has the most significant effect (negative effect) on the performance of the pollutant photodegradation. The degradation rate of acetamiprid increases with decreasing the initial concentration of this pollutant and the most important values of degradation rate are obtained when using lower concentrations of acetamiprid. This can be explained by the greater availability of reactive species photogenerated (OH). For high concentration of contaminant, the constant rate can be attributed to the decrease of active sites due to the competition of the intermediate product of the reaction (Pramauro et al. 1993). The catalyst concentration has a significant influence on the performance degradation and thus automatically influences the disappearance rate of acetamiprid. It presents a positive effect and the photodegradation percentage increases with increasing the catalyst concentration. The pH of the solution has a negligible effect on the reaction rate.

The interaction between the pollutant concentration and pH of the solution is not significant. The interaction between the type of used catalyst and the various studied parameters (pH, C_{pollutant} and C_{TiO₂}) have no considerable effect on the degradation performance.
To determine the contribution of each effect and their interactions on the response, the Pareto diagram was used (Herrmann et al. 1993). 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:

\[
P_i = \frac{b_i^2}{\sum b_i^2} \times 100
\]

where \( b_i \) is the regression coefficients given in the Equations (3) and (4).

Figure 5 shows the Pareto chart where the effects of each factor on the pollutant degradation rates were compared. The factors that most influenced this response were the concentration and type of TiO\(_2\) and pollutant concentration.

According to Pareto chart analysis, it can be concluded that the initial concentration of the pollutant affects the performance of the pollutant disappearance reaction in the presence of Degussa TiO\(_2\)-P25 by 92% and by 72% for TiO\(_2\)-T42. The type of used catalyst influences greatly the degradation performance. From the histograms of Figure 4, it is concluded that the influence of the catalyst concentration is greater when using TiO\(_2\)-T42 (20%) while the degradation does not exceed 1% for TiO\(_2\)-P25. Although this type of catalyst is performant and more than 70% of photodegradation is reached after 5 h of UV irradiation. The pH of the solution has an effect of 3–4% and the combined interactions between the various parameters have only an effect of 3%.

According to the obtained results on the basis of the experimental design, for a better performance and a quick disappearance of acetamiprid concentration, it is better to work with a low pollutant concentration (2 mg/L), acid or natural pH of the solution and a high concentration of TiO\(_2\)-T42 catalyst. The objective of this study is to degrade the maximum of pollutant using a small amount of catalyst to minimize the treatment cost. Since the catalyst TiO\(_2\)-P25 has a good performance and almost similar to that obtained using the highest value of TiO\(_2\)-T42, as indicated by the results illustrated in Table 3, it is better to use this catalyst for the degradation of acetamiprid.

**Response surface analysis**

The graphical presentation of results provides a simple method of optimization of the treatment rate and identification of interactions between variables. Two-dimensional surfaces and contour plots are a graphical representation of regression equation for the optimization of reaction conditions and are the most useful approach in revealing the conditions of the reaction system. The results of the interactions between two independent variables and dependent variable are shown in Figures 6–8. Each curve represents an infinite number of combinations between two variables when the third variable is maintained at a constant level.
The interaction between the effect of the catalyst amount using TiO$_2$-P25 and the concentration of acetamiprid for different pH set at 3, 6 and 9 was shown in Figure 6. The degradation yield of this pollutant was significantly influenced when increasing the concentration of TiO$_2$ in the region of low pollutant concentrations. This corresponds probably to the maximum absorption of the pollutant by the photocatalyst. Increasing the initial concentration of the contaminant, results in a considerable fall of the degradation yield from 85% to 45%. The degradation yield response curves have the form of vertical palatal. For low concentrations of acetamiprid (<10 mg.L$^{-1}$), the increase in TiO$_2$ concentration from the minimum to the maximum values increase the degradation rate to over 20%. This rate decreases with increasing pH from 3 to 9. When the initial concentration of the pollutant increases, the catalyst concentration effect becomes less important on the photocatalytic process efficiency, as shown in the Figure 6. In the case of TiO$_2$-T42 catalyst, Figure 6(b) shows that increasing the concentration of TiO$_2$ results in a degradation yield increase in the range of concentration below 10 mg/L. The effect of the catalyst amount is always positive in the chosen concentration range. These results agree well with experimental study of Tassalit et al. (2011).

<table>
<thead>
<tr>
<th>$C_{catalyst}$ (g/L)</th>
<th>$Y_{T42}$ (%)</th>
<th>$Y_{P25}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>48.06</td>
<td>69.28</td>
</tr>
<tr>
<td>0.2</td>
<td>50.06</td>
<td>70.21</td>
</tr>
<tr>
<td>0.3</td>
<td>52.00</td>
<td>71.09</td>
</tr>
<tr>
<td>0.4</td>
<td>53.87</td>
<td>71.89</td>
</tr>
<tr>
<td>0.6</td>
<td>57.43</td>
<td>73.31</td>
</tr>
<tr>
<td>0.8</td>
<td>60.72</td>
<td>74.47</td>
</tr>
<tr>
<td>1.00</td>
<td>63.76</td>
<td>75.36</td>
</tr>
<tr>
<td>1.5</td>
<td>70.22</td>
<td>76.00</td>
</tr>
</tbody>
</table>

**Figure 6** | Effect of catalyst concentration (TiO$_2$ concentration) and acetamiprid initial concentration on the degradation yield of acetamiprid when the value of pH was kept constant at 3, 6 and 9. (a) The used catalyst is TiO$_2$-P25; (b) the used catalyst is TiO$_2$-T42.
Concentration of pollutant is constant

The interaction between the catalyst and the pH of the solution was carried out when the concentration of pollutant was fixed at 2, 11 and 20 mg/L. Figure 7(a) illustrates the interaction between these two parameters using the TiO$_2$-P25. The results show that the degradation rate increases from 45% to more than 65% with increasing the concentration of TiO$_2$ and increases slowly in the direction of increasing the pH in the case of initial pollutant concentrations situated between 2 and 11 g/L. However, this increase on the degradation rate is dependent on the pH and the catalyst concentration simultaneously. In the case of high concentrations of pollutant (20 mg/L), it reaches a limit of 50% when the pH becomes basic.

In the case of second catalyst (TiO$_2$-T42) as shown in Figure 7(b), the yield is higher compared to the first catalyst (TiO$_2$-P25) and it is more important in the sense of increasing the catalyst amount and decreasing the pH value. In the case of high concentrations of the pollutant, it can be concluded that the influence of these two parameters on the performance of the photodegradation is insignificant and the yield is low. These results are in accordance with those obtained by Laoufi et al. (2008) and Chekir et al. (2015) for the degradation of phenol and methylene blue.

Catalyst concentration is constant

The interaction between the acetamiprid concentration and the pH of the solution is presented in Figure 8(a) (catalyst: TiO$_2$-P25). The given results show that the degradation rate is influenced linearly when increasing the pH of the solution in the case of high concentrations of pollutant. The contours graphs also show that the interaction between these two variables is more important for the level +1 of acetamiprid concentrations, whereas it is negligible for the level -1. For low values of pollutant concentration, the interaction effect of pH and $C_{\text{pollutant}}$ present circular
responses which have a local maximum performance in certain pH and C\text{pollutant} range. Furthermore, the degradation yield decreases away from the center of the circle.

In the case of TiO2-T42, the yield of the photodegradation increases by decreasing the pH and the concentration of the pollutant. The highest rates are obtained with pH values below 7 and reach 70 to 75% when using C_{TiO2} = 0.1 g/L, 70 to 80% for C_{TiO2} = 0.8 g/L and 75 to 85% for C_{TiO2} = 1.5 g/L.

Optimization of the factors influencing the photodegradation of acetamiprid

The objective of this study is to determine the optimal value of the different variables of the model obtained by the experience plan and experimental analysis. Previous work has tended to focus on how to optimize the target parameters (Laoufi et al. 2008; Tassalit et al. 2011; Chekir et al. 2015) and ignore some aspects of the study compared to the reaction conditions, such as economic cost, ecological factor, further processing. Therefore, in this work, the degradation rate is not only obtained from the optimization of specific conditions of pH, concentration of TiO2 and the initial concentration of the pollutant but also other aspects are taken into consideration:

- Table 4 shows the degradation yields obtained by experiments and by using experimental design. The experimental performance recorded by varying the initial concentration of the pollutant between 2 and 20 mg/L are in agreement with the results obtained by experimental design. These degradation yields increase with decreasing pollutant concentration to reach 70% for lower concentrations of pollutants. The maximum pollutant degradation yield is the main goal of the optimization study taking into account the initial concentration of this pollutant. For example: 41.7% degradation yield of acetamiprid initial concentration equal to 20 mg/L presents 8.3 mg/L while 71.6% degradation...
yield of an initial concentration equal to 2 mg/L presents only 1.4 mg/L as shown in Table 4.

- Results in Table 4 show the comparison of degradation yield obtained by experimentation and experimental design using different concentrations of TiO2-P25 catalyst. The yield values calculated by the two methods are very similar with a slight variation in the direction of increasing catalyst concentration. The use of a small amount of catalyst to minimize the cost of the treatment is suitable.

- Histograms shown in Figure 9 illustrate the comparison between yields obtained by photocatalysis experiments and experimental design. From these results, it is concluded that the pollutant degradation yields obtained by these two methods are very similar. The optimal level of the pH is as close to neutral as possible; working in acidic or basic pH requires no readjustment after the treatment before discharging it directly into the aquatic environment.

On the basis of the studied model and constraints related to treatment by photocatalysis, numerical optimization was performed, taking into account the value of each response. Optimal conditions for a degradation rate of the pollutant as large as possible were found to be as follows:

- A pH value close to 6.
- Using the TiO2-P25 catalyst.
- The lowest TiO2 concentration possible since the influence of the concentration of TiO2 is negligible.

Under these optimal conditions, the model predicted a maximum degradation rate of over 70%.

Finally, statistical tests and diagrams obtained allow considering the quadratic model as a good model to represent the results of the experimental design. This model will allow making predictions in the field of photodegradation kinetics study.

Under the optimal conditions, the predictive and experimental results were 93.78% and 92.85%, respectively. The two results are very close, indicating the adequacy of the semi-empirical expression to optimize the photocatalytic degradation of the acetamiprid.

### CONCLUSION

This study shows the application of statistical design of experiments and response surface analysis for determining the optimal operation variables influencing the photocatalytic degradation process of acetamiprid. The main objective is to study the interaction between the various parameters influencing the photodegradation of this pollutant. Experimental design organizing the photocatalytic system permitted an evaluation of the influence of three parameters: pollutant concentration, pH, TiO2 amount and type. It seems that in the defined domain, neither the pH, nor the CAcetamiprid/catalyst/pH interactions has a real influence on the degradation process. This result could mean that the application of this process can be considered to be relatively free of strong restraints.

### Table 4 | Comparison of degradation yields obtained by experimental design and experiments

<table>
<thead>
<tr>
<th><em>CTiO2-P25 (g/L)</em></th>
<th><strong>C Acetamiprid (mg/L)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Y experimental design (%)</td>
<td>69.4</td>
</tr>
<tr>
<td>Final acetamiprid degradation (mg/L)</td>
<td>6.9</td>
</tr>
<tr>
<td>Y experiments (%)</td>
<td>68.6</td>
</tr>
<tr>
<td>Final acetamiprid degradation (mg/L)</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Operating conditions: *C_Pollutant = 10 mg/L, Free pH. **C_TiO2-P25 = 0.1 g/L, Free pH.
After optimization and assessment of the interaction of three independent variables on photocatalytic efficiencies, the optimization conditions in the experimental area chosen for this study, under UV irradiation in a hexagonal reactor, were as follows:

- The most influencing effect is the concentration of acetamiprid, followed by the catalyst effect and the effect of pH.
- The type of used catalyst has important influence on the photodegradation ratio of acetamiprid. The results show that TiO$_2$-P25 is more efficient than TiO$_2$-T42 for the degradation of acetamiprid. Increasing the concentration of TiO$_2$-T42 catalyst increases the degradation rate, but in the case of TiO$_2$-P25, it has no significant effect on the photodegradation of acetamiprid.
- No interaction effects were observed between the experimental factors (catalyst amount, pH and pollutant concentration). The interaction was observed only for a paired combination of these factors.

The resulting model allows the prediction of the pollutant degradation yields without resorting to experimentation which is a considerable economic gain.

REFERENCES


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