

MULTIVARIABLE ANALYSIS OF 2,4-D HERBICIDE PHOTOCATALYTIC DEGRADATION

ANÁLISIS MULTIVARIABLE DE LA DEGRADACIÓN FOTOCATALÍTICA DEL HERBICIDA 2,4-D

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ABSTRACT: The 2,4-D herbicide degradation of TiO₂ suspensions in tap water was evaluated under artificial irradiation conditions. The response surface methodology (RSM) was applied to evaluate the effect of variables such as: catalyst concentration, herbicide concentration, pH, and the volumetric flow on the photocatalytic reaction in two kinds of photoreactors: flat plate and tubular reactor. The response variable was the pesticide mineralization expressed as the total organic carbon (TOC) removal percentage of the herbicide after four hours of irradiation. For the treatment carried out in the tubular reactor, the four effects had the same significance on the degradation; whereas for the flat plate reactor, the catalyst concentration and the pH were more significant. The results obtained suggest that the RSM is a suitable technique for obtaining optimal operating parameters of a photocatalytic process with a specific reactor and within a determined range of study.

KEYWORDS: Heterogeneous photocatalysis; 2,4-D herbicide; response surface methodology

RESUMEN: La degradación del herbicida 2,4-D en suspensiones de TiO₂ en agua real fue evaluada bajo condiciones de irradiación artificial. El análisis multivariable de metodología de superficie de respuesta (MSR), se aplicó para evaluar el efecto de variables como la concentración de catalizador y pesticida, el pH y el caudal volumétrico sobre la reacción fotocatalítica en dos fotorreactores catalíticos: placa plana y tubular. La variable de respuesta fue la mineralización del pesticida expresada como porcentaje de degradación de carbono orgánico total (COT) después de cuatro horas de irradiación. Para el fotorreactor tubular, los cuatro factores tuvieron la misma significancia sobre la degradación, mientras que para el fotorreactor de placa plana inclinada, sólo la concentración de catalizador y el pH tuvieron significancia. La MSR fue una técnica adecuada para obtener parámetros de operación óptimos de un proceso fotocatalítico con un reactor específico y dentro de un rango de estudio determinado.

PALABRAS CLAVE: Fotocatálisis heterogénea, herbicida 2,4-D, metodología de superficie de respuesta

1. INTRODUCTION

Due to extensive sugar cane crops, a large amount of polluted effluents are produced by the washing of containers and equipment used for sprinkling pesticides. The improper handling of these wastes are not quantified; nonetheless, the environmental and public health hazards involved in these activities is well known [1,2].

Most pesticides are not treatable by biological systems and it is necessary to find more efficient and

environmentally-friendly choices. Heterogeneous photocatalysis has been proven to be a suitable alternative for treating these pollutants, not only on laboratory and model scales, but on the industrial scale [3-6].

Contrary to other redox processes, photocatalysis performance is determined by the kind of reactor to be used. Depending on the reactor, the operating variables can affect the efficacy of the heterogeneous photocatalysis in organic compounds degradation, as reported in previous works [7,8]. The multivariable

analysis has been used as a tool to evaluate the main effects of the operating variables and their interactions on the Photo-Fenton degradation of various pesticides [9]. This set of mathematical and statistical techniques allowed us to model and analyze situations which involved an interest variable influenced by the effects considered and to optimize this interest variable.

The response surface methodology (RSM) has been used in other studies related to the heterogeneous photocatalytic degradation of diverse substances, such as methylene blue, using a tubular reactor and a compound parabolic collector (CPC) reactor under artificial UV radiation [10].

In this research, the RSM was used to evaluate the incidence of the following variables on the photocatalytic mineralization of the commercial herbicide 2,4-D: catalyst load, $[\text{TiO}_2]$, pollutant initial concentration, $[\text{2,4-D}]$, initial pH, and the flow rate, Q . A statistical model of the process was obtained which satisfactorily described the behavior of the photocatalytic systems selected (tubular and flat plate bench-scale reactors) with artificial UV radiation. In addition, it was possible to find optimal operating values for each reactor with the RSM and the plots of the main effects. These results obtained were congruent with the ones reported in the literature.

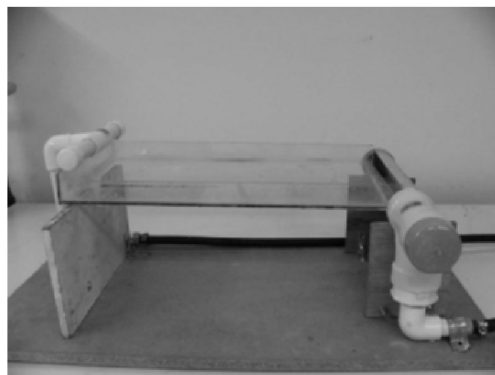
2. MATERIALS AND METHODS

2.1. Photocatalytic reactors

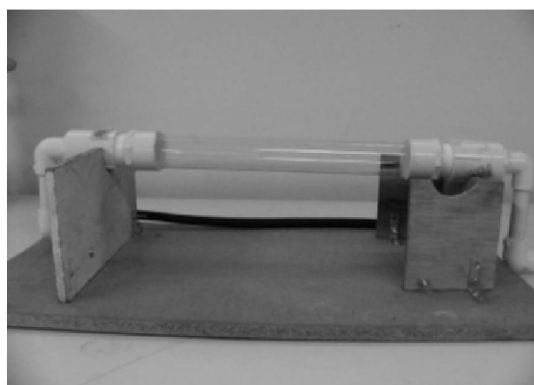
The catalyst used for the tests was titanium dioxide (Aeroxide® TiO_2 P25 from Degussa) as slurry. The pollutant selected was a commercial presentation of the 2,4-D herbicide (2,4-D Amina 4 from Proficol S.A®) and the solutions were prepared with tap water at different concentrations (30 - 60 ppm as TOC). The initial pH was adjusted at the beginning of each experimental run with 0.1 N solutions of NaOH (Merck) and HCl (Carlo Erba) after adding the solid catalyst.

The experimental tests were carried out at a flat plate photoreactor and at a tubular one. Each device had a recycling pump, a 5-liter storage tank, and a set of artificial UV lamps as recommended in previous studies [8,11]. Figure 1 shows the bench-scale photoreactors used for this study.

The artificial UV radiation was supplied by a set of 6 black Opalux® lamps with 25 W of nominal power each, and they were located 5 cm above the reactors. The incident radiation flux was measured with an ACADUS S85 UV radiometer within the 300 - 400 nm range and the average value was 20 W/m^2 .



(a)



(b)

Figure 1. Photocatalytic reactors. (a) Flat plate reactor, (b) tubular reactor

Table 1. Flat plate reactor specifications

Characteristic	Value
Length (m)	0.40
Width (m)	0.20
Height (m)	0.03
Average film thickness (m)	0.0015
Irradiated surface (m^2)	0.08
Operating flow rate (l/h)	120 - 230
Irradiated volume (l)	0.12
Total treated volume (l)	5.00

Table 2. Tubular reactor specifications

Characteristic	Value
Length (m)	0.36
Inside diameter (m)	0.038
Tube thickness (m)	0.002
Operating flow rate (l/h)	120 - 320
Irradiated volume (l)	0.342
Total treated volume (l)	5.00

Both systems operated in batch mode with recirculation. The main design and operating features are listed in Table 1 (flat plate) and Table 2 (tubular).

The oxygen dissolved in the slurry was supplied by the atmospheric air which interacted with the magnetically-stirred liquid suspension. The high turbulence in the storage-recycling tank provided by the magnetic stirrer ensured a perfect-mixture model. The oxygen concentration dissolved in the slurry was kept at an average value of 6.5 mg/l for the flat plate reactor and 5.0 mg/l for the tubular one. The average temperature observed during all the experiments was 33.5 °C.

2.2. Experimental design

For building a response surface plot, it is necessary to consider a full-composite experimental design which consists of a 2^k factorial design with central and star points, where *k* corresponds to the number of selected variables or main effects [12]. In this case, the response variable chosen was the TOC degradation of

the commercial pesticide and the levels of the main effects were established from the results obtained in previous works [13,14]. The main effects and their levels used for this experimental design were set as follows: catalyst load, 0.2 - 0.5 g/l; initial concentration of 2,4-D, 30 - 60 ppm; initial pH, 6 - 8; and flow rate, 140 - 230 l/h. The photocatalytic mineralization of the 2,4-D was estimated from the dissolved TOC removal after 4 hours of irradiation according to Eq. (1):

$$X = \frac{TOC_0 - TOC}{TOC_0} \times 100\% \tag{1}$$

where *TOC*₀ and *TOC* correspond to the initial and the final TOC concentration of the pollutant, respectively.

The coefficients of the linear and quadratic effects of the mathematical model obtained from the statistical analysis were estimated for each photoreactor using a multilinear regression analysis of minimal squares. The equations used for quantitatively describing the photocatalytic systems and the response surface plots were analyzed and interpreted with the Statgraphics® Trial Version 5.1 software.

3. RESULTS AND DISCUSSION

The results of the experimental runs are listed in Table 3 and the mathematical models of the 2,4-D mineralization obtained from these data are described by Eq. (2) for the flat plate reactor and Eq. (3) for the tubular one:

$$\begin{aligned} \%TOC\ removal &= 9,85(\pm 2,92) + 11,62(\pm 2,54) \times [TiO_2] - 2,7(\pm 2,54) \times [2,4 - D] - 21,23(\pm 2,54) \times pH + 1,86(\pm 2,54) \times Q \\ &+ 8,71(\pm 3,92) \times [TiO_2]^2 + 6,91(\pm 2,84) \times [TiO_2] \times pH - 8,88(\pm 2,84) \times [TiO_2] \times Q - 1,85(\pm 3,9) \times [2,4 - D]^2 \\ &+ 5,55(\pm 2,84) \times [2,4 - D] \times pH - 1,95(\pm 2,84) \times [2,4 - D] \times Q + 13,93(\pm 3,89) \times pH^2 + 2,11(\pm 2,84) \times pH \times Q - 3,99(\pm 3,9) \times Q^2 \end{aligned} \tag{2}$$

$$\begin{aligned} \%TOC\ removal &= 8,94(\pm 0,48) - 1,42(\pm 0,42) \times [TiO_2] - 1,29(\pm 0,42) \times [2,4 - D] - 2,25(\pm 0,42) \times pH + 1,13(\pm 0,42) \times Q \\ &- 2,34(\pm 0,65) \times [TiO_2]^2 + 0,56(\pm 0,47) \times [TiO_2] \times [2,4 - D] - 0,55(\pm 0,47) \times [TiO_2] \times pH - 0,48(\pm 0,47) \times [TiO_2] \times Q \\ &- 1,23(\pm 0,64) \times [2,4 - D]^2 - 0,41(\pm 0,47) \times [2,4 - D] \times pH - 0,16(\pm 0,47) \times [2,4 - D] \times Q - 1,88(\pm 0,64) \times pH^2 + 1,52(\pm 0,47) \times pH \times Q \\ &+ 2,44(\pm 0,64) \times Q^2 \end{aligned} \tag{3}$$

Table 3. Experimental results of the photocatalytic degradation of 2,4-D

Variables				Flat plate reactor		Tubular reactor	
A TiO ₂ (g/l)	B 2,4-D (ppm)	C pH	D Flow rate (l/h)	Observed value	Adjusted value	Observed value	Adjusted value
0.35	45.00	7.00	185	10.86	9.85	9.49	8.94
0.20	30.00	6.00	140	32.46	28.27	9.85	9.58
0.50	30.00	6.00	140	27.82	36.00	8.23	8.63

Variables				Flat plate reactor		Tubular reactor	
A TiO ₂ (g/l)	B 2,4-D (ppm)	C pH	D Flow rate (l/h)	Observed value	Adjusted value	Observed value	Adjusted value
0.20	60.00	6.00	140	8.59	15.06	7.88	8.31
0.50	60.00	6.00	140	42.69	36.61	8.95	8.47
0.20	30.00	8.00	140	4.16	8.26	6.66	6.77
0.50	30.00	8.00	140	3.75	-1.76	4.61	4.73
0.20	60.00	8.00	140	7.64	6.15	4.80	4.68
0.50	60.00	8.00	140	8.25	9.95	4.74	3.75
0.20	30.00	6.00	230	21.98	24.11	9.01	9.84
0.50	30.00	6.00	230	46.24	43.56	7.98	7.93
0.20	60.00	6.00	230	5.67	7.01	8.54	8.24
0.50	60.00	6.00	230	40.54	40.28	7.72	7.45
0.20	30.00	8.00	230	6.4	8.31	9.76	10.06
0.50	30.00	8.00	230	12.65	10.01	7.65	7.06
0.20	60.00	8.00	230	6.66	2.31	8.21	7.65
0.50	60.00	8.00	230	17.8	17.82	5.67	5.76
0.14	45.00	7.00	185	14.64	10.24	8.07	7.64
0.56	45.00	7.00	185	21.77	26.75	4.49	5.59
0.35	23.79	7.00	185	10.97	9.91	9.35	8.62
0.35	66.21	7.00	185	4.36	6.09	5.38	6.80
0.35	45.00	5.58	185	42.56	38.97	8.98	8.64
0.35	45.00	8.41	185	4.41	8.73	4.45	5.48
0.35	45.00	7.00	121	6.91	4.53	10.15	10.57
0.35	45.00	7.00	249	4.12	7.18	11.91	12.17
0.35	45.00	7.00	185	10.15	9.85	9.75	8.94

The positive coefficient of [TiO₂] in Eq. (2) indicates that an increase of the catalyst load favored the 2,4-D mineralization; whereas for the tubular reactor, Eq. (3), the opposite occurred. This behavior was observed because of a “clouding” effect of the solid catalyst in the tubular reactor which impairs the photon absorption, and therefore, the photocatalytic reaction performance. The optical thickness for the flat plate reactor is shorter than the tubular one’s; whereas the film thickness of the flat plate reactor is around 1 mm, the maximum optical pathway is 38 mm for the tubular one, corresponding to the inside diameter of the tube.

The initial pH effect has negative coefficients for both reactors; this means that the mineralization was faster in an acidic medium. It has been reported that the free hydroxyl radicals attack the aromatic ring preferably over the side chains at an acidic pH [15]. On the other hand, these results were congruent with the ones obtained in other related studies where the 2,4-D degraded better in an acidic medium [16-18].

The same occurred with the initial concentration of the pollutant. This effect presented negative coefficients

for both reactors. This means that the photocatalytic mineralization was faster at low concentrations of the substrate as is reported in the literature [19]. From these results, it can be considered that both variables, the initial pH and the initial pollutant concentration, affected the photocatalytic process regardless of the geometrical configuration and the optical properties of the photoreactor; and they may be related more to the chemical nature of the compound treated. Nonetheless, the effect of the initial concentration of pollutant on the photocatalytic degradation can be considered to be independent of the kind of photoreactor only when this substance does not change the optical properties of the slurry nor absorb UV photons within the photosensible range of the catalyst.

The effect of the flow rate was not significant in the case of the flat plate reactor; whereas for the tubular reactor, it had a positive influence. This can be explained by analyzing the flow regimes of both reactor geometries. It is known that the turbulent flow regime favors the mass transfer between phases in heterogeneous catalytic processes; therefore, Reynolds numbers (N_{Re}) greater than 15,000 are recommended for the case of tubular

photocatalytic reactors [20]. For the flat plate reactors, there are no known lower limits of N_{Re} that avoid these mass transfer limitations; however, it is documented that the turbulent regime appears with N_{Re} greater than 1000 [21]. In this analysis, the estimated N_{Re} for flat plate reactor was 1227.5 with a flow rate of 230 l/h; whereas the N_{Re} for the tubular reactor was 2,500 (estimated from the same flow rate). Both reactors operated in the turbulent regime, but the N_{Re} for the tubular reactor was very far from the suggested value of 15,000. The positive coefficient of Q in Eq. (3) clearly points to the fact that increasing the flow rate improves the photocatalytic mineralization of the 2,4-D; whereas, for the flat plate reactor, Eq. (2), this effect was not significant because the turbulence obtained was enough to keep the catalyst suspended and to avoid mass transfer limitations.

There was a synergic interaction between $[TiO_2]$ and the initial pH in Eq. (2); whereas for the tubular reactor, Eq. (3), this interaction was antagonistic. The effect was more significant for the tubular reactor due to the fact that the pH determines the surface charge of the solid catalyst. When the pH is lower than the zero charge point pH, pH_{zpc} , (6.25 for the Degussa P25), the catalyst surface become positively charged [3]. This favored the adsorption of anionic compounds into the catalyst surface, and therefore, the photocatalytic degradation rate. The antagonistic behavior for the tubular reactor was due to the “clouding” effect mentioned previously. The effect of pH on the particle size of catalyst also must be considered since the closer the pH gets to pH_{zpc} , the greater the particle size of the catalyst becomes [22]. This phenomenon can explain why the interaction between the pH and the catalyst load was more significant for the tubular reactor, since the mass transfer limitations could appear not only due to low flow rates but also larger particle sizes which favored the solid sedimentation.

The interaction between the 2,4-D concentration and the initial pH was also significant and it was related to the anionic character of the 2,4-D and its intermediates favored by the attack orientation of the oxidant species in an acidic medium, as mentioned before. This effect was more significant for the flat plate reactor, but it was synergic for both reactors. A simultaneous decrease of these two factors favors the 2,4-D mineralization regardless of the reactor geometry.

In both reactors, the initial pH was the main effect which most influenced the photocatalytic degradation since its coefficient was the largest in Eqs. (2) and (3).

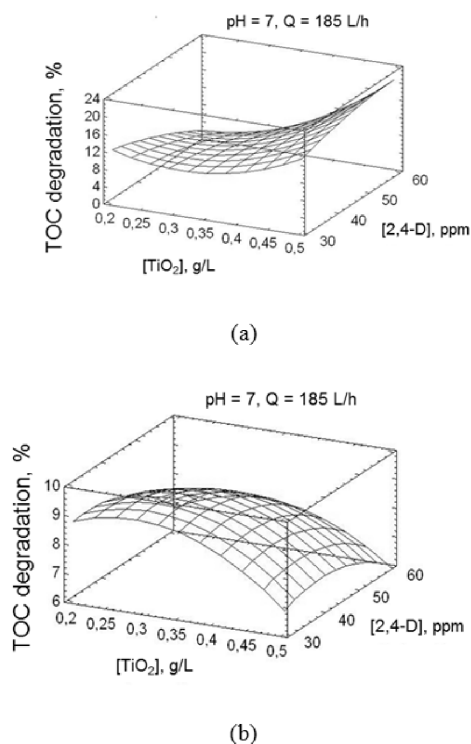


Figure 2. Response surfaces for the 2,4-D mineralization. (a) Flat plate reactor, (b) tubular reactor

Figure 2 shows the response surface plots obtained from Eqs. (2) and (3). The main effects $[TiO_2]$ and $[2,4-D]$ were assigned to x and y axes, respectively; and the TOC degradation percentage, as the response variable, to the z -axis perpendicular to the xy plane. The other main effects, such as the initial pH and the flow rate, were fixed at 7 and 185 l/h, respectively. For the flat plate reactor, the response surface plot was saddle-shaped with slight curvatures at the ends and it predicted a 20% TOC degradation at optimal conditions within the range studied. Nonetheless, the flat plate could handle higher catalyst loads for increasing the 2,4-D mineralization. For the tubular reactor, the plot obtained was tile-shaped and an optimum value for the catalyst load could be observed.

Table 4. Optimal values for the photoreactors

Variable	Flat plate	Tubular
pH	5.58	7.13
$[TiO_2]$ (g/l)	0.56	0.27
$[2,4-D]$ (ppm)	30.41	33.55
Q (l/h)	236.75	248.60
TOC degradation (%)	66.87	12.74

Table 4 shows the optimal conditions estimated from Eqs. (2) and (3). The optimal catalyst load for the tubular reactor was congruent with the values reported in a previous study where the RSM was used for obtaining optimal conditions in the photocatalytic degradation of methylene blue with the same photoreactor at similar conditions of UV irradiation and pH [10]. On the other hand, these results were also predicted by a mathematical approach that involved the maximization of the volumetric rate of photonic energy absorption (VREA) in tubular and CPC reactor geometries varying the catalyst loads [23].

Figure 3 shows the incidence of the main effects on the photocatalytic mineralization for each reactor. The greatest effects for the flat plate were the pH and the catalyst load; whereas for the tubular, the difference between the incidences of the effects was not significant. This was because of the low degradations achieved with the tubular reactor; whereas for the flat plate reactor, the difference between the degradations obtained was larger.

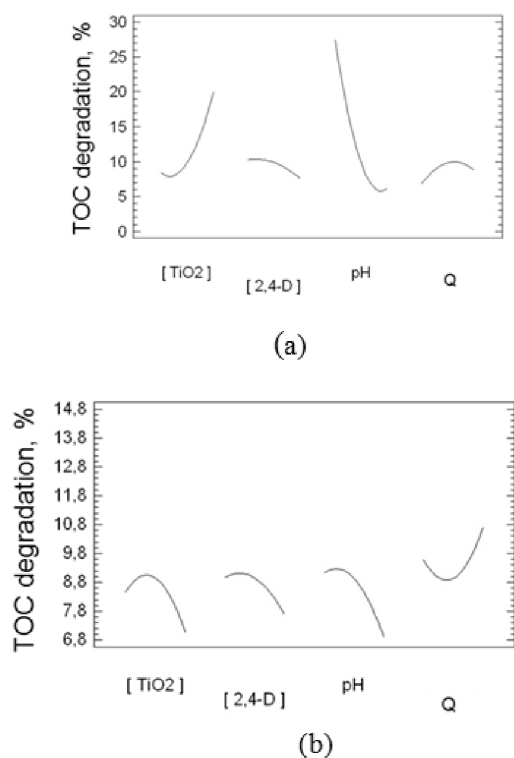


Figure 3. Main effects plot. (a) Flat plate reactor, (b) tubular reactor

4. CONCLUSIONS

It was possible to carry out a complete statistical analysis using a simple mathematical tool as the RSM. This allowed us to evaluate the effect of the main operating variables on the photocatalytic mineralization of the commercial pesticide 2,4-D in two bench-scale reactors. The greatest effects were the initial pH and the catalyst loads. An acidic pH favored the herbicide degradation, which was a result congruent with the ones reported in the literature. Regarding the catalyst load, an increase affected the 2,4-D mineralization positively in the flat plate case; whereas for the tubular reactor, the behavior observed was the opposite. This was due to the different optical properties and geometries of the photoreactors considered. The catalyst load that maximized the mineralization of the herbicide (0.27 g/l) in the tubular reactor was similar to the ones that were mathematically and experimentally estimated in previous works under similar conditions.

The effects of the initial pH and the initial pollutant concentration were independent of the kind of photocatalytic reactor, whereas the catalyst load and the flow rate were not.

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