Modeling and optimization of photo-Fenton degradation of 2,4-D using ferrioxalate complex and response surface methodology (RSM)

Agustina V. Schenone [a], Leandro O. Conte [a], María A. Botta [b], Orlando M. Alfano [a], [*]

[a] Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Universidad Nacional del Litoral (UNL), Ruta Nacional N° 168, 3000, Santa Fe, Argentina
[b] Facultad de Bioquímica y Ciencias Biológicas, Universidad Nacional del Litoral (UNL), Santa Fe, Argentina

ABSTRACT

This study reports the application of the photo-Fenton process for the degradation of the herbicide 2,4-dichlorophenoxyacetic (2,4-D). The objective of this research was the evaluation of the procedure at natural pH (pH = 5) using the ferrioxalate complex as iron source at two incident irradiation levels. For this purpose, different combinations of attenuation filters from a solar simulator were tested. Since the process depends on several parameters, the influence of the temperature (T) and peroxide to 2,4-D initial concentration ratio (R) were investigated and optimized by the application of a three-level factorial experimental design combined with the Response Surface Methodology (RSM). The significance of models and their coefficients were assessed with the analysis of variance (ANOVA). The found optimal conditions were: $T = 50\ °C$ and $R = 46.3$ and $T = 41.53\ °C$ and $R = 41.46$, achieving experimental conversions of 91.4 and 95.9% for the low and high radiation levels, respectively. The obtained results are very close to the values predicted by the quadratic models (93.8 and 100.0%). It was concluded that temperature and hydrogen peroxyde concentration have different influences on the response factor depending on the incident irradiation level. It was demonstrated that RSM is a good tool for studying the effects of different variables and their interactions on 2,4-D conversion percentage in the photo-Fenton process. In addition, solution acute toxicity was also evaluated during the treatments under optimum conditions, since some degradation by-products of 2,4-D can be more toxic than the parent compound. For this purpose, the commonly used Microtox® test based on the bacteria *Vibrio fischeri* was employed.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The great extension of the cultivated area in Argentina, mainly soybeans, wheat and maize, has led to an increase in the use of pesticides. Glyphosate, 2,4-dichlorophenoxyacetic acid (2,4-D) and atrazine are the most utilized herbicides. 2,4-D is an auxin-like herbicide most commonly used for the control of broadleaf weed species and is widely applied because of its low cost and high efficiency. However, the knowledge of the toxicity of this compound (EPA, 2005), has given rise to public concern and to the inclusion of 2,4-D in several legislations. Because of their application in crops, pesticides can enter watercourses from different practices, such as: wastewater from food processing industries and from plants producing pesticides, washing water from containers and spraying equipment. In Argentina, the triple washing technique is used to treat empty chemical containers (Allevato and Pórfido, 2002; Casafe, 2004). The resulting water contains residues of the agrochemical and needs to be treated properly. Furthermore, due to its relative high solubility in water, 2,4-D was detected in river and drainage water (Laganà et al., 2002). For these reasons, it is necessary to develop methods for the reduction or elimination of agrochemicals from water resources.

Biological systems are generally preferred due to their low cost and because they are environmentally friendly, but pesticide and herbicide elimination efficiencies are not always possible or satisfactory. On the other hand, advanced oxidation processes (AOPs) are effective remediation methods based on the generation of reactive species, such as hydroxyl radicals (HO•), which react rapidly and with low selectivity with a variety of toxic and nonbiodegradable compounds, yielding CO_2 and inorganic ions (Pignatello et al., 2006). Among the AOPs, processes using Fenton type reagent are relatively inexpensive and the oxidizing agent is

easily handled. The combination of the Fenton process with UV–Visible radiation results in photo-Fenton reaction, which has several advantages. Some of them are the increase of degradation rates and the possibility of using alternative energy sources, such as solar radiation. Thus, the photo-Fenton process has gained attention due to the possibility of reducing the demand of energy (Bauer and Fallmann, 1997; Bauer et al., 1999; Malato et al., 2002). In addition, this AOP has been successfully applied in order to degrade several residues of agrochemicals present in liquid wastes (Ahmed et al., 2011; Al Momani et al., 2007; Carra et al., 2013; Hincapié Pérez et al., 2006; Huston and Pignatello, 1999; Ikehata and Gamma El-Din, 2006; Janin et al., 2013; Oliveira et al., 2014; Zapata et al., 2010).

Generally, ferric sulfate is employed as iron source in photo-Fenton process and the reaction is commonly carried out at pH 2.8. In this condition, photo-active iron species predominate. At higher values, the concentration of the catalyst decreases as a consequence of the precipitation of Fe(III) as hydroxides (Malato et al., 2009; Pignatello et al., 2006). On the other hand, the need for acidification could be circumvented with the presence of complexing agents. The resulting iron complexes typically have higher molar absorption coefficients in the UV and visible regions than the aqueous complexes (Pignatello et al., 2006). Nogueira et al. (2005) studied the influence of ferrioxalate as iron source on the degradation efficiency of several organic compounds. This ferric complex strongly absorbs up to 550 nm, allowing that a higher portion of solar radiation be absorbed by the photo-Fenton process. Furthermore, Conte et al. (2014) investigated the degradation of 2,4-D employing different iron sources, demonstrating the effectiveness of the process by employing ferrioxalate complexes under conditions of pH close to neutrality.

Photo-Fenton treatment is affected by several parameters such as the temperature, iron concentration, hydrogen peroxide concentration and pH of the reaction medium. Moreover, operating conditions need to be carefully determined since they are specific for each contaminant. The aim of the present investigation was to optimize the procedure to obtain the maximum conversion and mineralization of 2,4-D in aqueous medium. It is known that the drawback of the traditional photo-Fenton process is the operating pH at 2.8. Hence, the objective of this research was the evaluation of the procedure at pH = 5, which is the natural value of 2,4-D active compound at the concentration under study, thus reducing the operating costs. In order to accomplish this, ferrioxalate complex was employed as iron source. It is a photoactive complex capable of expanding the usage of the solar spectrum range, which improves the oxidation efficiency of the process. Furthermore, it allows the use of iron concentrations below the discharge limit, avoiding its subsequent removal.

Another way of reducing the degradation process costs is to use solar technology. As a preliminary step to the study of the system in a solar pilot plant reactor, an artificial sunlight source was applied to analyze the viability of the process, considering the solar radiation in Santa Fe city (31°39′ S, 60°43′ W, 25 m above sea level), Argentina. Thus, two types of incident irradiation levels of a solar simulator were tested by different combinations of attenuation filters in order to match the output to the solar spectrum.

In addition, the effect of temperature on the homogeneous photo-Fenton degradation was investigated since it is a parameter which influences the kinetic of the reaction, generally causing an increase in the reaction rate at higher temperatures. Furthermore, the hydrogen peroxide concentration effect was taken into account because, according to the reaction temperature, different amounts of oxidizing agent could be consumed to reach the same level of 2,4-D conversion.

Three level factorial design and response surface methodology (RSM) were proposed to study the influence of two factors (temperature and H_2O_2 concentration) as well as their interactive influence. Several experimental designs have been used for photo-Fenton optimization in different applications (Ay et al., 2009; Colombo et al., 2013; Dopar et al., 2011; Prieto-Rodriguez et al., 2013; Trovó et al., 2013). Finally, experiments were performed at the optimized found conditions for each filter combination, in order to evaluate the results obtained with the predicted model.

2. Experimental

2.1. Chemicals and reagents

Analytical reagent-grade chemicals and ultrapure water were used. 2,4-dichlorophenoxiacetic acid ($C_8H_6Cl_2O_3$, 98%) was purchased from Aldrich. Potassium ferrioxalate solution was prepared according to the methodology described by Murov et al. (1993), using potassium oxalate monohydrate (Carlo Erba, 99.5%) and $FeCl_3.6H_2O$ (Merck). Hydrogen peroxide (H_2O_2, 30%, reagent-grade), sodium carbonate and sodium bicarbonate were obtained from Cicarelli. NaOH (Cicarelli) was employed for pH adjustment and HPLC grade methanol (Sintorgan) was used to stop the Fenton reaction. Acetonitrile and anhydrous acetic acid were purchased from Sintorgan and Anedra, respectively.

2.2. Experimental procedure

Experiments were performed in a lab-scale flat plate reactor of borosilicate glass with external recycle. A solar simulator (Oriel 9600) was used as the irradiation source. The storage tank features a pH-meter, a thermometer and a liquid sample valve. The experimental devise was connected to a thermostatic bath to ensure constant temperature during the reaction and a centrifugal pump to achieve a high recirculation flow rate and good mixing conditions. The total volume of the treated solution was 3.00 L, while the irradiated volume of the reactor was 69.94×10^{-3} L.

The next steps were followed to carry out the experimental runs: first, the temperature was set at the specified working condition. Then, the solutions of ferric complex ($C^0_{Fe^{3+}} = 0.054$ mmol L^{-1}) and 2,4-D ($C^0_{2,4-D} = 0.136$ mmol L^{-1}) were added to the reactor, followed by the pH adjustment to 5 using a concentrated NaOH solution. Next, the first sample was taken (defining the reaction time equal to zero) after the addition of the hydrogen peroxide to the storage tank. Finally, the lamp shutter was removed to start the run. During the photo-Fenton reaction, samples were withdrawn at different times.

The solar simulator was equipped with an ozone free xenon lamp of 150 W, which produces a collimated beam of 0.033 m diameter. In order to simulate various solar conditions, it is feasible to couple different filters to the device, such as air, liquid and attenuation filters, and redirect the beam with a set of reflecting mirrors. In the present study, two filter combinations were analyzed: (a) water filter, air mass filter AM0 and air mass filter AM1.5 Direct, and (b) water filter, air mass filter AM0 and air mass filter AM1 Direct, which will be called F-1.5D and F-1D, respectively. The selection was made regarding the radiation level in a pilot plant-solar reactor quantified in previous essays, considering the period of maximum incident solar radiation (noon) for clear summer days and standard relative humidity conditions (50—60%), in Santa Fe city, Argentina (Conte et al., 2012).

Radiation fluxes were measured with a modular USB spectrometer (USB2000, Ocean Optics). From the experimental results, the local radiation fluxes averaged over the reactor window (q_W) were determined: $q_W = 3.64 \times 10^{-8}$ E cm^{-2} s^{-1} and $q_W = 6.58 \times 10^{-8}$ E cm^{-2} s^{-1}, for F-1.5D and F-1D, respectively, in

the wavelength range 305–435 nm.

2.3. Analytical determinations

The concentrations of 2,4-D and 2,4-dichlorofenol (2,4-DCP) were monitored by HPLC (Waters) equipped with a dual UV–Vis detector. The maximum global errors were 0.16 and 0.09 mg L^{-1}, respectively (Miller and Miller, 2002). A LC-18 Supelcosil reverse phase column (Supelco) was employed and detection was done at 236 and 280 nm. A mixture of ultrapure water, acetonitrile and anhydrous acetic acid (49:50:1) was applied as the mobile phase, with a flow rate of 1.0 mL min^{-1}. The concentration of oxalate was determined by ion exchange chromatography, using a Water equipment and IonPac AS4A-SC analytical column. The eluent was a mixture of sodium carbonate and sodium bicarbonate (1:8), flowing at 0.7 mL min^{-1}. A modified iodometric technique was applied to determine hydrogen peroxide at 350 nm and the content of ferrous ions was quantified by absorbance measurements of the formed complex by means of 1,10-phenanthroline at 510 nm. Total organic carbon content was measured employing a Shimadzu TOC-5000A analyzer.

2.4. Toxicity assay

Microtox Model 500 Toxicity Analyser (Strategic Diagnostic Inc.) was used in order to carry out the acute bioluminescence assay and evaluate the toxicity of the samples during the photo-Fenton process. Toxicity was measured as the percentage of inhibition of light emission of the bacteria strain *Vibrio fischeri* NRRL-B-11177, after 5 min of incubation (I %). Sample pH was adjusted between 6 and 8 and hydrogen peroxide was removed prior to analysis using catalase (1500 mg L^{-1} of >2000 U mg^{-1} bovine liver) acquired from Fluka.

2.5. Experimental design

A three level factorial experimental design was employed to optimize the reaction conditions. The effect of the variables: hydrogen peroxide to 2,4-D initial concentration ratio (R) and temperature (T) on the herbicide conversion was assessed by using the RSM (Montgomery, 2005). For two variables and three levels, 12 experiments were performed including four central points in order to give statistical consistency to the mathematical model. The applied ranges of process parameters were: 25–50 °C and 7–50 for T and R, respectively. The percentage of 2,4-D conversion after 180 min of photo-Fenton reaction was chosen as the response factor. The same procedure was employed to each of the filter combinations: F-1.5D and F-1D, giving a total of 24 experiments.

The temperature range was chosen due to the fact that the potential samples would be at room temperature (25 °C) and could reach almost 50 °C in the case that the sample were treated in a pilot-plant solar reactor (Conte et al., 2012; Farias et al., 2009). The stoichiometric H_2O_2 to 2,4-D initial concentration ratio required for the 2,4-D complete mineralization is 7. However, Pignatello et al. (1992) have demonstrated that better conversion levels are reached with higher R values in a shorter time.

The RSM is useful for evaluating the relationship between the experimental factors and the measured response according to one or more selected criteria (Montgomery, 2005; Myers and Montgomery, 2002). In the 3^k design is common to denote low, intermediate and high levels as −1, 0 y +1, respectively. Each level of a factor is combined in the different experiments with all levels of the other factors. Once the results are obtained for the optimization experiments, a mathematical model is created to describe the relationship between the response and the studied factors. The

behavior of the system is represented by the following quadratic equation:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \varepsilon \qquad (1)$$

in which Y is the response (dependent variable), X_1 and X_2 the studied factors (R and T, respectively), β_i the model coefficients and ε the experimental error.

3. Results and discussion

All the experiments were performed with the same initial 2,4-D concentration ($C_{2,4-D}^0 = 0.136$ mmol L^{-1}, 30 mg L^{-1}). The herbicide concentration corresponds to the obtained quantity after the triple washing technique, which is widely used to treat empty chemical containers (Allevato and Pórfido, 2002; Casafe, 2004). The initial iron concentration was 0.054 mmol L^{-1} (3 mg L^{-1}); therefore, the treated effluent could be discharged to a surface watercourse (Res. N° 1089/82) or redirected to a biological treatment. The pH = 5 was selected because it is close to the value of an effluent with 30 mg L^{-1} of 2,4-D. Moreover, when the process is complete, the samples can be discharged without the need to modify this value, as it is in the case of the processes carried out at pH = 2.8. An oxalate/iron molar ratio of 10:1 was chosen in order to avoid iron compounds precipitation and to keep them in solution along the photo-Fenton process at pH = 5. Consequently, the initial oxalate ion concentration was 0.54 mmol L^{-1}. Note that the speciation of the complexes is influenced by the system pH value. Under these conditions, the dominant ferrioxalate complex is $Fe^{III}(C_2O_4)_3^{3-}$, although $Fe^{III}(C_2O_4)_2^{-}$ is also present. Compared with the aqueous complexes, these oxalate complexes have higher molar radiation absorption coefficients in the UV–Vis region (Conte et al., 2014; Pignatello et al., 2006).

3.1. Process optimization under low radiation level (F-1.5D)

Previous publications have demonstrated that the photo-Fenton process is highly influenced by some operating variables, such as temperature and hydrogen peroxide to pollutant initial concentration ratio (Benzaquen et al., 2014; Conte et al., 2012, 2014; Farias et al., 2009). Therefore, the RSM was applied in order to find the optimal conditions that maximizes the 2,4-D conversion. For this purpose, two solar simulator filter combinations were studied. In this section, the low radiation level ($q_W = 3.64 \times 10^{-8}$ E cm^{-2} s^{-1}) will be analyzed.

A two factor with three levels design was carried out. The design consisted of 12 experiments with independent variables combinations in the following ranges: R between 7 and 50, temperature from 25 to 50 °C, including three central points replicates (Table 1). All experiments were performed in random order to avoid introducing a bias on the measurements produced by uncontrolled (or external) factors.

After removing the outliers (Table 1) by applying the Cook's test (Myers and Montgomery, 2002), the herbicide conversions after 180 min for the experiments were fitted to a quadratic model (**Q1**). Multiple regression analysis was used to calculate the model coefficients and the analysis of variance (ANOVA) with 95% confidence level to validate them, resulting in the following expression:

$$X_{180}^{2,4-D} = -49.771 + 2.015T + 3.435R - 0.032T \times R - 0.020R^2 \qquad (2)$$

in which $X_{180}^{2,4-D}$ is the 2,4-D conversion at 180 min of photo-Fenton reaction.

Table 1
Results of 2,4-D conversion percentage at 180 min. 3^k factorial design with 2 independent variables for F-1.5D and F-1D.

Run	T (°C)[a,b]	R[b]	$X_{180}^{2,4-D}$[c]	
			F1.5D	F1D
1	35 (0)	7 (−1)	36.9	78.3
2	50 (+1)	50 (+1)	95.6	100
3	50 (+1)	7 (−1)	63.8	86
4	35 (0)	28.5 (0)	72.4	94.1
5	25 (−1)	50 (+1)	83.0	96.5
6	25 (−1)	28.5 (0)	73.0	92.6
7	50 (+1)	28.5 (0)	83.4	100
8	35 (0)	28.5 (0)	71.8	93.9
9	35 (0)	28.5 (0)	72.9	94.5
10	35 (0)	50 (+1)	84.8	100
11	25 (−1)	7 (−1)	16.4	53.7
12	35 (0)	28.5 (0)	70.0	94.8

[a] The calculated value for the T central point by the design was 37.5 °C, but it was set at 35 °C because of operational issues.
[b] Codified values for variables in parentheses.
[c] Outliers: F1.5D: #2, F1D: #5 and 11.

The ANOVA results are shown in Table 2. The p value represents the probability that F occurred due to noise; the smaller the value of p, the more significant is the corresponding parameter in the model (Montgomery, 2005). According to the high calculated values of F (198.41) and low values of p (<0.0001), **Q1** model can be characterized as statistically significant. As can be appreciated, the model terms are also significant ($p < 0.05$), while the lack of fit is non-significant ($p = 0.0704$). T^2 term was not taken into account because it was non-significant. Furthermore, the model was selected due to the low standard deviation (2.55) and the R^2 and adjusted R^2 satisfactory values (0.9925 and 0.9875, respectively). These results and the information on the model performance given in Supplementary material (Fig. S1) indicate that **Q1** properly describes the system behavior in the studied conditions.

The significance and contribution of each process parameter was evaluated. For this purpose, F and p values for each linear, interaction or quadratic model components were compared. The results presented in Table 2 indicate that the most important term is R ($F = 518.37$), followed by the other linear term, T, the interaction ($T \times R$) and finally the quadratic term corresponding to R^2. Moreover, the signs of these terms in Equation (2) provide physical significance to the obtained results. For instance, larger T values would result in a higher herbicide conversion, demonstrating the importance of its role in the photo-Fenton reaction. On the other hand, the influence of the quadratic term is negative due to the fact that an excess of H_2O_2 produces a scavenging effect, reducing the

catalytic activity (see Equation (3)) (Pignatello et al., 2006).

$$H_2O_2 + OH^\bullet \rightarrow H_2O + HO_2^\bullet \tag{3}$$

The interaction plot between T and R is presented in Fig. 1. As can be observed, keeping the temperature at 25 °C and varying the $H_2O_2/2,4$-D ratio, a larger amplitude of 2,4-D conversion is obtained (difference of 67% in the 2,4-D conversion) in comparison with the produced effect when the temperature is set at 50 °C (difference of 32% in the 2,4-D conversion). On the other hand, a high operating temperature would compensate a lower hydrogen peroxide concentration, which is important from an economical point of view. Accordingly, at $R = 7$ the difference in the conversion is 47% when the temperature is varied between 25 and 50 °C.

The overall effect can be observed in Fig. 2A, which shows the response surface that represents the **Q1** model for the photo-Fenton reaction with F-1.5D (Equation (2)). According to the shape of the surface, the $H_2O_2/2,4$-D ratio is more important when the low radiation level is used in the process at 25 °C. Furthermore, experimental conversion results are in accordance with the model predicted by applying multiple regression analysis.

The highest herbicide conversion (95.6%) was achieved for run #2 ($R = 50$ and $T = 50$ °C) after 180 min of reaction. On the other hand, the minimum conversion was 16.4%, obtained when the lowest values of each parameter, i.e. $T = 25$ °C and $R = 7$ (run #11), were used. At this T, an important increment of the conversion is observed when R is increased (83.0% in run #5). The same can be seen when R is kept at its lowest value and T is raised (63.8% in run #3), but the percentage of conversion is lower. This is in accordance with the F values gathered by the ANOVA of the model for R and T (518.37 and 153.51, respectively), showing the higher influence of the former in the model predictions.

The total organic carbon (TOC) was monitored as well. The lowest TOC after 180 min of operation was observed in run #2, with a final value of 9.86 mg L^{-1}, disregarding the contribution of oxalate. Furthermore, 2,4-DCP (principal reaction intermediate) was detected in this run at $t = 30$ min. The concentration of this organic compound also decreased up to 0.62 mg L^{-1} at the end of the reaction.

The optimal conditions for the highest 2,4-D conversion, predicted by **Q1**, are found to be: $T = 50$ °C and $R = 46.3$. The criteria which were followed for the optimization consisted on maximizing the response and, in the case of R and T, the goal was to maintain these factors in the range of study (7−50 and 25−50 °C, respectively). Under these conditions, the herbicide conversion predicted

Table 2
ANOVA results for **Q1** model.

Factors	Statistics				
	SS[a]	df[b]	MS[c]	F	p[d]
Model	5175.43	4	1293.86	198.41	<0.0001
T	1001.07	1	1001.07	153.51	<0.0001
R	3380.35	1	3380.35	518.37	<0.0001
$T \times R$	295.81	1	295.81	45.36	0.0005
R^2	229.67	1	229.67	35.22	0.0010
Residual	39.13	6	6.52		
Lack of fit	34.32	3	11.44	7.14	0.0704
Pure error	4.81	3	1.6		
Total	5214.56	10			

[a] Sum of squares.
[b] Degree of freedom.
[c] Mean square.
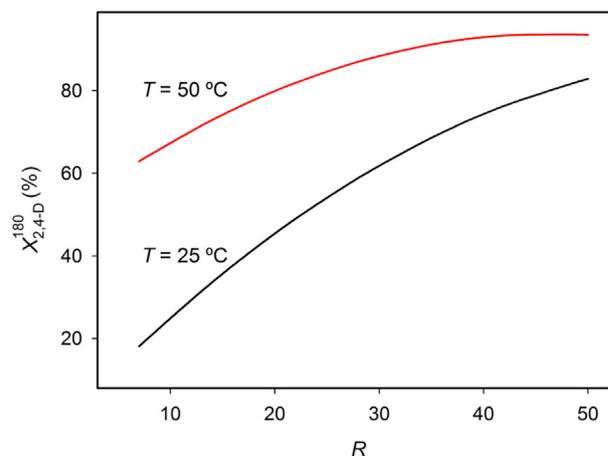[d] Considered significant when $p < 0.05$.

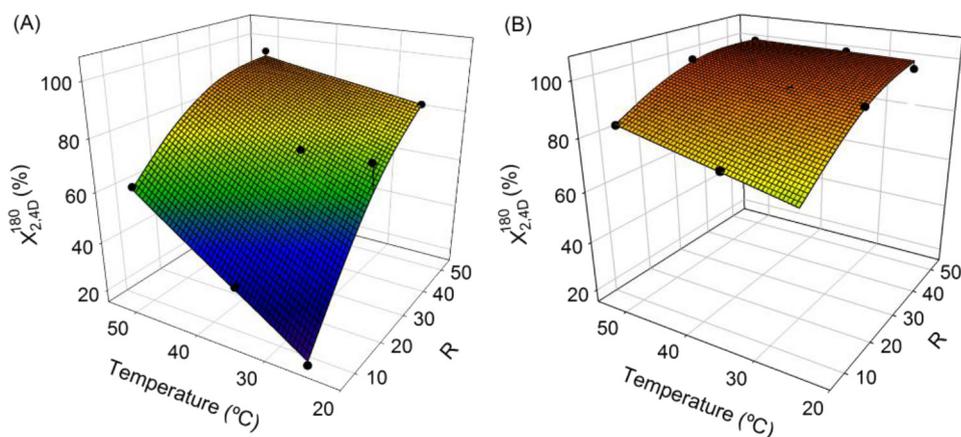**Fig. 1.** Interaction plot between T and R for **Q1** model.

Fig. 2. Response surface and experimental values (circles) for 2,4-D conversions after 180 min *versus* reaction temperature and H_2O_2/2,4-D inicial molar ratio. (A) F-1.5D and (B) F-1D.

by the model was 93.8%. In order to corroborate this value, an additional experiment was carried out under optimal conditions. Results are shown in a subsequent section of the paper.

3.2. Process optimization under high radiation level (F-1D)

In order to evaluate the influence of two variables (T and R) and to optimize 2,4-D conversion through the application of the photo-Fenton process with the F-1D filter combination ($q_W = 3.64 \times 10^{-8}$ E cm^{-2} s^{-1}), the same methodology employed above for F-1.5D was used. The application of multiple regression analysis on the experimental conditions and the chosen response described in Table 1, resulted in the quadratic model **Q2**:

$$X_{180}^{2,4-D} = +48.163 + 0.628T + 1.641R - 0.012T \times R - 0.013R^2$$

(4)

The ANOVA indicated that **Q2** model is significant ($p < 0.0001$), while the lack of fit is non-significant ($p = 0.0716$). The results are displayed in Table 3.

In addition, high regression coefficients were obtained: $R^2 = 0.9932$ and adjusted $R^2 = 0.9878$, as well as a low standard deviation value: 0.75. As in the previous section, the term T^2 resulted non-significant; thus, it was not taken into account in the final model.

Given the results summarized in Table 3, the terms of the model are significant in the following order: lineal R term, quadratic R

term, lineal T term and finally, the interaction between the two studied variable terms. All of them have a p value lower than 0.05 and a high F value. The impact of each independent variable in the oxidation process is attributable directly to its coefficient. From Equation (4), the positive contribution of T and R is observed, while the negative coefficient value of R^2 suggests that higher H_2O_2 concentrations reduce the herbicide conversion, such as in **Q1** model. Fig. S2 in Supplementary Material also demonstrates the good performance of the **Q2** model.

Predicted and experimental results for photo-Fenton reaction using the high radiation level is presented in Fig. 2B, which shows the 3D plot of 2,4-D conversion at $t = 180$ min as a function of R and T. Notice that higher conversions are obtained in comparison with those achieved with the F-1.5D filter combination. Moreover, the influence of R in **Q2** model is considered moderate, meanwhile the effect of T is lower.

Fig. 3 displays the interaction plot between T and R. In this case, when R is kept constant at 50, the change in temperature does not modify the 2,4-D conversion significantly. On the other hand, at the lowest R value ($R = 7$), a moderate effect is observed when the temperature is varied, increasing the conversion when going from 25 to 50° C (difference of 32% in the 2,4-D conversion).

In this case, almost the total 2,4-D conversion is achieved in three experiments (runs #2, 7 and 10 from Table 1). Furthermore, nearly complete conversion of the main reaction intermediate, 2,4-

Table 3
ANOVA results for **Q2** model.

Factors	Statistics				
	SS[a]	df[b]	MS[c]	F	p[d]
Model	415.17	4	103.79	183.50	<0.0001
T	45.06	1	45.06	79.67	0.0003
R	288.58	1	288.58	510.19	<0.0001
T × R	14.82	1	14.82	26.20	0.0037
R^2	68.09	1	68.09	120.39	0.0001
Residual	2.83	5	0.57		
Lack of fit	2.34	2	1.17	7.20	0.0716
Pure error	0.49	3	0.16		
Total	418.00	9			

[a] Sum of squares.
[b] Degree of freedom.
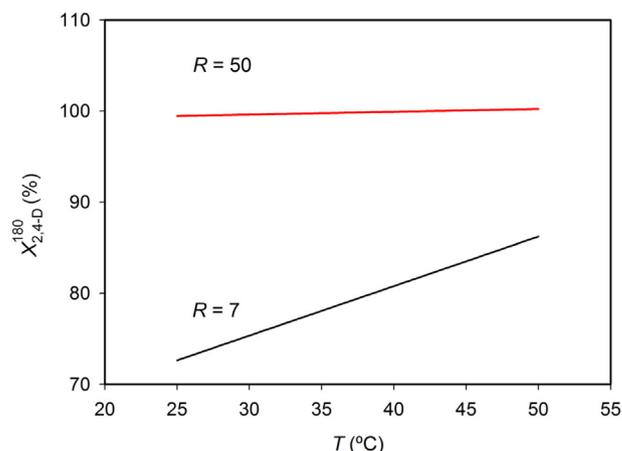[c] Mean square.
[d] Considered significant when $p < 0.05$.

Fig. 3. Interaction plot between T and R for **Q2** model.

DCP, was observed when the operating conditions were $R = 50$ and $T = 50\,°C$ (data not shown). In addition, TOC values at $t = 180$ min were 6.88 and 6.84 mg L^{-1}, disregarding the contribution of oxalate, under the operating conditions $R = 50$ and $T = 50\,°C$ and $R = 28.5$ and $T = 50\,°C$, respectively. These TOC values were the lowest for all the experiments.

The experimental conditions corresponding to the maximum 2,4-D conversion predicted by **Q2**, are found to be $T = 41.53\,°C$ and $R = 41.46$. As in the previous case for **Q1**, the criteria were to maximize the herbicide conversion as well as to maintain T and R in the evaluated range. The predicted result ($X_{180}^{2,4-D} = 100.0\%$) is checked and the results are shown in the following section.

3.3. Herbicide conversion under optimized conditions

The predicted values obtained in the multivariate optimization were confirmed for each filter combination. As previously explained, the aim was to maximize the herbicide conversion as well as to maintain T and R in the evaluated range. Accordingly, 2,4-D experimental conversions of 91.4 and 95.9% were obtained for F-1.5D and F-1D, respectively. Both results are very close to the values predicted by **Q1** and **Q2** models (93.8 and 100.0%), demonstrating satisfactory performances. Fig. 4 shows the evolution of 2,4-D, 2,4-DCP and H$_2$O$_2$ as a function of time for both optimized conditions,

F-1.5D and F-1D, during photo-Fenton experiments.

Comparing the results of both processes, once again it can be seen that F-1D is more effective for the treatment of aqueous samples with 2,4-D, which is in part due to the difference in the local radiation fluxes averaged over the reactor window. Furthermore, lower values of T and R were obtained as optimum in the higher radiation level, confirming that the influence of the parameters T and R is more pronounced in the case of F-1.5D.

The results showed that experimental design strategy and response surface methodology can be successfully employed to model the relationship between photo-Fenton variables and 2,4-D conversion. Furthermore, the optimum parameter values were found and corroborated.

Because of the possibility of transient formation of more toxic pollutants during AOP application, a toxicity test was carried out. It is based on the inhibition of bioluminescence of V. fischeri bacteria strains after 5 min of incubation.

Despite the nearly complete conversion of 2,4-D, a percentage of inhibition remained in solution at $t = 180$ min in both experiments, being $I\% = 60$ and 47% for F1.5D and F-1D, respectively. This fact indicates the existence of other toxic intermediates.

EC$_{50}$ values (concentration which causes 50% reduction of the bioluminescence) can be found in the literature. 2,4-D is appointed as moderately toxic (EC$_{50}$ = 59 mg L^{-1}) (Zona and Solar, 2003) and 2,4-DCP as toxic (EC$_{50}$ = 1.2–6.1 mg L^{-1}) (Kaiser and Palabrica, 1991). These values are in conformity with the bacteria growth inhibition. However, the observed concentration of 2,4-DCP in solutions is low to be the only reason of the total toxicity at $t = 180$ min. Therefore, residual toxicity could be also attributed to other compounds present in solution along with 2,4-DCP. Thus, formation of other intermediates during the herbicide degradation, such as chlorohydroquinones or chlorobenzoquinones, should focus larger attention. Fig. 5 shows a simplified degradation pathway of 2,4-D, taking into account the intermediates identified by Kwan and Chu (2004).

Finally, further work is under way in order to develop a kinetic model based on a detailed reaction scheme to study the photo-Fenton degradation of 2,4-D at natural pH, using the ferrioxalate complex as iron source. Moreover, the system will be analyzed in a pilot plant solar reactor in order to better assess the applicability of this methodology.

4. Conclusions

The photo-Fenton degradation of the herbicide 2,4-D at pH = 5, using the ferrioxalate complex as iron source and a solar simulator with different attenuation filters (F-1.5D and F-1D) was optimized. With the aim of studying the effects of the process parameters: temperature (T) and hydrogen peroxide to 2,4-D initial concentration ratio (R), a three-level factorial experimental design combined with response surface methodology was applied. It was shown that the investigated parameters strongly influence the herbicide conversion percentage under the studied conditions. It was also found that R over 50 should be avoided, since it causes a decrease in the process efficiency.

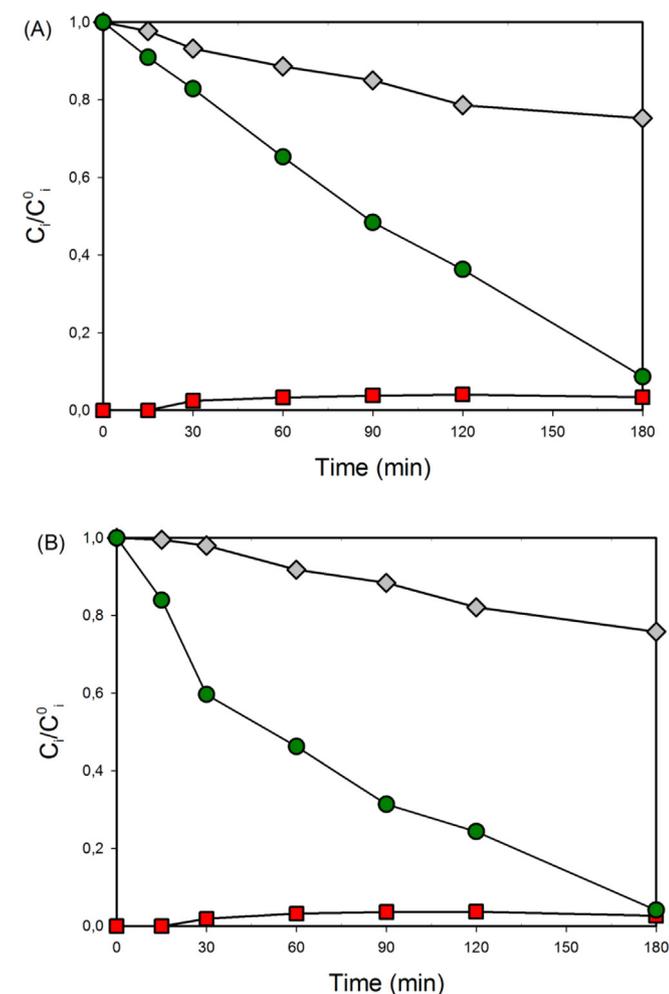The developed models, **Q1** and **Q2**, are found to be highly

Fig. 4. Experimental relative concentrations *versus* time for 2,4-D (circles), 2,4-DCP (squares) and hydrogen peroxide (diamonds) at the optimum conditions for (A) F-1.5D and (B) F-1D.
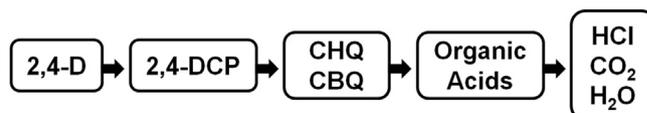

Fig. 5. Proposed pathway for 2,4-D degradation (CHQ: chlorohydroquinones, CBQ: chlorobenzoquinones).

accurate and predictive, according to the obtained statistical parameters. The conversion achieved by the F-1D filter at the optimal conditions ($T = 41.53\ ^\circ$C and $R = 41.46$, $X_{180}^{2,4-D} = 95.9\%$) was higher than that of F-1.5D filter at the optimal conditions ($T = 50\ ^\circ$C and $R = 46.3$, $X_{180}^{2,4-D} = 91.4\%$). The obtained results are very close to the values predicted by the quadratic models (93.8 and 100.0%, respectively). In addition, lower values of T and R were obtained as optimum with the higher radiation level, confirming that the influence of the parameters T and R is more pronounced in the case of F-1.5D.

The obtained mathematical models were able to explain the influence of the parameters under study in the degradation of 2,4-D by the photo-Fenton process at natural pH.

A significant percentage of inhibition remained in solution at $t = 180$ min in both experiments at the optimal conditions despite the nearly complete conversion of 2,4-D and the low 2,4-DCP concentration, indicating the existence of other toxic compounds along with the principal intermediate.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2015.03.028.

References

Ahmed, B., Limem, E., Abdel-Wahab, A., Bensalah, N., 2011. Photo-Fenton treatment of actual agro-industrial wastewaters. Ind. Eng. Chem. Res. 50, 6673–6680.

Al Momani, F.A., Shawaqfeh, A.T., Shawaqfeh, M.S., 2007. Solar wastewater treatment plant for aqueous solution of pesticide. Sol. Energy 81, 1213–1218.

Allevato, H., Pórfido, D., 2002. Report available on: www.msal.gov.ar/agroquimicos/pdf/EnvaAgro_CEPIS-OPS.pdf (accessed October 2014).

Ay, F., Catalkaya, E.C., Kargi, F.A., 2009. Statistical Experiment design approach for advanced oxidation of direct Red Azo Dye by photo-Fenton treatment. J. Hazard. Mater. 162, 230–236.

Bauer, R., Fallmann, H., 1997. The photo-fenton oxidation − a cheap and efficient wastewater treatment method. Res. Chem. Intermed. 23, 341–354.

Bauer, R., Waldner, G., Fallmann, H., Hager, S., Klare, M., Krutzler, T., Malato, S., Maletzky, P., 1999. The photo-fenton reaction and the TiO2/UV process for waste water treatment − novel developments. Catal. Today 53, 131–144.

Benzaquen, T.B., Isla, M.A., Alfano, O.M., 2014. Fenton and photo-Fenton processes for the degradation of atrazine: a kinetic study. J. Chem. Technol. Biotechnol. http://dx.doi.org/10.1002/jctb.4324.

CASAFE. Program AgroLimpio, 2004. Available on: http://www.casafe.org/quienes-somos/agrolimpio/ (accessed October 2014).

Carra, I., Casas López, J.L., Santos-Juanes, L., Malato, S., Sánchez Pérez, J.A., 2013. Iron dosage as a strategy to operate the photo-Fenton process at initial neutral pH. Chem. Eng. J. 224, 67–74.

Colombo, R., Ferreira, T.C.R., Alves, S.A., Carneiro, R.L., Lanza, M.R.V., 2013. Application of the response surface and desirability design to the Lambda-cyhalothrin degradation using photo-Fenton reaction. J. Environ. Manag. 118, 32–39.

Conte, L.O., Farias, J., Albizzati, E.D., Alfano, O.M., 2012. Photo-Fenton degradation of the herbicide 2,4-dichlorophenoxyacetic acid in laboratory and solar pilot-plant reactors. Ind. Eng. Chem. Res. 51, 4181–4191.

Conte, L.O., Querini, P., Albizzati, E.D., y Alfano, O.M., 2014. Photonic and quantum

efficiencies for the homogeneous photo-Fenton degradation of herbicide 2,4-D using different iron complexes. J. Chem. Technol. Biotechnol. http://dx.doi.org/10.1002/jctb.4284.

Dopar, M., Kusic, H., Koprivanac, N., 2011. Treatment of simulated industrial wastewater by photo-Fenton process. Part I: the optimization of process parameters using design of experiments (DOE). Chem. Eng. J. 173, 267–279.

Farias, J., Albizzatti, E.D., Alfano, O.M., 2009. Kinetic study of the photo-Fenton degradation of formic acid. Combined effects of temperature and iron concentration. Catal. Today 144, 117–123.

Hincapié Pérez, M., Peñuela, G., Maldonado, M.I., Malato, O., Fenández-Ibáñez, P., Oller, I., Gernjak, W., Malato, S., 2006. Degradation of pesticides in water using solar advanced oxidation processes. Appl. Catal. B Environ. 64, 272–281.

Huston, P.L., Pignatello, J.J., 1999. Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. Water Res. 33, 1238–1246.

Ikehata, K., Gamal El-Din, M., 2006. Aqueous pesticide degradation by hydrogen peroxide/ultraviolet irradiation and Fenton-type advanced oxidation processes: a review. J. Environ. Eng. Sci. 5, 81–135.

Janin, T., Goetz, V., Brosillon, S., Plantard, G., 2013. Solar photocatalytic mineralization of 2,4-dichlorophenol and mixtures of pesticides: kinetic model of mineralization. Sol. Energy 87, 127–135.

Kaiser, K.L.E., Palabrica, V.S., 1991. Photobacterian phosphoreum. Toxicity data Index. Water Pollut. Res. J. Can. 26, 361–431.

Kwan, C.Y., Chu, W., 2004. A study of the reaction mechanisms of the degradation of 2,4-dichlorophenoxyacetic acid by oxalate-mediated photooxidation. Water Res. 38, 4213–4221.

Laganà, A., Bacaloni, A., Leva, I.D., Faberi, A., Fago, G., Marino, A., 2002. Occurrence and determination of herbicides and their major transformation products in environmental waters. Anal. Chim. Acta 462, 187–198.

Malato, S., Blanco, J., Vidal, A., Richter, C., 2002. Photocatalysis with solar energy at a pilot-plant scale: an overview. Appl. Catal. B Environ. 37, 1–15.

Malato, S., Fernández-Ibañez, P., Maldonado, M.I., Blanco, J., Gernjak, W., 2009. Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. Catal. Today 147, 1–59.

Miller, J.N., Miller, J.C., 2002. Statistics and Chemometrics for Analytical Chemistry. Pearson-Prentice Hall, New York, USA.

Montgomery, D.C., 2005. Desing and Analysis of Experiments. John Wiley and Sons, New York, USA.

Murov, S., Carmichael, I., Hug, G., 1993. Handbook of Photochemistry, second ed. Marcel Dekker, New York, pp. 299–305.

Myers, R.H., Montgomery, D.C., 2002. Response Surface Methodology: Process and Product Optimization Using Designed Experiments, second ed. John Wiley & Sons, New York, USA.

Nogueira, R.F.P., Silva, M.R.A., Trovo, A.G., 2005. Influence of the iron source on the solar photo-Fenton degradation of different classes of organic compounds. Sol. Energy 79, 384–392.

Oliveira, C., Alves, A., Madeira, L.M., 2014. Treatment of water networks (waters and deposits) contaminated with chlorfenvinphos by oxidation with Fenton's reagent. Chem. Eng. J. 241, 190–199.

Pignatello, J.J., 1992. Dark and photoassisted Fe^{3+} catalyzed degradation of chlorophenoxy herbicides by hydroxen peroxy. Environ. Sci. Technol. 26, 944–951.

Pignatello, J.J., Oliveros, E., MacKay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Crit. Rev. Env. Sci. Technol. 36, 1–84.

Prieto-Rodriguez, L., Spasiano, D., Oller, I., Fernandez-Calderero, I., Aguera, A., Malato, S., 2013. Solar photo-Fenton optimization for the treatment of MWTP effluents containing emerging contaminants. Catal. Today 209, 188–194.

Resolution N° 1089/82. Santa Fe, Argentina. Available on http://www.santafe.gov.ar/index.php/web/content/view/full/28842/(subtema)/112857 (accessed October 2014).

Trovó, A.G., Silva, T.F.S., Gomes Jr., O., Machado, A.E.H., Neto, W.B., Muller Jr., P.S., Daniel, D., 2013. Degradation of caffeine by photo-Fenton process: optimization of treatment conditions using experimental design. Chemosphere 90, 170–175.

United States Prevention Agency (EPA), 2005. Prevention, Pesticides and Toxic Substances (7508C). Reregistration Eligibility Decision for 2,4-D. http://www.epa.gov/oppsrrd1/REDs/24d_red.pdf (accessed October 2014).

Zapata, A., Oller, I., Rizzo, L., Hilgert, S., Maldonado, M.I., Sánchez-Pérez, J.A., Malato, S., 2010. Evaluation of operating parameters involved in solar photo-Fenton treatment of wastewater: interdependence of initial pollutant concentration, temperature and iron concentration. Appl. Catal. B Environ. 97, 292–298.

Zona, R., Solar, S., 2003. Oxidation of 2,4-dichlorophenoxyacetic acid by ionizing radiation: degradation, detoxification and mineralization. Radiat. Phys. Chem. 66, 137–143.