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A new substrate and by-product kinetic model for the photodegradation of 4-chlorophenol with KrCl exciplex UV lamp and hydrogen peroxide

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Abstract

4-Chlorophenol removal has been studied with many different methods. One of these methods is their UV oxidation. Among chemical oxidation, excimer and exciplex lamps are attractive alternatives to commonly used mercury lamps, mainly because they are free of elemental mercury, present long life and geometric freedom. It has been described that the first step in 4-chlorophenol photodegradation process is the break of the C-Cl bond leading to the formation of primary photoproducts after further reactions. Besides, it is described that the photodegradation of 4-chlorophenol in the presence of hydrogen peroxide improve the formation of oxygenated products increasing their removal. In previous studies the kinetics of these reactions has been described by pseudo-first order

reaction models but none of these studies has taking into account the photoproducts in the kinetic equations. In this work, a new kinetic model that considers 4-chlorophenol and the photoproducts has been formulated. The validation of the model has been done with previously obtained experimental data.

Keywords: 4-chlorophenol; kinetic model; photodegradation; excilamp; hydrogen peroxide

1 Introduction

In the last decades many papers have been published about the removal of phenolic compounds from wastewater. Despite all of this research, the problem is still opened and a definitive solution has not been reached. Typical methods for the removal of those compounds include physical (solvent extraction [1], membrane technology [2, 3], and adsorption on different supports [4, 5]), biological (microbial degradation [6] and enzyme oxidation [7, 8]) and chemical methods (traditional oxidation treatments [9, 10] or advanced oxidation processes).

Among chemical treatments for phenolic compounds removal, systems based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have aroused increasing interest due to their high oxidant power. Such systems are commonly named Advanced Oxidation Processes (AOPs), and, the radicals are produced by combining ozone, hydrogen peroxide and UV radiation. The combination of hydrogen peroxide with ferrous ions in the so-called Fenton reagent is also used [11, 12]. [Some authors have studied](#)

the influence of some groundwater and surface waters constituents such as carbonate or chloride on the degradation process [13].

AOPs embrace a number of degradation methods for removal [14]. The use of UV radiation and strong chemical oxidizing agents constitutes one type of combined advanced oxidation process that can be particularly effective in the removal of toxic chlorophenols from water and wastewater [15-20].

In general, high-, medium- and low-pressure UV mercury lamps, at a wavelength of primarily 254 nm, are typically used in photolysis of chlorophenols [14, 21]. Current research in UV oxidation using excimer and/or exciplex lamps is showing promise as an alternative to traditional UV sources [22, 23]. Excimer lamps, or excilamps, are a class of spontaneous radiation sources based on transitions of exciplex (rare gas halides) or excimer molecules (rare gas or halogen dimers), whose main advantage is the emission of UV radiation in a narrow band. They are attractive alternatives to commonly used mercury lamps because they have some important advantages including the absence of elemental mercury, long lifetime, geometric freedom and high photon flux [23-25]. Excimer lamps have been successfully used for the removal of phenolic compounds, alone or in combination with oxidants such as H₂O₂ to improve the removal process and facilitate complete mineralization [26-32].

In several studies [21, 33] about 4-chlorophenol photodegradation, all the authors agree that the first step in the photodegradation process is the break of the C-Cl bond giving two main unstable compounds: 4-hydroxyphenil and 4-oxocyclohexa-2,5-dienylidene. Further reactions of these intermediates result in the formation of primary photoproducts, mainly hydroquinone and benzoquinone and in less amount 1,2,4-trihydroxybenzene, catechol, resorcinol and

chlorodihydroxibencenes. The primary photoproducts are degraded to smaller compounds until the formation of CO₂ and water.

The presence of hydrogen peroxide [11, 21, 33, 34] in the reaction media has demonstrated to improve 4-chlorophenol degradation rate in the photodegradation process, and also improve the formation of oxygenated products, due to the presence of free HO• radicals. The main photoproducts in the case of 4-chlorophenol oxidation with UV/H₂O₂ are hydroquinone and 1,2,4-trihydroxybenzene when the concentration of hydrogen peroxide is 20 times higher than 4-chlorophenol concentration. Benitez et al. [11] also studied the influence of hydroxyl radicals in the chlorophenol advanced oxidation processes. They concluded that the presence of hydrogen peroxide in the media does not exert a significance influence on the compound decomposition constant and they established the global reaction rate of the photodegradation process as the sum of the reaction rate of the direct photolysis, without H₂O₂, and an additional reaction rate between the generated hydroxyl radicals and the phenolic compound, being the contribution of the direct photolysis to the overall reaction rate higher than that of the reaction with hydroxyl radicals.

According to Pera-Titus [14] and Czaplicka [21] the kinetics and the mechanism of these reactions are highly dependent on experimental conditions such as wavelength of irradiation, pH of solution, concentration of dissolved oxygen and/or hydroxyl radicals and the presence of other dissolved organic material, which can act as a potential photo-sensitizer. Taking into account all of these conditions, the reaction of chlorophenol and hydroxyl radicals has been described by pseudo –first order reaction models, but as far as we know, there is no studies where kinetic equations for the photoproducts were proposed.

With the experience of a first model formulated in a previous study for the photodegradation of 4-chlorophenol [27] and taking into account the mechanisms proposed by Czaplicka [21] and Rayne et al. [33] and their intermediates compounds, a new kinetic model has been formulated. In order to check the validity of the proposed model, the results obtained in a previous work [29] related with 4-chlorophenol photodegradation with a KrCl excilamp and H₂O₂ has been used.

2. Materials and methods

2.1. Reagents

4-Chlorophenol (99%), 4-chlorocatechol (97%), resorcinol (99%), 4-chlororesorcinol (98%), chlorohydroquinone (85%), p-benzoquinone (98%), hydroquinone (99%), catechol (99%) and hydrogen peroxide (30%) were purchased from Sigma-Aldrich Fine Chemicals. Phenol was supplied by BDH and 1,2,4-trihydroxibenzene (99%) by Alfa Aesar. Other chemicals were of analytical grade and were used without further purification.

2.2. Materials

A KrCl excilamp, emitting maximum UV radiation at 222 nm, has been used. The excilamp is of cylindrical geometry covered by a metal case having an UV exit window with an area of 75 cm². The exit window is oriented vertically in close proximity to a quartz tube with an operating length of 22 cm and external diameter of 2.6 cm. The output power of the excilamp was measured with a H8025-222 photodetector (Hamamatsu Photonics KK) and tested using

an electrochemical actinometer. The average radiation intensity delivered to the solution was determined at 2.47 mW cm^{-2} .

2.3. 4-Chlorophenol phototreatment method

The phototreatment of 4-chlorophenol with the UV excilamp has been carried out, alternatively, without hydrogen peroxide (direct photolysis) and in the presence of hydrogen peroxide at different H_2O_2 : 4-chlorophenol molar ratios.

For the experiments with the UV lamp without hydrogen peroxide (direct photolysis), 4-chlorophenol at two different concentrations, 100 and 250 mg L^{-1} (0.78 and 1.95 mM) were used. Samples of 10 mL were placed into quartz reaction tubes covered with a reflector and UV irradiated at laboratory temperature ($24 \pm 1^\circ\text{C}$) under static conditions for periods up to 60 minutes.

For the experiments with the UV lamp and hydrogen peroxide, 4-chlorophenol at 100 and 250 mg L^{-1} was combined with hydrogen peroxide at appropriate concentrations (molar ratios H_2O_2 : 4-chlorophenol of 1:1, 10:1, 25:1 and 50:1 were used), placed into quartz reaction tubes covered with a reflector and UV irradiated following the above procedure. Figure 1 shows a scheme of the experimental set-up.

2.4. Determination of 4-chlorophenol and photoproducts

4-chlorophenol and different photoproducts remaining following UV treatment were analysed by HPLC analysis. Detection of photoproducts was done at 283 nm, using a Varian Prostar 210 chromatograph with UV-vis detector and a C18 reverse phase column. The mobile phase

was a mixture of methanol, acetic acid and water (60:2.5:37.5 v/v) with a flow rate of 1 mL min⁻¹. The retention time of the different photoproducts was the following ones: 1,2,4-trihydroxibenzene, 1.9 min, hydroquinone, 2.1 min, resorcinol, 2.26 min, p-benzoquinone, 2.39 min, 4-chlorohydroquinone, 2.46 min, catechol, 2.59 min, 4-chlororesorcinol, 3.06 min, phenol, 3.49 min, 4-chlorocatechol, 4.2 min and 4-chlorophenol, 6.2 min.

3. Theoretical analysis: kinetic model

3.1. Proposed scheme of the mechanism

As it was mentioned in the Introduction, there are many papers on the degradation mechanism of 4-chlorophenol and, as a consequence, the mechanism is well established as we can see, as example, in the excellent revisions of Czaplicka [21] and Rayne et al. [33]. By this, in this work authors don't propose a new mechanism but use the mechanism described in these revisions to propose a kinetic scheme as a basis to derive the kinetic equations.

According to these mentioned revisions, the first step of the degradation pathway is the breaking of the C-Cl bond and the formation of two main radical intermediates: a 4-hydroxyphenyl radical and a γ -ketocarbene, 4-oxocyclohexa-2,5-dienylidene. From these unstable species primary photoproducts appear that, in further steps, give the secondary photoproducts and, finally, total degradation to CO₂ and H₂O₂ can be achieved.

Also, studies about the influence of hydroxyl radicals on the photo-degradation of chlorinated phenols by UV/H₂O₂ advanced oxidation processes can be found in the literature [11, 33].

From these studies, the main conclusion is that the reaction mechanism for the photo-degradation of these organic compounds is very complex and, as a consequence, a rigorous kinetic study cannot be performed. Therefore, an approach to the kinetic study can be

performed by assuming that the photochemical decomposition reaction follows a pseudo-first-order kinetics.

Assuming this kinetic approach, Benitez et al. [11] established that the overall reaction rate, for the photo-degradation process, is the sum of the reaction rate of the direct photolysis, without H_2O_2 , and an additional reaction rate between the generated hydroxyl radical and the phenolic compound. Additionally, it was observed that the contribution of the direct photolysis to the overall reaction rate was higher than that of the reaction with hydroxyl radicals. Despite this general result, this influence was dependent on the position of chlorine in the phenolic compound, being significant for 2- and 3-chlorophenol and almost no significant for 4-chlorophenol, where the overall photo-degradation reaction rate, in the presence of H_2O_2 , was only slightly higher than the one for the direct photolysis.

As resume of all above considerations, we can say that until now, despite the degradation mechanism of 4-chlorophenol is well established, only kinetic models for the 4-chlorophenol (most of them consisting in pseudo-first order kinetic models) have been proposed and no kinetic equations have been derived and solved for the by-products. Only the authors, in a previous paper [27], proposed a first simplified kinetic model for the main photoproducts of the direct photolysis: hydroquinone and benzoquinone.

By this, and on the basis of the mechanism established in the literature authors proposed, in this work, a kinetic scheme, not only to confirm the mechanism but mainly to derive kinetic equations both for the 4-chlorophenol and for the primary photoproducts. From now on, the kinetic scheme and equations are presented.

Figure 2 shows the scheme of the proposed 4-chlorophenol photodegradation model. As it can be observed, the intermediate compounds I and J are formed from the initial substrate. Both of them are unstable and easily degrade to form the N primary photoproducts P_i , which will degrade further to produce the secondary photoproducts Q_i (not identified in this study) that will finally produce CO_2 and H_2O . From this mechanism, the mass balance equations for 4-chlorophenol, the intermediates and the different primary photoproducts can be formulated and the corresponding equations of concentration change versus time can be obtained, as described below.

3.2. Variation of 4-chlorophenol concentration with time

From the proposed mechanism, a new constant k_0 can be defined as follows:

$$k_0 = k_{01} + k_{02} \quad (1)$$

As a result, the 4-chlorophenol degradation rate is given by:

$$\frac{d[4CP]}{dt} = -k_0[4CP] \quad (2)$$

with the initial condition:

$$t = 0; [4CP] = [4CP]_0 \quad (3)$$

The previous equation can be easily integrated leading to:

$$[4CP] = [4CP]_0 e^{-k_0 t} \quad (4)$$

3.3. Intermediate compounds I and J

The intermediate compounds *I* and *J* are formed from the 4-chlorophenol and during the photodegradation process they lead to the *N* primary photoproducts *P_i*. Within these photoproducts, the ones from *i* = 1 to *M* are formed from the intermediate compound *I* and the rest (from *i* = *M* + 1 to *N*) are formed from the intermediate *J*.

For the intermediate compound *I*, and by defining a *k_I* constant:

$$k_I = \sum_{i=1}^M k_i \quad (5)$$

it can be verified that:

$$\frac{d[I]}{dt} = k_{01}[4CP] - k_I [I] \quad (6)$$

with the initial condition:

$$t = 0; [I] = 0 \quad (7)$$

Equation (7) is a linear differential equation of first order and constant coefficients, with initial conditions equal to 0, which can be solved by using the Laplace Transform. The obtained result is indicated below:

$$[I] = \frac{k_{01}[4CP]_0}{k_I - k_0} (e^{-k_0 t} - e^{-k_I t}) \quad (8)$$

In a similar way, another constant can be defined for the intermediate compound J :

$$k_J = \sum_{i=M+1}^N k_i \quad (9)$$

And the equation for the variation of this compound over time would be:

$$\frac{d[J]}{dt} = k_{02}[4CP] - k_J[J] \quad (10)$$

with the initial condition:

$$t = 0; [J] = 0 \quad (11)$$

Equation (10) can be solved in the same way that equation (6) giving:

$$[J] = \frac{k_{02}[4CP]_0}{k_J - k_0} (e^{-k_0 t} - e^{-k_J t}) \quad (12)$$

3.4. Primary photoproducts, P_i

For each one of the M primary photoproducts, P_i , formed from the intermediate compound I , it can be verified:

$$\frac{d[P_i]}{dt} = k_i[I] - k_{i2}[P_i] \quad (13)$$

with the initial condition:

$$t = 0; [P_i] = 0 \quad (14)$$

This equation is also a linear differential one with constant coefficients, so it can be solved by the Laplace Transform with the following result:

$$[P_i] = \frac{k_i k_{01} [4CP]_0}{k_I - k_0} \left(\frac{1}{(k_{i2} - k_0)} (e^{-k_0 t} - e^{-k_{i2} t}) - \frac{1}{(k_{i2} - k_I)} (e^{-k_I t} - e^{-k_{i2} t}) \right) \quad (15)$$

The previous equation is valid for: $M \geq i \geq 1$

The same procedure can be applied to the primary photoproducts formed from the intermediate compound J , leading to:

$$[P_i] = \frac{k_i k_{02} [4CP]_0}{k_J - k_0} \left(\frac{1}{(k_{i2} - k_0)} (e^{-k_0 t} - e^{-k_{i2} t}) - \frac{1}{(k_{i2} - k_J)} (e^{-k_J t} - e^{-k_{i2} t}) \right) \quad (16)$$

In this case: $N \geq i \geq M + 1$

3.5. Model fitting

The fitting of the proposed model to the experimental results has been done using the software Sigma Plot V8.2. Equation (4) has been used directly for the fitting of 4-chlorophenol experimental conversions. However, some modifications have been introduced in equations (15) and (16) to make them suitable to be used in the previously mentioned software. Since both equations have been modified in the same way, only the new equation (15) is shown, as follows:

$$[P_i] = \frac{k_i k_{01} [4CP]_0}{(k_I - k_0)(k_{i2} - k_I)} \left(e^{-k_{i2}t} - \frac{k_{i2} - k_0}{k_I - k_0} e^{-k_I t} + \frac{k_{i2} - k_I}{k_I - k_0} e^{-k_0 t} \right) \quad (17)$$

By defining the following **auxiliary** parameters:

$$a = \frac{k_i k_{01} [4CP]_0}{(k_{i2} - k_0)(k_{i2} - k_I)} \quad (18)$$

$$b = k_{i2} \quad (19)$$

$$c = \frac{k_{i2} - k_0}{k_0 - k_I} \quad (20)$$

$$d = k_I \quad (21)$$

$$f = k_0 \quad (22)$$

It is finally obtained:

$$[P_i] = a(e^{-bt} + ce^{-dt} - (1+c)e^{-ft}) \quad (23)$$

being the parameter $f = k_o$ known after the 4-chlorophenol fitting.

In particular, if $b \rightarrow 0$ (no significant formation of Q_i) the previous equation leads to:

$$[P_i] = a(1 + ce^{-dt} - (1+c)e^{-ft}) \quad (24)$$

3.6. Fitting procedure

In the fitting of the model, experimental data obtained in a previous work were used [29].

The general procedure used in the fitting of the data has been the following one:

- In the series of variation of the molar ratio H_2O_2 :4-chlorophenol, with constant initial chlorophenol concentration, the experimental data of 4-chlorophenol variation over time was fitted to equation (4), since it was previously observed [28] that the molar ratio has no influence on the 4-chlorophenol removal rate. In this way, a unique value of the constant k_o was obtained, being this value the f parameter of equations (23) and (24), which was kept constant for the fitting of the different primary photoproducts in this series so that only the remaining parameters, a , b , c and d , needed to be determined.

- Additionally, the value of the parameter d obtained from the best fitting of the previous series (the one with higher correlation coefficient) was selected as the value of the constant k_I for the intermediate compound. This value was kept constant in equations (23) and (24) and the fitting of all the by-products was repeated, giving new values for the parameters a , b and c .

- Under these conditions, when a good degree of fitting of the different photoproducts to the proposed model was obtained (high values of the correlation coefficients) it was assumed that the chosen value for the parameter d was appropriate, also indicating that all the primary photoproducts had been formed from the same intermediate. In case any photoproduct did not show a good fitting, the value of the parameter d leading to an optimum fitting was determined. This new value would correspond, according to the proposed mechanism, with the degradation constant of the other intermediate compound.

- Those fittings leading to a negative value of the parameter b were not accepted since this parameter, corresponding with the value of the kinetic constant k_{i2} , cannot be negative. In these cases the value of b was considered rather negligible and was given the value 0, using equation (24) for the fitting.

4. Results and Discussion

4.1. Progress curves of 4-chlorophenol and photoproducts

Figures 3, 4 and 5 show 4-chlorophenol and photoproducts concentrations fitting to the equations depicted in equations (4) and (23). The dots shown in the Figures represent the experimental data and the continuous lines the values calculated with the model.

Figure 3 shows the fitting of 4-chlorophenol concentration variation to equation (4). Figure 3A is for the experiments done with 4-chlorophenol initial concentration of 100 mg L^{-1} (0.778 mM) both for direct photolysis and for the four molar ratios $\text{H}_2\text{O}_2/$ 4-chlorophenol assayed. The continuous line is the representation of equation (7) of the model for a value of $k_0 = 0.419 \text{ min}^{-1}$. This value was obtained from the mean value of 4-chlorophenol concentration without hydrogen peroxide and the ones for the four molar ratios. As can be observed in Figure 3A, the individual values for each molar ratio show no significance deviation from the mean value, what agrees with the previous results described by Benitez et al. [11].

The same behaviour is observed in Figure 3B for a 4-chlorophenol initial concentration of 250 mg L^{-1} (1.946 mM). Besides, the apparent pseudo-first kinetic constant decreases when 4-chlorophenol initial concentration is increased, being the value of the constant $k_0 = 0.111 \text{ min}^{-1}$ for this series. This behaviour agrees with the previously obtained in absence of hydrogen peroxide [27], where it was observed that when the initial concentration of 4-chlorophenol increases longer irradiation time was needed to reach total 4-chlorophenol degradation.

Figure 4 shows altogether 4-chlorophenol and photoproducts concentration variation over time for the series of initial 4-chlorophenol concentration of 100 mg L^{-1} , both for the direct photolysis and the four $\text{H}_2\text{O}_2/$ 4-chlorophenol molar ratios assayed. The same representation

is shown in Figure 5 but for a 4-chlorophenol initial concentration of 250 mg L⁻¹. In both cases and for the **most** of the photoproducts a good **degree of fitting** is obtained with a unique value of the parameter *d*, which is the **kinetic constant for the disappearance of one of the unstable intermediate photoproducts**, I or J. This parameter *d*, has taken an alternative value for the case of low molar ratios H₂O₂/4-chlorophenol. The predominant values of the parameter *d* have been 0.390 min⁻¹ and 0.102 min⁻¹ for the series of 4-chlorophenol initial concentrations of 0.778 and 1.924 mM, respectively, with correlation coefficient in all the cases higher than 0.9 and in some cases very close to the unity.

4.2. Kinetic constants

From the values of auxiliary parameters *a*, *b*, *c*, *d* and *f*, values of the kinetic constants that appear in the mechanism can be determined as follows:

- The pseudo-first order kinetic constant of 4-chlorophenol, *k₀*, is obtained from Eq. (22), being equal to the parameter *f*: $k_0 = f$ (min⁻¹).
- For the unstable intermediates *I* or *J*, the pseudo-first order kinetic constants, *k_I* or *k_J*, are obtained from Eq. (21), being equal to the parameter *d*: $k_I = d$ (min⁻¹).
- In the same way, the kinetic constant *k_{i2}*, for the consumption of the different primary photoproducts *P_i*, can be obtained from Eq. (19): $k_{i2} = b$ (min⁻¹).
- In the model there is not a direct relationship between the kinetic constant *k_i*, for the rate of formation of the primary photoproducts *P_i* from the unstable intermediates, and the auxiliary parameters. Only, by using Eq. (18), the product *k_ik₀₁* or, alternatively, *k_ik₀₂*, can be obtained from the value of the auxiliary parameter *a*, the initial concentration of 4-chlorophenol, [4CP]₀, and the previously determined values of constants *k₀*, *k_I* and *k_{i2}*, as follows:

$$k_i k_{01} = \frac{a(k_{i2} - k_0)(k_{i2} - k_I)}{[4CP]_0} \quad (\text{min}^{-2})$$

In Tables 1, 2 and 3, the values of the kinetics constants are shown, for the different experimental conditions assayed and for 4-chlorophenol and each one of the primary photoproducts determined in this work. Also in the Tables, on the right of the constants values, the correlation coefficient, R, and standard deviation, St_D, obtained in the fitting of each one of the individual progress curves are shown. As it can be seen in the Tables, in most cases high values of R were obtained. In Table 1, the kinetic constants for direct photolysis are shown, and in Tables 2 and 3 it can be seen the kinetic constants for the series with initial concentration of 4-chlorophenol of 100 and 250 mg/L, respectively, and the different H₂O₂ : 4-chlorophenol molar ratio assayed.

From the values of the different kinetic constants that appear in Tables 1, 2 and 3, it is follows:

- For each one of the initial 4-chlorophenol concentration assayed, the kinetic constant of 4-chlorophenol degradation, k_0 , is the same both in the direct photolysis and in the assays with different H₂O₂ : 4-chlorophenol molar ratio. Also, this value decreases when the initial 4-chlorophenol concentration increases, in good agreement with the results obtained in a previous work [27].
- In the same way, the kinetic constants k_I or k_J , for the consumption of the unstable intermediates I or J , are the same both in the direct photolysis and in the assays with different H₂O₂ : 4-chlorophenol molar ratio, and this value also decreases when the initial 4-chlorophenol concentration increases. For each one of the two initial 4-chlorophenol concentrations tested, there is a predominant value for these constants and only in a few cases a different value was obtained. It is in good

agreement with the kinetic scheme proposed, where two different unstable intermediates I and J were assumed.

- Related to the values of the kinetic constant of consumption of the primary photoproducts, k_{i2} , it can be seen in Tables 1-3 that there is a different value for each one of the different photoproducts. Also it can be observed in the Tables that for the different experimental conditions tested different values were obtained. The influence of the initial 4-chlorophenol was the same that the one observed for the others kinetic constants: as this concentration increases, the value of the kinetic constant decreases. And for the influence of the hydrogen peroxide we can see in Tables 1-3 that, for the same initial concentration of 4-chlorophenol, the values of k_{i2} increase when increases the H_2O_2 : 4-chlorophenol molar ratio, in good agreement with the experimental decreasing in the concentration of the different primary photoproducts with the increasing of the amount of hydrogen peroxide in the reaction medium.
- Due to that no individual values of k_i and k_{01} or k_{02} were obtained with the model, it is not possible to establish a reliable correlation between these kinetics constants and the experimental conditions.

4.3. Comparison of experimental and calculated concentrations: ANOVA test

Finally, and with the main objective to check the overall degree of fitting of the proposed model, all the concentration experimental data have been represented versus the concentration values calculated by the model for all the experiments done and all the compounds (4-chlorophenol and the primary photoproducts) and an ANOVA test has been carried out. The results are depicted in Figure 6 and Table 4 and, as it can be seen, a good

degree of approximation to the diagonal was obtained, with a high value of the determination coefficient, $R^2 = 0.9943$, and a high significance level, which confirms the validity of the proposed model.

5. Conclusions

A new kinetic model that takes into account 4-chlorophenol degradation and the formation of primary photoproducts has been proposed. The results show that the proposed model fit to the experimental data with a good degree of approximation.

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Figure captions

Figure 1. Experimental set up.

Figure 2. Proposed 4-chlorophenol photodegradation model.

Figure 3. Fit of 4-chlorophenol concentration variation over time to the proposed model: (A) $[4CP]_0 = 0.778$ mM; (B) $[4CP]_0 = 1.946$ mM; $[H_2O_2]_0/[4CP]_0$: \blacklozenge 0/1, \blacksquare 1/1, \blacktriangle 10/1, \times 25/1
* 50/1, — Model.

Figure 4. Fit of photoproducts concentration variation over time to the proposed model.
 $[4CP]_0 = 0.778$ mM; $[H_2O_2]_0/[4CP]_0$: (A) = 0/1; (B) = 1/1; (C) = 10/1; (D) = 25/1; (E) = 50/1.
 \blacklozenge 4-Chlorophenol, \blacksquare 4-Chlorocatechol; \blacktriangle Hydroquinone; \times Benzoquinone;
* 1,2,4-Trihydroxibencene; \bullet Resorcinol; + Chlorohydroquinone: - 4-Chlororesorcinol;
 \diamond Phenol; — Model.

Figure 5. Fit of photoproducts concentration variation over time to the proposed model.
 $[4CP]_0 = 1.946$ mM; $[H_2O_2]_0/[4CP]_0$: (A) = 0/1; (B) = 1/1; (C) = 10/1; (D) = 25/1; (E) = 50/1.
 \blacklozenge 4-Chlorophenol, \blacksquare 4-Chlorocatechol; \blacktriangle Hydroquinone; \times Benzoquinone;
* 1,2,4-Trihydroxibencene; \bullet Resorcinol; + Chlorohydroquinone: - 4-Chlororesorcinol;
 \diamond Phenol; — Model.

Figure 6. Experimental and calculated concentrations of 4-chlorophenol and photoproducts for all the experimental conditions assayed.