Photochemical oxidation processes for the elimination of phenyl-urea herbicides in waters

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Abstract

Four phenyl-urea herbicides (linuron, chlorotoluron, diuron, and isoproturon) were individually photooxidized by monochromatic UV radiation in ultra-pure aqueous solutions. The influence of pH and temperature on the photodegradation process was established, and the first-order rate constants and quantum yields were evaluated. The sequence of photodecomposition rates was: linuron > chlorotoluron > diuron > isoproturon. The simultaneous photooxidation of mixtures of the selected herbicides in several types of waters was then performed by means of UV radiation alone, and by UV radiation combined with hydrogen peroxide. The types of waters used were: ultra-pure water, a commercial mineral water, a groundwater, and a lake water. The influence of the independent variables in these processes – the presence or absence of *tert*-butyl alcohol, types of herbicide and waters, and concentration of hydrogen peroxide – were established and discussed. A kinetic study was performed using a competitive kinetic model that allowed various rate constants to be evaluated for each herbicide. This kinetic model allows one to predict the elimination of these phenyl-urea herbicides in contaminated waters by the oxidation systems used (UV alone and combined UV/H$_2$O$_2$). The herbicide concentrations predicted by this model agree well with the experimental results that were obtained.
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1. Introduction

The application of pesticides, in general, and herbicides, in particular, onto agricultural soils is a well established and effective practice in controlling weed growth. However, because of the extension of intensive agriculture worldwide during the last 30 years, the varieties and amounts of pesticides used to improve the yield of crops have increased markedly. Indeed, pesticides have become some of the most frequently occurring organic pollutants in natural waters and, therefore, great concern has arisen about their possible effects on human health and the environment. Less than 1% of total applied pesticides reaches the target pests. Most pesticides are dispersed into the aquatic environment via agricultural runoff or leaching [1]. In response to this concern, the European Union has moved to establish a maximum permissible concentration of 0.1 μg L^{-1} for any particular pesticide in drinking waters, and a total concentration of 0.5 μg L^{-1}

for the sum of all pesticides, including their degradation products [2]. In the specific case of herbicides, since they are applied to soils repeatedly, and because of their fairly slow degradation [3,4], their presence in both ground and surface waters has become ever more frequent.

The environmental problem generated by the herbicide contamination of water resources has led to increasing interest in reliable technologies for their removal. This can be achieved by appropriate physico-chemical methods, such as adsorption onto activated carbon and membrane filtration. A disadvantage of activated carbon adsorption, however, is the high cost of reactivating the spent activated carbon, and the poor removal of polar pesticides. Membrane filtration is also a relatively expensive process, although the cost can be reduced if membrane filtration can be combined with other processes, e.g., the possibility of removing and/or degrading the herbicides by chemical oxidation, as is currently being done with increasing success during the disinfection step carried out at drinking water treatment plants.

Among these chemical processes, photodegradation is a process to which pesticides may be subjected, and thus UV radiation

is widely used in advanced water disinfection methods to induce photoreactions of organic pollutants [5]. Chemical oxidation using UV radiation in the presence of hydrogen peroxide is also a very promising technique for the oxidative degradation of organic compounds. Mercury lamps emitting at 254 nm are the UV sources most commonly used to dissociate H_2O_2, and the generally accepted mechanism for this H_2O_2 photolysis is the cleavage of the molecule into hydroxyl radicals which are highly powerful oxidizing species. Once these radicals are generated, they can oxidize organic compounds, and produce additional organic radicals simultaneously, which are highly reactive and can be further oxidized [6,7].

Phenyl-urea derivatives are reported to be among the most widely used herbicides in agriculture today [8]. They are used for a variety of purposes [9], including as systemic herbicides (isoproturon and chlorotoluron) to control broadleaf and grassy weeds in cereals and other crops, in cotton fields (linuron), as total herbicides in urban areas (diuron), and as algicides in paints and coatings (diuron) [10]. These herbicides have received particular attention in recent years because of their toxicity and possible carcinogenic properties, and because several weeks, or even months, are required for their removal from environment [11].

Given this context, the present study was designed to evaluate the photodegradation by UV radiation alone and by the combined system UV/H_2O_2 of four selected phenyl-urea herbicides—linuron ((dichloro-3,4 phenyl)-3-methoxy-1*N*-methyl-1 urea), chlorotoluron (3-(3-chloro-4-methylphenyl)-1,1 dimethylurea), diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), and isoproturon (3-(4-isopropylphenyl)-1-1-dimethylurea). The chemical structures of the four herbicides are shown in Fig. 1. The published information in this research field is not abundant. Although there have been some studies of the photolysis of diuron [12], linuron [13], and isoproturon and chlorotoluron [14], these studies [12–14] have focused primarily on the analysis and identification of the main photoproducts with proposals for the reaction mechanisms for the photoreactions. The quantum yields values reported in these studies [12–14] will be compared to the values obtained in the present study.

Due to the lack of knowledge on the basic kinetic parameters in these photoprocesses, the objective of the first stage of the present study was to establish the influence of some of the independent variables on the individual photochemical oxidation of the herbicides in ultra-pure water, as well as the evaluation of several basic kinetic parameters (rate constants and quantum yields) for different experimental conditions (pH and temperature). In a second stage, the study focused on the simultaneous photooxidation of the herbicides when they are present together in different types of waters. After establishing the influence of the independent variables, a model was constructed for the prediction of the elimination of these herbicides in different types of waters under conditions that are similar to those in drinking water treatments. This model uses the two oxidation systems of the present study (UV radiation alone and in combination with hydrogen peroxide) and some of the kinetic parameters evaluated previously.
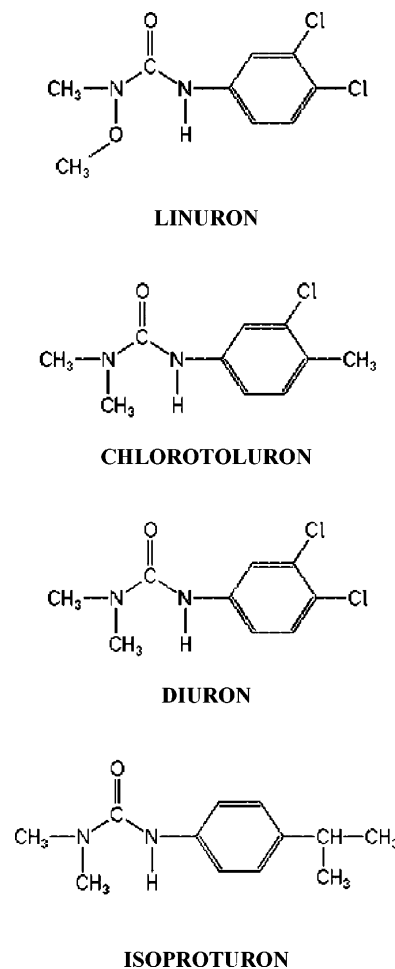

Fig. 1. Chemical structures of the phenyl-urea herbicides.

2. Experimental procedures

The experiments subjecting the phenyl-urea herbicides in ultra-pure water (Milli-Q water system, Millipore) to UV radiation were carried out in a 500-cm^3 cylindrical glass reactor. The radiation source was a low pressure mercury vapor lamp (Hanau TNN 15/32, electrical power 15 W), which emits monochromatic radiation at 254 nm, placed axially within the reactor. A quartz sleeve housed the lamp. Chemical actinometry experiments using hydrogen peroxide as actinometer were conducted to determine the radiation intensity emitted by the lamp into the reactor I_0, with the results of these experiments yielding a value $2.03 \times 10^{-6}\,E\,s^{-1}$.

In the first group of experiments, the photodegradation was performed individually for each of the selected phenyl-ureas, and the reactor was thermostatted at the desired temperature, which ranged from 10 to 40 °C. In order to attain the required pH, the solutions were buffered with a phosphoric acid/phosphate buffer (0.05 M). For each experiment, the reactor was filled with 350 cm^3 of an aqueous solution of the selected herbicide, with an initial concentration of 25 ppm in all cases, and the lamp was connected. During each experiment, samples were withdrawn from the reactor at regular time intervals for assay.

In the second group of experiments, mixtures of the selected herbicides dissolved in four types of waters were simultaneously photodegraded by UV radiation alone and in combination with H_2O_2, in the same reactor and at a constant temperature of 20 °C. In the combined UV/H_2O_2 experiments, the required amount of hydrogen peroxide was also introduced into the reactor.

The four waters used included ultra-pure water, a bottled mineral water of the commercial brand "Los Riscos", and two natural waters collected from two locations in the Extremadura Community (SW Spain)—a groundwater, and water from the lake "Peña del Aguila". These natural waters were filtered within 24 h after sampling and stored at 4 °C until use. The measured absorbances at 254 nm were 0, 0.002, 0.050, and 0.179 for the ultra-pure water (value assumed), the mineral water, the groundwater, and the "Peña del Aguila" lake water, respectively.

Herbicides of the highest purity available were purchased from Sigma–Aldrich, and all of the other chemicals used for the solutions (hydrogen peroxide, eluents, buffers, etc.) were of reagent grade. The phenyl-urea concentrations in each sample in both the individual photodegradation experiments in ultra-pure water and the simultaneous photodegradation experiments in several water types were determined by HPLC, using a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Waters Spherisorb Column (Nova-Pak C18, 3.9 mm × 150 mm). Each run was performed in isocratic mode with a 1 cm^3 min^{-1} mobile phase of methanol-aqueous solution of phosphoric acid (10^{-2} M), and the detection was made at 248 nm for all the samples.

3. Results and discussion

3.1. Photochemical oxidation of individual herbicides in ultra-pure water

The individual photooxidation of the selected phenyl-urea herbicides in ultra-pure aqueous solutions by the monochromatic UV radiation source described in Section 2 was performed by varying the pH and the temperature. Table 1 presents the corresponding experimental conditions, and Fig. 2 depicts the evolution of the herbicide concentration *vs* reaction time in the experiments carried out at pH 2 and $T = 20$ °C. As can be seen, linuron had the highest oxidation rate, followed by chlorotoluron, diuron, and isoproturon, in that order. The same order of reactivity was observed for the other values of pH and temperature.

Fig. 3 shows the effect of pH on the photooxidation process at 20 °C for isoproturon and chlorotoluron taken as examples. One observes that the decay in concentration for each compound was almost the same for both values of pH (2 and 9). The behaviour of linuron and diuron was similar. Thus, pH has no significant influence on the herbicide photodegradation. On the contrary, the reaction temperature had a significant effect on the degradation rates. For example, as shown in Fig. 4, the rate of degradation of linuron increases with increasing temperatrure, as expected. Similar results were obtained for the other phenyl-ureas.

Since the reaction mechanisms for the photodegradation of organic compounds, in general, and the studied herbicides, in
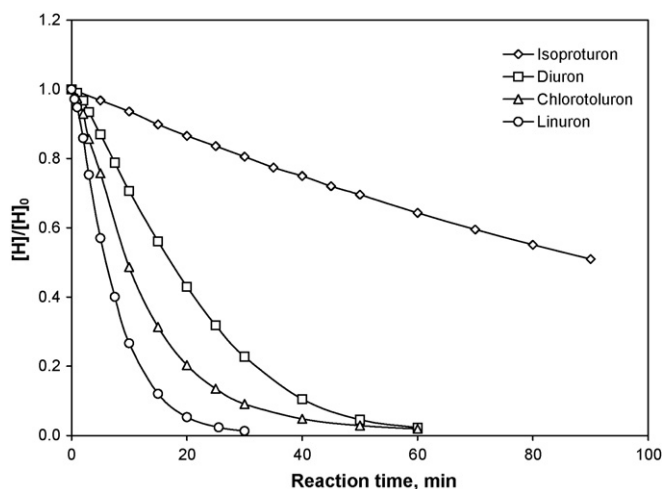

Fig. 2. Herbicide photooxidation curves with reaction time in ultra-pure water at 20 °C and pH 2. Herbicide initial concentrations = 25 ppm, equivalent to: [isoproturon]$_0$ = 121 μM; [chlorotoluron]$_0$ = 117 μM; [diuron]$_0$ = 107 μM; [linuron]$_0$ = 100 μM.

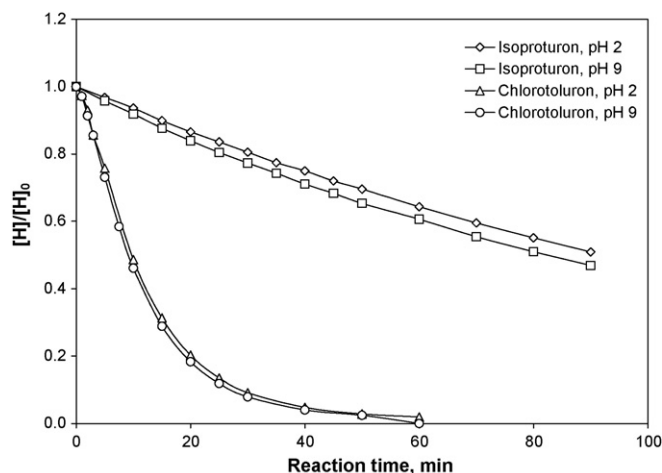Fig. 3. Influence of pH on the photooxidation of chlorotoluron and isoproturon at 20 °C. Herbicide initial concentrations = 25 ppm, equivalent to: [isoproturon]$_0$ = 121 μM; [chlorotoluron]$_0$ = 117 μM.
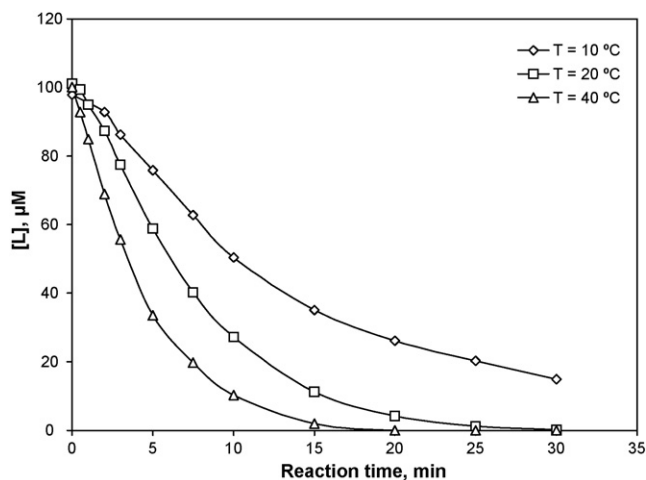

Fig. 4. Influence of temperature on the photooxidation of linuron at pH = 7, [linuron]$_0$ = 100 μM.

Table 1
Individual photooxidation of phenyl-urea herbicides in ultra-pure water

Herbicide	Experiment	T (°C)	pH	$k_{UV} \times 10^3$ (min^{-1})	$\phi \times 10^3$ (mol E^{-1})
Linuron	UVL-1	20	2	149.6	34.5
	UVL-2	20	5	158.6	38.2
	UVL-3	20	7	146.8	34.5
	UVL-4	20	9	154.0	36.7
	UVL-5	40	7	255.5	55.0
	UVL-6	10	7	71.5	19.2
Chlorotoluron	UVC-1	20	2	73.7	30.9
	UVC-2	20	9	69.7	32.8
	UVC-3	40	7	177.8	53.3
	UVC-4	10	7	40.3	14.8
Diuron	UVD-1	20	2	48.8	11.8
	UVD-2	20	9	53.3	11.2
	UVD-3	40	7	103.3	23.8
	UVD-4	10	7	22.3	5.7
Isoproturon	UVI-1	20	2	7.5	3.5
	UVI-2	20	9	8.4	3.9
	UVI-3	40	7	15.4	6.6
	UVI-4	10	7	7.2	3.6

particular, are complex, a first approximation to the process can be made by assuming that the photochemical oxidation follows simple first-order kinetics as follows:

$$H + h\upsilon \xrightarrow{\phi \mu I_0} H_{oxid} \tag{1}$$

where ϕ, μ, and I_0 are the quantum yield of the reaction, the absorbance of the solution, and the radiation intensity, respectively, for the wavelength of the monochromatic irradiation source that was used (254 nm). The rate equation for the herbicide elimination then can be written in the following form:

$$\ln \frac{[H]_0}{[H]} = k_{UV}t \tag{2}$$

where k_{UV} is the first-order rate constant.

Thus, a plot of $\ln [H]_0/[H]$ versus time for each herbicide should result in a straight line with a slope of k_{UV}. As an example, Fig. 5 shows this plot for the diuron experiments. The plots for the other herbicides were similar. As illustrated in Fig. 5, the data points are sufficiently close to straight lines such that the first-order rate constants could be deduced from semi-log linear regression analyses (Table 1). The resulting values for the rate constants confirm the trend noted above for the herbicide concentration decay curves; i.e., the highest k_{UV} corresponded to linuron, and the lowest to isoproturon, with chlorotoluron and diuron having intermediate rate constants. Since the pH
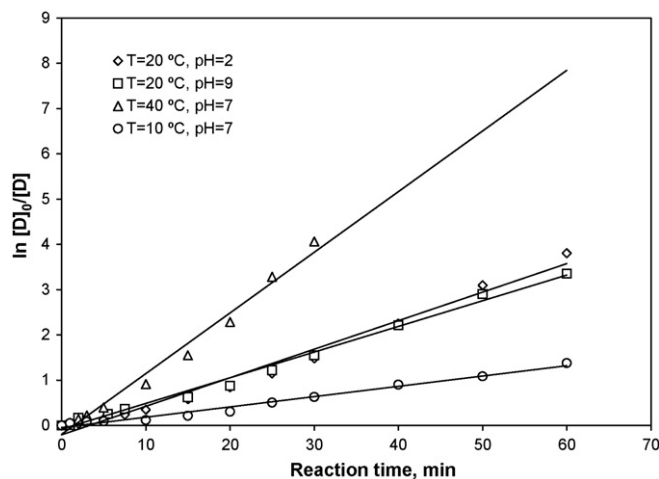

Fig. 5. Determination of the first-order rate constants for the photooxidation of diuron, [diuron]$_0$ = 107 μM. (Experiments performed with the diuron-UV radiation system, see Table 1.)

does not affect these first-order rate constants, one can propose for each herbicide an average value at 20 °C obtained from the different experiments. These values are given in Table 2 as 152.3×10^{-3} min^{-1} for linuron, 71.7×10^{-3} min^{-1} for chortoluron, 51.1×10^{-3} min^{-1} for diuron, and 8.0×10^{-3} min^{-1} for isoproturon.

A more rigorous procedure then was applied with the aim of evaluating the quantum yields ϕ for the photodegradation of these phenyl-ureas. The quantum yield is defined as the number of molecules reacted (or decomposed) per photon absorbed [15]. For this purpose, we took into account the results reported by other workers for the photooxidation of similar organic compounds [5,6] which indicate that the herbicide is the principal absorber. For conditions similar to those in the present study. We therefore used the reaction model described in detail in [16]. This model provides a general equation for the disappearance rate of each herbicide as a function of the absorbed radiation flux W_{abs} as follows:

$$-\frac{d[H]}{dt} = \frac{\phi}{V} W_{abs} \tag{3}$$

Integration of Eq. (3) with the initial condition gives the following final expression:

$$[H] = [H]_0 - \frac{\phi}{V} \int W_{abs} \, dt \tag{4}$$

The procedure for determining W_{abs} also is described in Ref. [16]. One uses a radiation source model which describes the

Table 2
Parameters obtained in the individual photooxidation of phenyl-urea herbicides in ultra-pure water, by using a monochromatic UV radiation lamp with a wavelength of 254 nm

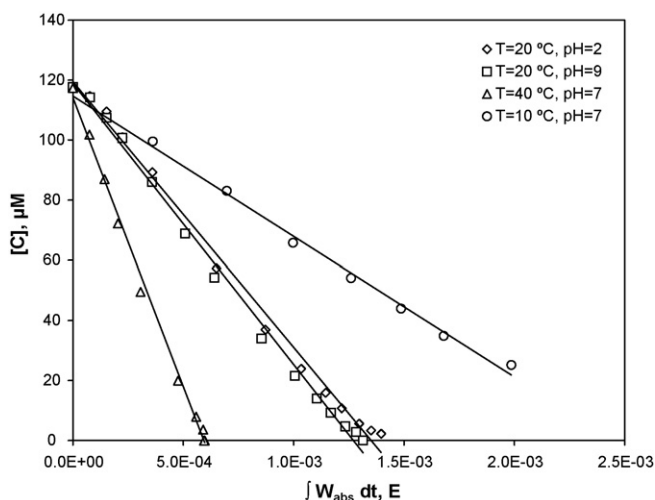| Herbicide	$k_{UV} \times 10^3$ (min^{-1})	ε (M^{-1} cm^{-1})	$\phi \times 10^3$ (mol E^{-1})	E_a (kcal mol^{-1})	ε_0 (mol E^{-1})
Linuron	152.3	13437	36.0	5.943	815.7
Chlorotoluron	71.7	6080	31.9	8.670	79777.8
Diuron	51.1	15699	11.5	8.146	12203.8
Isoproturon	8.0	6068	3.7	5.779	71.7

Fig. 6. Determination of the quantum yields for the photooxidation of chlorotoluron, [chlorotoluron]$_0$ = 117 μM. (Experiments performed with chlorotoluron and UV radiation see Table 1.)

distribution of radiant energy within the reactor. In this case, the line source spherical emission model [17] was selected.

Application of this model requires prior knowledge of the molar extinction coefficients ε. These coefficients were determined for the selected herbicides by measuring spectrophotometrically the absorbances of solutions with known concentrations. Then, according to the Lambert–Beer law, the slopes of the linear regressions of these absorbances against the solution concentrations represented the desired molar extinction coefficients ε. The average values obtained using this procedure also are given in Table 2 as 13,437, 6080, 15,699, and 6068 M^{-1} cm^{-1} for linuron, chlorotoluron, diuron, and isoproturon, respectively.

With W_{abs} determined for any reaction time, the integral $\int W_{abs}\, dt$ was calculated numerically. For this purpose and for every herbicide concentration [H], the experimental data (W_{abs}, t) were fitted to a polynomial expression by least squares regression, and the resulting function was integrated. With the integral terms evaluated according to Eq. (4), a plot of the herbicide concentration [H] versus the corresponding integral $\int W_{abs}\, dt$ should describe a straight line with an intercept [H]$_0$ and a negative slope ϕ/V. As the reactor volume is known (350 cm^3), the overall quantum yield ϕ of the photoreaction can be determined from this slope.

Fig. 6 shows this plot for the different photodegradation experiments conducted for chlorotoluron. As shown, the resulting data points essentially describe straight lines, confirming the representativeness of the model. A regression analysis for all the experiments then yielded the slopes ϕ/V and, together with the volume of the reacting mass, the overall quantum yields ϕ were evaluated. The resulting values obtained, with coefficients of determination $R^2 > 0.99$, are also listed in Table 1. The trends observed for the rate constants k_{UV} are also reproduced for the quantum yields; i.e., linuron > chlorotoluron > diuron > isoproturon. Similar to the case of the first-order rate constants, there was almost no influence of the pH on these ϕ values. Therefore, an average value at 20 °C obtained from the different experiments also can be proposed for each herbicide. These

values, given in Table 2, were 36.0 × 10^{-3} mol E^{-1} for linuron, 31.9 × 10^{-3} mol E^{-1} for chortoluron, 11.5 × 10^{-3} mol E^{-1} for diuron, and 3.7 × 10^{-3} mol E^{-1} for isoproturon. For comparison, Jirkovsky et al. [12] reported a value of 0.02 mol E^{-1} for diuron, while Faure and Boule [13] reported a value of 0.05–0.06 mol E^{-1} at 254 nm for linuron. Both values are in the same range as those of the present research, but an exact comparison is not possible because the temperature and pH were not specified for the referenced values. Similarly, for chlorotoluron and isoproturon, Tixier et al. [14] reported values of 0.031 and 0.002 mol E^{-1}, respectively, for the quantum yield at 254 nm, although again without specification of the temperature and pH of their experiments. The former is in perfect agreement with, and the latter is quite similar to, the respective values determined in the present work at 20 °C.

Increasing the temperature, however, led to an increase in the quantum yield in all cases. A regression analysis of these quantum yields an Arrhenius-type function of temperature of the form:

$$\phi = \phi_0 \exp\left(-\frac{E_a}{T}\right) \qquad (5)$$

where the ϕ_0 and E_a values are listed in Table 2. The correlation of this equation with the experimental results was satisfactory for all four phenyl-urea herbicides.

3.2. Photochemical oxidation of herbicide mixtures in different types of waters

Following the initial stage of investigating the individual photooxidation of the selected herbicides in ultra-pure water, we then studied the photolysis of mixtures of these herbicides dissolved in the different types of waters previously noted. Oxidation was carried out by means of UV radiation alone, and UV radiation combined with two different concentrations of H$_2$O$_2$ in order to generate the very reactive and oxidizing hydroxyl radicals. Additionally, for the photooxidation by UV radiation alone, experiments were conducted both with and without the presence of tert-butyl alcohol (t-BuOH).

The operating conditions that were maintained constant in these experiments were pH 7, $T = 20$ °C, and initial concentrations of 25 ppm for the herbicides. The two initial concentrations of hydrogen peroxide in the combined UV/H$_2$O$_2$ system were 1×10^{-3} and 5×10^{-3} M, and the concentration of t-BuOH when present was 0.1 M.

Firstly, we shall discuss the effect of the presence or absence of t-BuOH in the reactor. As is well known, t-BuOH is a scavenger of hydroxyl radicals [18], such that direct photolysis was expected to be the only significant pathway for the photooxidation process when t-BuOH was present. Fig. 7 presents the decay curves against reaction time for isoproturon and diuron (taken as examples) in photooxidation experiments with the ultra-pure water using UV radiation alone. The two degradation curves in Fig. 7 are quite similar for each herbicide, and are independent of the presence of t-BuOH, indicating a negligible contribution of the radical pathway to the overall reaction rate in the radiation process. In other words, few radicals are produced in the pho-
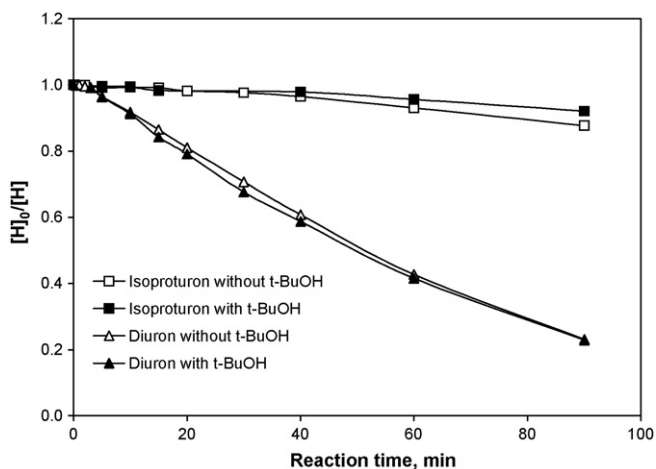
Fig. 7. Influence of the presence of t-BuOH on the photooxidation of diuron and isoproturon in ultra-pure water. Herbicide initial concentrations = 25 ppm, equivalent to: [isoproturon]$_0$ = 121 μM and [diuron]$_0$ = 107 μM.

Fig. 9. Influence of the nature of the phenyl-urea herbicides on the simultaneous photooxidation of the herbicides in the lake water by the combined system UV/H$_2$O$_2$. Herbicide initial concentrations = 25 ppm, equivalent to: [isoproturon]$_0$ = 121 μM; [chlorotoluron]$_0$ = 117 μM; [diuron]$_0$ = 107 μM; [linuron]$_0$ = 100 μM. [H$_2$O$_2$]$_0$ = 5 × 10^{-3} M.

tooxidation of these organic compounds by UV radiation alone and, therefore, the only pathway acting is direct photolysis.

Fig. 8 shows the decrease in diuron concentration as a function of reaction time in experiments carried out with UV radiation alone and in combination with hydrogen peroxide in ultra-pure water. The similar results were similar for the other herbicides and waters. One clearly observes the expected positive effect of the combined UV/H$_2$O$_2$ system relative to the photodegradation by UV radiation alone, and of the higher initial concentration of H$_2$O$_2$ on the combined UV/H$_2$O$_2$ process, with a higher disappearance rate for the greater initial concentration.

Similarly, it is interesting to establish the influence of the nature of the herbicide on the photooxidation rate. For example, Fig. 9 shows the degradation curves of the selected herbicides with reaction time in the photodegradation by the UV/H$_2$O$_2$ combination (with initial hydrogen peroxide concentration of 5 × 10^{-3} M) in the water from the "Peña del Aguila" lake. As

shown, isoproturon presents the lowest oxidation rate, followed by chlorotoluron and diuron with quite similar rates, and linuron with the highest rate. This same oxidation ranking was found for the other waters, and coincides with that previously described for the quantum yields during the individual photooxidation of each herbicide in ultra-pure water solutions.

Finally, the effect of the type of water on the herbicides photooxidation is illustrated in Fig. 10, which shows as an example the concentration curves of chlorotoluron versus reaction time in experiments performed with UV radiation alone. The fastest degradation occurs in the ultra-pure water solutions, followed by mineral water and groundwater, and finally the slowest elimination in the "Peña del Aguila" lake water. Similar results were obtained for the other herbicides with both UV radiation alone and in combination with the two concentrations of H$_2$O$_2$.

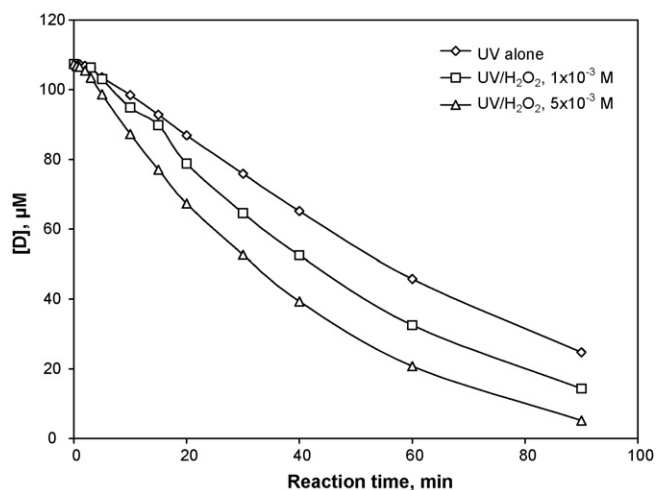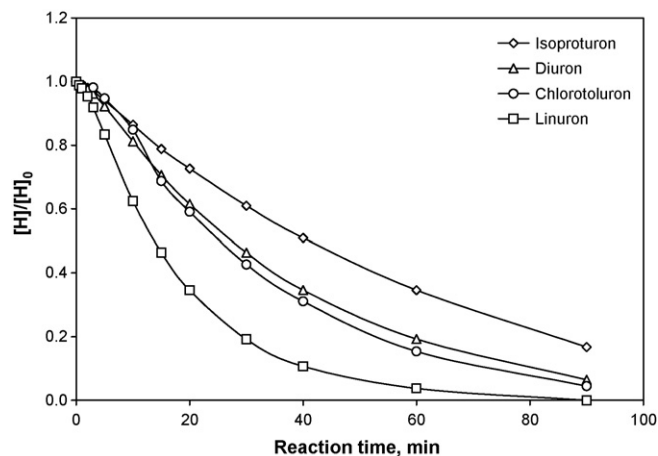The higher rates of herbicide elimination in the ultra-pure and mineral waters are due to the absence or near absence of

Fig. 8. Influence of the type of oxidation process on the photooxidation of diuron in ultra-pure water, [diuron]$_0$ = 107 μM, and [H$_2$O$_2$]$_0$ = 1 × 10^{-3} M (□) or 5 × 10^{-3} M (△).
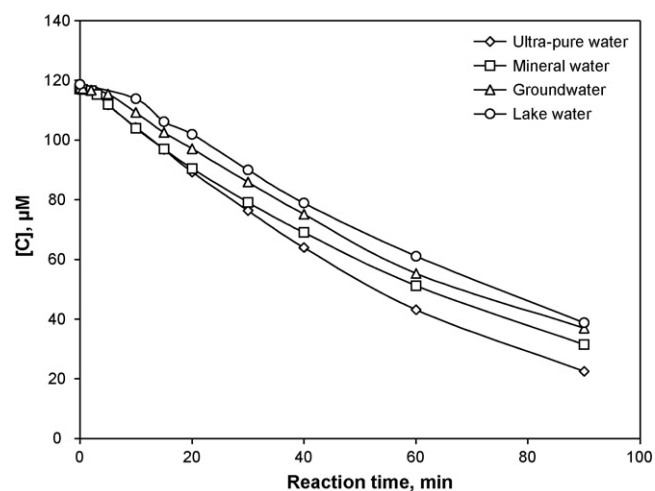

Fig. 10. Influence of the type of water on the photooxidation of chlorotoluron by UV radiation alone, [chlorotoluron]$_0$ = 117 μM.

organic and inorganic compounds that could consume radiation and hydroxyl radicals. On the contrary, in the groundwater and lake water, with some organic compound and bicarbonate ion content, a smaller concentration of OH radicals is available to react with the herbicides, resulting in a lower rate of herbicide degradation. In natural waters of this type, therefore, a higher dose of oxidants is required if greater contaminant removal is desired. These results are confirmed by the measured absorbances at 254 nm of these waters previously presented: i.e., an assumed zero value for ultra-pure water, and 0.002, 0.050, and 0.179 for the mineral water, groundwater, and "Peña del Aguila" lake water, respectively. The measured absorbances and observed herbicides elimination rates in he different types of waters indicate that the herbicides and hydrogen peroxide are competing with the organic matter which may be present for the absorption of UV. In particular, in the ultra-pure aqueous solution and mineral waters, with lower absorbance values, more UV radiation is available for the oxidation of herbicides and hydrogen peroxide.

3.3. Kinetic study of the photochemical processes of herbicide mixtures

As was indicated above, a kinetic study was performed with the objective of being able to predict and model the photodegradation rate of some pollutants (specifically, the selected herbicides) in a mixture of organic substances that could be present in any kind of water. These pollutants may be simultaneously photodegraded in a general purification process of the selected water by each of the oxidant systems used in the present work—UV radiation alone or the combination UV/H$_2$O$_2$. Once such a photodecomposition rate equation has been established, the concentration profile for each compound at any reaction time can be evaluated. To this end, we will use some of the kinetic parameters obtained previously, and others yet to be determined.

We will assume a very simple reaction mechanism for this oxidation system. This considers that the overall oxidation of each substance in the herbicide mixture is the result of the contribution of two individual reaction pathways: the direct photochemical reaction, and the radical reaction between the organic compound and the hydroxyl radicals generated in the UV/H$_2$O$_2$ system.

In addition, we will use a competitive kinetic model describing the simultaneous degradation of mixtures of several organic compounds by any oxidant or combination of oxidants. One of these substances must be taken as the reference compound R, with known degradation rate constants. The other substances are taken as the target compounds P, with unknown rate constants. This procedure is reliable when measuring the rates of fast reactions in aqueous solutions, and is based on assuming that the reaction between the oxidant and each organic compound is second-order overall, and first-order with respect to both reactants.

In order to consider the aforementioned reaction mechanism, one must set up rate equations for the two reactions (direct and radical pathways). For the direct photochemical reaction of an absorbing compound (such as the reference compound R in the present case) by a monochromatic radiation source, the disappearance rate equation is well established [19]:

$$-\frac{d[R]}{dt} = 2.303[R]\ell\phi\varepsilon\frac{I_0}{V} \tag{6}$$

where ϕ, I_0, and ε are the same as previously defined, i.e., quantum yield of the reaction, radiation intensity (with the measured value 2.03×10^{-6} E s^{-1}), and molar extinction coefficient, respectively, for the wavelength of the monochromatic irradiation source used (254 nm)—and l is the reactor's optical path length. As given by Zamy et al. [19], the integrated form of Eq. (6) is as follows:

$$\ln\frac{[R]_0}{[R]}\bigg|_d = 2.303\ell\phi\varepsilon\frac{I_0}{V}t = k'_{\phi-R}t \tag{7}$$

where $k'_{\phi-R}$ represents an apparent first-order rate constant for the direct photodecomposition of this reference compound which includes the factor $(2.303l\Phi\varepsilon I_0/V)$.

Similarly, for each target compound, one can write:

$$\ln\frac{[P]_0}{[P]}\bigg|_d = k'_{\phi-P}t \tag{8}$$

with $k'_{\phi-P}$ being the pseudo first-order rate constant for the direct photochemical decomposition of this target compound.

For the radical reaction between the reference compound and the hydroxyl radicals, the second-order kinetics leads to the following rate equation:

$$-\frac{d[R]}{dt} = k_{OH-R}[OH][R] = k'_{OH-R}[R] \tag{9}$$

As the concentration of hydroxyl radicals remains almost constant (they are consumed, but at the same time continuously generated), the product (k_{OH-R} [OH·]) can be converted into a pseudo first-order rate constant k'_{OH-R} for this radical reaction. After integration, one obtains:

$$\ln\frac{[R]_0}{[R]}\bigg|_r = k'_{OH-R}t \tag{10}$$

Similarly for the target compounds, with the same consideration for the second-order kinetics and the transformation into pseudo first-order, one has:

$$\ln\frac{[P]_0}{[P]}\bigg|_r = k'_{OH-P}t \tag{11}$$

In a general process where both reaction pathways (direct and radical reactions) contribute significantly, and taking into account the equations described above, the following kinetic equation may be proposed for the reference compound:

$$\ln\frac{[R]_0}{[R]} = k'_R t = \ln\frac{[R]_0}{[R]}\bigg|_d + \ln\frac{[R]_0}{[R]}\bigg|_r = (k'_{\phi-R} + k'_{OH-R})t \tag{12}$$

Similarly, for any target compound P:

$$\ln\frac{[P]_0}{[P]} = k'_P t = \ln\frac{[P]_0}{[P]}\bigg|_d + \ln\frac{[P]_0}{[P]}\bigg|_r = (k'_{\phi-P} + k'_{OH-P})t \tag{13}$$

In Eqs. (12) and (13), k'_R and k'_P represent the pseudo first-order rate constants for the overall decomposition reactions of the reference and targets compounds.

Given the proposal of the reaction mechanism, one now applies the aforementioned competitive kinetics method. Several researchers have used this general dynamic approach to describe the oxidation of some organic compounds by different oxidants such as ozone [20,21], UV radiation [19,22,23], and hydroxyl radicals [16,24–26]. In the present case, for the photooxidation by UV radiation alone, when the only contribution to the overall degradation rate is from direct photolysis, the application of this competitive kinetic model yields the following final expression [19,22,23]:

$$\ln \left. \frac{[P]_0}{[P]} \right|_d = \frac{\phi_P \varepsilon_P}{\phi_R \varepsilon_R} \ln \left. \frac{[R]_0}{[R]} \right|_d \quad (14)$$

where ϕ_P and ε_P, and ϕ_R and ε_R, represent the quantum yields and molar extinction coefficients for the target and reference compounds, respectively.

Similarly, for the case when the only contribution to the overall degradation rate is from hydroxyl radicals, the competitive kinetic model yields the following expression [16,24–26]:

$$\ln \left. \frac{[P]_0}{[P]} \right|_r = \frac{k_{OH-P}}{k_{OH-R}} \ln \left. \frac{[R]_0}{[R]} \right|_r \quad (15)$$

where k_{OH-P} and k_{OH-R} are the second-order rate constants for the reaction between OH radicals and the target and the reference compounds, respectively.

Substituting Eqs. (14) and (15) into Eq. (13), and then using Eqs. (7) and (10), one finally has

$$\ln \frac{[P]_0}{[P]} = k'_P t = \frac{\phi_P \varepsilon_P}{\phi_R \varepsilon_R} k'_{\phi-R} t + \frac{k_{OH-P}}{k_{OH-R}} k'_{OH-R} t \quad (16)$$

The value of Eq. (16) is clear. Once the kinetic rate constants ($k'_{\phi-R}$ and k'_{OH-R}) that characterize the photodegradation of a reference compound in a particular water are known, the overall rate constant k'_P for any target compound in that specific water can be evaluated if the quantum yields ϕ_R and ϕ_P, molar extinction coefficients ε_R and ε_P, and rate constants with OH radicals k_{OH-R} and k_{OH-P} are known for both the reference and the target compounds. Additionally, the concentration of P at any reaction time can also be predicted by using Eq. (16).
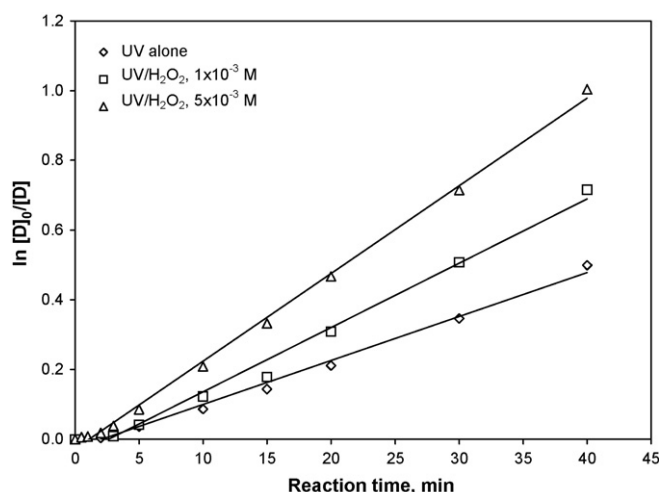

Fig. 11. Determination of the first-order rate constants for the photooxidation of the reference compound (diuron) in ultra-pure water by the combination UV/H$_2$O$_2$, [diuron]$_0$ = 107 μM, and [H$_2$O$_2$]$_0$ = 1 × 10^{-3} M (□) or 5 × 10^{-3} M (△).

In the present study, we applied the above model to the photodegradation of mixtures of the four selected phenyl-urea herbicides in different types of water, by both UV radiation alone and the UV/H$_2$O$_2$ combination. In this specific case, diuron was selected as the reference compound R because diuron presents an intermediate reactivity with respect to photochemical processes (see Fig. 9), and also because of the special relevance of diuron as a priority pollutant present in natural waters. According to Eq. (12), plots of ln([R]$_0$/[R]) versus reaction time should be straight lines. This result is apparent in Fig. 11, which shows the elimination of diuron in ultra-pure water by UV radiation alone, and by the two combined UV/H$_2$O$_2$ systems. The rate constants k'_R were determined as the slopes of the linear regressions for these experiments with the four types of water. The values are listed in Table 3.

Obviously, in the case of the photooxidation experiments by UV radiation alone, the contribution of the radical pathway to the overall reaction is inexistent, i.e., $k'_{OH-R} = 0$, and consequently the value of k'_R coincides with $k'_{\phi-R}$ (see Eq. (12)). On the contrary, in the experiments performed with the UV/H$_2$O$_2$ systems, the contribution of the radical reaction is significant. Therefore, the slopes obtained from the regression analysis correspond to the overall rate constants k'_R, and, according to Eq. (12), sub-

Table 3
First-order rate constants obtained for the reference compound (diuron)

Type of water	$k'_R \times 10^3 = k'_{\phi-R} \times 10^3$ (min^{-1})[a]	$k'_R \times 10^3$ (min^{-1})[b]	$k'_{OH-R} \times 10^3$ (min^{-1})[b]	$k'_R \times 10^3$ (min^{-1})[c]	$k'_{OH-R} \times 10^3$ (min^{-1})[c]
Ultra-pure	13.1	18.4	5.3	25.1	12.0
Mineral	12.6	14.5	1.9	29.8	17.2
Groundwater	11.6	14.1	2.5	23.4	11.8
Lake	11.3	14.0	2.7	24.2	12.9

Experimental conditions: pH 7, $T = 20\,^{\circ}$C and [herbicide]$_0$ = 25 ppm.
[a] Experiments with UV radiation alone.
[b] Experiments with UV/H$_2$O$_2$ system: [H$_2$O$_2$]$_0$ = 1 × 10^{-3} M.
[c] Experiments with UV/H$_2$O$_2$ system: [H$_2$O$_2$]$_0$ = 5 × 10^{-3} M.

Table 4
Model-predicted values obtained for the first-order rate constants for linuron, chlorotoluron and isoproturon

Herbicide	Type of water	$k'_P \times 10^3$ (min^{-1})[a]	$k'_P \times 10^3$ (min^{-1})[b]	$k'_P \times 10^3$ (min^{-1})[c]
Linuron	Ultra-pure water	35.7	39.2	45.4
	Mineral water	33.1	36.4	43.7
	Groundwater	31.3	33.9	41.6
	Lake water	30.1	33.3	42.8
Chlorotoluron	Ultra-pure water	14.1	18.9	29.2
	Mineral water	13.5	15.4	28.7
	Groundwater	12.4	14.7	23.4
	Lake water	12.1	14.7	24.2
Isoproturon	Ultra-pure water	1.6	8.1	20.7
	Mineral water	1.6	3.2	20.5
	Groundwater	1.4	4.6	15.1
	Lake water	1.4	4.2	14.7

Experimental conditions: pH 7–8, $T = 20\,^{\circ}C$ and [herbicide]$_0$ = 25 ppm.

[a] Experiments with UV radiation alone.
[b] Experiments with UV/H$_2$O$_2$ system: [H$_2$O$_2$]$_0$ = 1×10^{-3} M.
[c] Experiments with UV/H$_2$O$_2$ system: [H$_2$O$_2$]$_0$ = 5×10^{-3} M.

tracting the already evaluated $k'_{\phi-R}$ values from the constants k'_R yields the first-order rate constants for the radical pathway k'_{OH-R}. Table 3 also lists these rate constants for this reference compound. As expected, the experiments with the higher initial hydrogen peroxide concentration gave higher values for k'_{OH-R}, reflecting a greater generation of hydroxyl radicals.

Once the kinetic constants $k'_{\phi-R}$ and k'_{OH-R} for the reference compound have been determined, they can be used to predict the elimination of the remaining herbicides when photooxidized simultaneously with diuron, by using Eq. (16) and the remaining parameters contained therein. The ϕ and ε values were determined experimentally in the first part of this study, and are listed in Table 2. These values must be taken as ϕ_R and ε_R for diuron, and ϕ_P and ε_P for linuron, chlorotoluron and isoproturon. The rate constants for the reaction between each herbicide and OH radicals (i.e., k_{OH-R} for diuron, and the respective values of k_{OH-P} for linuron, chlorotoluron, and isoproturon) were determined and reported in a previous publication [27]. Their values are 4.6×10^9 L mol^{-1} s^{-1} for diuron, 4.3×10^9 L mol^{-1} s^{-1} for linuron, 4.3×10^9 L mol^{-1} s^{-1} for chlorotoluron, and 5.2×10^9 L mol^{-1} s^{-1} for isoproturon.

Table 4 lists the k'_P values obtained for the target compounds (linuron, chlorotoluron, and isoproturon) after the application of Eq. (16). Once again, the trends discussed above in the influence of the independent variables are confirmed: i.e., higher reactivity of the herbicides in the ultra-pure and mineral waters, followed by the groundwater and the "Peña del Aguila" lake water. There were also higher rates with the UV/H$_2$O$_2$ system than with UV radiation alone. As a test of the utility of the model, Fig. 12 shows as an example the concentration decay curves of the herbicides predicted theoretically (lines) from Eq. (16), as well as the experimental values obtained during the treatment of the mineral water by UV radiation combined with H$_2$O$_2$ (initial concentration 1×10^{-3} M). Similar plots were obtained for the other waters and oxidation systems. Satisfactory agreement between the predicted and experimental values is apparent, confirming the goodness of the proposed model. In effect, all the
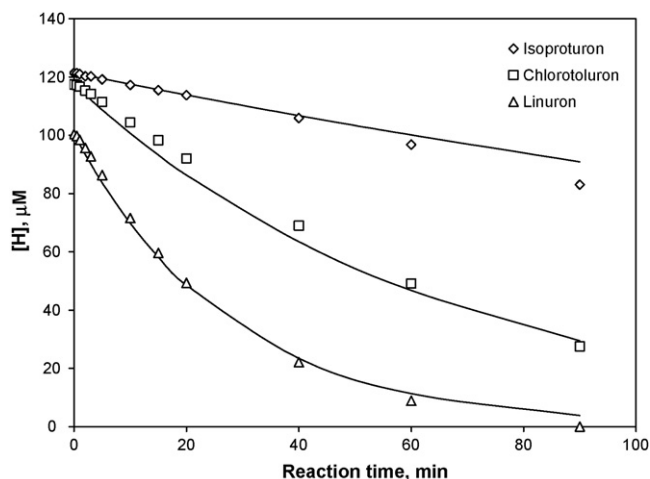

Fig. 12. Comparison of the predicted (lines) and experimental (symbols) concentrations of linuron, chlorotoluron, and isoproturon in the photooxidation by the combination UV/H$_2$O$_2$ in the mineral water. Herbicide initial concentrations = 25 ppm, equivalent to: [isoproturon]$_0$ = 121 μM; [chlorotoluron]$_0$ = 117 μM; [linuron]$_0$ = 100 μM. [H$_2$O$_2$]$_0$ = 1×10^{-3} M.

predicted values deviated less than 3% from the corresponding experimental ones.

In summary, the proposed kinetic approach allows one to predict the elimination rate of each pollutant present in a mixture in any kind of water during its photochemical treatment. A minimal set of experiments must be carried out with that water in the presence of a reference compound, by applying both UV radiation alone and the combination UV/H$_2$O$_2$ (in order to evaluate the rate constants $k'_{\phi-R}$ and k'_{OH-R}). The quantum yields, the molar extinction coefficients, and the rate constants with OH radicals must be known *a priori* for all the compounds involved.

4. Conclusions

The individual photooxidation of the selected phenyl-urea herbicides in ultra-pure water by a monochromatic UV irradi-

ation showed linuron to have the highest oxidation rate, isoproturon the lowest, and diuron and chlorotoluron intermediate values. Almost no influence on the photodegradation process was observed by increasing the pH from 2 to 9, while increasing the temperature led to an increase in the reaction rate. The first-order rate constants were evaluated in a first-order kinetic approximation. The application of the line source spherical emission model to the experimental results allowed us to determine the absorbed radiation flux and the photochemical quantum yields. The average values of the latter at 20 °C and independently of the pH were 36.0×10^{-3} mol E^{-1} for linuron, 31.9×10^{-3} mol E^{-1} for chlorotoluron, 11.5×10^{-3} mol E^{-1} for diuron, and 3.7×10^{-3} mol E^{-1} for isoproturon.

The simultaneous photooxidation of mixtures of these phenyl-ureas in different types of water (ultra-pure water, commercial mineral water, groundwater, and lake water) showed the same trend of reactivities to both UV radiation alone and the UV/H$_2$O$_2$ combination: i.e., linuron > chlorotoluron > diuron > isoproturon. The presence of *t*-BuOH did not modify the photoreaction rate, which seems to indicate that direct photolysis is the only pathway involved in photodegradation by UV radiation alone. The oxidation rate for each herbicide was highest in the ultra-pure water, followed by the mineral water, groundwater, and lake water, in that order. This result was consistent with their experimentally measured absorbances, which constitute a measure of their organic matter content. For a specific herbicide in any type of water, the presence of H$_2$O$_2$ enhanced the photodegradation rate due to the generation of oxidizing hydroxyl radicals. From a perspective of competitive kinetics, a kinetic model was proposed that allows one to predict and model the elimination of phenyl-ureas in any type of water, using some of the basic parameters determined previously for these herbicides (rate constants and quantum yields). The concentrations predicted with this model agreed well with the experimental results, indicating that the model could be of use for the drinking water treatments applied in water purification plants.

Acknowledgements

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