Effects of the H$_2$O$_2$ concentration and spectral distribution of the UV lamp output power on the photooxidation of a water pollutant

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Abstract Previous kinetics studies have been extended to analyze some practical issues concerning this process. Hence, in this work we have studied additional aspects of the H$_2$O$_2$ enhanced, UV degradation of 2,4-dichlorophenoxyacetic acid (2,4-D), namely: (i) the effect of the H$_2$O$_2$/2,4-D initial molar ratio and (ii) the effect of the irradiation power and, particularly, the characteristics of the wavelength distribution of the lamp output emission. The work was done on a well stirred, discontinuously operated tank reactor irradiated from its bottom. A UV, tubular lamp and a cylindrical reflector of parabolic cross section were used [actually, two germicidal lamps (254 nm) of different output power per unit lamp length and a medium pressure, mercury arc lamp with polychromatic emission between 220 and 760 nm]. 2,4-D concentration and TOC were the main variables used to investigate the degradation rate. There is an optimal initial concentration ratio for each 2,4-D initial concentration. It was also observed that increasing the lamp output power at 254 nm (output from 0.08 W/cm to 0.6 W/cm) favors the reaction rate. However, much more significant is the effect produced by employing a polychromatic lamp with some emission below 254 although this photonic contribution is relatively small (just 0.21 W/cm below 250 nm). A kinetic model, having parameters independent of the reactor configuration and derived from mechanistic considerations was used to analyze the experimental data.

Keywords Advanced oxidation technologies; 2,4-dichlorophenoxyacetic acid; ultraviolet radiation; hydrogen peroxide; reaction kinetics

Introduction
Increasing concern for protecting the environment has led to growing efforts in the application of advanced oxidation technologies for the treatment of air and water. Among them, the use of UV irradiation combined with the presence of different oxidants is a typical example. The objective is to produce the in situ generation of highly reactive chemical species to oxidize organic contaminants. Usually, UV radiation is used in conjunction with ozone, hydrogen peroxide (HP) or a mixture of hydrogen peroxide and ferric salts. In all cases and with different rates a large variety of water pollutants can be degraded. The final objective may be the total mineralization of the organic compound (e.g., transform 2,4-D in CO$_2$, H$_2$O and HCl) or partial oxidation to reach products of much higher biodegradability (i.e., higher BOD).

In the past we have studied the degradation of a widely spread water contaminant, the 2,4-dichlorophenoxyacetic acid (2,4-D) under the following conditions: (1) employing UV alone (Cabrera et al., 1997) and (2) employing UV + HP (Cabrera et al., 1999, Alfano et al., 2000).

Two important technical questions were not addressed in those studies: (1) the existence of an optimal initial concentration ratio for the system HP/2,4-D, including the existence of a single value for this relationship and (2) the selection of the most appropriate radiation source as far as the spectral characteristics of its output power (wavelengths of emission).

The change in the HP concentration may have two different and opposite effects (Stefan et al., 1996): (i) at low HP concentration, radiation absorption may be too low and so will be
the OH radical generation, and (ii) at high HP concentration it acts as a radical trapping agent, thus competing with the pollutant degradation path and rendering lower degradation rates. Thus, an optimal concentration ratio should be expected. An additional question is related to the potential uniqueness of this optimal ratio and its relationship with the reaction stoichiometry.

The second aspect that must be also analyzed is the effect of the spectral distribution of the radiation source emission (Hager, 1990). The main alternatives may be defined as follows: (i) low pressure mercury lamps (germicidal type) with substantial emission at 253.7 nm and (ii) medium or high pressure mercury lamps with a much broader range of emission, usually from 220 nm to sometimes even more than 800 nm. In the first case, absorption by HP is not too high, leading to rather low reaction rates. But usually, in a properly designed reactor, more than 90% of the energy produced by the lamp will be used in the degradation reaction. Sometimes, at this wavelength, the pollutant may compete with the HP in radiation absorption leading to a parallel direct photolysis (as it is the case with 2,4-D) but reducing the energy availability for the generation of OH• radicals. Conversely, the second group of lamps will have emission in a region of much higher radiation absorption by the HP (λ < 250 nm) producing higher degradation rates. This beneficial effect is achieved with a relatively high consumption of energy because of radiation emission in wavelengths above 300 nm, where neither absorption by HP nor direct photolysis will occur. A third group of lamps is also possible: there exist Excimer UV lamps with almost monochromatic emission at 222 nm but they are rather expensive and not regularly produced in large sizes.

Objectives
1. To determine the existence of an optimum hydrogen peroxide/contaminant concentration ratio for the UV degradation of 2,4-D and to decide if this value is unique.
2. To quantify the efficiency of irradiating the hydrogen peroxide/contaminant mixture with radiation below 250 nm.
3. To develop a kinetic model for the degradation reaction, independent of the reactor configuration and operating conditions.

Experimental
The reaction was studied in a well stirred, batch reactor irradiated from the bottom with a tubular lamp. The UV lamp is placed at the focal axis of a cylindrical reflector of parabolic cross section (see Table 1 and Cabrera et al., 1997).

We have used three different types of lamps: two of them were of the germicidal type having nominal input powers of 15 and 40 W with almost monochromatic output at 254 nm and producing a per unit length emission of 0.08 W/cm and 0.6 W/cm of output power respectively. The third lamp was a medium pressure, mercury arc type with 360 W of nominal input power. The dimensions and main characteristics are also described in Table 1. The output power of this lamp in the entire range of emission is 4 W/cm and below 254 nm just 0.21 W/cm.

The bottom of the reactor was made of Suprasil quartz to ensure the admission of the desired irradiation wavelength. Very good stirring conditions were always present and the temperature was kept constant. Other employed materials and operating methods have been described in Cabrera et al. (1997). Experimental runs lasted from 2 to 6 hours depending upon the lamp output power and the initial 2,4-D and H₂O₂ concentrations.
Table 1 Reacting system and lamp characteristics

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Lamp Heraeus UVC NNI40/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>2000 (cm³)</td>
</tr>
<tr>
<td>Irradiated area</td>
<td>132.7 (cm²)</td>
</tr>
<tr>
<td>Reflector</td>
<td></td>
</tr>
<tr>
<td>Parabola characteristic constant</td>
<td>2.1 (cm)</td>
</tr>
<tr>
<td>Distance reflector vertex to reactor</td>
<td>8.4 (cm)</td>
</tr>
<tr>
<td>Length</td>
<td>15.8 (cm)</td>
</tr>
<tr>
<td>Diameter</td>
<td>1.5 (cm)</td>
</tr>
<tr>
<td>Arc length</td>
<td>20 (cm)</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Lamp GE 360 UA-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal power</td>
</tr>
<tr>
<td>Output power at 220–300 nm</td>
</tr>
<tr>
<td>Output power at 220–760 nm</td>
</tr>
<tr>
<td>Diameter</td>
</tr>
<tr>
<td>Arc length</td>
</tr>
</tbody>
</table>

Results and discussion

Effect of the hydrogen peroxide concentration

The degradation reaction with UV and hydrogen peroxide is rather slow. To reduce the reaction time, these studies were performed using the monochromatic, 40 W, Heraeus germicidal lamp. Figure 1 portrays experimental results corresponding to initial photodegradation reaction rates as a function of the initial molar concentration ratio \( r = \frac{\text{H}_2\text{O}_2}{2,4\text{-D}} \) for two initial pollutant concentrations: 30 and 90 ppm. It can be clearly seen that rates increase with \( r \) and that for values of \( r \) between 25 and slightly over 30 the maximum initial reaction rate is reached.

During the course of the reaction, equally toxic reaction intermediates were observed such as 2,4 dichlorophenol and chlorohydroquinone (Alfano et al., 2000). Thus, it is convenient to add an additional variable to control, from a practical standpoint, the pollution abatement. Total organic carbon (TOC) has been chosen as an indicator. Figure 2 shows the results of the TOC conversion (after a reaction time \( t = 4 \text{ h} \)) vs. the initial molar ratio of \( \text{H}_2\text{O}_2/2,4\text{-D} \), for two different initial concentrations of the water pollutant. These results indicate that for a 2,4-D initial concentration of 90 ppm the initial optimal HP/2,4-D concentration ratio is about 32, whereas for an initial concentration of 30 ppm this ratio is smaller (ca. 20). Consequently, a single value for this optimal ratio does not exist. Moreover, it was observed that this optimal initial concentration ratio increases with the increase in pollutant concentration. In other words, there is no direct relationship between the stoichiometric demand of OH( radicals and this optimal ratio.

![Figure 1](https://iwaponline.com/ws/article-pdf/1/2/73/408271/73.pdf)

**Figure 1** Initial reaction rate of 2,4-D vs. \( \frac{\text{H}_2\text{O}_2}{2,4\text{-D}} \) initial molar ratio \( r \)

![Figure 2](https://iwaponline.com/ws/article-pdf/1/2/73/408271/73.pdf)

**Figure 2** TOC conversion vs. \( \frac{\text{H}_2\text{O}_2}{2,4\text{-D}} \) initial molar ratio \( r \)
Effects of the lamp spectral emission characteristics

Results with three different UV lamps are reported in this section (see Table 1). Figure 3(a) shows results of 2,4-D concentration vs. time for a molar ratio of \( r = 8 \), an initial 2,4-D concentration of 30 ppm and for the three employed lamps. With the 360 W polychromatic lamp the time needed to reach a significant reduction of the pollutant concentration is greatly shortened. For example: (i) half of one hour for the 360 W lamp, (ii) 2 hours for the 40 W lamp, and (iii) 4 hours with the 15 W lamp. It is fair to note that the 15 W lamp (0.08 W/cm) is not totally used because only 15.8 cm are inside the reflector that is used to irradiate the reactor; i.e. approximately only 5 W of its nominal input power are really being used in the illuminating system. Figure 3 (b) shows an important increase in the required time and this result is directly related to the initial pollutant concentration (90 ppm for this case).

If we use the TOC measurements, we obtain results as shown in Figures 4 (a) and (b). The operating conditions are the same as described before: three different lamps, \( r = 8 \) and initial 2,4-D concentrations of 30 and 90 ppm. In this case, the observed differences are much more pronounced. For the 15 W lamp, after 6 hs the TOC decrease is still unacceptable. Good improvement is obtained with the 40 W lamp but the most noticeable result is obtained employing radiation below 254 nm. In this case, after 2 hs the TOC drops to an almost negligible value (4 hs for 2,4-D initial concentration of 90 ppm.). However, it should be noted that complete mineralization is not always required. Sometimes, after an
initial oxidation, a less expensive treatment (e.g., biological purification) can be applied. In other cases, as long as the intermediate reaction products are non-toxic the desired degradation can be stopped once the maximum tolerable TOC is achieved (very often expressed in terms of chemical oxygen demand, COD).

The initial degradation rates of 2,4-D are presented in Figure 5 (a) and (b) for the three lamps, two initial concentrations and two different molar ratios: \( r = 0 \) (direct photolysis) and \( r = 8 \) (\( \text{H}_2\text{O}_2 \) enhancement). In all cases, a noticeable increment in the degradation rate (between 6 to 32 times) is observed when \( \text{H}_2\text{O}_2 \) is added. Even better yields are obtained employing radiation below 250 nm. After comparing the 360 W lamp (between 220 and 300 nm, 0.92 W/cm) with the 40 W lamp (0.6 W/cm), the initial rate increases up to 4 times for the UV-HP combined process and up to 18 times when direct photolysis alone is used.

Clearly, absorption by hydrogen peroxide below 250 nm becomes significant and yields a better use of the inputted energy.

Figure 6 (a) and (b) shows a similar representation but the dependent variable is the TOC conversion. Using the 360 W (only 3.14 W from 220 to 250 nm, 3.95 W at 254 nm and 6.87 W from 260 to 300 nm), for \( r = 8 \) the following results are obtained: (i) an increase from 3.0 to 3.5 times when moving from the 40 W lamp [approx. 12(15.8/20) = 9.5 effective W at 254 nm], and (ii) an increase from 6.9 to 7.8 times with respect to the 15 W [approx. 3.6(15.8/44.7) = 1.3 effective W at 254 nm]. The lamp with emission below 250 nm is the only one that achieved a 90% TOC conversion after 2 hs (starting from 30 ppm of initial 2,4-D concentration) and after 4 hs (for 90 ppm of initial 2,4-D).

It should be noted that the change in the output energy of the 360 W in the range of 220 to 300 nm with respect to the 40 W lamp is just 16% higher. Thus, the observed beneficial effect is produced by the existence of a rather small emission at lower wavelengths (below 250 nm) where absorption by the HP becomes much more important.
Conclusions are not the same if we think in terms of the total energy consumption. Figure 7 shows two different ways of defining quantum efficiencies. The first plot [Figure 7 (a)] is obtained in terms of the absorbed energy. It can be seen that the best yield corresponds to the 360 W lamp, but in terms of the energy consumption [Figure 7 (b)] this lamp produces the poorest result. This is a consequence of all the unnecessary energy consumed in producing radiation above 300 nm that is totally useless. This result should be a strong stimulus to produce monochromatic, excimer lamps with emission at 220 nm, having larger sizes and lower costs.

The kinetic model

Reaction scheme

The macroscopic reaction path can be described as follows:

\[
\begin{align*}
\text{Chlorohydroquinone} & \rightarrow 2,4\text{-D} \rightarrow \text{Humic acids} \rightarrow \text{Low MW products} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{HCl} \\
\downarrow & \quad \downarrow \\
\text{Dichlorophenol} &
\end{align*}
\]

We developed and used a kinetic model that can account for the reaction rates of 2,4-D (D), 2,4-dichlorophenol (DCP), chlorohydroquinone (CHQ), and hydrogen peroxide (P). The model includes the following variables: the local volumetric rate of photon absorption (LVRPA), the direct photolysis quantum yields (\(\phi_i\)), and the kinetic parameters corresponding to the HP/UV reactions (\(k_i\)). Table 2 shows the reaction scheme used to explain the observed kinetics.

In Table 2, RH stands for any hydrocarbon present in the system. With this kinetic representation the following limiting behaviors can be described (Luñak and Sedlák, 1992): (i) for low and intermediate HP concentrations and low irradiation levels, the HP reaction rate is directly proportional to the HP concentration and to the square root of the LVRPA, and (ii) for high irradiation rates, the HP reaction rate is zero order with respect to the HP concentration and directly proportional to the LVRPA.

Mass balances

A mass balance for each stable reacting species inside the batch, well stirred tank photoreactor gives the following set of five non-linear, first order, ordinary differential equations (Alfano et al., 2000):
Here, AH stands for humic acids, a not well defined family of polymeric chains resulting from condensation of polyphenols. Very often they are part of natural environments in river waters and are considered non-toxic intermediate products. Details corresponding to the derivation of Eqs. (1) to (5) as well as an explicit description of the expressions corresponding to each one of the kinetic parameters included in the mass balances can be found elsewhere (Alfano et al., 2000). The quantum yield for direct photolysis of humic acids is negligible and has not been included in Eq. (5). Eqs. (1) to (5) can be integrated with the following initial conditions:

\[ C_i(t=0) = C_i^0 \quad (i = D, P) \quad \text{and} \quad C_i(t=0) = 0 \quad (i = DCP, CHQ, HA) \quad (6) \]

Volumetric rate of photon absorption (VRPA)

It has been proposed in previous reports (Cabrera et al., 1997, 1999) that, in this reactor-reflector-lamp system, the following one-dimensional model can describe the monochromatic LVRPA:

\[ e_i^v(y,t) = k_i(t)G_W \exp[-k_i(t)y] \quad (i = D, DCP, CHQ, P) \quad (7) \]

Here, \( e_i^v \) stands for humic acids, a not well defined family of polymeric chains resulting from condensation of polyphenols. Very often they are part of natural environments in river waters and are considered non-toxic intermediate products. Details corresponding to the derivation of Eqs. (1) to (5) as well as an explicit description of the expressions corresponding to each one of the kinetic parameters included in the mass balances can be found elsewhere (Alfano et al., 2000). The quantum yield for direct photolysis of humic acids is negligible and has not been included in Eq. (5). Eqs. (1) to (5) can be integrated with the following initial conditions:

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In Eq. (7) $\kappa_i$ corresponds to the absorption coefficient of the compound that absorbs radiation and undergoes a specific reaction, whereas the total absorption coefficient $\kappa_T$ (for total radiation attenuation in the reaction space) includes the radiation absorption of all existing compounds. Thus,

$$\kappa_T(t) = \sum_{j=1}^{N} \alpha_j C_j(t) \quad (j: \text{D, DCP, CHQ, P, HA})$$  \hspace{1cm} (8)$$

Values of $\alpha$ for the different, well defined compounds can be directly measured. The value corresponding to HA has been obtained with an extension of the methodology described by Cabrera et al. (1997). It provides $\alpha_{HA}$ as a function of the properties of all the other compounds analyzed in the solution; i.e., the concentration of humic acids was obtained by difference between the initial values of the 2,4-D concentration and the actual concentrations of 2,4-D, CHQ and DCP.

Finally, the expressions employed to compute the reactor length averaged LVRPA and the reactor length averaged of the square root of the LVRPA, are:

$$\langle \epsilon_i^2(y, t) \rangle_{L} = \frac{\kappa_T(t)}{\kappa_T(t)} G_W \frac{1}{y_L} \left\{ 1 - \exp \left[-\kappa_T(t)y_L \right] \right\} \quad (i = \text{D, DCP, CHQ, P})$$  \hspace{1cm} (9)$$

$$\left\langle \left[ \epsilon_i^2(y, t) \right]^{1/2} \right\rangle_{L} = \left[ \frac{\kappa_T(t) G_W}{\kappa_T(t)} \right]^{1/2} \frac{2}{y_L} \left\{ 1 - \exp \left[-\frac{\kappa_T(t)y_L}{2} \right] \right\}$$  \hspace{1cm} (10)$$

Evaluation of the kinetic parameters

According to the kinetic model, eleven unknowns have been obtained: (i) four direct photolysis quantum yields, that have been independently measured, and (ii) seven kinetic parameters for the HP+UV reaction. Employing a non-linear, regression parameter estimator applied to the complete reaction and reactor model, the full set of the kinetic constants has been obtained. The values of the unknown parameters, are:

$$\phi_{D,DCP} = 0.0107 \quad k_{D,DCP} = 21.88 \quad k_{HA} = 13.17 \quad k_{P1} = 0.519$$

$$\phi_{D,CHQ} = 0.0024 \quad k_{D,CHQ} = 23.25 \quad k_{CHQ,HA} = 110.04$$

$$\phi_{DCP} = 0.0184 \quad k_{DCP,HA} = 158.86 \quad k_{P2} = 0.00569$$

$$\phi_{CHQ} = 0.0426 \quad k_{CHQ,HA} = 110.04$$

Note that $k_{P2}$ is almost negligible compared to $k_{P1}$, an expected result when the irradiation rate is not very low. Figure 8 (a) and (b) shows the theoretical and experimental concentrations as a function of time, for a 2,4-D initial concentration of 30 ppm and a initial HP/2,4-D molar ratio $r = 16$. Good agreement between model predictions and experimental data can be observed. It should be mentioned that the experimental concentrations of humic acids were obtained by subtracting the sum of 2,4-D, DCP, CHQ and acetic acid concentrations from the TOC measurements. This procedure is responsible for the higher errors observed for this family of organic compounds when experimental data are compared with model predictions.

It must be observed that results with the polychromatic lamp have not been included in the model. The reason is simple: we do not have reliable information concerning the humic acids absorption coefficient when polychromatic light is employed. Additional work is being conducted to extend the model for the case when the reactor employs polychromatic illumination.
Conclusions

- The degradation rate is greatly increased by addition of HP to the process. Even for rather low initial molar ratios of HP/2,4-D ($r = 8$), the reaction rate increases from 6 to 32 times with respect to the direct photolysis.

- For an initial 2,4-D concentration of 30 ppm the optimal HP/2,4-D concentration ratio is close to 20. This value is about 30 for an initial 2,4-D concentration of 90 ppm. These results were obtained employing monochromatic light (254 nm) using a lamp with an effective output power of 9.5 W.

- The use of a lamp with emission below 250 nm, with a slight increase in the output power (13.96 W between 220 and 300 nm as compared with 9.5 W at 254 nm for the monochromatic lamp) produces an increment in the degradation rate of 2,4-D. A factor of 4 was observed when HP+UV was used and a factor of 18 with respect to results with UV alone. When these results are expressed in terms of TOC, the increasing effect was traduced in a factor of 3.0 to 3.5 with respect to the 9.5 W output power lamp and a factor of 6.9 to 7.8 with respect to the lamp with an effective output power of 1.3 W.

- Using a value of $r = 8$, the lamp with emission below 250 nm is the only one that reduces the initial TOC to very low values (90% conversion). However, this yield is obtained with a lamp that has significant emission above 300 nm (47.44 W) where radiation is almost useless for this process. Energy consumption will be a crucial factor.

- A kinetic model has been developed to describe the photo-oxidation of the 2,4-dichlorophenoxyacetic acid in water solution. The kinetic parameters are obtained from the experimental data by application of the full model to the time evolution of the degradation reaction. When predictions of the kinetic model are compared with experimental results for two germicidal lamps, a reasonably good representation of the reacting species evolution is obtained.

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Nomenclature

\[ \begin{align*}
C & \quad \text{molar concentration, mol m}^{-3} \\
e^a & \quad \text{LVRPA, einstein s}^{-1} \text{m}^{-3} \\
G_W & \quad \text{incident radiation at the wall, einstein s}^{-1} \text{m}^{-2} \\
k & \quad \text{kinetic constant, varies with reaction order} \\
r & \quad \text{HP/2,4-D initial molar ratio, dimensionless} \\
R & \quad \text{Reaction rate, mole s}^{-1} \text{m}^{-3} \\
t & \quad \text{Time, s} \\
V & \quad \text{Volume, m}^3 \\
X & \quad \text{Conversion, dimensionless} \\
y & \quad \text{Cartesian coordinate, m} \\
\end{align*} \]

Greek Letters

\[ \begin{align*}
\alpha & \quad \text{molar absorptivity, m}^2 \text{mol}^{-1} \\
\kappa & \quad \text{Absorption coefficient, cm}^{-1} \\
\lambda & \quad \text{wavelength, nm} \\
\phi & \quad \text{direct photolysis quantum yield, mol einstein}^{-1} \]

References


