Removal of Phenylurea Herbicides from Waters by using Chemical Oxidation Treatments

F. Javier Benitez*, Carolina Garcia, Juan Luis Acero and Francisco J. Real

Abstract—Four phenylurea herbicides (isoproturon, chlortoluuron, diuron and linuron) were dissolved in different water matrices in order to study their chemical degradation by using UV radiation, ozone and some advanced oxidation processes (UV/H₂O₂, O₃/H₂O₂, Fenton reagent and the photo-Fenton system). Thewaters used were: ultra-pure water, a commercial mineral water, a groundwater and a surface water taken from a reservoir. Elimination levels were established for each herbicide and for several global quality parameters, and a kinetic study was performed in order to determine basic kinetic parameters of each reaction between the target phenylureas and these oxidizing systems.

Keywords—Phenylurea herbicides; UV radiation; Ozone; Fenton reagent; Hydroxyl radicals; Rate constants; Quantum yields.

I. INTRODUCTION

PESTICIDES are one of the most commonly organic compounds found in surface and ground waters, which are dispersed in aqueous medium by direct agricultural runoff or leaching [1]. Furthermore, the manufacture pesticide industries also produce pesticide pollution at high levels, reaching concentrations of 500 mg L⁻¹ [2]. Among these industries also produce pesticide pollution at high levels, or leaching [1]. Furthermore, the manufacture pesticide reagent; Hydroxyl radicals; Rate constants; Quantum yields.

European Union. In general, the different technologies matrices until the permissible levels established by the herbicides makes necessary their removal from waters in the field of water policy is established.

II. EXPERIMENTAL SECTION

A. Materials and reagents

Commercial phenylurea herbicides and p-chlorobenzoic acid (p-CBA) were purchased from Sigma-Aldrich (Steinheim, Germany) with the highest purity available. All the other chemicals used for the solutions (hydrogen peroxide, HPLC eluents, buffers, etc.) were of reagent grade, and they were provided by Panreac (Barcelona, Spain).

A Milli-Q water system (Millipore) was used for obtaining the ultra-pure water, and other three water matrices were also employed: a mineral water of the commercial brand “Los Riscos”, and two natural waters (groundwater and surface water taken from the reservoir “Peña del Aguila”), both collected from the Extremadura Community (southwest of Spain). The absorbances at 254 nm for these waters were 0.004, 0.064, and 0.125; the DOC contents were 1.2, 2.6 and 6.7 mg L⁻¹, and the alkalinity was 1.20, 1.15 and 0.47 x10⁻³ M in HCO₃⁻, for mineral, groundwater and reservoir water, respectively.

B. Experimental procedures

Photochemical reactions were carried out in a 500-mL
cylindrical glass reactor equipped with a low pressure mercury vapor lamp (Hanau TNN 15/32, 15 W), which emits a monochromatic radiation at 254 nm, placed axially within the reactor. A quartz sleeve housed the lamp. For each experiment, the reactor was thermostated at the desired temperature and was filled with buffered solutions of the selected phenylureas. The required amount of hydrogen peroxide for each specific experiment in the UV/H\textsubscript{2}O\textsubscript{2} system or in the combination Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} (Fenton and photo-Fenton systems), was added before connecting the lamp. Once this UV lamp was turned on, samples were withdrawn from the reactor at regular time intervals for assay.

The first group of ozonation experiments was performed at 20 °C, pH 2 and in the presence of tert-butyl alcohol as OH scavenger, with the aim of determining the rate constant for the direct reactions between ozone and each phenylurea herbicide. These experiments were performed by using a gas-liquid reactor containing the herbicide solution with a reference compound (fenuron), and the oxygen/ozone stream was produced by a laboratory ozone generator (Yemar, mod. HPA) with a gas flow of 40 L h\textsuperscript{-1}.

Furthermore, another experimental serie was performed for the reaction of selected phenylureas and p-CBA (reference compound) with ozone or O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} in the three natural waters already described. These experiments were conducted in a 500-mL flask reactor by adding dissolved ozone in aqueous solution, and hydrogen peroxide was also added in the combined O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} experiments. At regular reaction times, two samples were withdrawn: one was introduced into an indigo solution for the analysis of ozone remaining concentration, and the other was introduced into a vial containing potassium thiosulfate, and was subsequently assayed for the herbicide and p-CBA concentrations.

The experiments with the single Fenton system were performed in 250-mL Erlenmeyer flasks, and the reaction solutions were homogenized by means of a magnetic stirrer. Each flask was filled with the corresponding herbicide aqueous solution, which was previously buffered at the selected pH by adding perchloric acid/perchlorate, acetic acid/acetate or phosphoric acid/phosphate buffer. The required amounts of ferrous ion and hydrogen peroxide were also added to the reactor. A competition kinetics method was applied in order to determine rate constants of the herbicides with OH radicals, by using p-CBA as a reference compound, which was also added to the reactor in the corresponding experiments.

Finally, global quality parameters such as chemical oxygen demand (COD), dissolved organic carbon (DOC), UV absorbance at 254 nm and chloride ion concentration were measured in several experiments carried out in order to evaluate these parameters and to identify some reaction by-products formed in the oxidation of phenylurea herbicides by means of UV alone, ozone and Fenton’s reagent.

C. Analytical methods

The remaining concentrations of herbicides and p-CBA were determined by high-performance liquid chromatography (HPLC), using a Waters chromatograph equipped with a 2487 dual absorbance detector and a Waters Nova-Pak C18 column (15 cm x 0.39 cm) (Waters Corp., Milford, U.S.A.). The mobile phase was constituted by phosphoric acid in aqueous solution (10\textsuperscript{-2} M) and methanol in different proportions, and herbicides detection was performed at 248 nm.

The ozone concentration in the inlet gas-ozone stream was determined iodometrically, while the ozone concentration of the liquid stock solutions was determined by measuring their UV absorbance at 258 nm (\(\varepsilon = 3150\) M\textsuperscript{-1} cm\textsuperscript{-1}). The remaining concentration of ozone in reaction samples was analyzed by measuring its absorbance at 600 nm in the presence of indigo solution [7].

![Fig. 1 Chemical structures of selected phenylureas.](image-url)

III. RESULTS AND DISCUSSION

A. Photochemical oxidation of phenylurea herbicides

The oxidation of the selected phenylureas dissolved in pure...
water by single UV radiation was performed by varying pH and temperature. It was observed the following reactivity order: linuron > chlortoluron > diuron > isoproturon. The decay in concentration of each compound was almost the same for the range of pH 2-9, so it can be deduced that pH caused almost no effect on the degradation of phenylurea herbicides by direct photolysis. On the contrary, the reaction temperature had a significant effect on the degradation rates, as expected: the elimination rates of selected phenylureas increased with increasing temperature in all the cases.

A kinetic study was applied in order to evaluate the quantum yields $\phi$ for the photochemical reactions of these herbicides. The quantum yield is defined as the number of molecules reacted per photon absorbed [8]. By using the reaction model described in detail in a previous publication [9], a general equation for the removal of each herbicide P as a function of the absorbed radiation flux $W_{abs}$ is suggested as follows:

$$\frac{d[P]}{dt} = \phi \frac{W_{abs}}{V}$$

Integration of eq (1) with the initial condition provides the following final expression:

$$[P] = [P]_0 - \phi \frac{W_{abs}}{V} dt$$

The procedure for determining $W_{abs}$ is also described in [9]. In this case, the Line Source Spherical Emission Model [10] was selected to describe the distribution of radiant energy within the reactor. Previously, it was necessary to determine the molar extinction coefficients $\varepsilon$ for the selected herbicides; the average values spectrophotometrically obtained were 13,437, 6,080, 15,699 and 6,068 M$^{-1}$cm$^{-1}$ for linuron, chlortoluron, diuron and isoproturon, respectively. Then, by applying eq (2) to the experimental data it was possible to evaluate the quantum yields $\phi$ of the photochemical reactions carried out. The resulting values obtained at 20 ºC are listed in Table I. These quantum yields are in agreement with the values reported by other authors [11]-[13].

In a next step of this research, the photolysis of mixtures of the selected herbicides dissolved in several water matrices (commercial mineral water, groundwater and surface water) was performed at 20 ºC and pH 7. In these experiments, the initial dosage of H$_2$O$_2$ was modified in the range 0-5x$10^{-3}$ M.

Fig. 2 shows, as an example, the degradation curves of the selected herbicides with the reaction time in their photodegradation by UV alone or combined with H$_2$O$_2$ 5x$10^{-3}$ M, in the reservoir water matrix. It was clearly observed that the combined UV/H$_2$O$_2$ system exerted a positive effect on the photodegradation by UV alone. A higher initial concentration of hydrogen peroxide caused also an increase of the degradation rate of the target compounds. Similarly, it is interesting to establish the influence of the nature of herbicide on the oxidation rate. Thus, Fig. 2 shows the following order of reactivity: linuron > chlortoluron > diuron > isoproturon, as expected, accordingly to the quantum yields previously determined. Similar results were observed in the remaining water matrices.

**Fig. 2 Degradation curves of phenylurea herbicides in the reservoir water by means of UV irradiation alone (a) and combined with H$_2$O$_2$ 5x$10^{-3}$ M (b); T = 20 ºC, pH 7, [P]$_0$ = 1x$10^{-4}$ M.**

Furthermore, the effect of the type of water could also be established. The fastest oxidation rate of phenylureas occurred in the ultra-pure water matrix, followed by mineral water and groundwater; and finally, the slowest elimination took place in the reservoir water. This result is a consequence of the organic matter content of these water matrix, which competes with the herbicides in the absorption of UV. Thus, in the ultra-pure and mineral water, with low content in natural organic matter (NOM), more UV radiation was available for the oxidation of herbicides and hydrogen peroxide, and they were eliminated more rapidly; on the contrary, in the groundwater and reservoir water, with higher NOM content, less UV radiation was available to react with the selected phenylureas.

Finally, experiments were performed with the aim of evaluating global pollutant parameters like COD, DOC, absorbance at 254 nm and concentration of chloride ion in the photolysis of the selected phenylureas dissolved in ultra-pure water, at pH 7 and 20 ºC. The measures of DOC and COD

**TABLE I**

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>$\phi$, mol E$^{-1}$</th>
<th>$k_{O_3,P}$, M$^{-1}$s$^{-1}$</th>
<th>$k_{H_2O_2,P}$, M$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linuron</td>
<td>0.0360</td>
<td>1.9</td>
<td>5.6 x 10$^9$</td>
</tr>
<tr>
<td>Chlortoluron</td>
<td>0.0319</td>
<td>393.5</td>
<td>7.5 x 10$^9$</td>
</tr>
<tr>
<td>Diuron</td>
<td>0.0115</td>
<td>16.5</td>
<td>7.1 x 10$^9$</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>0.0037</td>
<td>2191</td>
<td>5.7 x 10$^9$</td>
</tr>
</tbody>
</table>
provided the following trend of degradations: isoproturon > chlortoluron > diuron = linuron. In effect, this sequence is in agreement with the theoretical values of organic carbon present in each herbicide molecule, being the number of carbon atoms 12, 10, 9 and 9 in isoproturon, chlortoluron, diuron and linuron, respectively. Moreover, Fig. 3 shows, as an example, the evolution of these parameters with the reaction time in the photolysis of chlortoluron, with similar results obtained for the rest of herbicides. As it is seen, COD and DOC presented almost constant values with reaction time, because the total mineralization of parent compounds was not reached. On the contrary, it was observed a slight decrease of absorbance at 254 nm with time, which can be attributed to the formation of by-products derived from phenylureas that presented lower absorbances at the mentioned wavelength.

In these photochemical reactions, several of these by-products were identified by using HPLC techniques. Thus, for the photolysis of diuron, 3,4-dichlorophenylurea and 3,4-dichlorophenyl isocyanate were found; both organic compounds were also identified in the photolysis of linuron, in addition to 3,4-dichloroaniline. For chlortoluron, 3-chloro-4-methylphenylurea and 3-chloro-4-methylphenyl isocyanate were identified. Finally, in the photolysis of isoproturon, 4-isopropylphenyl isocyanate and 4-isopropylaniline were detected. These organic compounds were also identified by other authors [11] [14] [15] in similar works. Other by-products were observed but not identified, which could correspond to intermediate phenylureas. The formation of the mentioned by-products indicates the existence of an initial attack of UV irradiation to C-N bonds, removing in this way the methyl substituents from the aliphatic chain [11] [15]. Other possible degradation pathway could be the attack of hydroxyl radicals (indirect photolysis) to the aromatic ring, producing intermediate phenylureas. To assess this hypothesis, the concentration of chloride ion in the reaction medium was also measured. Fig. 4 represents the evolution of chloride ion with the reaction time for the photolysis of chlortoluron, linuron and diuron (isoproturon has not chlorine atoms in its chemical structure, see Fig. 1). In all the cases, there was an increase of the concentration of chloride ions in the reaction bulk, which indicates an attack of OH radicals to the aromatic ring of phenylureas, leading to the formation of intermediate by-products with lower chlorine atoms in their structure, and subsequently, increasing the chlorine content in the reaction medium.

![Absorbance at 254 nm](image)

**Fig. 3** Evolution of global quality parameters with reaction time in the photolysis of chlortoluron at 20 °C and pH 7; [P]₀ = 2x10⁻⁴ M.

In this study, the target compounds were the selected phenylureas, and the reference compound used for chlortoluron and diuron was fenuron. This pollutant was selected because it is also a phenylurea herbicide, and previous experiments revealed that it presents reactivity toward ozone in the same order of magnitude than chlortoluron and diuron. The rate constant for its reaction with ozone was reported by Acero et al. [17], being 208 M⁻¹s⁻¹. Later, chlortoluron was used as a reference compound for isoproturon, and diuron was selected as reference compound for ozone toward fenuron, because the total mineralization of parent compounds was not reached.

**B. Ozonation of phenylurea herbicides**

Determination of the rate constants for direct reactions between each phenylurea herbicide and ozone (k_O3-P) was performed by conducting ozonation experiments under the following operative conditions: T = 20 °C, pH 2 and the presence of tert-butylalcohol. Under these conditions, it was expected that molecular ozone attack was the only significant pathway for the oxidation of the selected herbicides. With this purpose, the competition kinetics model already reported [16] was applied. It is based on considering a second-order kinetic rate for a target compound P and a reference compound R, which presents a rate constant with molecular ozone previously known (k_O3,R). Then, it is possible to determine the desired rate constant k_O3-P for the target compound by applying eq (3) to the experimental data:

\[
k_{O3-P} = k_{O3-R} \frac{\ln([P]_0/[P])}{\ln([R]_0/[R])}
\]  

(3)

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for linuron, once their rate constants were previously evaluated. Once this procedure was developed, the average values obtained for \( k_{O3-P} \) are listed in Table I. A reasonable agreement between these values and those reported by De Laat et al. [18] are observed for linuron and diuron; however, much smaller values were proposed by the mentioned authors for chlortoluron and isoproturon. This is due to the fact that atrazine (reference compound used in [18]) has a much lower reactivity with ozone than chlortoluron and isoproturon, and therefore atrazine is not probably an adequate reference compound in those cases. As the competition kinetics model establishes, the reactivity of the reference compound and the target compound must be in the same order of magnitude.

In a later stage, simultaneous ozonation experiments of these herbicides were performed in natural water systems (the mentioned mineral, groundwater and reservoir waters), at 20 °C and pH 7.0-7.5. The initial concentrations of ozone (1-5 \( \times 10^{-5} \) M) and hydrogen peroxide (0-1 \( \times 10^{-5} \) M) were modified, and all the experiments were carried out in the presence of p-CBA, used as reference compound. In these cases, it was observed that ozone was completely consumed during the first 5-10 minutes of the oxidation process; moreover, the presence of hydrogen peroxide accelerated the ozone decomposition rate, and ozone disappeared almost instantaneously. Similarly, the increase in the initial ozone dose led to a subsequent increase in the degradation level of each phenylurea. It was also observed that after some time of reaction (around 8 minutes), the concentration of each phenylurea herbicide remained almost constant, as a consequence of the total consumption of ozone. When \( \text{H}_2\text{O}_2 \) was present, the removal of herbicides was faster and ozone was totally consumed much earlier, affecting negatively on the oxidation of isoproturon, which presents a higher ozone demand (see Table I).

Regarding to the influence of the type of water used, the ozone consumption was faster in the reservoir water, followed by groundwater and mineral water. This effect is again due to the amount of NOM present in each type of water, which also consumes ozone. As was previously noted, the sequence of NOM was reservoir water > groundwater > mineral water. Thus, for the low NOM content in mineral water, ozone consumption was slower than in ground and reservoir waters, with higher NOM content. The type of water also affected to the removal of the selected phenylureas, as shown at Fig. 5 which represents, as an example, the decay curves of linuron in experiments where the initial dose of ozone was 2\( \times 10^{-5} \) M and without addition of hydrogen peroxide. It can be observed that the degradation was faster in mineral water, intermediate in groundwater, and slower in reservoir water, with similar results obtained for the remaining herbicides; it is again due to the competition of the target phenylureas with NOM for the consumption of oxidizing reagents (ozone and OH radicals, in this case), which is higher in the reservoir water than in ground and mineral water, as was mentioned before.

Finally, the following order of reactivity for each phenylurea herbicide with ozone and \( \text{O}_3/\text{H}_2\text{O}_2 \) system was found: isoproturon > chlortoluron > diuron > linuron, as expected from the observation of second order rate constants for the reaction of phenylurea herbicides with molecular ozone (\( k_{O3-P} \), see Table I).

![Fig. 5 Influence of the type of water on the ozonation of linuron with \([\text{O}_3]_0 = 2\times10^{-5} \text{ M}, T = 20^\circ \text{C}, \text{pH} 7-7.5, [\text{P}]_0 = 1\times10^{-6} \text{ M}.\)](image)

Furthermore, the same global quality parameters (DOC, COD, absorbance at 254 nm, and chloride ions) were evaluated at pH 2 during the ozonation of the phenylurea herbicides. Fig. 6 represents, as example, the evolution of these global parameters with the reaction time in the ozonation of isoproturon at pH 2 and 20 °C, conditions that minimize the presence of OH radicals in the reaction medium.

![Fig. 6 Evolution of global quality parameters with reaction time in the ozonation of isoproturon at 20 °C and pH 2; \([\text{P}]_0 = 2\times10^{-7} \text{ M}\).](image)

It is observed that there is a slight decay in DOC values due to the incomplete mineralization of the parent compounds by applying ozone as oxidizing reagent; whereas the decay in COD with time is more significant at initial reaction times. The sequence for both parameters was again isoproturon > chlortoluron > diuron = linuron. At the same time, the decay in absorbance at 254 nm was important in all cases, due to the
attack of molecular ozone to the aromatic ring of phenylureas [19], breaking this ring and leading to the reduction of aromatic compounds in the reaction medium, which present a high absorbance at this wavelength.

In these experiments were also detected some by-products from the ozonation of phenylurea herbicides by using HPLC techniques. Thus, the following organic compounds were found in the oxidation of phenylureas by molecular ozone: 3,4-dichlorophenyl isocyanate (diuron and linuron), 3,4-dichlorophenol, 3,4-dichloroaniline (linuron), 3-chloro-4-methylphenyl isocyanate (chlortoluron) and 4-isopropylaniline (isoproturon). The presence of these by-products was confirmed by other authors results [19] [20], and they indicate the electrophylic character of molecular ozone, which produces abstraction of H atoms and breaks C-N bonds. On the other hand, the rest of compounds not identified could correspond to intermediate ureas generated by an attack of ozone to the aromatic ring [19]. Fig. 7 shows the evolution of chloride ion concentration with the reaction time for the ozonation of chlortoluron, diuron and linuron; it is clearly observed that the presence of chloride ions in the reaction medium increases with the ozonation time, which confirms the attack of ozone to the aromatic ring of phenylureas by incorporating chlorine atoms to the aqueous matrix.

Fig. 7 Evolution of chloride ion concentration with reaction time in the ozonation of phenylureas at 20 °C and pH 2; [P]₀ = 1-2x10⁻⁴ M.

C. Oxidation of phenylurea herbicides by Fenton and photo-Fenton processes

Oxidation experiments of phenylureas by means of the combination H₂O₂/Fe²⁺ (Fenton’s reagent) were performed for each individual herbicide in pure water at 20 °C, by varying the initial concentrations of ferrous ions (0.5-5 x10⁻⁴ M) and hydrogen peroxide (1-10 x10⁻⁴ M), as well as the pH and the type of buffer used. Previous experiments carried out in the absence of H₂O₂ or Fe²⁺ did not show any degradation of the selected herbicides. When applying the H₂O₂/Fe²⁺ system, it was observed that the elimination percentage of each herbicide increased with the increase of the initial hydrogen peroxide concentration, due to increases in the amount of ferrous ion regenerated and OH radicals formed. Similarly, an increase in the phenylurea removal was obtained by increasing the initial Fe²⁺ concentration, both factors previously noted by other authors [21]. Thus, for the removal of phenylurea herbicides at concentrations of 4 x10⁻³ M, the following Fenton’s reagent doses can be proposed: 5 x10⁻⁴ for hydrogen peroxide, and the range 2.5-5 x10⁻⁴ M for ferrous ion.

In these Fenton’s reagent experiments, the pH value was modified in the range 2-4. It was observed that the best herbicide removals were obtained for pH 3.3, which confirms the optimum range of pH (2.5-3.5) already proposed by other authors [21, 22]. At the same time, the influence of the type of buffer used to make stable the pH in the solutions was also investigated and it was concluded that the best removals were obtained with perchlorate buffer, followed by phosphate buffer; and the lowest eliminations were reached with acetate buffer. As Pignatello [23] pointed out, some buffers reduce the efficiency of Fenton’s reagent owing to the formation of stable complexes of Fe²⁺ and Fe³⁺ that reduce their reactivity with hydrogen peroxide and cause a subsequent reduction in the regeneration of ferrous ions.

The application of a competition kinetics model permitted the evaluation of the rate constants for the direct reaction between each selected phenylureas and the oxidizing hydroxyl radicals (kOH-P), by considering that the rate of phenylurea oxidation by OH radicals follows a second-order kinetic model [24]. Similarly to the ozonation process described before, the following expression was applied to the experimental data in order to determine the kOH-P values:

\[ k_{OH-P} = k_{OH-R} \frac{\ln([P]_0)}{\ln([R]_0)} \]

In this work, p-CBA was used as a reference compound with a previously known rate constant for its oxidation by OH radicals: kOH-R = 5 x10⁹ M⁻¹s⁻¹ [6]. The application of eq (4) provided the values for kOH-P that are listed in Table I. These second order constants are also compared with those reported by De Laat et al. [18]: 4.3, 4.6, 4.3 and 5.2 x10⁹ M⁻¹s⁻¹ for linuron, diuron, chlortoluron and isoproturon, respectively, with a satisfactory agreement between both groups of rate constants.

Similarly to the preceding oxidation systems, several reactions of phenylurea herbicides with Fenton’s reagent were performed in ultra-pure water, at 20 °C and pH 3.3, in order to evaluate global quality parameters such as absorbance at 254 nm and chloride ion concentration, whose evolutions with the reaction time are represented in Figs. 8 and 9, respectively. As it can be observed in Fig. 8 for herbicides chlortoluron, diuron and linuron, a reduction of absorbance (254 nm) at the initial reaction times took place, and later, this parameter remained almost constant. However, an increase in absorbance at initial times was found for isoproturon, and later, a slight
decay was observed. As Gallard and De Laat [25] reported, the elimination rate of phenylurea herbicides by Fenton’s reagent depends on the relative importance of initial oxidation stages produced by OH radicals. Thus, whereas chlortoluron, diuron and linuron undergo attack of OH radicals on their dimethylurea group or their aromatic ring [26] (which is confirmed by their decay in absorbance at 254 nm), this initial attack of OH radicals in the case of isoproturon occurs on its isopropyl group [25]; this fact explains the different reactivity towards OH radicals of isoproturon on one hand, and the remaining herbicides on the other hand.

On the other hand, Fig. 9 shows the evolution of chloride ion concentration with the oxidation time for chlortoluron, diuron and linuron. It can be observed that an increase of the chloride ion concentration is produced during the first 30 minutes, and later, this concentration remains constant. This effect can be explained by the attack of OH radicals to the aromatic ring where are placed the chlorine atoms (see Fig. 1), and then, they are liberated into the aqueous medium.

Finally, several oxidation experiments for the degradation of chlortoluron, diuron, linuron and isoproturon in pure water were performed by applying Fenton’s reagent with the additional presence of UV irradiation, i.e. the photo-Fenton system, at 20 °C and pH 3.3. Fig. 10 shows, as an example, the degradation curves of linuron by means of Fenton and photo-Fenton systems under the same operating conditions.

As observed, a significant improvement is obtained in the removal by the photo-Fenton system at advanced reaction times, as expected; this effect is due to the additional generation of OH radicals through several reaction pathways. Furthermore, Fig. 10 shows that an increase of the initial dosage of ferrous ion caused a positive effect on the degradation of linuron. Similar results were obtained for the remaining herbicides.

IV. CONCLUSIONS

Chemical oxidation processes are adequate to remove phenylurea herbicides from ground and surface waters, and they can be used in real water treatment plants. The advanced
oxidation processes used in this work are recommended to eliminate the herbicides isoproturon, chlorotoluron, diuron and linuron, which are resistant to other classic oxidants such as chlorine and permanganate. Specifically, as it has been deduced from the present research at lab scale, the ozonation of phenylurea herbicides is probably the most efficient process to remove the selected micropollutants from natural waters, although the most adequate method at real scale will depend of the operating conditions and the global cost which must be calculated by means of an economical study applied to each specific case.

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