KINETICS OF ISOPROTURON AND MONURON DEGRADATION BY THE UV/H_2O_2 PROCESS

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Abstract: *Both isoproturon and monuron are selective phenyl urea herbicides used in large quantities and recently detected as pollutants of drinking water sources. The degradation and mineralization of these pollutants from water by the combined hydrogen peroxide (H_2O_2) and ultraviolet radiation (UV) oxidation have been explored in this work. Aqueous solutions containing 0.2 mM (40 ppm) monuron or 0.05 mM (10 ppm) isoproturon have been irradiated with a UV lamp ($5x10^{-6}$ Es/s incident photonic flux) in a cylindrical stirred batch photo reactor (0.5 L volume)in the presence of hydrogen peroxide(doses from 0.0 to 20 mM), at constant temperature. Samples have been taken at programmed reaction times (5, 10, 15, 20, 30, 40, 50 60 minutes). The unconverted pollutant and the residual total organic carbon (TOC) of each sample have been analyzed. The pseudo- first- order rate constants, at different hydrogen peroxide doses, have been identified for each compound, using the integral method and the experimental data. In addition, a more complex mathematical model of the photochemical process has been proposed. The model is based on the assumption of hydroxyl radical steady state concentration.*

Keywords: *photo degradation, mineralization, kinetic curves, rate constant, mathematical model.*

Introduction

Isoproturon (ISO) and monuron (M) are selective herbicides in pre- and post-emergence control of blackgrass, silky bentgrass, wild oats, annual meadow grass, ryegrass, and many broad leaf weeds found in fields of spring and winter barley, spring and winter wheat, and winter rye (Parra, 2000). They are two substituted phenyl urea, chlorinated (M) and unchlorinated (ISO) respectively. These chemical compounds act as inhibitors of photosynthesis. In general, these chemicals are characterized by long lifetimes in the environment and thus can be found as contaminants of surface-, ground waters and wastewater treatment plants effluents (Garmouma, 1997; Gerecke, 2001; Sorensen, 2005). This fact indicates that these herbicides are difficult to eliminate by a conventional biological wastewater treatment process.

A promising way to perform the mineralization of these type of substances is the application of advanced oxidation processes (AOP), that are characterized by the "in situ" production of •OH radicals under mild experimental conditions (Siminiceanu, 2003). Among the new oxidation methods, chemical oxidation using ultraviolet radiation (UV) in the presence of the hydrogen peroxide (H_2O_2) is a very promising technique. The mechanism adopted for the photolysis of H_2O_2 is the cleavage of the molecule into hydroxyl radicals which are highly powerful oxidizing species.

The photodegradation of monuron (3-(4-chlorophenyl)-1,1-dimethylurea) and isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea) in aqueous solutions UV irradiation has been conducted in this study. On the basis of substrate conversion degree and the mineralization degree the efficiency of the involved advanced oxidation process was evaluated and the kinetics of the process was investigated.

Materials and methods

Isoproturon was purchased from Riedel-de Haen and monuron from Aldrich and were used without further purification. The initial concentrations were 40 ppm (2 x 10^{-4} M) for monuron and 10 ppm (5 x 10^{-5} M) for isoproturon. All the other chemicals were of the highest grade commercially available and were used as obtained. Grade 1 water was obtained from a Milli-Q ultrapure water purification system (Millipore, USA). All the solvents used were HPLC grade.

All the photodegradation experiments were performed in a cylindrical quartz glass vessel ($V = 0.5$ L) under magnetically stirring. The irradiation source was a UV lamp with an incident photonic flux of 5 x 10^{-6} Es s^{-1}, determined by a phenylglyoxilic acid actinometry (Bobu, 2006). The samples were taken at different times from the reaction mixture, with single used syringes. The consumption of H_2O_2 during the reaction was followed by Quantofix Peroxide 25 sticks (Machery & Nagel, Düren, Germany).

Total Organic Carbon (TOC) measurements were performed using a TOC analyzer (Shimadzu, model 5000 A) with autosampler. Concentrations of unreacted pesticides were determined by large volume injection micro-liquid chromatography with UV detection (μ-LC-UV) at 244 nm (Bobu, 2006). The composition of the mobile phases for the analytical column was presented in a previous paper (Bobu, 2008). All the mobile phases contained 0.1% formic acid and were degassed with helium before use.

The degradation of isoproturon and monuron were measured with UV-VIS Hitachi U 2000 spectrophotometer at 244 nm. Calibration plot based on Beer-Lambert's law was established by relating the absorbance to the concentration.

Results and Discussion

The photodegradation of the isoproturon and monuron, two phenyl urea herbicides, was examined in the presence of H_2O_2 and UV light. Pesticide (A) concentration versus irradiation time was determined by HPLC measurements and the conversion of the original substrate, X_A (%), was used to define the efficiency of the degradation.

$$X_A = 100\left(1 - \frac{C_A}{C_A^0}\right) \qquad (1)$$

where C_A and C_A^0 refers to the pesticide molar concentrations values at reaction time τ and 0, respectively.

The complete conversion of monuron and isoproturon molecules lead to the reaction intermediates accumulation. A general pathway for the mineralization of phenyl urea herbicides is initiated by the attack of hydroxyl radicals on the mother molecule at the N-terminal group leading to several by-products. For both photocatalytic processes the degradation is initiated by the attack of hydroxyl radicals at the N-terminal group and consists of two sequential N-dealkylations followed by hydrolysis to aniline derivates. Further oxidations steps involve oxidative opening of the aromatic ring, leading to small carboxylic acids and inorganic ions (Bobu, 2006). In order to asses the mineralization degree the total organic carbon values were recorded during the photo-degradation procedures. The TOC removal ratio of the reaction solution was defined as below:

$$X_{TOC} = 100\left(1 - \frac{TOC}{TOC_0}\right) \qquad (2)$$

where TOC and TOC_0 refer to the TOC values at reaction time τ and 0, respectively.

The kinetics in this study only refers to apparent reaction kinetics considering that several processes can contribute to the overall degradation of the organic pollutant. The apparent degradation kinetics of isoproturon (monuron) in aqueous solution is described according the pseudo first-order equation:

$$-\frac{dC_A}{d\tau} = k_{ap} C_A \qquad (3)$$

where C_A is the isoproturon's (or monuron) molar concentration in water, τ is the reaction time and k_{ap} is the pseudo first-order rate constant.

By plotting $-\ln(C/C_0)$ as a function of reaction time τ, through linear regression, the k_{ap} constants could be derived from the slopes of the straight lines, through linear regression, using the experimental data. The k_{ap} values calculated from the experimental data, using the above method, are listed in the Table 1.

Table 1 Rate constants and maximal conversions at different doses of hydrogen peroxide in UV/H_2O_2 process (60 min. irradiation, 298 K, C^0_{IPU} = 0.05 mM).

0.05 mM isoproturon		0.2 mM monuron	
$C^0_{H_2O_2}$, mM	k_{ap}, s^{-1}	$C^0_{H_2O_2}$, mM	k_{ap}, s^{-1}
0.0	0.19×10^{-4}	0	0.17×10^{-4}
0.1	1.44×10^{-4}	1	0.29×10^{-4}
0.5	2.00×10^{-4}	2	1.72×10^{-4}
1.0	1.67×10^{-4}	10	2.33×10^{-4}
		20	2.22×10^{-4}

1. Hydrogen peroxide concentration influence

UV-based AOPs also transform pollutants in two ways. Some organic chemicals absorb UV light directly, and absorption of this high-energy radiation can cause destruction of chemical bonds and subsequent breakdown of the contaminant (Siminiceanu, 2003). However, some organic species do not degrade very quickly or efficiently by direct UV photolysis. Therefore, addition of H_2O_2 to the UV process creates AOPs conditions, often increasing the rate of contaminant degradation significantly. H_2O_2 absorbs UV light, and breaks down into $HO\bullet$ radicals, degrading the contaminant via $HO\bullet$ radical oxidation.

The mechanism for the formation of hydroxyl radicals in UV/H_2O_2 system takes place through the homolytic decomposition of hydrogen peroxide molecule under UV irradiation. The most important factor that influences the efficiency of this process is the initial dose of the hydrogen peroxide. Fig. 1 illustrates the photodegradation of monuron (A) and isoproturon (B) under UV irradiation for solutions containing various H_2O_2 concentrations.

A preliminary experiment was performed in order to establish the contribution of UV irradiation to the process efficiency. In the absence of H_2O_2 the isoproturon concentration decreased from 0.050 to 0.048 mM during one hour radiation (X_M = 4.5%) resulting in a mineralization degree of 3%. There was no dramatic decay of the monuron concentration when the irradiation was carried out in the absence of H_2O_2, neither; X_M = 4.5% and the removal of TOC was 3.8%.

The results indicated a considerable decrease in the concentration of the both herbicides when the sample was irradiated by UV in the presence of H_2O_2.

This loss can be related to the production of hydroxyl radicals, which is a powerful oxidizing agent. The removal rates increases considerably with increasing H_2O_2 concentration from zero to 1 mM, reaching a maximum value at a H_2O_2 dose of 0.5 mM (Table 1).

When the H_2O_2 concentration raises from 0.5 to 1 mM a significant inhibition of isoproturon conversion and mineralization rates occurs (Fig. 2A). This could be explained by two opposing effects. With increasing H_2O_2 concentration: (i) More hydroxyl radicals are available to attack the aromatic rings and the rate of reaction increases (Eq. 4); (ii) Above the critical value of H_2O_2 concentration, hydroxyl radicals efficiently reacts with H_2O_2 and produces $HO_2\bullet$ (Eq. 6), radicalic species less reactive than $HO\bullet$.

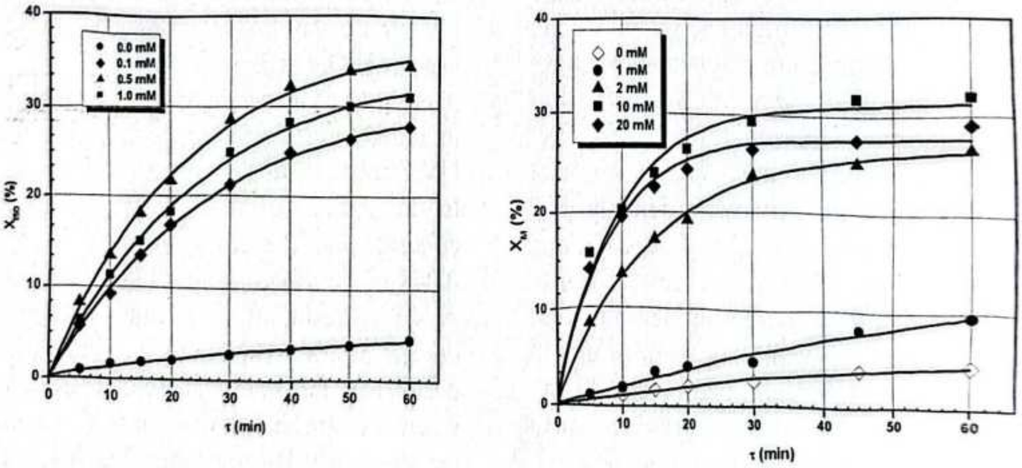
$$H_2O_2 \xrightarrow{h\nu} 2HO\bullet \qquad (4)$$

$$A + HO\bullet \xrightarrow{k_A} Products \qquad (5)$$

$$H_2O_2 + HO\bullet \xrightarrow{k_{H_2O_2}} H_2O + HO_2\bullet \qquad (6)$$

After one hour irradiation, using the optimal hydrogen peroxide concentration (0.5 mM H_2O_2) a 34.6% conversion of the initial ISO concentration and a 14.5% mineralization degree were achieved.

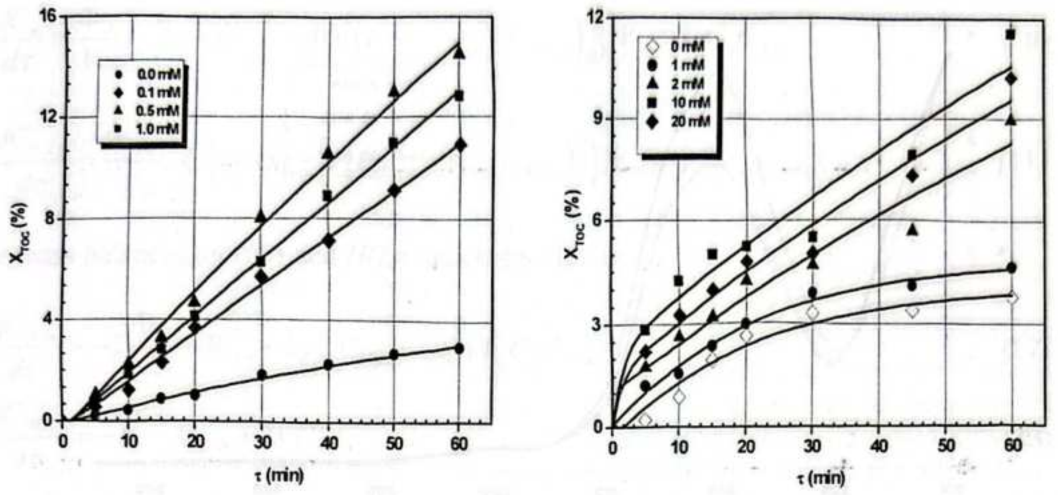
The presence of H_2O_2 has a beneficial effect on the monuron degradation since more hydroxyl radicals are available to attack the aromatic ring and the rate of reaction increases (Table 2). As H_2O_2 concentration increases from 1 to 20 mM, the conversion and mineralization accelerates up to a critical value of 10 mM (Fig. 2B). When a higher concentration is used (20 mM), the TOC reduction and monuron conversion decreases due to the scavenger effect of excess H_2O_2. After one hour of irradiation, conversion and mineralization range between 9.6-29.1% and 4.7-10.2% depending on the hydrogen peroxide concentrations. The optimal hydrogen peroxide concentration was found to be 10 mM H_2O_2, for 0.2 mM monuron solution.



A.

B.

Figure 1 The influence of initial concentration of hydrogen peroxide in UV/H_2O_2 photodegradation of isoproturon (A) and monuron (B) at 298 K.



A. B.

Figure 2 The influence of initial concentration of hydrogen peroxide on mineralization degree profile at 298 K (A: 0.05 mM isoproturon, B: mM monuron)

Complete removal of the initial concentration was observed after 180 min of irradiation in hydrogen peroxide presence. This poor TOC reduction may be due to the weak photolysis of H_2O_2 (Eq. 4) that absorbs only UV light with a wavelength below 300 nm.

The complete herbicide removal demands several hours of irradiative treatment, which will damage to the lamp life and it will increase the operative cost of the process.

The optimal hydrogen peroxide concentration was found to be 0.5 mM H_2O_2 for 0.05 mM isoproturon and 10 mM H_2O_2 for 0.2 mM monuron respectively. The overall stoichiometry for the mineralization of ISO and M by *HO•* radicals can be written as:

$$C_9H_{11}ClN_2O + 54HO\bullet \rightarrow 9CO_2 + HCl + 2HNO_3 + 31H_2O \qquad (7)$$

$$C_9H_{11}ClN_2O + 54HO\bullet \rightarrow 9CO_2 + HCl + 2HNO_3 + 31H_2O \qquad (8)$$

On the basis of those equations, 47 moles of H_2O_2 are theoretically needed to completely degrade 1 mol of isoproturon and 27 moles of H_2O_2 for 1 mol of monuron respectively. In the present study, the optimal $[H_2O_2]/[ISO]$ and $[H_2O_2]/[M]$ molar ratios equal 10. These values are larger than the theoretical value. It can be concluded that an excess amount of H_2O_2 is required to reach the maximum degradation of both herbicides.

The changes in the absorption spectra of monuron solutions during the photodestruction run at different irradiation times are shown in Figure 3. The decrease of the absorption peak at $\lambda = 244$ nm indicates a rapid degradation of the herbicide. The maximum of the main absorption band is located near 244 nm. A band of lower intensity is located near 280 nm. The absorption is very low at wavelengths longer than 380 nm.

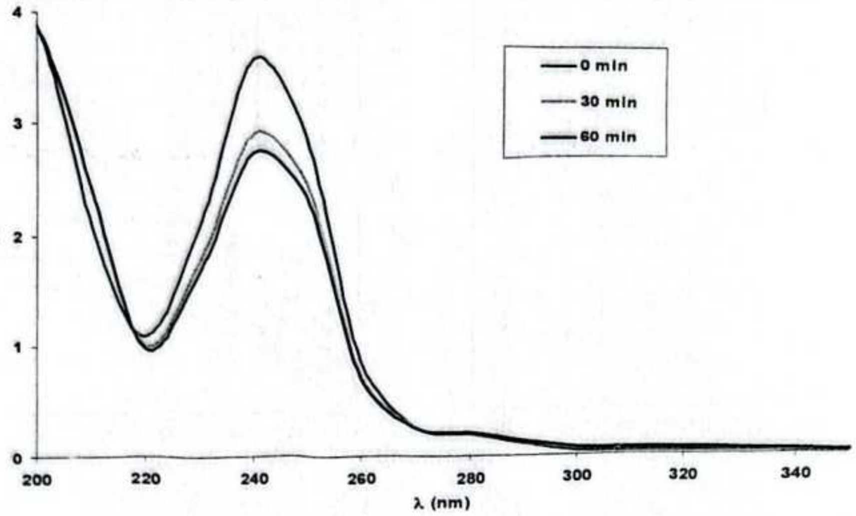


Figure 3 The evolution of the UV spectrum of monuron.

Several intermediary products have been chromatographically (μ-LC) identified in samples collected during the oxidative treatment of both herbicides aqueous solutions (Bobu, 2006). During the first minutes of oxidative degradation the detected compounds are continuously accumulating in the solution, reaching a maximal value when the original substrate is totally removed. The amount of the intermediary products is decreasing after further oxidative treatment, due to the hydroxyl radicals attack. Since the intermediates are detected at the same wavelengths as the original compound, it is assumed that these secondary oxidation products might have similar structures and spectral proprieties as the parent compound. This could be the explanation of low absorbance decrease at 244 nm (24% after 60 min in optimal conditions).

2. Kinetic assessment

A system where UV radiation is applied to a solution containing the organic substrate (A) and H_2O_2 can be described by the following set of rate-limiting reaction steps:

$$H_2O_2 \xrightarrow{h\nu} 2HO\bullet \qquad (4)$$

$$A + HO\bullet \xrightarrow{k_A} products \qquad (5)$$

$$H_2O_2 + HO\bullet \xrightarrow{k_{H_2O_2}} H_2O + HO_2\bullet \qquad (6)$$

$$2HO_2\bullet \xrightarrow{k_t} H_2O_2 + O_2 \qquad (9)$$

A kinetic investigation for the oxidation of herbicides with UV/H_2O_2 system has been carried out considering that: the substrate disappearance due to the UV direct photolysis is negligible compared to that obtained during UV/H_2O_2 oxidation process (Fig. 1), H_2O_2 concentration remains constant at the initial value during the experimental runs, and assuming that: the concentration of the reaction intermediates does not influence that of the $HO^{\bullet}$ radicals.

The initial step for the UV/H_2O_2 oxidation process is represented by the photolysis of hydrogen peroxide and the generation of hydroxyl radicals (Eq. 4). These radicals attack the organic molecules (Eq. 5) and the excess of hydrogen peroxide (Eq. 6).

The substrate and hydrogen peroxide degradation rates can be written as:

$$-\frac{dC_A}{d\tau}=\frac{\Phi_A}{V_L}I_0\left\{1-\exp-\left[2.303l\left(\varepsilon_A C_A+\varepsilon_{H_2O_2}C_{H_2O_2}\right)\right]\right\}\Psi_A+k_A C_A C_{HO\bullet} \tag{10}$$

$$-\frac{dC_{H_2O_2}}{d\tau}=\frac{\Phi_{H_2O_2}}{V_L}I_0\left\{1-\exp-\left[l\left(\varepsilon_A C_A+\varepsilon_{H_2O_2}C_{H_2O_2}\right)\right]\right\}\Psi_{H_2O_2}+k_{H_2O_2}C_{H_2O_2}C_{HO\bullet}-k_t C^2_{HO_2\bullet} \tag{11}$$

The mass balances on *HO•* and *HO₂•* radical species are:

$$-\frac{dC_{HO\bullet}}{d\tau}=-2\frac{\Phi_{H_2O_2}}{V_L}W_{abs}+k_{H_2O_2}C_{H_2O_2}C_{HO\bullet}+k_A C_A C_{HO\bullet} \tag{12}$$

$$-\frac{dC_{HO_2\bullet}}{d\tau}=-k_{H_2O_2}C_{HO\bullet}+2k_t C^2_{HO_2\bullet} \tag{13}$$

Where: W_{abs} is the radiation power absorbed by the solution. W_{abs} can be expressed as:

$$W_{abs}=I_0\left\{1-\exp-\left[l\left(\varepsilon_A C_A+\varepsilon_{H_2O_2}C_{H_2O_2}\right)\right]\right\}\Psi_{H_2O_2} \tag{14}$$

By assuming the "steady-state" hypothesis for radical species ($-\frac{dC_{HO\bullet}}{d\tau}=0$ and $-\frac{dC_{HO_2\bullet}}{d\tau}=0$), the stationary *HO•* and *HO₂•* concentrations can be expressed as:

$$C_{HO\bullet}=\frac{2\Phi_{H_2O_2}}{V_L}I_0\left\{\frac{1-\exp-\left[l\left(\varepsilon_A C_A+\varepsilon_{H_2O_2}C_{H_2O_2}\right)\right]}{k_{H_2O_2}C_{H_2O_2}+k_A C_A}\right\}\Psi_{H_2O_2} \tag{15}$$

$$C^2_{HO_2\bullet}=\frac{k_{H_2O_2}\Phi_{H_2O_2}}{k_t V_L}I_0\left\{\frac{1-\exp-\left[l\left(\varepsilon_A C_A+\varepsilon_{H_2O_2}C_{H_2O_2}\right)\right]}{k_{H_2O_2}C_{H_2O_2}+k_A C_A}\right\}C_{H_2O_2}\Psi_{H_2O_2} \tag{16}$$

Substituting the obtained equations (15 and 16) in (10) and (11) gives:

$$-\frac{dC_A}{d\tau}=\frac{\Phi_A}{V_L}I_0\left\{1-\exp-\left[l\left(\varepsilon_A C_A+\varepsilon_{H_2O_2}C_{H_2O_2}\right)\right]\right\}\Psi_A+$$

$$+k_A\frac{2\Phi_{H_2O_2}I_0}{V_L}\left\{1-\frac{\exp-\left[l\left(\varepsilon_{H_2O_2}C_{H_2O_2}+\varepsilon_A C_A\right)\right]}{k_{H_2O_2}C_{H_2O_2}+k_A C_A}\right\}C_A\Psi_{H_2O_2} \tag{17}$$

$$-\frac{dC_{H_2O_2}}{d\tau}=\frac{\Phi_{H_2O_2}}{V_L}I_0\left\{1-\exp-\left[l\left(\varepsilon_A C_A+\varepsilon_{H_2O_2}C_{H_2O_2}\right)\right]\right\}\Psi_{H_2O_2}+$$

$$+k_{H_2O_2}\frac{\Phi_{H_2O_2}I_0}{V_L}\left\{\frac{1-\exp\left[-l\left(\varepsilon_{H_2O_2}C_{H_2O_2}+\varepsilon_A C_A\right)\right]}{k_{H_2O_2}C_{H_2O_2}+k_A C_A}\right\}\Psi_{H_2O_2} \tag{18}$$

where:

Φ_A : primary quantum yields of the direct photolysis at 254 nm of herbicides ($\Phi_A = 1.8 \times 10^{-2}$ mol Es^{-1})
$\Phi_{H_2O_2}$: quantum yield of the direct photolysis at 254 nm of hydrogen peroxide ($\Phi_{H_2O_2} = 0.5$ mol Es^{-1})
V_L : the volume of the aqueous solution (0.5 L)
I_0 : the measured incident UV-light intensity (5×10^{-6} Es s^{-1})
l : optical path length ($l = 2.5$ cm)
ε_A : molar extinction coefficient of substance A (L mol^{-1} cm^{-1})
$\varepsilon_{H_2O_2}$: molar extinction coefficient of H_2O_2 at 254 nm ($\varepsilon_{H_2O_2} = 18.6$ L mol^{-1} cm^{-1})
Ψ_A : the fraction of UV irradiation absorbed by substance A
$\Psi_{H_2O_2}$: the fraction of UV irradiation absorbed by H_2O_2
$k_{H_2O_2}$: pseudo-first order rate constant of the reaction (6) ($k_{H_2O_2} = 2{,}7 \times 10^7$ L mol^{-1} s^{-1})
k_t : pseudo-first order rate constant of the reaction (9) ($k_t = 8{,}3 \times 10^5$ L mol^{-1} s^{-1})

Preliminary photolytic runs without hydrogen peroxide addition allowed the determination of quantum yield of the direct photolysis of monuron and isoproturon. Once the value of the parameter k_A is known, (17) and (18) can be integrated with the initial conditions: $\tau = 0$, $C_A = C_A^0$ and $C_{H_2O_2} = C_{H_2O_2}^0$ and the concentrations of the substrate and hydrogen peroxide calculated at varying reaction time.

Conclusion

The removal of two phenyl urea herbicides from aqueous solutions has been studied using UV/H_2O_2 system. For the adopted experimental conditions the investigated AOP leads to a 32% conversion degree and 12% mineralization degree for 0.2 mM monuron and 10 mM hydrogen peroxide. After one hour irradiation, using the optimal hydrogen peroxide concentration (0.5 mM H_2O_2) a 34.6% conversion of the initial isoproturon concentration and a 14.5% mineralization degree were achieved. Reaction kinetics has been evaluated in experimental runs for different hydrogen peroxide concentrations.

The presence of a halogen atom on the ring has a significant influence on the photochemical behavior of phenyl urea herbicides in aqueous solution: monuron and isoproturon have completely different reactivities. The difference in photo-reactivity between the two pesticides suggests that the degradation rate is directly related to the electron-donor and electron-withdrawing character of the different substitutes in the herbicides aromatic ring, which can activate or deactivate the ring with respect to the elecrophilic attack of the HO• radical. Isoproturon was the most reactive substance due probably to the presence of the isopropyl group, which is benzene ring activating. Monuron has one halogen group bound to the aromatic ring, which is considered as deactivating. Further investigations must be done in order to validate the differential aquations proposed using the experimental data and to use them for the photo-react or design and scale-up.

Acknowledgments

This research was undertaken at the Department of Chemistry, University of Oslo, Norway, under the frame of a Marie Curie grant.

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