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Monuron Photodegradation Products in Aqueous Solution

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Abstract: The photodegradation of monuron (3-(4-chlorophenyl)-1, 1-dimethylurea) in aqueous solutions under simulated solar irradiation has been conducted in this study by different advanced oxidation processes (UV/H_2O_2, UV/H_2O_2/Fe^{2+}, UV/H_2O_2/TiO_2, UV/TiO_2). The degradation rates were always higher for the homogenous catalysis in photo-Fenton reactions (UV/H_2O_2/Fe^{2+}) when compared with the heterogeneous photocatalytic systems (TiO_2/UV and UV/H_2O_2/TiO_2). Optimal concentrations of Fe^{2+} and H_2O_2 for the abatement of the herbicide in the photo-Fenton system were found. Several intermediary products were identified using large volume injection micro-liquid chromatography with UV detection, LC-MS and GC-MS techniques and from the analytical data, a degradation mechanism was proposed. The degradation mechanism of monuron is initiated by the attack of hydroxyl radicals at the N-terminal group and consists of two sequential N-dealkylations followed by hydrolysis to an aniline derivate (4-chloroaniline). Further oxidations leads to ring opening and smaller organic molecules, easier to oxidize.

Keywords: Monuron, μ-LC-MS, μ-LC-UV, photocatalysis, degradation products.

1. Introduction

Since their appearance shortly after the Second World War phenyl urea herbicides has grown to be one of the most important classes of herbicides used worldwide. Phenyl urea herbicides are applied for pre- or post-emergence control of weeds in cotton, fruit or cereal production, and also on non-cultivated areas such as roads and railways. They 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 and groundwater [1-3].

Among the phenylurea herbicides, monuron and linuron are already reported to be possibly carcinogenic in humans [4]. The other herbicides could also cause serious damage to humans [5].

In this work, the photocatalytic degradation of monuron was investigated. Since monuron is subject to a quite slow transformation in moist soils, with a mean persistence in the environment of about 10 months [6], there are relevant risks of its leaching into groundwater. Monuron has a half-life time of 8 weeks in the river waters [7].

The presence of herbicides in groundwaters, surface waters, effluents of wastewater treatment plants and other sources of drinking water indicates that conventional biological treatment processes are very slow or non-destructive for these kinds of compounds. A promissing 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 [8].

The photodegradation of monuron (3-(4-chlorophenyl)-1, 1-dimethylurea) in aqueous solutions under simulated solar irradiation has been conducted in this study by different advanced oxidation processes (UV/H_2O_2, UV/H_2O_2/Fe^{2+}, UV/H_2O_2/TiO_2, UV/TiO_2). On the basys of substrate conversion degree (X_M, %) and the mineralization degree (X_{TOC}, %) the efficiency of the involved AOPs was evaluated. The intermediary products were identified using large volume injection micro-liquid chromatography with UV detection, LC-MS and GC-MS techniques and from the analytical data, a degradation mechanism was proposed.

2. Experimental

Monuron was purchased from Aldrich (Steinheim, Germany) and was used without further purification. The initial concentration was 40 ppm (2 x 10^{-4} M) monuron. 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. The intermediary products standards 4-chlorophenylurea and 1-(4-chlorophenol)-3-methyurea were purchased from the Sigma-Aldrich library of rare chemicals (Millwaukee, WI, USA), hydroquinone (HPLC purity, 99.0 %) from Fluka (France) and 4-chloroaniline (98 %) from Aldrich (Steinheim, Germany).

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 [9].

The samples taken at different times from the reaction mixture, with single used syringes have been filtered before analysis through 0.2 μm Minisart cellulose nitrate filters (Sartorius). 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 monuron and some of the secondary products were determined by large volume injection micro-liquid chromatography with UV detection (μ-LC-UV) at 244 nm [9]. The mobile phase for the analytical column was acetonitrile-methanol-water (20/20/60, v/v). All the mobile phases contained 0.1% formic acid and were degassed with helium before use.

The identification of secondary products was done by μ-LC-MS, μ-LC-UV, and GC-MS techniques [9, 10].

3. Results and discussion

3.1. Photodegradation experiments

Monuron concentration versus irradiation time was determined by HPLC measurements and the conversion of the original substrate, X_M (%), was used to define the efficiency of the degradation.

$$X_M = 100\left(1 - \frac{C_M}{C_M^0}\right) \quad (1),$$

where C_M and C_M^0 refers to monuron molar concentrations values at reaction time τ and 0, respectively. It is well accepted that complete conversion does not mean that the organic compound has been completely oxidized into CO_2, H_2O and inorganic ions. Reaction intermediates are usually formed in the solution and are involved in different reactions during the degradation process.

The TOC removal ratio of the reaction solution was defined as below:

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

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

The apparent degradation kinetics of monuron in aqueous solution is described according the pseudo first-order equation as given below:

$$-\frac{dC_M}{d\tau} = k_{ap,M} C_M \quad (3),$$

where C_M is the monuron concentration in water, τ is reaction time and $k_{ap,M}$ is the pseudo first-order rate constant.

The TOC removal rate can be expressed by a pseudo first-order kinetic equation with respect to TOC value as follows:

$$\ln\frac{TOC_0}{TOC} = -\ln(1 - X_{TOC}) = k_{ap,TOC}\tau \quad (4),$$

where $k_{ap,\ TOC}$ stands for the apparent mineralization rate constant.

Figure 1 presents the time course of the mineralization degree when some advanced oxidation systems are applied to the aqueous monuron solution (0.2 mM). From data depicted in figure 1, the kinetics of degradation of the different studied AOPs has been deduced and the corresponding kinetic rate constants obtained are summarized in Table 1.

The UV/H_2O_2 process (trace ● in Fig. 1) causes a slow degradation and the decrease in monuron concentration in 60 min was only 32% and the mineralization degree was 12%. This poor efficiency may be due to the weak photolysis of hydrogen peroxide that absorbs only UV light with a wavelength bellow 300 nm [11]. Chromatograms recorded by μ-LC-UV revealed that during the monuron degradation an intermediate having a retention time of 9.4 min is formed. The nature of this intermediary product, having a retention time smaller than that of monuron (10.5 min), will be discused in the section 3.2.

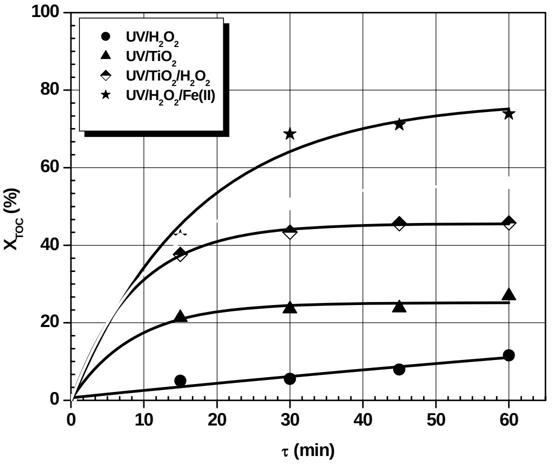


Figure 1. Time course of the mineralization degree during the application of the UV/H_2O_2, $UV/H_2O_2/Fe^{2+}$, $UV/H_2O_2/TiO_2$, UV/TiO_2, at 298 K; 0.2 mM monuron, 10 mM H_2O_2, 1 g l^{-1} TiO_2 and 1 mM Fe^{2+}

In order to improve the H_2O_2 photolysis, a small amount of iron salt was added ($UV/H_2O_2/Fe(II)$, homogeneous photocatalysis). This had a beneficial effect on the degradation of monuron: the original product was completely removed after 5 minutes, and the mineralization degree after 60 minutes achieved 74%. Since the other aim of the study was to identify the intermediates of photo-Fenton process some slower degradation experiments were also performed and analyzed by μ-LC-UV, μ-LC-MS and GC-MS. The recorded μ-LC-UV chromatograms recorded (Fig. 2) showed the appearence of 3 intermediaty products (retention times of 4.3 min, 6.5 min and 9.4 min) while the monuron disipears.

TABLE 1. Conversion degree, mineralization degree, pseudo first order rate constant based on the molar concentration and pseudo first order rate constant based on the total organic carbon concentration, respectively, of the different investigated Advanced Oxidation Processes in 0.2 mM aqueous monuron solution at 298 K, 10 mM H_2O_2, 1 g l^{-1} TiO_2 and 1 mM Fe^{2+}

Advanced Oxidation Process	X_M (%)	X_{TOC} (%)	$k_{ap,\ M}$ (s^{-1})	$k_{ap,\ TOC}$ (s^{-1})
UV/H_2O_2	32.01	11.56	2.91×10^{-4}	3.46×10^{-5}
$UV/H_2O_2/Fe(II)$	99.99	73.88	3.33×10^{-3}	4.44×10^{-4}
UV/TiO_2	67.09	26.94	4.17×10^{-4}	8.72×10^{-5}
$UV/H_2O_2/TiO_2$	91.69	45.77	7.50×10^{-4}	1.60×10^{-4}

The UV/TiO_2 heterogeneous catalysis causes a reduction of monuron concentration of 67% and a TOC value decreased with 27%. The μ-LC-UV chromatogram revealed 5 intermediary products (Fig. 3). One of the intermediates had a retention time significantly higher than that of monuron (18 minutes) (Table 2), and consequently, is more hydrophobic. The formation of nonpolar compounds is rather unusual in photocatalytic degradation of aromatics, and the identity of this compound was pursued using GC-MS as described latter.

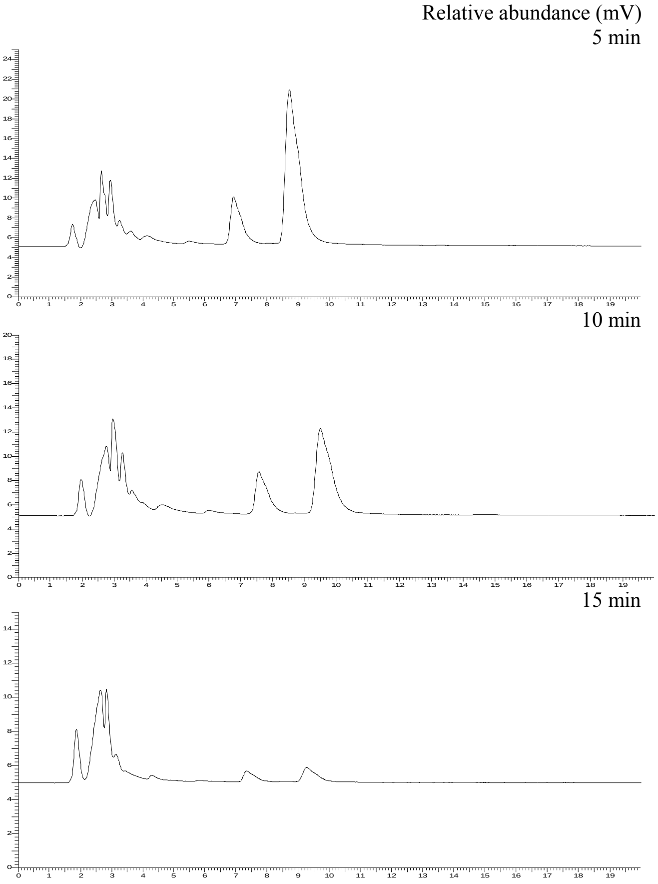


Figure 2. μ-LC-UV chromatograms recorded for photo-Fenton degradation at 5, 10 and 15 min samples (0,2 mM monuron, 0.02 mM Fe(II), 0.2 mM H_2O_2, pH=3, 298 K). Initial sample (τ=0) had a peak high of 125 mV)

Addition of H_2O_2 made the process even more effective (Fig. 1), since H_2O_2 is an efficient electron scavenger and generates additional HO• radicals. The addition of 10 mM H_2O_2 leaded a conversion of the original substrate of 91% in 60 minutes, and the TOC value decreased with 46%.

3.2. Identification of intermediary products

During the photodegradation of monuron solution formation of different photoproducts was detected by the μ-LC coupled to a UV detector (Fig. 2). The identity of these secondary products was studied by μ-LC-MS, μ-LC-UV and GC-MS analyses with the co-injection of some commercially available standards (Table 2).

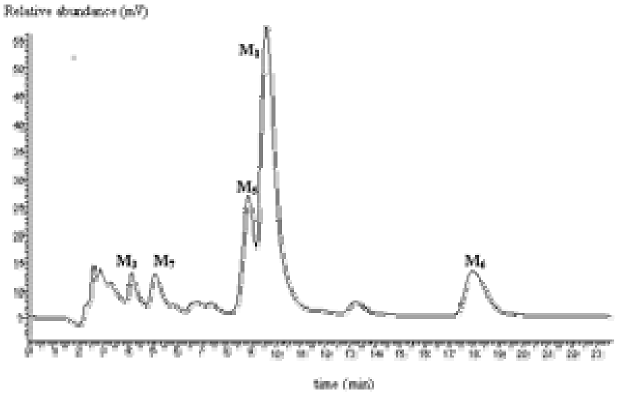


Figure 3. μ-LC-UV chromatograms recorded for photo-Fenton degradation at 5, 10 and 15 min samples (0,2 mM monuron, 0.02 mM Fe(II), 0.2 mM H_2O_2, pH=3, 298 K). Initial sample (τ=0) had a peak high of 125 mV)

μ-LC-MS analyses (Fig. 4) of the samples collected during the photo-Fenton degradation of monuron revealed the chemical structure of the by-products presented in Table 2. The identification of the compounds was performed by comparing their retention time with standard compounds. Identification of the products with lower molecular weights than hydroquinone or structures with open ring, according to the mechanism suggested by others [12] was not possible with the present μ-LC-MS method, due to mobile phase interferences.

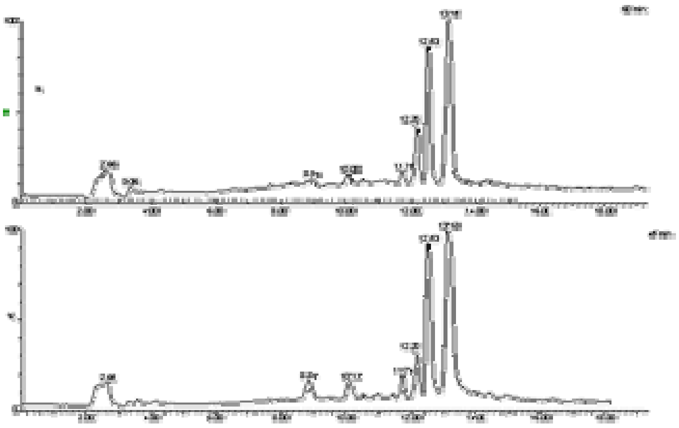


Figure 4. μ-LC-UV chromatograms recorded for photo-Fenton degradation at 5, 10 and 15 min samples (0,2 mM monuron, 0.02 mM Fe(II), 0.2 mM H_2O_2, pH=3, 298 K). Initial sample (τ=0) had a peak high of 125 mV).

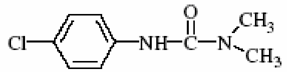
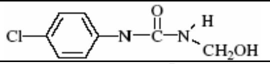
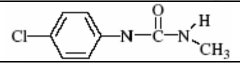
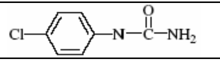
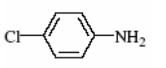
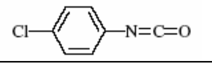
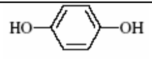
Analyses of the heterogeneous photocatalysis degradation

samples revealed the presence of the same by-products like in photo-Fenton experiments. The nature of the intermediary product with retention time 18 min could not be found by the μ-LC-MS method. Therefore GC-MS analysis was performed, and on the basis of coincidence with library mass spectra it was found to be 4-chlorophenyl isocyanate.

Thus, 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. The degradation mechanism of this phenylurea herbicide and the identification of the secondary products were made by several authors [1, 12-13] but in our study new analytical methods were involved (μ-LC-MS, μ-LC-UV).

TABLE 2. Monuron and its degradation products

Nr.	Chemical structure	Name	M	Analytical method	T_R (min)		Values *m/z* identified by GC-MS
					μLC-UV	μLC-MS	
M_1		Monuron	198,65	μ LC-UV μ LC-MS GC-MS	10,5	13,13	72, 90, 99, 125, 153, 198, 201
M_2		1-(4-clorofenil)–3–hidroxil metil ureea	200,62	μ LC-MS		12,20	
M_3		1-(4-clorofenil)–3–metil ureea	184,62	μ LC-MS μ LC-UV	4,3	12,53	
M_4		4-clorofenil ureea	170,60	μ LC-MS		11,74	
M_5		4 – cloro anilina	127,57	μ LC-MS μ LC-UV GC-MS	9,4	10,11	129, 127, 92, 100, 73, 65
M_6		4-clorofenil izocianat	153,75	GC-MS	18,0		155, 153, 90, 127, 125, 63
M_7		Hidrochinona	110,00	GC-MS μ LC-UV	7,5		110, 81, 55, 53

Even though the presence of a special intermediate product (4-chlorophenyl isocyanate) could be observed in the TiO_2 catalysis experiments we could not conclude that the mechanism of monuron degradation has different pathways, for heterogeneous catalysis with TiO_2 and for homogenous catalysis with Fe^{2+} (photo-Fenton). The presence of this product could be explained by the fact that heterogeneous catalysis has a slower degradation rate and that some intermediary products are longer present than in the photo-Fenton system.

4. Conclusions

Different advanced oxidation processes, i.e. the systems UV/H_2O_2, TiO_2/UV, $TiO_2/UV/H_2O_2$ and $Fe^{2+}/UV/H_2O_2$, have been studied and their performances for the degradation of monuron were compared. The experimental results presented demonstrated that both heterogeneous photocatalysis with TiO_2 and homogenous photocatalysis (photo-Fenton reactions) are suitable methods for the mineralization of this compound. However, the degradation rate was higher for the photo-Fenton reaction as compared to the heterogeneous photocatalytic systems. Through this work we have found that the optimal concentrations of 1 mM Fe^{2+} and 10 mM H_2O_2 for the mineralization of a 0.2 mM monuron solution (X_{TOC}=73.9%).

Several intermediate products were identified after different irradiation times and different oxidation systems. When monuron was degraded, an intermediate more hydrophobic that the starting product was also produced in the heterogeneous photocatalytic system together with the predictable aromatic degradation products.

This compound, identified as 4-chlorophenyl isocyanate, undergoes further decomposition to 4-chloroaniline, an intermediary product that is common for both heterogeneous and homogenous catalysis.

The presence of this product could be explained by the fact that heterogeneous catalysis has a slower degradation rate and that some intermediary products are present longer than in the photo-Fenton system.

The degradation mechanism of phenylurea herbicides is initiated by the attack of hydroxyl radicals at the N-terminal group and consists of two sequential N-dealkylations followed by hydrolysis to ananiline derivate. Further oxidations leads to ring opening and smaller organic molecules, that are easier to oxidize, and elimination of phenylurea herbicide from aqueous solution in less than 10 minutes using the most efficient method, photo-Fenton.

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