*ANNALS of the Suceava University – **FOOD ENGINEERING**, Year VII, No. 1 - 2008*

PHOTOCATALYTIC DEGRADATION OF PHENYLUREA HERBICIDES IN AQUEOUS SOLUTION

Maria-Magdalena Bobu[1,2], Ilie Siminiceanu[2], Ramona Tătaru[2], Steven Wilson[3], Elsa Lundanes[3]
[1] "Stefan cel Mare" University of Suceava, Food Engineering Faculty
[2] "Gh. Asachi" Technical University of Iaşi, Chemical Engineering Department, Iaşi
[3] University of Oslo, Department of Chemistry, N-315 Oslo, PO Box 1033, Norway

Abstract

The photodegradation of two phenyl urea herbicides (monuron and isoproturon) in aqueous solutions under simulated solar irradiation has been conducted by different advanced oxidation processes, i.e. the systems TiO_2/UV, $TiO_2/UV/H_2O_2$ *and* $Fe^{2+}/UV/H_2O_2$. *The initial concentration of monuron aqueous solution was of* $2x10^{-4}$ *M while that of isoproturon of* $5x10^{-5}$ *M. During the phototreatment, experiments were made to obtain information concerning the evolution of organic carbon* (X_{TOC}), *the initial compound concentration* (X_I) *and the chemical nature of the intermediates. The optimal parameters for the abatement of both herbicides have been identified for each process. The degradation rates were always higher for the photo-Fenton reactions when compared with the heterogeneous photocatalytic system. Several intermediary products were identified using large volume injection micro-liquid chromatography with UV detection (μ-LC-UV), μ-LC-MS and GC-MS techniques and a degradation mechanism has been proposed.*

***Keywords**: Monuron, Isoproturon, μ-LC-MS, μ-LC-UV, Photo-Fenton,* TiO_2 *photocatalysis.*

Introduction

The history of agriculture can be divided into three main ages. The first, which goes to the XVIIIth century, had a subsistence ratio of 3/1 (three farmers produced and substantiated only one person involved in non agricultural activities).

During the second age, the mechanical age, the subsistence ratio increased from 4/9 in 1830 to 1/10 in 1930. After the Second World War, in the "chemical age", the intensive and extensive use of chemical fertilizers and pesticides in the industrial world increased the subsistence ratio to 1/80.

The value of pesticides sold in 2001 was over 40.9 billion USD, the share of herbicides being of 53% (Monaco, 2002).

Phenyl urea herbicides are applied for pre- and post-emergence control of weeds in many crops and they act as inhibitors of photosynthesis. Their prolonged use involves the risk of their retention in crops and soils. More than 98% of the applied substance is not used to kill the target weeds but dispersed in the environmental compartments, mainly in aquatic one via runoff or leaching.

Monuron has a half-life time of 8 weeks in the river waters (Eichelberger, 1971) and up to 170 days in the soil. Isoproturon persist more than 22-48 days in soil and 145-237 days in water (Perrin-Ganier, 1996). Among the phenyl urea herbicides, monuron and linuron are already reported to be possibly carcinogenic in humans (Ragsdale, 1989). Isoproturon is one of the most used herbicides in Europe ant it is often found in contaminated groundwater, surface water and effluents of wastewater treatment plants (Parra, 2000).

This finding suggests that these herbicides are difficult to be removed by the municipal wastewater treatment plants. The limitations of conventional removal techniques can be overcome by the application of advanced oxidation processes (AOPs), a group of chemical reactions characterized by the *in situ* generation of hydroxyl radicals (HO•) (Siminiceanu, 2003). This radical is the most powerful oxidizing species (E^o=2.8V) after fluorine and is much stronger than the conventional oxidants (Cl_2, ClO_3, O_3).

In the present study the photochemical degradation of monuron and isoproturon was investigated in order to compare the efficiency of two catalytic systems ($Fe^{2+}/UV/H_2O_2$ and $TiO_2/UV/H_2O_2$) and to identify the mechanism of organic substrate oxidation.

Experimental

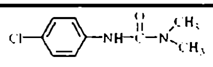
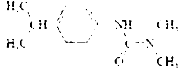
The degradation experiments have been performed in a cylindrical quartz glass vessel (V=0.5 L) under magnetically stirring using a UV lamp with an incident photonic flux of $5x10^{-6}$ Es s^{-1}. The incident flux was determined by a phenylglyoxilic acid actinometry as described in detail previously (Bobu, 2006).

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).

Isoproturon was purchased from Riedel-de Haen and monuron from Aldrich and were used without further purification. The initial concentrations were 40 ppm ($2x10^{-4}$ M) for monuron and 10 ppm ($5x10^{-5}$ 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.

Table 1: The main properties of the monuron and isoproturon

	Monuron	**Isoproturon**
Chemical formula		
CAS number	150-68-5	34123-59-6
Chemical name	3-(4-clorophenyl)-1,1-dimethylurea	3-(4-izopropylphenyl)-1,1-dimethylurea
Molecular formula	$C_9H_{11}ClN_2O$	$C_{12}H_{18}N_2O$
Molecular weight	198.1	206.3
Trade names	CNV-Weed-Killer; Rosuran; Karmex-W; Telvar	Arelon, Tolkan, Bison, Azur, Panther, Puma, Pasport, Pestanal
Physical state	Colorless crystalline solid	White crystalline powder
Solubility in water, mg L^{-1}	230 at 298 K	70.2 at 293 K
Toxicity hazards LD_{50} (oral, rat), mg kg^{-1}	3600	2500
Melting point, K	443.5	428.5
Boiling point, K	458- 473	373

Total Organic Carbon (TOC) measurements were performed using a TOC analyzer (Shimadzu, model 5000 A) with autosampler. Concentrations of unreacted herbicides and some of the secondary products 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 phase for the analytical column is presented in Table 2. All the mobile phases contained 0.1% formic acid and were degassed with helium before use.

Table 2: Data on the µ-LC-UV method

Herbicide	Molecular weight	Mobile phase			T_t (± 0,5 min)	R^2
		H_2O	CH_3CN	CH_3OH		
Monuron	$C_9H_{11}ClN_2O$	60	20	20	10.5	0.9971
Isoproturon	$C_{12}H_{18}N_2O$	60	40	-	8.5	0.9983

The identification of secondary products was done by µ-LC-MS. For MS detection, the analytical column (0.5 mm I.D.x3.5 µm C_{18} Zorbax column, Palo Alto, CA, USA) was connected to a Micromass LCT TOF-MS (Micromass, Manchester, UK). The TOF-MS was equipped with a Z-spray atmospheric pressure ionization source for ESI, which was modified to handle flow rates in the low µL min^{-1} range. Ionization was performed in positive mode.

The following voltages were used: 3.5 kV on the capillary, 20 V on the sample cone and 3 V on the extraction cone. In order to obtain a stable spray performance and aid solvent vaporization, nebulizer gas and desolvation gas were applied at 50 L h^{-1} and 250 L h^{-1}, respectively.

The TOF-MS instrument was controlled by MassLynx v4.0 software. For the identification of intermediary products with µ-LC-MS the loading phase was acetonitrile-water (5/95, v/v) and for the gradient elution on the analytical column channel A contained acetonitrile-water (5/95, v/v) and channel B acetonitrile-water (95/5, v/v).

All this three solvents contained 0.1% formic acid and the gradient was: linear increase from 1% B to 50% B for 10 minutes and 50% B for additional 10 more minutes at a flow of 10µL min^{-1}.

An HP (Avonade, PA, USA) 5890 gas chromatograph was operated by ChemStation B 02.05. For analysis of samples a CP-Sil 5 CB fused silica capillary column (30 m x 0.25 mm I.D., 0.25 µm film thickness, Chrompack, Middelburg, The Netherlands) was used and samples of 2 µl were injected. The column was connected to the injector via a deactivated retention gap of 1.5 m x 0.32 mm I.D. (J&W Scientific, Folsom, CA, USA). The injector temperature was 523 K and samples were injected in pulsed splitless mode with a pulse pressure of 1.72 bars for 1.5 min. Helium (99.99%) was used as carrier gas and separation was performed at a constant flow of 1.2 mL min^{-1}. The chromatographic separation was performed with following temperature program: initial column temperature 313 K for 3 minutes, than raised by 10 K min^{-1} to 573 K, which was held constant for 8 minutes. The mass spectrometer, an HP 5989 MSD, was operated in the electron ionization mode. The temperatures were 373 K, 473 K and 573 K for the quadruple, the ion source, and the interface, respectively.

Results and Discussion

In ***homogeneous photocatalysis*** (photo-Fenton system) the radical mechanism can be resumed by the following equations:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO\bullet \qquad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^{+} + HO\bullet \qquad (2)$$

$$H_2O_2 + h\nu \rightarrow 2HO\bullet \qquad (3)$$

Eq. (1) is the classical Fenton reaction, followed by the UV regeneration of Fe^{2+} (Eq. (2). The photocatalytic nature (Eq. (3)) of the system is demonstrated by the sum of Eq. (1) and Eq. (2). The number of HO• radicals becomes double compared to Fenton reaction.

Comparing the efficiency of classic Fenton reaction and Fe^{2+}/UV/H_2O_2 system (Table 2) it was observed that the maximal effect of degradation was obtained when the solution was irradiated. For the Fenton reaction the TOC values of samples taken at 60 minutes reaction time was 36% of the original value.

The concentration of monuron was found to decrease after 30 minutes of reaction and 97% was transformed into secondary reaction products, and this could explain the small TOC reduction. In the UV light absence, hydroxyl radicals are only generated according to Eq. (1) and when the depletion of H_2O_2 is achieved, the production of radicals stops. In the photo Fenton system both reactions are involved, so the photoreduction of Fe^{3+} to Fe^{2+} takes place with the production of a new HO• radical.

The efficiency of photo-Fenton reactions depends on parameters like the initial value of pH and the concentrations of involved reactive species. In all experiments in the present study the same pH value (pH=3) was used (Siminiceanu, 2002).

Table 2 is summarizing the experiments made in order to find the optimal values of concentration ratios of the oxidizing agents for the complete mineralization of a 0.2 mM monuron solution. As one of our aims was to identify the intermediates, some slower degradation processes were also performed (II, III, V) and analyzed by μ- LC-MS and GC-MS.

In order to find the optimal concentration of iron salt (I, IV and VII) different ratios of oxidizing agents were used and it was found that the optimal iron concentration was 1 mM (see table 2). In experiment IV, where the concentration of oxidized agents were quite high (2 mM Fe^{2+} and 20 mM H_2O_2) the TOC removal was 48.5 %, which was less than in experiment I with 1 mM Fe^{2+}.

Table 2: Photo-Fenton experiments performed with a 0.2 mM monuron solution and initial pH 3 for 60 minutes
(*Value achieved after 5 minutes: **Fenton reaction (without UV irradiation)

Experiment	Fe^{2+} concentration (mM)	H_2O_2 concentration (mM)	Monuron reduction (%)	TOC reduction (%)
I	1	20	99.9*	51.2
II	0.2	2	97.9*	23.9
III	0.02	0.2	95.0	19.1
IV	2	20	97.0*	48.5
V	0.1	1	95.5*	20.9
VI	1	4	99.5*	64.5
VII	1	10	99.9*	73.9
VIII	1	0	15.7	16.6
IX	0	10	32.0	11.6
X**	1	10	99.2	36.0

Same phenomena could be observed for the isoproturon experiments (figure 1a) when the iron salt concentration was increased from 0.01 mM to 0.5 mM. The lower than expected reduction in TOC may be attributed to the formation of an orange-brown iron precipitate (ferric hydroxide) in the reaction solution during the photochemical treatment, hindering effective light absorption and hence ferric iron photo-reduction. The excess of Fe^{2+} ions has a scavenger effect for the formation of HO• radicals.

The increase of H_2O_2 concentration has a beneficial effect on the mineralization of phenyl urea herbicides. Fig. 1b presents the TOC conversion of isoproturon for different H_2O_2 concentration and a constant dose of Fe^{2+}. From the results obtained for monuron degradation at a constant Fe^{2+} concentration (1 mM), presented in Table 2, it can be observed that at 4 mM H_2O_2 the reduction of TOC value was 64.5 % and at 10 mM 73.9 %. When a larger concentration was used (20 mM), the TOC reduction decreased to 51.2 %, because of the scavenger effect of H_2O_2 excess (eq (4)).

$$H_2O_2 + HO\bullet \rightarrow H_2O + HO_2\bullet \qquad (4)$$

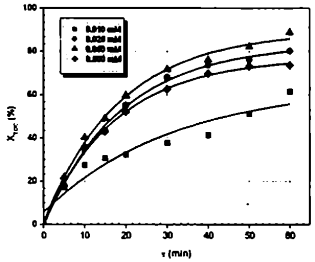


Fig. 1(a) : The influence of Fe^{2+} concentration on photo-Fenton degradation of 0.05 mM isoproturon using 10 mM H_2O_2 at pH = 3, 298 K)

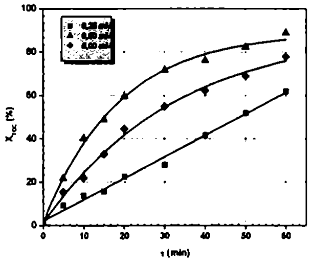


Fig. 1(b) : The influence of H_2O_2 concentration on photo-Fenton degradation of 0.05 mM isoproturon using 0.05 mM Fe^{2+} at pH = 3, 298 K)

In conclusion, for the mineralization of a 0.2 mM monuron solution the optimal conditions for photo-Fenton process were fond to be pH 3; 1 mM Fe^{2+} and 10 mM H_2O_2 and for 0.05 mM isoproturon were pH 3; 0.05 mM Fe^{2+} and 10 mM H_2O_2.

In ***heterogeneous photocatalysis*** (TiO_2/UV, TiO_2/UV/H_2O_2) the mechanism of the semiconductor–catalyzed oxidative degradation of organic compounds in aqueous systems can be explained by the band-gap model (Legrini, 1993). The first step is a light induced generation of a hole (h^+)/electron (e^-) pair (Eq. (5)).

$$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+) \tag{5}$$

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^- \bullet \tag{6}$$

$$O_2^- \bullet + H^+ \rightarrow HO_2 \bullet \tag{7}$$

$$O_2^- \bullet + HO_2 \bullet + H_2O \rightarrow HO \bullet + O_2 + H_2O_2 \tag{8}$$

$$2HO_2 \bullet \rightarrow O_2 + H_2O_2 \tag{9}$$

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + HO^- + HO \bullet \tag{10}$$

$$TiO_2(h^+) + H_2O_{ad} \rightarrow TiO_2 + HO_{ad} \bullet + H^+ \tag{11}$$

$$TiO_2(h^+) + RX_{ad} \rightarrow TiO_2 + RX_{ad}^+ \bullet \tag{12}$$

$$TiO_2(h^+) + HO_{ad}^- \rightarrow TiO_2 + HO_{ad} \bullet \tag{13}$$

On the surface of the catalyst oxygen or other electron acceptors (H_2O_2) are reduced (Eqs. (6) and (10)). The oxidation of absorbed water (Eq. (11)) or hydroxyl ions (Eq. (13)) by holes in the valence band at the exited surface produces the hydroxyl radicals. It has also been shown that the addition of H_2O_2 enhances the rate of photodegradation (Eq. (13)). Organic pollutants adsorbed onto the surface of the TiO_2 particles will then be oxidized by HO• radicals.

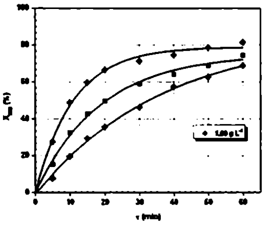


Fig. 2: The influence of TiO_2 concentration on TiO_2/UV degradation of 0.05 mM isoproturon (1 g L^{-1} TiO_2, 298K).

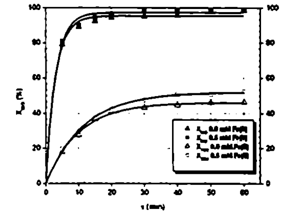


Fig. 3: The influence of Fe presence on TiO_2/UV/H_2O_2 process (0.05 mM isoproturon, 1 g L^{-1} TiO_2, 10 mM H_2O_2 at 298 K)

TiO_2 catalyst loading is the main factor that influences the efficiency of the process. The influence of the TiO_2 dose on the conversion of isoproturon was determined (Fig. 3). The degradation efficiency was found to increase with the increasing concentration of TiO_2 and approaching a limiting value at high concentration. The concentration used in future degradation experiments was 1g L^{-1} TiO_2. At higher concentrations the efficiency will be negatively affected by two main factors: (i) the aggregation of titanium dioxide particles will cause a decrease in the number of surface active sites and, (ii) increase of the opacity and light scattering of the TiO_2 particles lead to a decrease in the passage of irradiation through the solution.

When the optimal catalyst dose was use (1g L^{-1}) for the oxidation of a 0.05 mM isoproturon solution, an 81.5% conversion and a mineralization degree of 32.5% were achieved. The reduction of monuron concentration at the same titanium dioxide concentration was 65% and the TOC value decreased with 27%, and the µ-LC-UV chromatogram revealed 5 intermediary products. One of the intermediates had a retention time significantly higher than that of monuron (18 minutes) (Table 3), 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. In order to suppress the recombination reaction of electrons and holes different substances, which are able to trap electrons are added.

Addition of H_2O_2 made the process even more effective (Fig. 3), since H_2O_2 is an efficient electron scavenger and generates additional HO• radicals (Eq. (10)). The addition of 0.5 mM H_2O_2 increased the conversion of isoproturon (0.05 mM) to 98.6% and the mineralization degree to 46.1% after one hour treatment.

For monuron (0.2 mM) degradation 10 mM H_2O_2 were used in order to achieve a conversion of the original substrate of 91% in 60 minutes, and the TOC value decreased with 46%.

The efficiency of the titanium dioxide catalytic processes can be increased by the addition of transition metals. These metals can increase the degradation rate of pollutants by trapping the electron photogenerated by TiO_2 particles:

$$Fe(III) + e^- \rightarrow Fe(II) \qquad (14)$$

In addition, iron presence in the system can increase the amount of HO• radicals via the Fenton reaction. Fig. 3 presents the improvement in isoproturon degradation when 0.5 mM Fe^{2+} are added to the $TiO_2/UV/H_2O_2$ process. After 60 minutes irradiation the conversion of original substrate is almost total (98.6%) and the mineralization degree is 46.3%.

Identification of intermediary products

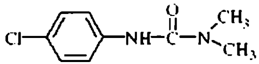
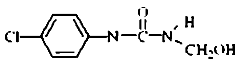
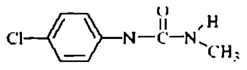
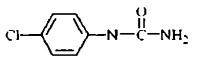
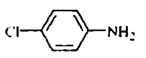
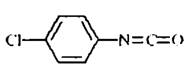
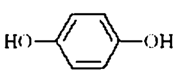
During the photocatalytic degradation of monuron and isoproturon solutions formation of different photoproducts was detected by the μ-LC coupled to a UV detector.

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 3 and 4). Sørensen (2003), proposed a general degradation pathway for phenyl urea herbicides consisted in two sequential N-dealkylations followed by hydrolysis to an aniline derivative.

μ-LC-MS analyses of the samples collected during the photo-Fenton degradation of monuron revealed the chemical structure of the by-products presented in Table 3. 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 (Pramauro, 1993) was not possible with the present μ-LC-MS method, due to mobile phase interferences.

Table 3: Monuron and its degradation products

No	**Chemical structure**	**Name**	**M**	**Identification by**	**t_R in μ LC-UV system (min.)**	***m/z* values from GC-MS**
M_1		Monuron	198.65	μ LC-UV μ LC-MS GC-MS	10.5	72, 90, 99, 125, 153, 198, 201
M_2		1-(4-chlorophenyl)-3-hydroxyl methylurea	200.62	μ LC-MS		
M_3		1-(4-chlorophenyl)-3-methylurea	184.62	μ LC-MS μ LC-UV	4.3	
M_4		4-chlorophenylurea	170.60	μ LC-MS	-	-
M_5		4 – chloroaniline	127.57	μ LC-MS μ LC-UV GC-MS	9.4	129, 127, 92, 100, 73, 65
M_6		4-chlorophenyl isocyanate	153.75	GC-MS	-	155, 153, 90, 127, 125, 63
M_7		hydroquinone	110	GC-MS μ LC-UV	7.5	110,81,55, 53

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 minutes 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.

On the basis of the analytical results a degradation scheme can be proposed which accounts for the simultaneous attack of HO• radicals on different points of the isoproturon molecule (figure 4).

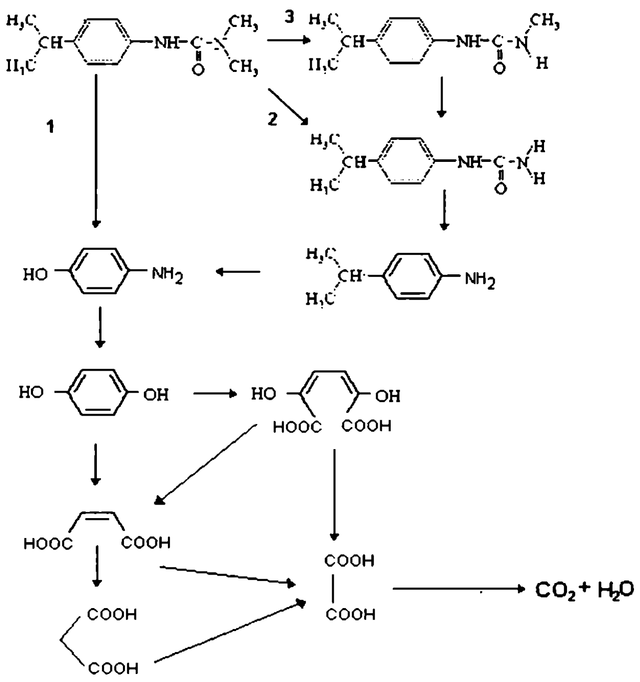


Fig. 4: Isoproturon degradation scheme (1: Photo-Fenton, 2: $TiO_2/UV/H_2O_2$, 3: TiO_2/UV)

During the photo-Fenton process (**1**) the original molecule is rapidly N-dealkylated and hydrolyses to an aniline derivative (4-hydroxy-aniline). During the TiO_2 photocatalysis (**3**), the degradation is slower and it was possible to identify both intermediary products resulted from consecutive N-dealkylation. When H_2O_2 was added (**2**) the degradation is faster and the appearance of some intermediary products couldn't be recorded. 4-hydroxy-aniline is hydrolyzed to hydroquinone and the further radicals attack will lead to the opening of the aromatic ring and the formation of dihydroxylic aliphatic acids.

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.

Even though the presence of a special intermediate product (4-chlorophenyl isocyanate) could be observed in the heterogeneous 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.

Conclusions

Different advanced oxidation processes, i.e. the systems 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 two herbicides 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 these compounds.

However, the degradation rates were always higher for the photo-Fenton reactions as compared to the heterogeneous photocatalytic systems. Through this work we have found that the optimal concentrations of Fe^{2+} and H_2O_2 are 1 mM Fe^{2+} and 10 mM H_2O_2 for mineralization of a 0.2 mM monuron solution (X_{TOC}=73.9%); 0.05 mM Fe^{2+} and 10 mM H_2O_2 for 0.05 mM isoproturon solution (X_{TOC}=87.8%).

For the heterogeneous photocatalysis with TiO_2 the optimal concentrations of TiO_2 and H_2O_2 are 1 g L^{-1} and [illegible] mM, respectively, for the degradation of both herbicides, mineralization degree ranging from 27% for monuron to 32.5% for isoproturon.

The difference in photoreactivity 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 (Table 1), 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. This could explain its lower reactivity when compared with the other herbicide.

The degradation mechanism of this phenylurea herbicide and the identification of the secondary products were made by several authors (Sørensen, 2003; Měšt'ánková, 2004; Pramauro, 1993; Tahmasseb, 2002) but in our study new analytical methods were involved (µ-LC-MS, µ-LC-UV). 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.

Acknowledgements

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

References

Bobu, M., Wilson, S., Greibrokk, T., Lundanes, E., Siminiceanu, I. (2006). Comparison of advanced oxidation processes and identification of monuron photodegradation products in aqueous solution. *Chemosphere*, *63*, 1718-1727.

Eichelberger, J. W., Lichtenberg, J. J. (1971). Persistence of pesticides in river water. *Environmental Science and Technology*, *5*, 541-544.

Legrini, O., Oliveros, E., Braun, A. M. (1993). Photochemical processes for water treatment. *Chemical Reviews*, *93*, 671-698.

Měšt'ánková, H., Mailhot, G., Pilichowski, J. K., Krysa, J., Jirkovsky, J., Bolte, M. (2004). Mineralization of monuron photoinduced by Fe(II) in aqueous solution. *Chemosphere*, *57*, 1307-1315.

Monaco, J. T., Ashton, M. F., Weller, C. S., (2002). *Weed Science: Principles and Practices*. Wiley, New York.

Parra, S., Sarria, V., Malato, S., Péringer, P., Pulgarin, C. (2000). Photochemical versus coupled photochemical-biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon. *Applied Catalysis B: Environment*, *27*, 153-168.

Perrin-Ganier, C., Breuzin, C., Portal, J.M., Schiavon, M. (1996). Availability and persistence of isoproturon under field and laboratory conditions. *Ecotoxicology and Environmental Safety*, *35* (3), 226-230.

Pramauro, E., Vincenti, M., Augugliaro, V., Palmisano, L. (1993). Photocatalytic degradation of monuron in aqueous TiO_2 dispersions. *Environmental Science and Technology*, *27*, 1790-1795.

Ragsdale, N. N., Menzer, R. E. (1989). Carcinogenicity and Pesticides: Principles, Issues, and Relationships. *American Chemical Society*, Washington, DC.

Siminiceanu, I., Bobu, M. (2002). La valeur optimale du pH dans le procede photo-Fenton. *Cofroca-Deuxieme Colloque Franco-Roumain de Chimie Apliquee*, Bacau.

Siminiceanu, I. (2003). Procese fotochimice aplicate la tratarea apei, *Tehnopress*, Iasi.

Sørensen, S. R., Bending, G. D., Jacobsen, C. S., Walker, A., Aamand, J. (2003). Microbial degradation of isoproturon and related phenylurea herbicides in and below agricultural fields. *FEMS Miceobiology Ecology*, *45*, 1-11.

Tahmasseb, L. A., Néliu, S., Kerhoas L., Einhorn J. (2002). Ozonation of chlorophenylurea pesticides in water: reaction monitoring and degradation pathways. *The Science Total Environment*, *291*, 33-44.