Monuron and Isoproturon Mineralization in Water by a Heterogeneous Photo-Fenton Process

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The paper presents new experimental results on the photodegradation of two important phenyl urea herbicides in water: Monuron and Isoproturon. The photodegradation was performed by two Advanced Oxidation Processes (AOPs): the homogeneous photo-Fenton process ($UV\text{-}H_2O_2 - Fe^{3+}$) and a heterogeneous photo- Fenton reaction using an iron pillared Laponide- RD catalyst (Fe-Lap-RD). The Fe-Lap-RD catalyst was prepared from iron nitrate 0.2 M solution and a suspension of Laponite- RD clay. The precipitate was calcinated at 623 K for 20 hours. The product was characterized by XPS/ ESCA technique. The main objective of the work was to compare the mineralization degree obtained by the two methods in similar conditions. The initial concentration of the Monuron aqueous solution was of 40 ppm while that of Isoproturon of 25 ppm. The Total Organic Carbon (TOC) measurements have been performed with a TOC Shimadzu analyzer model TOC 5000A. The results have shown that the mineralization degree (X_{TOC}) of both herbicides was superior by about 10% when the Fe-Lap-RD catalyst was used. The reaction mechanisms are also proposed on the basis of the experimental results.

Keywords: photo degradation, pesticides, water treatment, Laponite RD, photo- Fenton

During the „chemical age" of the agriculture, started after 1950, the intensive use of chemical fertilizers and pesticides in the industrial world increased the subsistence ratio to 1/80 (one farmer produces and subsistences 80 persons involved in non agricultural activities) compared to a maximum of 1/10 during the „mechanical age", in 1930. The use of agrochemicals is a vital necessity for a growing population of the world. The value of pesticides sold in 2001 was over 40.9 billion USD, the share of herbicides being of 53% [1]. Monuron and Isoproturon are two of the most important phenyl urea herbicides. Their essential properties are listed into the table 1. Monuron has a half life of more than 56 days in river water and up to 170 days in the soil. It is a persistent and bio recalcitrant pollutant [2]. Isoproturon has been found in the effluents of wastewater treatment plants [2]. This indicates that these herbicides are difficult to remove by a conventional wastewater treatment process.

Advanced Oxidation Processes (AOPs) have been proposed in recent years as an effective method to remove non biodegradable organic pollutants from ground water, surface water, and wastewater. The objective of a previous work [3] was to study the Isoproturon and Monuron photodegradation in water by four AOPs (UV/H_2O_2, UV/TiO_2, UV/H_2O_2 / Fe (II), UV/H_2O_2 / TiO_2). The results have shown that photo-Fenton was the most effective process for the mineralization of these two herbicides. However, this process has an important drawback: the large volume of sludge generated at the end of the treatment by neutralization and precipitation of the iron ions. To eliminate this major disadvantage, studies have been done to find a solid support for the iron catalyst [4]. The first objective of this work was to prepare a Laponite RD clay-based iron nanocomposite by the pillaring technique. The product has been characterized by the XPS/ESCA technique. The second objective was to test the catalytic activity of the Fe-Laponite RD nanocomposite for the degradation of the two herbicides in water in order to compare the effectiveness of the new heterogeneous photo- Fenton process with those of the conventional homogeneous one.

Experimental part

The Fe-Lap-RD nanocomposite was prepared through reaction between a solution of 0.2 M Fe $(NO_3)_3$ and dispersion (2g clay /100 mL water) of synthetic Laponite-RD supplied by *Kremer Pigments*. The suspension was stirred for 2 h, followed by aging at 373 K for 48 h. The precipitate was recovered by centrifugation, washed and dried. The dried solid was calcined at 623 K for 20h. The product, named Fe-Lap-RD nanocomposite, was analyzed by the X-Ray Photoelectron Spectroscopy (XPS) technique, using a VG Scientific MICROLAB Mk III with $AlK\alpha$ radiation ($h\nu$ = 1486.6 eV). The photo-catalytic activity of the Fe-Lap-RD was tested in the photo-assisted degradation of Monuron and Isoproturon in the presence of H_2O_2 and UV light.

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 5. 10^{-6} Es/s. The incident flux was determined by the phenylglyoxylic acid actinometer as described in a previous paper [3]. The samples taken at different times (5, 10,15, 20, 20, 40, 50, 60, 90, 120 min) from the reaction mixture, with single used syringes, have been filtered before analysis through 0.45 μm and 0.2 μm (Minisart cellulose nitrate filter from Sartorius). *Isoproturon* was purchased from Riedel-de Haën and *Monuron* from Aldrich and were used without further purification. The main properties of the two herbicides are presented in the table 1. Grade 1 water was obtained from a Milli-Q ultrapure water purification system (Millipore, USA). Aqueous solutions of Isoproturon (25 ppm) and Monuron (40 ppm) were prepared by dissolving the proper amount of herbicide in grade 1 water and stored protected from the light. The *p*H 3 adjustment was made with HCl 1M solution.

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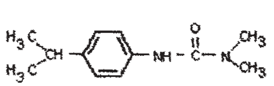
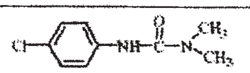
Table 1
THE MAIN PROPERTIES OF THE ISOPROTURON AND OF THE MONURON [3]

Chemical formula		
Chemical name	3- (4- isopropylphenyl)-1, 1-dimethylurea	3- (p- clorophenyl)-1, 1-dimethylurea
Trade names	*Isoproturon*, Tolkan, Bison, Azur, Panther, Puma, Pasport	*Monuron*, Monurex, Telvar
Formulations/ Application mode	Concentrate 50% / foliar spray , max 1.5 kg/ha	Wettable powder 80%, and technical 98%
Type	Substituted urea herbicide	Substituted urea herbicide
Molecular formula/weight	$C_{12}H_{18}N_2O$/ 206.3 g/mol	$C_9H_{11}ClN2O$/ 198.7 g/mol
Physical state	White crystalline powder	Colorless crystalline solid
Water solubility	70.2 mg/L water, at 293 K	230 mg/L water, at 298 K
Melting point	428.5 K	447.5 K
Toxicity Hazards	LD_{50}=2500 mg/kg (oral, rat). Very toxic to aquatic organisms.	LD_{50}=3600 mg/kg (oral, rat)

Total Organic Carbon (TOC) measurements were performed using a TOC analyzer Shimadzu (model 5000 A) with auto-sampler.

Results and discussions

The results of the XPS characterization of the synthesized Fe-Lap-RD are presented in the Table 2.The binding energy of the identification peaks are closed to those reported in the literature [5]. It was observed that the Fe (2p1/2) line was narrow. Therefore, it was very difficult to deconvolute the line into two components that correspond to Fe (II) and Fe (III), respectively. The detailed spectra in figure 2 show that the Fe ions leaching out from the Fe- Lap- RD in acidic solution is negligible. This was also proved analytically: the Fe ion concentration in solution, at the end of each run, was less than 1 mg/L [6,7].

The results of the Fe-Lap-RD catalytic activity testing are presented in the figures 3 to 5. Figure 3 presents the TOC conversion of Monuron for different Fe-Lap-RD doses and

Table 2
THE BINDING ENERGY (eV) AND THE ATOMIC CONCENTRATION (At %) OF Fe-Lap-RD AFTER 4x . 2h REACTION

Element	Binding energy(eV)	At%
Mg (1s)	1303.65	9.75
Fe (2p1/2)	711.30	6.09
Fe (2p3/2)	725.30	
O (1s)	531.60	59.06
C (1s)	284.80	5.31
Si (2p)	102.35	18.08

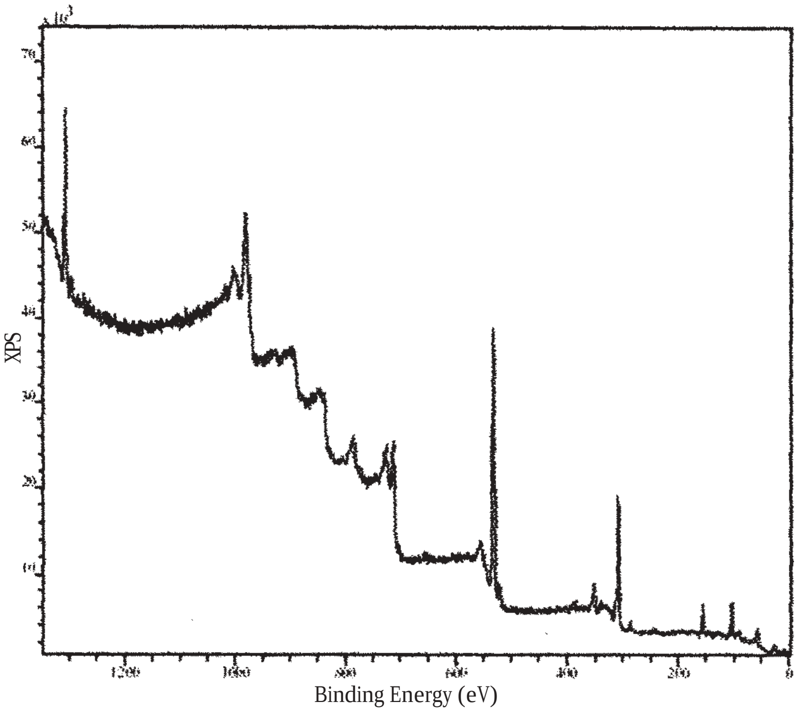


Fig.1. XPS survey spectrum of Fe- Lap- RD

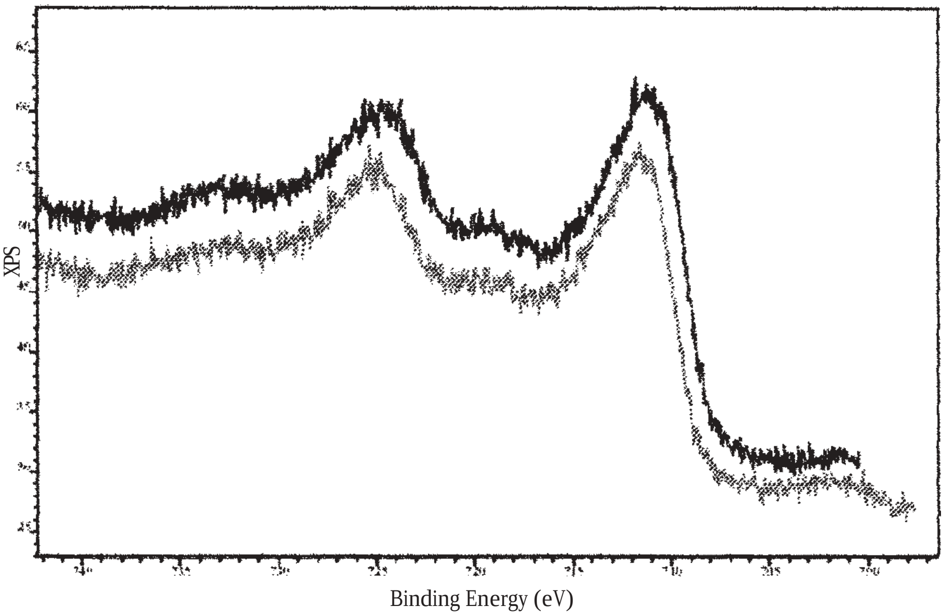


Fig.2. XPS spectra of Fe- Lap- RD: before (up) and after 4 . 2h reaction (down)

a constant dose of H_2O_2 (10 mM). The TOC conversion is a correct measure of the pollutant mineralization degree. The curve with 0.0 g/L Fe-Lap-RD was generated by adding 1 mM Fe (III). This corresponds to the homogeneous photo-Fenton process. The results allow a comparison of the Fe-Lap-RD heterogeneous catalyst effectiveness to those of the homogeneous photo- Fenton system. The TOC conversion is always superior being maximal for a 1.0 g/L dose of Fe-Lap-RD. Similar results have been obtained for the degradation of Isoproturon (fig.4). The conversions are even grater in the case of Isoproturon. Doses of 0.25 g/L Fe-Lap- RD were irrelevant in this case. The effects of increasing doses of hydrogen peroxide, from 10 mM to 40 mM, on the TOC conversion of Isoproturon in the presence of 1 g/L Fe-Lap- RD are presented in the figure 5. The experiments proved that higher doses are not necessary. A higher excess of hydrogen peroxide favours the generation of $HO_2^{\cdot}$ radicals which are less oxidants than hydroxyl radicals ($HO^{\cdot}$). The existence of an optimal dose of H_2O_2 has been proved in the UV- H_2O_2 degradation of other pollutants [8,9].

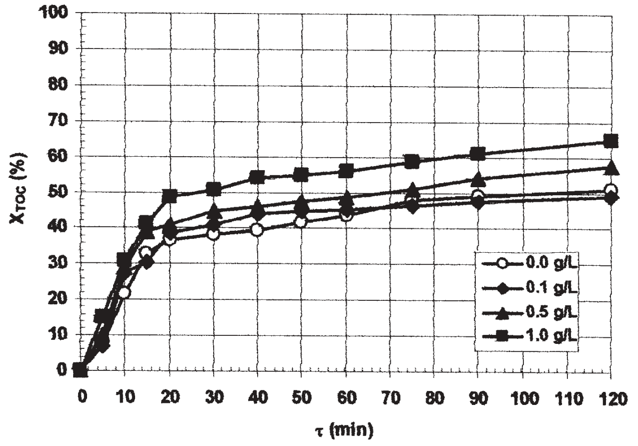


Fig. 3. Influence of Fe-Lap-RD dose on TOC conversion of a Monuron 40 ppm aqueous solution

Reaction mechanisms

On the basis of previously published results [6, 7] and of our new experimental data presented in the figures 3 to 5, two possible mechanisms can be postulated: M-I and M-II. These two mechanisms are present simultaneously when Fe-Lap-RD is used as a heterogeneous catalyst for the degradation of Monuron and Isoproturon in the presence of UV light and hydrogen peroxide.

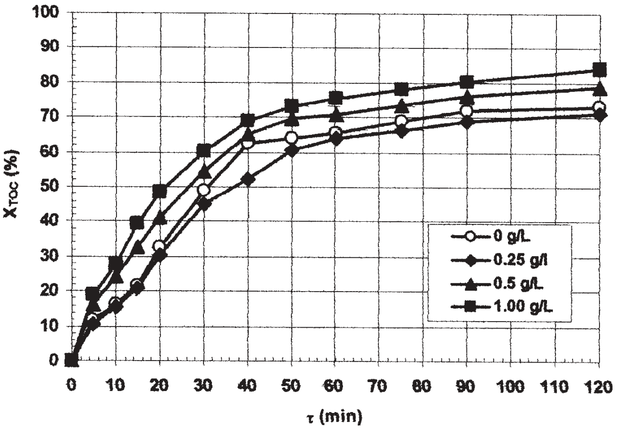


Fig. 4. Influence of Fe-Lap-RD dose on TOC conversion of a Isoproturon 25 ppm aqueous solution

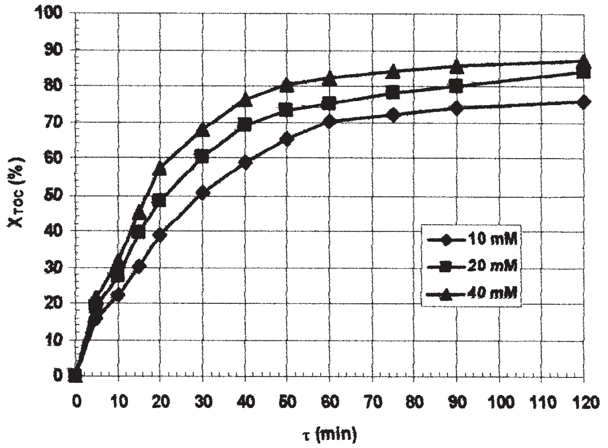


Fig. 5. Influence of H_2O_2 dose on TOC conversion of Isoproturon 25 ppm solution, 1 g/L Fe-Lap-RD

M-I: Fe-Lap-RD acts as a photo-Fenton catalyst.

The reactions are initiated by the photo- reduction of Fe (III) to Fe (II) on the surface of Fe-Lap-RD under UV irradiation:

$$Fe\,(OH)^{2+}_{(s)} + h\nu \rightarrow Fe^{2+}_{(s)} + HO^{\cdot} \qquad (1)$$

The ions Fe^{2+} formed on the surface generate $HO^{\cdot}$ radicals through the Fenton reaction:

$$Fe^{2+}_{(s)} + H_2O_2 = Fe^{3+}_{(s)} + HO^{\cdot} + HO^{-} \qquad (2)$$

The hydroxyl radicals attack the substrate (A) adsorbed on the surface of Fe-Lap-RD resulting in intermediates which are finally completely oxidized into mineral products.

$$A_{ads} + HO^{\cdot} \rightarrow Intermediates + HO^{\cdot} \rightarrow Mineral\ products \qquad (3)$$

The overall stoechiometric equation of Monuron mineralization by $HO^{\cdot}$ radicals is (4), and that of Isoproturon is (5):

$$C_9H_{11}ClN_2O + 54\ HO^{\cdot} = 9\ CO_2 + 31\ H_2O + HCl + 2\ HNO_3 \qquad (4)$$

$$C_{12}H_{18}N_2O + 74\ HO^{\cdot} = 12\ CO_2 + 45\ H_2O + 2\ HNO_3 \qquad (5)$$

M-II: Fe-Lap-RD acts as a simple photochemical catalyst.

According to this mechanism, a charge transfer between A and Fe_2O_3 in Fe-Lap-RD occurs:

$$Fe_2O_3\ (\text{ in Fe-Lap-RD }) + A + h\nu \rightarrow A^{*}\ \text{on}\ Fe_2O_3\ (\text{ in Fe-Lap-RD}) \rightarrow \qquad (6)$$

$$\rightarrow A^{\cdot+} + Fe_2O_3\ (\text{ in Fe-Lap-RD}) + e^{-} \qquad (7)$$

$$A^{\cdot+} \rightarrow Intermediates \rightarrow Final\ mineral\ products \qquad (8)$$

Our results demonstrated that the mechanism M-I dominated the degradation and mineralization of the two herbicides.

Conclusions

The herbicides used as substrates in this work are very popular because of their effectiveness and selectiveness in weed control. Nevertheless, most of the substance applied (about 98%) is unused by plants and moves through soil into the groundwater. They are both persistent and biorecalcitrant pollutants. Therefore, AOPs must be applied for treatment of water containing herbicides like Monuron and/or Isoproturon.

A novel laponite RD clay-based Fe nanocomposite(Fe-Lap-RD) has been synthesized ,and characterized by XPS/ESCA technique. This Fe-Lap-RD composite consists of Fe_2O_3 and $FeSi_4O_{10}(OH)_2$ and has a high specific surface area as well as a high pore volume. The XPS spectra have shown that the surface Fe (III) was not leach- out in the acidic solution after four uses of two hours in the photo-assisted degradation of the two herbicides. This confirmed the good stability of the new catalyst.

The catalytic activity of the novel catalyst has been evaluated by the photodegradation of two herbicides (Monuron and Isoproturon) in water. The TOC conversion (mineralization degree) was higher then that with the homogeneous photo- Fenton process which needs the addition of a soluble Fe (III) salt. The TOC conversion of Isoproturon (25 ppm) with the new heterogeneous catalyst (1g/L) was 87% compared to 73% with the homogeneous photo- Fenton (by adding 1 mM $Fe^{3+)}$ in other identical conditions (298 K, *p*H 3, 10 mM H_2O_2).

Two reaction mechanisms have been proposed on the basis of the results obtained. The mechanism (M1) which considers the Fe-Lap-RD as a photo- Fenton catalyst seems to be dominant in this heterogeneous process.

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