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Photodegradation of chlortoluron sensitised by iron(III) aquacomplexes

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Abstract

The degradation of chlortoluron photoinduced by Fe(III) aquacomplexes has been investigated under continuous irradiation at 365 nm. The determined quantum yields of chlortoluron disappearance give evidence for the involvement of the most photoactive species $Fe(OH)^{2+}$, which leads to the formation of hydroxyl radicals and Fe(II); the importance of oxygen in the degradation process was also demonstrated. According to the nature of the obtained photoproducts, the attack of $^{\bullet}OH$ radicals on two sites of chlortoluron are favoured: the aromatic ring and the methyl group of the urea function. A homogenous photocatalytic process based on the oxidation of Fe(II) into Fe(III) is responsible for the continuous production of hydroxyl radicals in such a system. This photocatalytic cycle allows the total mineralisation of compounds like chlortoluron using conditions compatible with a safe aquatic environment.

Keywords: Chlortoluron; Fe(III) aquacomplexes; Phototransformation; Homogeneous photocatalysis; Mineralisation

1. Introduction

The application of herbicides on agricultural soils is a well-established and effective practice to control weed growth. Since their discovery in the early 1950s, the substituted phenyl ureas have increased into the most prominent and diversified group of herbicides. Due to their slow biodegradation process [1,2] and to the washing and leaching processes these substances pass to surface and ground waters. The pollution of surface and ground waters by herbicides and their by-products can be a real problem for the environment. The presence of different herbicides in waters was detected by Martinez et al. [3] in several water samples at levels ranging from the detection limit to $1.2\,\mu g\,l^{-1}$. The highest values were found for chlortoluron that is used in cereal cultures. Chlortoluron, a selective herbicide of the phenylurea family derivatives, is absorbed by the roots and foliage and inhibits the photosynthesis of many broad-leaved and weeds of winter cereals [4]. Chlortoluron is one of the most used herbicides in agricultural field and it presents a long lifetime: 30–40 days in the soil and more than 200 days in waters [4].

Degradation by light, reaction with hydroxyl radicals $^{\bullet}OH$ and hydrolysis are the principal processes of herbicide abiotic degradation in the environment and can provide an alternative way to biodegradation. The major abiotic reactions (excepted the hydrolysis) are connected with irradiation by sunlight. If the herbicide does not absorb solar light, its transformation can be photoinduced by different absorbing species present or added in the aquatic medium (nitrate [5], humic substances [6], Fe(III) complexes [7], . . .). The common point of these species is the formation under irradiation of highly oxidative species, mainly hydroxyl radicals $^{\bullet}OH$, which degrade many organic compounds in water with rate constants close to that of a diffusion controlled process [8]. The formation of these oxidative species has been used in different chemical processes, designated as advanced oxidation processes (AOPs), to eliminate organic compounds in aqueous solutions. Among the different AOPs, the TiO_2 photocatalysis, the photo-Fenton reaction using Fe(II), H_2O_2 and UV-Vis irradiation, the UV-Vis photolysis of ferrioxalate in the presence of hydrogen peroxide process and the Fe(III) photooxidation process in aqueous solutions are commonly used to mineralise pollutants [9–13]. This last mentioned process has been studied for 10 years in our laboratory and we have reported in previous studies the efficiency of Fe(III) aquacomplexes for the photogeneration of hydroxyl radicals [7,14–16]. Among the Fe(III) aquacomplexes, $Fe(OH)^{2+}$ (which refers to $(Fe(OH)(H_2O)_5)^{2+}$) is photolysed with the highest quantum yield according to the reaction [17,18]:

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + {}^{\bullet}OH$$

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This electron transfer process has been efficiently used to achieve the degradation of several pollutants in aqueous solution ([19] and references therein). In most cases, the total mineralisation of the pollutant was observed.

In the present paper, the chlortoluron degradation, photoinduced by Fe(III) aquacomplexes, investigated from the primary reactions to the complete mineralisation, is reported. We identified the major photoproducts and proposed the major ways of the phenylurea derivative degradation.

2. Materials and methods

2.1. Reagents and solutions

All reagents were of the purest grade commercially available and were used without further purification.

Chlortoluron (3-(3-chloro-4-methylphenyl)-1-1-dimethyl urea) was a Riedel-de-Haën product (99.7%). Ferric perchlorate nonahydrate ($Fe(ClO_4)_3{\cdot}9H_2O$; >97%) was a Fluka product kept in a dessicator. The Fe(III) solutions for the studies were prepared by diluting stock solutions (2.0×10^{-3} mol l^{-1} in $Fe(ClO_4)_3{\cdot}9H_2O$) to the appropriate Fe(III) concentration. 8-Hydroxyquinoline-5-sulfonic acid (HQSA; 98%) monohydrate and *N*,*N*-dimethyl urea (99%) were purchased from Aldrich. 2-Propanol and acetonitrile were HPLC grade products and purchased from Merck and Carlo Erba, respectively.

All solutions were prepared with de-ionised ultra-pure water ($\rho = 18.2\,M\Omega\,cm$). When necessary, the solutions were degassed at room temperature either by bubbling with Argon for 30 min in 5 ml quartz cell or by bubbling continuously with nitrogen in the reactor of irradiation (100 ml). We checked that there was no outcome of chlortoluron during the bubbling. The pH was measured with an ORION pH meter to ±0.1 pH unit (pH = 3.3 for a solution with a concentration in Fe(III) equal to 3.0×10^{-4} mol l^{-1}). The ionic strength was not controlled.

2.2. Apparatus

In order to measure the quantum yields, monochromatic irradiations at 365 nm were carried out with a high-pressure mercury lamp (Osram HBO 200 W) equipped with a grating monochromator (Bausch and Lomb). The beam was parallel and the reactor was a cylindrical quartz cell of 2 cm path length. The light intensity was measured by ferrioxalate actinometry [20]: $I_{0,365\,nm} \approx 3.0\times10^{15}$ photons s^{-1} cm^{-2}.

The apparatus for the irradiations of larger volume ($V = 100$ ml) at $\lambda_{exc.} = 365$ nm was an elliptical stainless steel container used for kinetic and analytical experiments. A high-pressure mercury lamp (Philips HPW type 125 W), whose emission at 365 nm (93%) was selected by an inner filter, was located at a focal axis of the elliptical cylinder. The reactor, a water-jacketed Pyrex tube (diameter = 2.8 cm), was centred at the other focal axis. The reaction medium was continuously stirred.

UV-Vis spectra were recorded on a CARY 3 double beam spectrophotometer.

HPLC experiments were carried out using a Waters 540 chromatograph equipped with two pumps Waters 515 and a Waters 990 photodiode array detector. The flow rate was 1 ml min^{-1} and the eluent a mixture of pure water and acetonitrile (v/v 60/40). The column was a Touzard and Matignon Kromasil C18 of 250 mm × 4.6 mm with a particle diameter of 5 μm and a pore diameter of 100 Å.

The ^1H NMR spectra were recorded on a Bruker AC 400 MHz Fourier transform spectrometer.

2.3. Analysis

The method of measuring the monomeric concentration of Fe(III) (mainly $Fe(OH)^{2+}$ in our experimental conditions) was modified from Kuenzi's procedure [21] and described in our previous papers [15,16]. The measurement is based on the formation of the complex $Fe(HQS)_3$ between HQSA and Fe(III) monomeric species which presents a maximum at 572 nm with a molar absorption coefficient equal to 5075 l mol^{-1} cm^{-1} [16].

Fe(II) concentration was determined by complexometry with *ortho*-phenanthroline, using $\varepsilon_{510} = 1.118\times10^4$ l mol^{-1} cm^{-1} for the Fe(II)–phenanthroline complex [20].

The concentrations of chlortoluron and its photoproducts were followed by HPLC analysis ($\lambda_{detection} = 241$ nm).

Total organic carbon (TOC) measurements, based on the combustion of carbon detected by infrared gas analysis method, were followed with a TOC analyser Shimadzu model TOC-5050A. The calibration curves within the range 1–15 mg l^{-1} were obtained by using potassium hydrogen phthalate and sodium hydrogen carbonate for organic and inorganic carbon, respectively.

3. Results

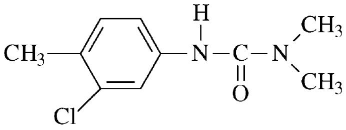
3.1. Characterisation of chlortoluron and Fe(III) in aqueous solution

Under our experimental conditions ([Fe(III)] = 3.0×10^{-4} mol l^{-1} and pH = 3.3±0.1), $Fe(OH)^{2+}$ is the predominant monomeric Fe(III) hydroxy complex [17]. However, the composition of Fe(III) solutions changed in time due to hydrolysis and oligomerisation processes. While the content of $Fe(OH)^{2+}$ in a freshly prepared solution of $Fe(ClO_4)_3$ (3.0×10^{-4} mol l^{-1}) decreased from 100 to 30% after 1 h, following first-order kinetics, the absorbance of the same solution measured at 365 nm in a 1 cm path length cell changed from 0.1 to 0.52 approximately. These changes corresponded to the formation of oligomeric forms of Fe(III) that present absorption at longer wavelengths [22]. The hydrolytic and oligomerisation processes controlled the proportion among the various Fe(III) species that differed in their photoactivities and thus influenced the rate of hydroxyl radical production [16]. By the HQSA method (see Section 2.3), we were able to determine the percentage of $Fe(OH)^{2+}$ in solution:

$$\mathrm{Fe(OH)^{2+}}\ (\%) = \frac{[\mathrm{Fe(OH)^{2+}}]}{[\mathrm{Fe(III)}]t_0} \times 100$$

$[Fe(III)]t_0$ is the starting concentration of total dissolved Fe(III). The different percentages of $Fe(OH)^{2+}$ were obtained by the use of Fe(III) solutions of different ageing.

Chlortoluron is slightly soluble in water (74 mg l^{-1} or 3.5×10^{-4} mol l^{-1} at 25 °C) [4]. A stock solution of 2.0×10^{-4} mol l^{-1} concentration was prepared under stir during 48 h.



A concentration of 1.0×10^{-4} mol l^{-1} was used all along this work. Chlortoluron is stable in aqueous solution, no degradation was observed in the dark and at room temperature after one month. The UV-Vis spectrum (Fig. 1) of chlortoluron in aqueous solution presents three maxima, at 280 nm (ε = 1150 l mol^{-1} cm^{-1}), 241 nm (ε = 15,500 l mol^{-1} cm^{-1}) and 209 nm (ε = 31,000 l mol^{-1} cm^{-1}).

A mixture of chlortoluron and Fe(III) was stable in the dark and at room temperature for a few weeks in terms of chlortoluron concentration. No complexation was observed between chlortoluron and Fe(III) in the ground state. Moreover, the classical kinetic of $Fe(OH)^{2+}$ disappearance in the dark [23] was not affected by the presence of chlortoluron. This result confirms the absence of interaction between chlortoluron and Fe(III) in aqueous solution and in the dark.

Table 1
Influence of the monomeric species concentration and oxygen concentration on the initial quantum yields of chlortoluron disappearance

	Aerated solution				Deaerated solution	
$Fe(OH)^{2+}$ (%)	93	60	30	16	65	59
Quantum yield ($\times 10^{-3}$)	2.3	0.85	0.35	0.20	0.46	0.34

3.2. Degradation of chlortoluron photoinduced by Fe(III)

Chlortoluron does not absorb at wavelengths higher than 300 nm (Fig. 1); there was no degradation when chlortoluron was irradiated alone at 365 nm or by solar light.

Irradiation of the mixture chlortoluron (1.0×10^{-4} mol l^{-1}) and Fe(III) (3.0×10^{-4} mol l^{-1}) was first carried out with about 100% of monomeric species $Fe(OH)^{2+}$ in aerated conditions and at 365 nm. The concentration of chlortoluron continuously decreased (very fast at the beginning) and the complete degradation was reached within 7 h (Fig. 2).

3.2.1. Influence of the monomeric species concentration

In this set of experiments, the percentage of $Fe(OH)^{2+}$ species was taken as 93, 60, 30 and 16%. The initial quantum yields of chlortoluron disappearance are collected in Table 1. The results show that the rate of chlortoluron disappearance is strongly affected by the $Fe(OH)^{2+}$ percentage: the higher the percentage, the faster the degradation is. This result is linked to the nature of Fe(III) hydroxo species present in solution, $Fe(OH)^{2+}$ being the most photoactive species in terms of $^{\bullet}OH$ radicals production [17,18].

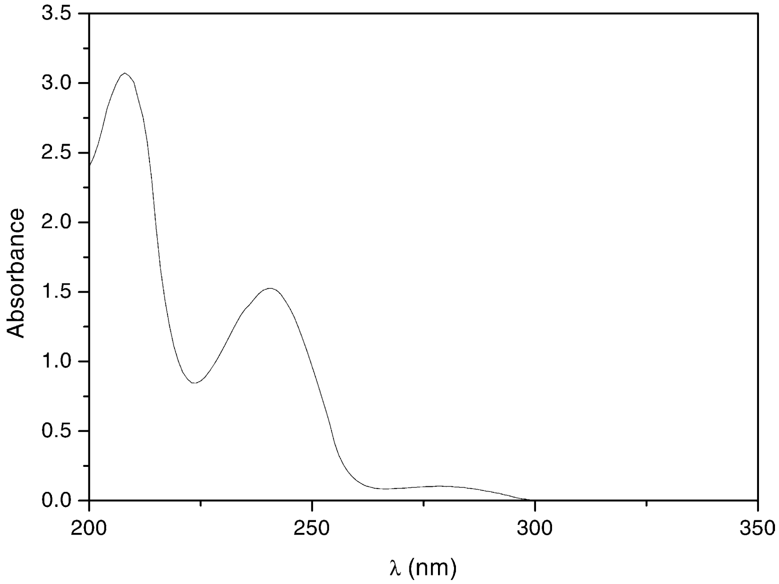


Fig. 1. UV absorption spectrum of chlortoluron (1.0×10^{-4} mol l^{-1}) (1 cm path length).

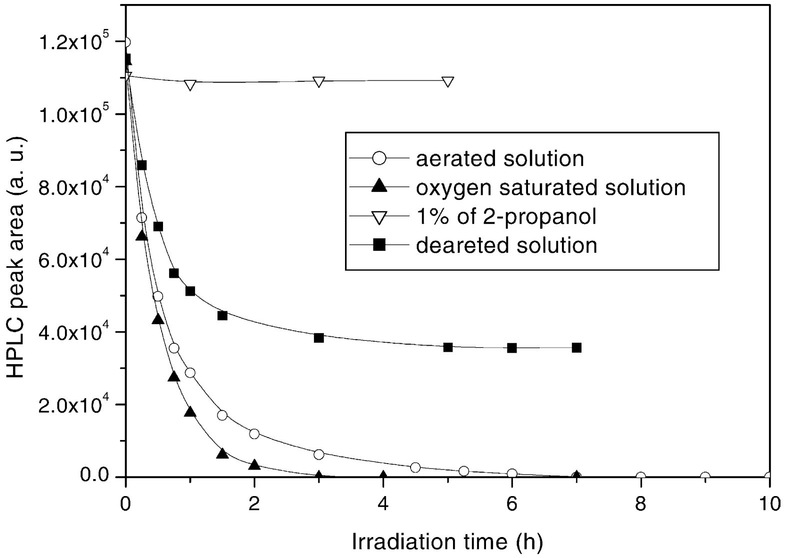


Fig. 2. Degradation of chlortoluron upon irradiation at 365 nm of Fe(III) (3.0×10^{-4} mol l^{-1}, 97% $Fe(OH)^{2+}$)/chlortoluron (1.0×10^{-4} mol l^{-1}) mixture at various oxygen concentrations and in the presence of 2-propanol.

3.2.2. *Irradiation in the presence of 2-propanol*

The degradation of chlortoluron can be directly attributed to the attack of $^{\bullet}OH$ radicals as demonstrated by the complete inhibition of the degradation during irradiation at 365 nm in the presence of 2-propanol (1% v/v), a known $^{\bullet}OH$ radical scavenger (Fig. 2): $^{\bullet}OH$ radicals are the only radical species present in the early stages upon irradiation of such solutions [16].

3.2.3. *Influence of oxygen*

The initial quantum yield of chlortoluron disappearance is approximately divided by two in the absence of oxygen (Table 1). This result was confirmed by the kinetic measurements (Fig. 2). In the absence of oxygen the degradation of chlortoluron was slower and reached a plateau value after 3 h of irradiation and its degradation stopped. On the contrary, in oxygen saturated solution, the degradation is faster and the herbicide is completely eliminated in 4 h of irradiation. These results show that oxygen plays a very important role in the degradation of chlortoluron.

3.2.4. *Formation of Fe(II)*

From the beginning of irradiation, we observed a very fast increase of Fe(II) concentration until a pseudo-constant value ($\approx 2.5 \times 10^{-4}$ mol l^{-1}) (Fig. 3). For longer irradiation times, after 5 h, the Fe(II) concentration

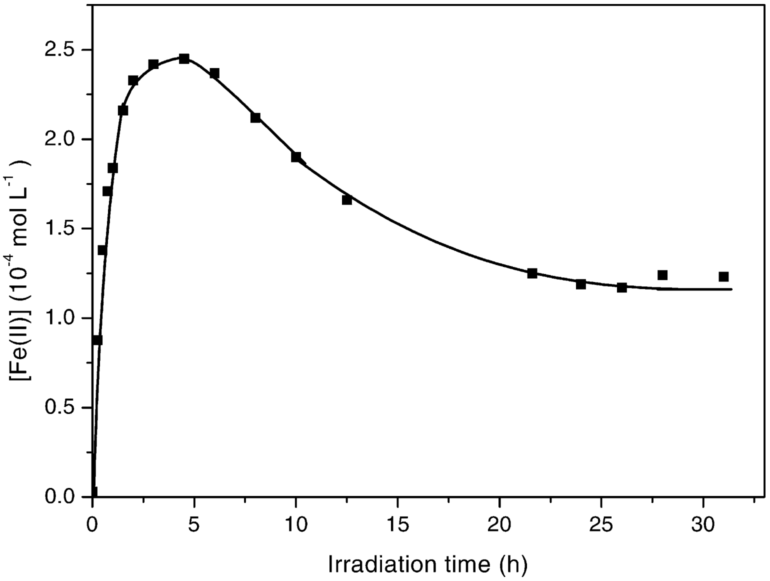


Fig. 3. Kinetic of Fe(II) concentration as a function of irradiation time (365 nm) of a mixture Fe(III) (3.0×10^{-4} mol l^{-1}, 97% $Fe(OH)^{2+}$)/chlortoluron (1.0×10^{-4} mol l^{-1}).

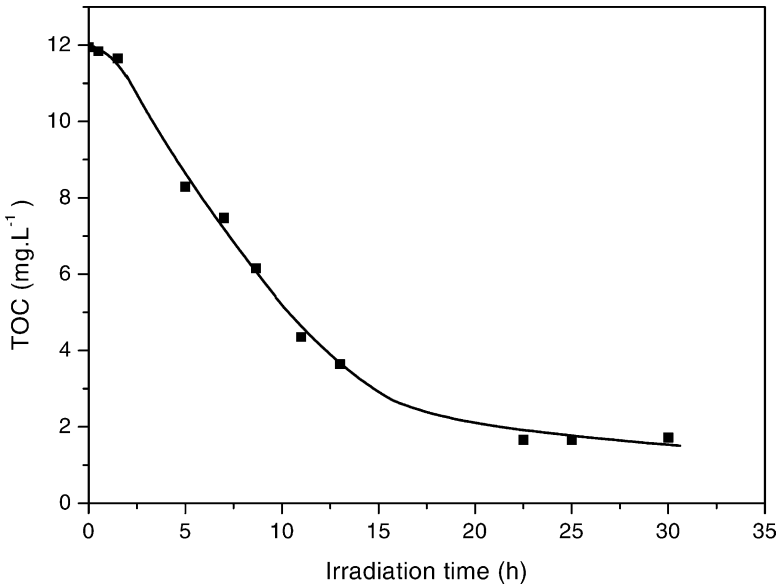


Fig. 4. Time evolution of TOC values during irradiation (365 nm) of Fe(III) (3.0×10^{-4} mol l^{-1}, 97% Fe(OH)$^{2+}$)/chlortoluron (1.0×10^{-4} mol l^{-1}) mixture.

decreased slowly and reached a new plateau value ($\approx 1.3 \times 10^{-4}$ mol l^{-1}).

3.2.5. Mineralisation

As already mentioned in the introduction, one of the aims of the present work was to test the efficiency of chlortoluron removal from the water, when the degradation is photoinduced by Fe(III). TOC experiments were undertaken in order to make evidence for the complete mineralisation of chlortoluron. As shown in Fig. 4, the total mineralisation of chlortoluron 1.0×10^{-4} mol l^{-1} (12 mg l^{-1} of organic carbon) was achieved after 25 h of irradiation. A lag period of about 2 h was observed. This is due to the formation of primary organic photoproducts at the beginning of the irradiation.

3.3. Photoproducts identification

During the irradiation of Fe(III) (3.0×10^{-4} mol l^{-1})/ chlortoluron (1.0×10^{-4} mol l^{-1}) mixture at 365 nm, different photoproducts were detected by HPLC coupled to a photodiode array detector. We noted the appearance of five main new peaks, their kinetics of formation are represented in Fig. 5 ($\lambda_{\text{detection}} = 241$ nm). One photoproduct (V) was less polar than chlortoluron which has a retention time of 11.6 min in the same elution conditions. Three photoproducts (II, IV and V) were identified by co-injection of authentic samples synthesised by organic chemists at SEESIB (Chemistry Laboratory of the Université Blaise Pascal, Clermont-Ferrand, France). The two other photoprod-

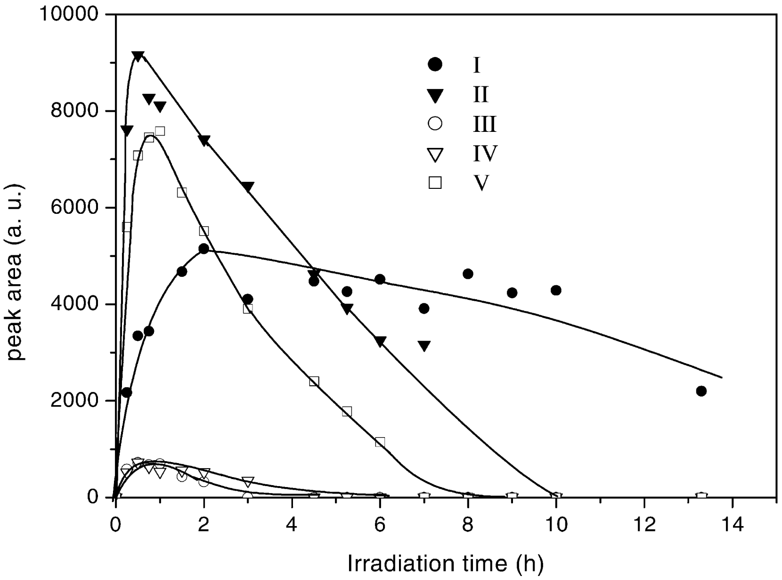
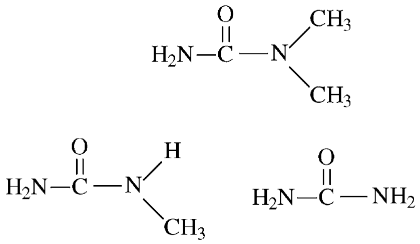
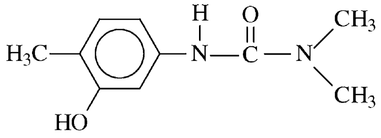
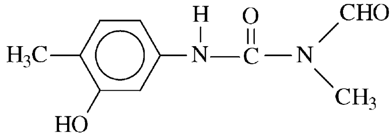
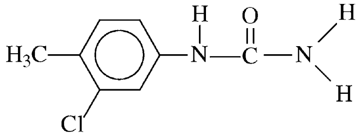
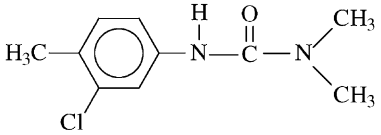
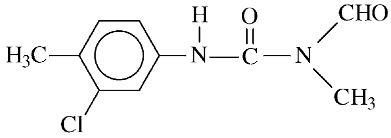


Fig. 5. Kinetics of photoproducts formation ($\lambda_{\text{detection}} = 241$ nm).

Table 2
Structure of the main photoproducts

Number	Retention time (min)	Structure
I	2.3	Urea derivatives 
II	4.2	
III	7.7	
IV	10.0	
Chlortoluron	11.6	
V	21.8	

ucts (I and III) were isolated and identified by NMR analysis. The structures of the main photoproducts are represented in Table 2. The three urea derivatives, urea, monomethylurea and dimethylurea were eluted together (I) due to their high polarity. We also identified the monodemethylated chlortoluron as a minor photoproduct.

4. Discussion

Fe(III) species are the only absorbing species when a mixture of chlortoluron and Fe(III) in aqueous solution was irradiated at 365 nm. Fe(III) in aqueous solution, under irradiation, is known to undergo a redox reaction giving rise to Fe(II) and $^{\bullet}$OH radicals. Among the Fe(III) species, $Fe(OH)^{2+}$ is the most photoreactive species in terms of $^{\bullet}$OH radical production and accordingly the most efficient one to induce chlortoluron disappearance. The experiment in the presence of isopropanol, clearly shows that the first stage of the photochemical process is the attack of $^{\bullet}$OH radical on chlortoluron.

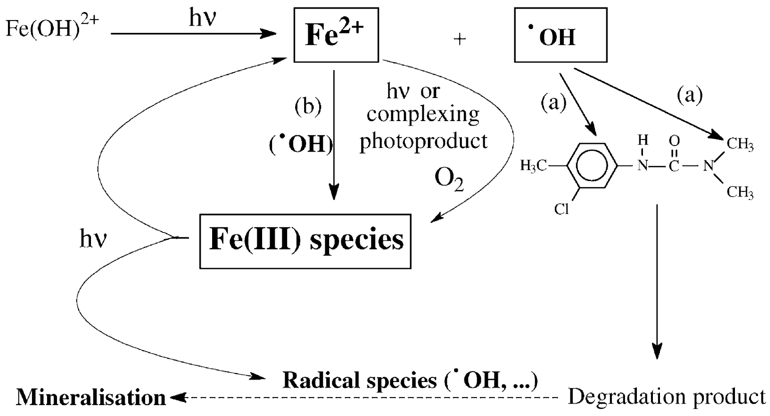
The nature of the identified photoproducts shows the presence of two main sites of attack by $^{\bullet}$OH radical: the aromatic ring and the methyl group of the urea function. This result is in agreement with the results obtained on the former studies [24,25]. For the phenylurea derivatives, we observed mainly four types of primary photoproducts corresponding to:

- the hydroxylation of the aromatic ring,
- the loss of one or two methyl group of the urea function replaced by a hydrogen atom,
- the formation of *N*-formyl derivatives,
- the formation of urea derivatives.

Oxygen appears to be a very important parameter in our process. In the absence of oxygen, the disappearance of chlortoluron is effective but with a rate divided by two and after 6 h of irradiation the degradation process is completely stopped (Fig. 2). On the other hand, in the presence of oxygen, we obtained the complete mineralisation of the chlortoluron for prolonged irradiations (20–25 h). This very interesting result, in terms of decontamination process, is obtained because of the continuous formation of radicals species, among them $^{\bullet}OH$ radicals. These radicals are formed by a photoredox process of Fe(III) species. Oxygen plays a key role in our process due to its role for the regeneration of Fe(III), which is the source of radical species responsible for the pollutant degradation, by oxidation of Fe(II).

The evolution of Fe(II) concentration which is described in Fig. 3 is a multistep phenomenon. The very fast formation at the beginning of the irradiation results from the photoredox process of $Fe(OH)^{2+}$ species. Then, the Fe(II) concentration reaches a pseudo-constant value (between 3 and 6 h of irradiation) corresponding to a photostationary equilibrium between Fe(III) and Fe(II). Afterwards, the concentration of Fe(II) decreases continuously and reaches, after 20 h of irradiation, a second plateau value ($\approx 1.2 \times 10^{-4}$ mol l^{-1}). This second constant value corresponds to the photostationary equilibrium between Fe(III) and Fe(II) in the absence of any organic compound as evidence by the irradiation of Fe(III) (3.0×10^{-4} mol l^{-1}, 97% of $Fe(OH)^{2+}$) alone in aqueous solution: the same photostationary equilibrium was reached. This result was also confirmed by the correlation, for the last stages, between Fe(II) formation and the total organic carbon concentration in solution (Fig. 4). The decrease of the carbon organic concentration is slow at the beginning of the irradiation and can be related to the accumulation of organic photoproducts. Moreover, the evolution of the toxicity measured by microtox test, as described elsewhere [25], shows a strong increase during the early stages of the degradation mainly due to the formation of the *N*-formyl derivatives (photoproducts III and V).

In agreement, with the kinetic results and according to the nature of the photoproducts, we can proposed the following scheme for the photochemical process:



There are two competitive reactions for the attack of radicals species ($^{\bullet}OH$): (a) on chlortoluron and on its photoproducts permitting the degradation and (b) on Fe(II) regenerating Fe(III), the absorbing species. The oxidation of Fe(II) into Fe(III) can also be due to other reactions like (i) the presence of oxygen and a complexing agent of Fe(III) (formed during the photochemical process or added in the medium) strongly favoured the oxidation of Fe(II), (ii) the attack of the radical species formed by a photoredox process in such Fe(III) complexes, (iii) the oxygen photoassisted Fe(II) oxidation giving rise to Fe(III) and superoxide anion [26]. We are in a presence of a homogenous photocatalytic process based on the couple Fe(III)/Fe(II) giving rise to a continuous formation of radical species and permitting the complete mineralisation of chlortoluron for prolonged irradiation (20 h).

This work gives evidence for the efficiency of chlortoluron removal from water by a process of homogeneous photocatalysis. This process can be used in a specific stage of a wastewater treatment to remove refractory pollutants or to treat effluent from industry production. Moreover, the concentrations in Fe(III) used in the process are low enough to make the treated solutions compatible with a safe environment.

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