Photochemical & Photobiological Sciences

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DOI: 10.1039/C6PP00441E

The effect of natural iron oxide and oxalic acid on the photocatalytic degradation of Isoproturon: a kinetics and analytical study

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Abstract

The photocatalytic degradation of isoproturon, a persistent toxic herbicide, was investigated in the presence ofnatural iron oxide, oxalic acid and under UV irradiation. The influence of relevant parameters as the pH, iron oxide and oxalic acid concentration has been studied.Results show that the system natural iron oxide and oxalic acid effectively allows degradation of isoproturon, whereas the presence of t-butyl alcohol adversely affects the phototransformation of the target pollutant, thus indicating an OH radical initiated degradation mechanism. The degradation mechanism of isoproturon was investigated by means of GC-MS analysis. Both oxidation of the terminal N-$(CH_3)_2$and isopropyl groups are the initial processes leading to the N-monodemethylated ($NHCH_3$), N-formyl ($N(CH_3)CHO$), and $CHCH_3OH$ as the main intermediates. The substitution of isopropyl group by OH is also observed as a side process.

Keywords: Isoproturon, Iron oxide,photocatalysis, oxalic acid, GC-MS

1.Introduction

Isoproturon (IP), 3-(4-isopropylphenyl)-1,1-dimethylurea, is a systemic non-biodegradableherbicide acting as a photosynthesis inhibitor, intensively used in agriculture for controlling annual grasses and broad-leaved weeds in cereals. Found both in surface and groundwater, IP is toxic and carcinogenic and it has

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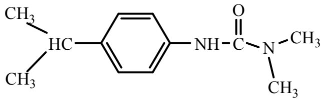
beenincluded in the European “black list” of hazardous compounds[1, 2].The structure of Isoproturon is showed in Scheme 1.



Scheme1. Structure of isoproturon

Therefore, it is important to understand the fate of this herbicide in the environment in order to assess its environmental impact.Several authors have investigated the photodegradationofisoproturon in aqueous solution[3-6].In recent decades, different strategies have been developed for removal of pollutants from water and a great deal of interest has been devoted to photocatalytic degradation of isoproturon by semiconductor compounds[7-15]. Photocatalytic treatmentofisoproturonover TiO_2/Al-MCM-41 and TiO_2/HY composite systemsusing solar light is reported to be very efficient in the destruction of the herbicide[7, 8].

Iron oxides are minerals naturally occurring in rocks, soils, hot brines, marine environments and also synthesized in various organisms[16].Among them hematite (α-Fe_2O_3)is one of the most promising materialsfor photocatalytic applications due toits widespread availability and high visible light absorbance (band gap 2.2 eV) [17], thus resulting economically advantageous for environmental remediation[18-22].

It is well known that ligands containing carboxylic groups (RCO_2^-) such us oxalic acid form complexes with Fe(III) which, under irradiation of suitable wavelength, undergo photo-induced ligand to metal charge transfer (LMCT) according to the following Equation 1[23].

$$[Fe(III)(RCO_2)]^{2+} + h\nu \rightarrow Fe^{2+} + R^{\bullet} + CO_2 \qquad (1)$$

This reaction results in the reduction of Fe(III) and the oxidation of the ligand with evolution of CO_2[24].

In the presence of dissolved oxygen, hydrogen peroxide (H_2O_2) is formed from the photodegradation of organic carboxylic acid. The Fe(II) and H_2O_2 thus produced, may react via the so-called Fenton reaction to produce hydroxyl radicals $HO^{\bullet}$, which eventually degrade the organic pollutants present in the system [25].Although the presence of oxalic acid poses criticisms due to the introduction of additional organic matter to the system, adding oxalic acid is preferred with respect to hydrogen peroxide for large scale water treatment. Indeed, problems arising from handling and storage of this highly oxidizing compound and the consequent safety issues, strongly limit its real industrial application. Recently, natural organic matter (NOM) have been proposed as substitutes of oxalic acid due to their ability to create complexes with iron ions present in solution and to undergo excitation under visible light irradiation [26, 27].

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Its use is justified by taking into account that oxalic acid is a natural compound produced by plants and that it allows degradation of organic pollutants without adding H_2O_2 to the system, thus implying cheaper and safer environmental actions.

The aim of this work was to obtain kinetic data on the photocatalytic degradation of IP in the presence of natural iron oxide and to identify the intermediates produced during its degradation. The effect of different parameters like pH, presence of t-butanol, and amount of iron oxides and oxalic acid on the photocatalytic activity has been evaluated.

2. Experimental part

2.1.Chemicals

Solutions were prepared starting from deionized water obtained by means of a Millipore device (Milli-Q). IPanalytical grade (>99.9% pure) was purchased from Riedel-de Haën, $HClO_4$ (70%)from Merck and Oxalic acid (99.5%) from Prolabo. The pH of solutions was measured using an Orion pH-meter with a combined electrode. HPLC grade acetonitrile was purchased from Carlo Erba. Chemicals were used without further purifications.The used NIO used in this study was collected from iron deposits located in North-East Algeria. This catalyst have been fully characterized in the relevant literature [20,21], is mostly composed of hematite, its specific surface area is 79.015 m^2g^{-1}, and the total pore volume is 0.0892 cm^3g^{-1}.

2.2. Photochemicalreactor

The runs were carried out in a 50 mL Pyrex glass reactor, cylindrical in shape (2 cm i.d.). The reacting mixture was perfectly mixed by means of a magnetic stirrer. Irradiation was externally performed with a HPW black light 125 W Philips lamp with a maximum emission at 365 nm. Temperature was kept constant (at ca. 25 °C) by using tap-water circulating through a thimble around the reactor. The initial IP concentration and the natural iron oxide load were 0.1 mM and 1 g L^{-1}, respectively. Samples (1 mL) were taken at regular intervals during irradiation and filtered through 0.45 µm syringe filters (Millipore).

2.3.Analyses

IP concentration during the runs was determined by using a Shimadzu HPLC equipped with an UVdetector set at 240 nm and a C_{18}reverse phase column Supelcosil^{TM} LC-18 (250×4.6mm). The mobile phase was a mixture acetonitrile/water (1:1 v/v) circulating at a flow rate of 1 $mLmin^{-1}$.

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After irradiation,the reacting suspension was acidified with HCl (pH ≤ 2), extracted with diethyl ether, concentrated under highly pure nitrogen and finally dried with anhydrous Na_2SO_4. This residue was analyzed by means of a QP2010 Shimadzu GC-MS instrument equipped with a capillary Varian WCOT fused silica column CP-SE30 (25 m x 0.25 mmx 0.25 µm), a trace GC 2010 gas chromatograph and a GCQ plus ion trap mass spectrometer. Identification of the transformation products was carried out under the following chromatographic conditions: the injector temperature was 250 °C (1µL manual split injection); the oven temperature was kept at 70°C for 4 min, then increased at 7°C min^{-1}until 280°C and was finally maintained for 5 min; Helium was used as the carrier gas at 0.76 mL min^{-1}. The MS operated in electron ionization mode with a potential of 70 eV.

3. Results and Discussion

3.1. Photodegradation of isoproturon under different reaction conditions

The characterization of natural iron oxide (NIO) used in this study has beenelsewhere reported[20, 21]. Prior to irradiation, suspensions were stirred in the dark during 1 hour to establish adsorption/desorption equilibrium. IP concentration decreased of 0.15% in the dark showing negligible adsorption on the surface of iron oxide.UV light irradiation of homogeneous IP solutions, in the absence of iron oxide and oxalic acid, did not produce IP degradation. In the presence of iron oxide but without oxalic acid, only 4% of the initial IP was degraded after 60min irradiation. In the presence of 1.0mM oxalic acid and 1 g L^{-1}iron oxide under UV irradiation (Fig.1) the IP removal significantly increased reaching 77% after 120 min. These results show the synergistic effect produced in the presence of both iron oxide and oxalic acid. The degradation of IP in the iron oxide-oxalic acid system can be described by a first-order kinetic which may be expressed by the following Equation 2.

$$\ln(C/C_0) = -kt \qquad (2)$$

Where C and C_0represent the IP concentrations at irradiation time t and t=0, respectively, and k is the apparent first order rate constant of the degradation reaction. The value of the apparent rate constant obtained by linear fit is $k = 1.2 \times 10^{-2}\ min^{-1}$ ($R^2 = 0.94$).

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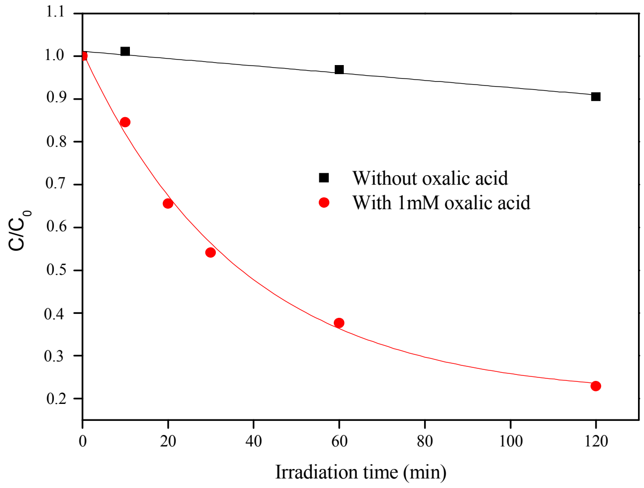

Fig.1. Photocatalytic degradation of IP (initial concentration: 0.1 mM) in the presence of NIO (1 g/L) with (red circles) and without (black squares) oxalic acid (1mM) under UV light irradiation.

3.1.1. Effect of iron oxide concentration

The influence of the amount of NIO in the system was studied by using 0.5, 1 and 2 g L^{-1}of iron oxide, being the same the concentration of oxalic acid (1.0 mM) and IP (0.1 mM). Results are shown in Figure 2. The highest reaction rate was obtained in the presence of 1g L^{-1} NIO so that further experiments were carried out in these conditions. Indeed, the reaction rate increases with increasing NIO concentration until the UV light penetration through the suspension becomes the limiting step inducing a decrease of the photocatalytic activity [9, 20].

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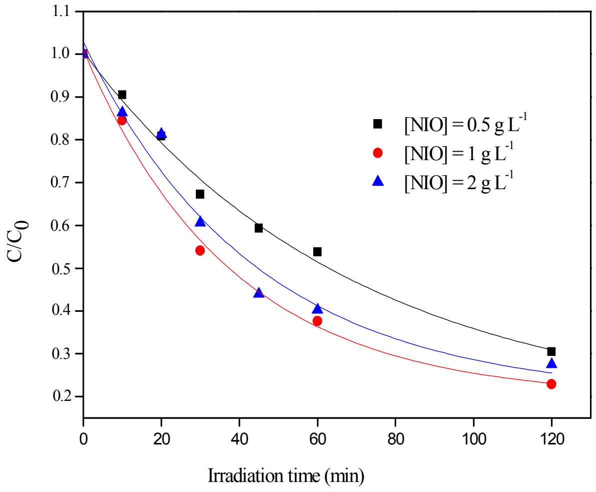

Fig. 2. Influence of different amounts of NIO (0.5 g L^{-1} black squares, 1 g L^{-1} red circles, 2 g L^{-1} blue triangles) on the IP degradation in the presence of 0.1 mM IP and 1.0 mM oxalic acid under UV light irradiation.

3.1.2. Effect of Oxalic Acid Concentration

The dosage of oxalic acid is one of the most important parameters to be considered to determine the optimum operative conditions in this kind of systems. Indeed, it is significant to determine the optimum dosage in order to minimize costs and sludge formation, by maximizing at the same time the photodegradation performances.Fig.3 shows the dependence of IP photodegradation on the initial concentration of oxalic acid ranging from 0 to 10 mM.Fig. 4 reports the apparent first order rate constants obtained for tests carried out at different oxalic acid concentrations. Theamount of oxalic acid concentration affording the highest isoproturon degradation rate, in the presence of 1 g L^{-1} of NIO, was 0.1 mM.Insufficient or overdosing oxalic acid resulted in poor photodegradation efficiencies. The role of oxalic acid in enhancing the photocatalytic degradation rate in the presence of iron oxide particles has been deeply studied in literature[28, 29]. Oxalic acid is first adsorbed on the surface of iron oxide to form iron oxide-oxalate complexes as $[\equiv Fe^{III}(C_2O_4)_n]^{3-2n}$ (Eq. 3). These species are photoactive so that, under irradiation of suitable wavelength, electron transfer processes may give rise to a series of radicals including oxalate radical $(C_2O_4)^{\bullet-}$, carbon-centered radical $(CO_2)^{\bullet-}$ and superoxide ion radical $(O_2^{\bullet-})$ (Eqs. 4-7). These highly oxidizing species initiate the photodegradation process. Furthermore, superoxide radical anions are able to reduce Fe^{3+} to Fe^{2+}ions. In

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acidic solution these latter react with $O_2^{\bullet -}$ to form H_2O_2 and Fe^{3+} as described by Eq. 9.The amount of H_2O_2 generated was estimated to be ca. $2\cdot 10^{-4}$ M in the presence of 1 mM oxalic acid, by means of a colorimetric method reported in the relevant literature [30]. This value is in agreement with that reported by[21] for the degradation of 1-naphtol. Finally, Fenton (Eq. 10) and photo-Fenton processes (Eq. 11) may simultaneously occur thus increasing the degradation rate by means of hydroxyl radicals thereby generated.

$$\text{Iron oxide} + \mathrm{nH_2C_2O_4} \rightarrow \equiv \mathrm{Fe[C_2O_4)_n]^{(2n-3)-}} \qquad (3)$$

$$\equiv \mathrm{Fe[C_2O_4)_n]^{(2n-3)-}} + \mathrm{h\nu} \rightarrow Fe(C_2O_4)_2^{2-} / \equiv Fe(C_2O_4)_2^{2-} + C_2O_4^{\cdot -} \qquad (4)$$

$$Fe^{III}[\mathrm{C_2O_4)_n}]^{3-2n} + \mathrm{h\nu} \rightarrow Fe^{II}[\mathrm{C_2O_4)_{(n-1)}}]^{4-2n} + C_2O_4^{\cdot -} \qquad (5)$$

$$C_2O_4^{\cdot -} \rightarrow CO_2 + CO_2^{\cdot -} \qquad (6)$$

$$CO_2^{\cdot -} + O_2 \rightarrow CO_2 + O_2^{\cdot -} \qquad (7)$$

$$O_2^{\cdot -} + Fe^{3+} \rightarrow Fe^{2+} + O_2 \qquad (8)$$

$$O_2^{\cdot -} + nH^+Fe^{2+} \rightarrow Fe^{3+} + H_2O_2 \qquad (9)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \mathrm{OH^-} + \mathrm{HO\cdot} \qquad (10)$$

$$\mathrm{Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + OH\cdot + H^+} \qquad (11)$$

On the other hand, an excessive oxalicacid concentration showed a negativeeffect on the photodegradation of IP. This maybedue to the competitivereaction of oxalate ionswithhydroxylradicals (Eq.12)which become relevant at higher oxalic acid concentrations [31].

$$\mathrm{{}^{\bullet}OH + HC_2O_4^{-} \longrightarrow CO_2 + O_2^{\bullet -} + H_2O} \qquad (12)$$

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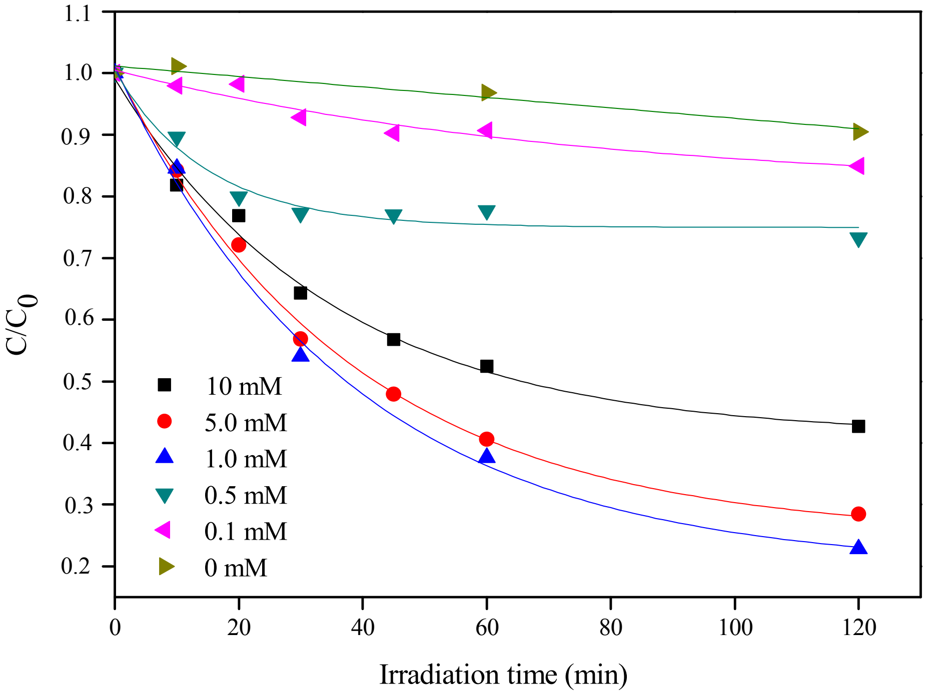

Fig. 3. Influence of oxalic acid concentration on the photocatalytic degradation ofisoproturon ([IP] = 0.1mM, [NIO] = 1g L^{-1})

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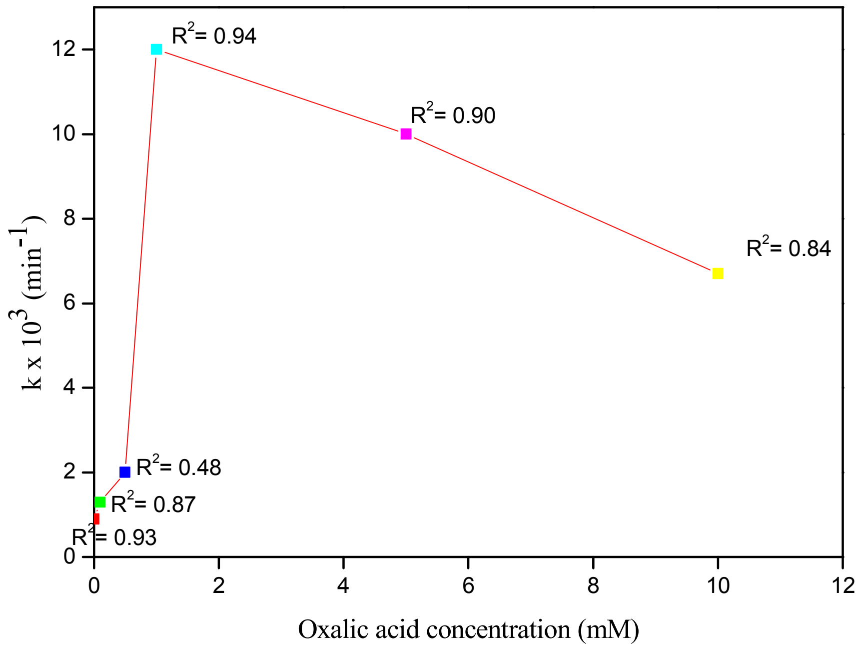

Fig. 4. Dependence of the first-order rate constant (k) of IP photodegradation on the initial concentration of oxalic acid.R^2 is the correlation coefficient of fitting.

3.1.3. Effect of t-butanol additions

T-Butyl alcohol (t-BuOH) was added to the reaction system as its OH scavenging ability is well established in literature [20]. The effect of thescavenger on the photocatalytic degradation of isoproturon is shown in Fig.5. It is evident that the addition of t-BuOHalmost completely stopsthe photocatalytic degradation of IP.This result suggests that hydroxyl radicals generated through the Fenton processes are the main oxidizing agents for the degradation of isoproturon.

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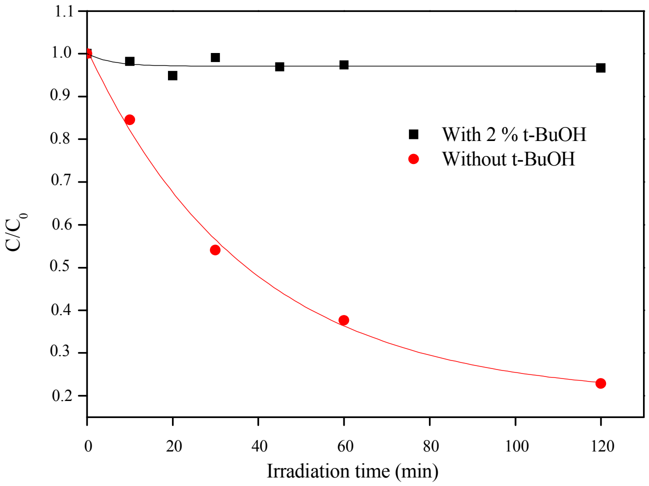

Fig.5. Influence of t-BuOHon the UV light induced photodegradation of IP (0.1 mM) in the presence of NIO (1g L^{-1}) and oxalic acid 1mM. Black squares and red circlesindicate the normalized isoproturon concentration in the presence and in the absence of 2% t-BuOH, respectively.

3.1.4. Effect of pH

The effect of pH is of paramount importance for Fenton and Photo-Fenton like processes[25, 32]. A set of experimental runs was carried out in the presence of IP (C=0.1 mM), NIO (1 g L^{-1}) and oxalic acid (1 mM) and by adjusting the initial pH of the suspension by means of $HClO_4$. Fig. 6 shows the photodegradation of IP at pH 2, 3, 4 and 5 being the same the other experimental conditions. Fitting the experimental data by means of the above mentionedfirst order model, allowed to retrieve the pseudofirst order rate constants k associated to each pH value (see Table 1). Results show that the IP photodegradation rate increased going from pH 2 to 3 and then decreased at higher pH values. This is in agreement with the pH dependence of the photodegradation of oxalate ions in similar systems according to the relevant literature [32].

Indeed, the main species present in the system at pH 3 are $[Fe^{III}(C_2O_4)_2]^-$ and $[Fe^{III}(C_2O_4)_3]^{3-}$, which possess high photoactivity[25].In our study, the $[Fe^{III}(C_2O_4)_2]^-$ and $[Fe^{III}(C_2O_4)_3]^{3-}$species might exist in a higher concentration in the solution and on thesurface $[\equiv Fe^{III}(C_2O_4)_2]^-$ and $[\equiv Fe^{III}(C_2O_4)_3]^{3-}$. On the other hand, the

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Fe^{III}–oxalate species mainly present at pH 4 or 5 is $[\equiv Fe^{III}(C_2O_4)]^+$ and$Fe^{III}(C_2O_4)]^+$, which is lessphotoactive[33].

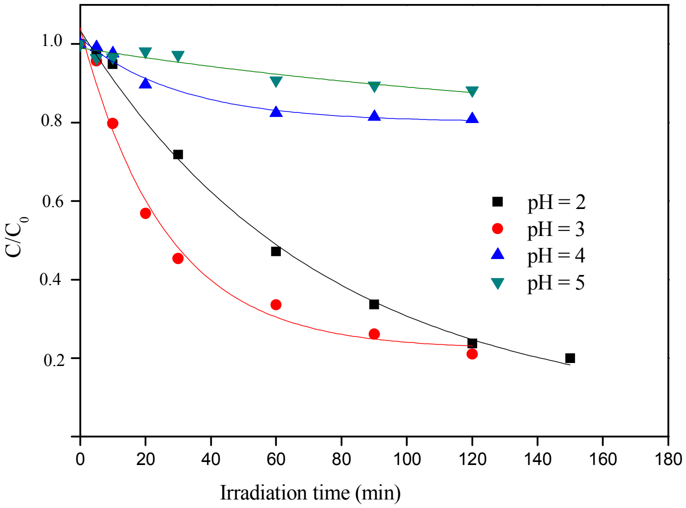

Fig.6. Photodegradation runs of IP (C_0 = 0.1 mM) in the presence of NIO (1 g L^{-1})and oxalic acid (1 mM), under UV irradiation at different initial pH values.

Table 1: The pseudo first-order kinetic constant (k), correlation coefficient (R^2) and removal percentage for photodegradation of IP (0.1mM) with NIO (1g L^{-1}) and oxalic acid (1 mM)at different pH values after 1h irradiation.

pH	k x 10^{-2} min^{-1}	R^2	Removal percentage after 1h
2	1.24	0.99	53
3	1.30	0.91	66
4	0.17	0.96	18
5	0.10	0.87	10

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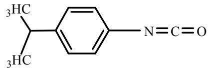
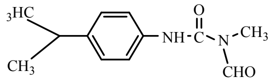
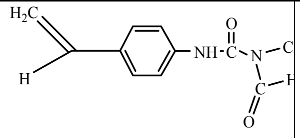
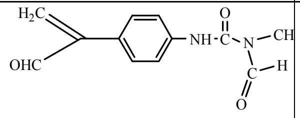
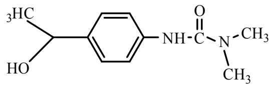
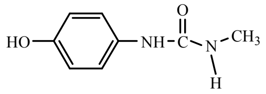
3.2. Identification of some reaction intermediates

The plausible mechanism of the photocatalytic degradation of IP was studied by performing the reaction under the aforementioned optimum experimental conditions (concentration of IP and oxalic acid 0.1 mM and 1 mM, respectively, amount of natural iron oxide 1g L^{-1}, 1h irradiation) and by extracting the products as described in the experimental part. Among the several by-products detected by means of HPLC analysis, six could be identified by using GC–MS. Some of the identified compounds have been also previously reported as intermediates of different oxidation processes of IP [11, 34].The IUPAC names, structures, retention times, the m/z ratios,and the relative amountof the main fragments are listed in Table 2.

Table 2: GC-MS retention times (Rt; min), structure, relative amount, and spectral characteristics of IP major photoproducts

NO.	Name Herbicide-photoproducts	structure	Mol. wt.	R_t (min)	*m*/*z* ratios of main mass (MS) fragments	Relative amount (%)
P1	4-isopropylphenylisocyanate		161	9.0	161,146, 128, 118, 41	1.20
P2	1-formyl-3-(4-isopropylphenyl)-1-methylurea		220	14.7	220, 205, 189, 177, 145	12.81
P3	1-formyl-1-methyl-3-(4-vinylphenyl)urea		204	21.1	204, 188, 158, 132, 105	1.14
P4	1-formyl-1-methyl-3-(4-(1-oxopropan-2-en-2-yl)phenyl)urea		232	21.4	230, 215, 185, 132, 55	3.52
P5	3-(4-(1-hydroxyethyl)phenyl)-1,1-dimethylurea		208	23.6	207, 149, 123, 71, 44	3.92
P6	1-(4-hydroxyphenyl)-3-methylurea		166	28.6	167, 149, 108, 57	54.18

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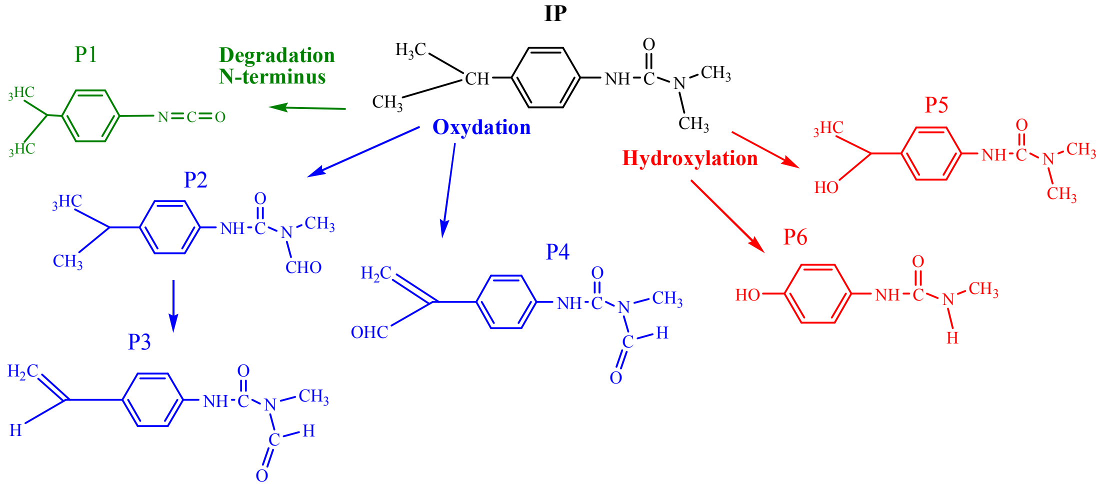
The degradation of IP mainly proceeds through oxidation or through elimination of the side chains groups. 4-isopropylphenylisocyanate (P1) may be obtained through theelimination of the terminal amine group –$N(CH_3)_2$ followed by the loss of an H atom to yield the isocyanate. This intermediate has been identified during the photodegradation of the herbicide monuron by means of advanced oxidation process and in the presence of nitrate ions[35, 36]. The intermediates P2 and P4 may be obtained by oxidation of urea chain and also isopropyl group for P2. These products have been identified in the degradation of the herbicide diuron[37].P3 was obtained firstly by the attack of OH radicals on the dimethylamine group, this assignment could also be confirmed by the fragment at 188 which can be ascribed to the loss to oxygen atom and secondly by loss of the -CH_3 in the isopropyl group. Compounds P5 may be obtained through OH radical attack of the isopropyl group and P6of the aromatic ring after elimination of the isopropyl group, respectively.On the basis of the above reported results the following IP degradation mechanism can be hypothesized (Scheme 2).



Scheme2. Proposed photodegradation pathway of isoproturon.

4. Conclusions

The photodegradation of isoproturon has been successfully carried out in the presence of natural iron oxide, oxalic acid and under UV light irradiation. The best oxalic acid concentration was 0.1 mM in the presence of 1 g L^{-1} of natural iron oxide. The highest degradation rate was obtained at pH 3. The degradation of isoproturon can be described by a pseudo-first-order kinetics. Experiments in the presence of t-butyl alcohol suggest that the photodegradation of isoproturon in the present experimental conditions proceed

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through OH radicals' oxidation. Mass spectrometry analysis allowed identifying six of the reaction intermediates. These results suggest that natural iron oxide can be used as an inexpensive and efficient photocatalyst for water and environmental detoxification.

Acknowledgments

The authors wish to thank the Algerian Ministry of Higher Education and Scientific Research.

References:

[1] S. von Wirén-Lehr, M. del Pilar Castillo, L. Torstensson, I. Scheunert, 2001. Degradation of isoproturon in biobeds, Biology and Fertility of Soils. 33, 535-540.

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

[3] H. Allemane, M. Prados-Ramirez, J. P. Croue, B. Legube, 1995. Recherche et identification des premiers sous-produits d'oxydation de l'isoproturon par le système ozone/peroxyde d'hydrogène, Revue des sciences de l'eau/Journal of Water Science.8, 315-331.

[4] B. M. Magdalena, S. Ilie, L. Elsa. Photodegradation of Isoproturon in Water by Several Adavanced Oxidation Processes, Chem bull. 50, 1-2.

[5] S. Sanches, M. T. B. Crespo, V. J. Pereira, 2010. Drinking water treatment of priority pesticides using low pressure UV photolysis and advanced oxidation processes, Water Research. 44, 1809-1818.

[6] Y. C. Lu, S. Zhang, H. Yang, 2015. Acceleration of the herbicide isoproturon degradation in wheat by glycosyltransferases and salicylic acid, Journal of hazardous materials. 283, 806-814.

[7] M. P. Sharma, V. D. Kumari, M. Subrahmanyam, 2008. Photocatalytic degradation of isoproturon herbicide over TiO_2/Al-MCM-41 composite systems using solar light, Chemosphere. 72, 644-651.

[8] M. V. Phanikrishna Sharma, K. Lalitha, V. Durgakumari, M. Subrahmanyam, 2008. Solar photocatalytic mineralization of isoproturon over TiO_2/HY composite systems, Solar energy materials and solar cells. 92, 332-342.

[9] S. Malato, P. Fernández-Ibáñez, M. I. Maldonado, J. Blanco, W. Gernjak, 2009. Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, Catalysis Today. 147, 1-59.

[10] S. Thomas, A. Alatrache, M.-N. Pons, O. Zahraa, 2014. Degradation of the herbicide isoproturon by a photocatalytic process, Comptes Rendus Chimie. 17, 824-831.

[11] M. Lopez-Munoz, A. Revilla, J. Aguado, 2013. Heterogeneous photocatalytic degradation of isoproturon in aqueous solution: Experimental design and intermediate products analysis, Catalysis today.209, 99-107.

View Article Online
DOI: 10.1039/C6PP00441E

[12] R. Xie, L. Zhang, H. Xu, Y. Zhong, X. Sui, Z. Mao, 2015. Fabrication of Z-scheme photocatalyst Ag–AgBr@ Bi_{20} TiO_{32} and its visible-light photocatalytic activity for the degradation of isoproturon herbicide, Journal of Molecular Catalysis A: Chemical. 406, 194-203.

[13] P. García-Muñoz, J. Carbajo, M. Faraldos, A. Bahamonde, 2014. Photocatalytic degradation of phenol and isoproturon: effect of adding an activated carbon to titania catalyst, Journal of Photochemistry and Photobiology A: Chemistry. 287, 8-18.

[14] A. Verma, N. Prakash, A. Toor, 2014. An efficient TiO_2 coated immobilized system for the degradation studies of herbicide isoproturon: Durability studies, Chemosphere.109, 7-13.

[15] A. K. R. Police, S. Basavaraju, D. K. Valluri, S. Machiraju, 2013. Bismuth modified porous silica preparation, characterization and photocatalytic activity evaluation for degradation of isoproturon, Journal of Materials Science & Technology. 29, 639-646.

[16] H. Gupta B. Gupta, 2015. Photocatalytic degradation of polycyclic aromatic hydrocarbon benzo [a] pyrene by iron oxides and identification of degradation products, Chemosphere.138, 924-931.

[17] V. M. da Silva Rocha, M. de Godoi Pereira, L. R. Teles, M. O. da Guarda Souza, 2014. Effect of copper on the photocatalytic activity of semiconductor-based titanium dioxide (anatase) and hematite (α-Fe_2O_3), Materials Science and Engineering: B. 185, 13-20.

[18] M. Mahadik, S. Shinde, V. Mohite, S. Kumbhar, K. Rajpure, A. Moholkar, *et al.*, 2013. Photoelectrocatalytic oxidation of Rhodamine B with sprayed α-Fe_2O_3 photocatalyst, Materials express.3, 247-255.

[19] C. Liu, F. Li, X. Li, G. Zhang, Y. Kuang, 2006. The effect of iron oxides and oxalate on the photodegradation of 2-mercaptobenzothiazole, Journal of Molecular Catalysis A: Chemical. 252, 40-48.

[20] S. Belaidi, T. Sehili, L. Mammeri, K. Djebbar, 2012. Photodegradation kinetics of 2, 6-dimetylphenol by natural iron oxide and oxalate in aqueous solution, Journal of Photochemistry and Photobiology A: Chemistry. 237, 31-37.

[21] L. Mammeri, T. Sehili, S. Belaidi, K. Djebbar, 2015. Heterogeneous photodegradation of 1-naphthol with natural iron oxide in water: influence of oxalic acid, Desalination and water treatment. 54, 2324-2333.

[22] J. Dhal, B. Mishra, G. Hota, 2015. Ferrous oxalate, maghemite and hematite nanorods as efficient adsorbents for decontamination of Congo red dye from aqueous system, International Journal of Environmental Science and Technology. 12, 1845-1856.

[23] C. Weller, S. Horn, H. Herrmann, 2013. Photolysis of Fe (III) carboxylato complexes: Fe (II) quantum yields and reaction mechanisms, Journal of Photochemistry and Photobiology A: Chemistry. 268, 24-36.

[24] V. Balzani V. Carassiti, 1970. Photochemistry of Coordination Compounds, Academic Press, London. chapter 10, 145-192.

[25] M. E. Balmer B. Sulzberger, 1999. Atrazine degradation in irradiated iron/oxalate systems: effects of pH and oxalate, Environmental Science & Technology. 33, 2418-2424.

View Article Online
DOI: 10.1039/C6PP00441E

[26] T. Weber, T. Allard, E. Tipping, M. F. Benedetti, 2006. Modeling iron binding to organic matter, Environmental science & technology. 40, 7488-7493.

[27] H. Gao R. G. Zepp, 1998. Factors influencing photoreactions of dissolved organic matter in a coastal river of the southeastern United States, Environmental Science & Technology. 32, 2940-2946.

[28] B. C. Faust R. G. Zepp, 1993. Photochemistry of aqueous iron (III)-polycarboxylate complexes: roles in the chemistry of atmospheric and surface waters, Environmental Science & Technology. 27, 2517-2522.

[29] C. Siffert B. Sulzberger, 1991. Light-induced dissolution of hematite in the presence of oxalate. A case study, Langmuir. 7, 1627-1634.

[30] V. Amin N. Olson, 1967. Spectrophotometric Determination of Hydrogen Peroxide in Milk1, Journal of Dairy Science. 50, 461-464.

[31] B. Sulzberger H. Laubscher, 1995. Reactivity of various types of iron (III)(hydr) oxides towards light-induced dissolution, Marine Chemistry. 50, 103-115.

[32] Q. Lan, H. Liu, F.-b. Li, F. Zeng, C.-s. Liu, 2011. Effect of pH on pentachlorophenol degradation in irradiated iron/oxalate systems, Chemical engineering journal. 168, 1209-1216.

[33] F. Li, X. Li, X. Li, T. Liu, J. Dong, 2007. Heterogeneous photodegradation of bisphenol A with iron oxides and oxalate in aqueous solution, Journal of colloid and interface science.311, 481-490.

[34] J. Fenoll, P. Sabater, G. Navarro, G. Pérez-Lucas, S. Navarro, 2013. Photocatalytic transformation of sixteen substituted phenylurea herbicides in aqueous semiconductor suspensions: intermediates and degradation pathways, Journal of hazardous materials. 244, 370-379.

[35] H. Boucheloukh, T. Sehili, N. Kouachi, K. Djebbar, 2012. Kinetic and analytical study of the photo-induced degradation of monuron by nitrates and nitrites under irradiation or in the dark, Photochemical & Photobiological Sciences. 11, 1339-1345.

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

[37] M. Shankar, S. Nélieu, L. Kerhoas, J. Einhorn, 2007. Photo-induced degradation of diuron in aqueous solution by nitrites and nitrates: kinetics and pathways, Chemosphere. 66, 767-774.