

# PHOTODEGRADATION OF 3-(3,4- DICHLOROPHENYL)-1,1-DIMETHYLUREA IN PRESENCE OF NATURAL IRON OXIDE UNDER UV IRRADIATION

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## Abstract

Heterogeneous photodegradation of Linuron under UV irradiation was investigated. Natural iron oxide (NIO) was used in this study, to take a closer look at its adsorption capacity in the dark. The results obtained showed that the substrate photolysis is very slowly in artificial light ( $\lambda = 365\text{nm}$ ). However, the introduction of oxalic acid (Ox) in the system improves the degradation process greatly. The dependence of Linuron degradation was attributed to the formation of the dissolved Fe-Ox in the solution and the adsorbed Fe-Ox on the surface of natural iron oxide. The effect of different parameters such as the oxalate concentration, pH and initial concentration of NIO on the photodegradation were studied in the iron oxide/ oxalate system. The results demonstrated that the optimal pH should be in the range of 2–3. The system efficiency is directly proportional to the concentration of polycarboxylate ions. The optimum mass of NIO used a good inducing disappearance of linuron was  $1\text{g.L}^{-1}$ . Furthermore, changes in the concentrations of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions in the photo-reaction were also strongly dependent on the initial oxalate and iron oxide concentration. The use of 2% of isopropanol as a scavenger confirmed the intervention of hydroxyl radicals in the photodegradation of linuron.

**Keywords:** Photodegradation, Natural iron oxide, Linuron, Oxalic acid, Hydroxyl radicals.

## Résumé

Nous nous sommes intéressés à l'étude de la photodégradation en milieu hétérogène du Linuron sous irradiation UV. Un oxyde de fer naturel a été utilisé, sa capacité d'adsorption a été étudiée dans l'obscurité. Les résultats obtenus ont montré que le substrat est peu photolysable en lumière artificielle ( $\lambda = 365\text{nm}$ ). En revanche, l'introduction de l'acide oxalique dans le système améliore d'une manière considérable le processus de dégradation. La dégradation du linuron dans ce système est due à la formation de complexe Fer-oxalate dissous dans la solution et adsorbé à la surface de l'oxyde de fer naturel. L'effet de différents paramètres tel que la concentration en oxalate, le pH et la concentration initiale en oxyde de fer sur la photodégradation du substrat ont été étudiés dans le système oxyde de fer/ oxalate. Les résultats ont montré une meilleure disparition de linuron pour une gamme de pH située entre 2 et 3. L'efficacité du système est directement proportionnelle à la concentration en ions polycarboxylate. La masse optimale d'oxyde de fer utilisée induisant une bonne disparition du linuron est de  $1\text{g/L}$ . En outre, les variations des concentrations en ions  $\text{Fe}^{3+}$  et  $\text{Fe}^{2+}$  au cours de la photo-réaction dépendent de la concentration initiale d'oxalate et d'oxyde de fer. L'utilisation de 2 % d'isopropanol en tant que piège a montré que le processus de photodégradation du linuron emprunte majoritairement la voie de dégradation par les radicaux hydroxyles.

**Mots-clés:** Photodégradation, oxyde de fer naturel, Linuron, Oxalate, Radical Hydroxyle.

## ملخص

قمنا بدراسة التحلل الضوئي لمبيد الحشائش (لينورون) في وسط غير متجانس تحت الأشعة فوق البنفسجية. درسنا سعة امتزازه في الظلام. أظهرت النتائج المتحصل عليها أن نسبة التحلل منخفضة عند ( $\lambda = 365\text{nm}$ ). لكن مع إدخال حمض الأكساليك، فإن نظام التحليل يحسن بطريقة كبيرة. ويرجع تحلل اللينورون في هذا النظام إلى تكوين أكسالات الحديد الذائبة في المحلول و المتواجدة على سطح أكسيد الحديد الطبيعية. وقد تم دراسة تأثير العوامل المختلفة مثل تركيز الأكسالات، ودرجة الحموضة وتركيز أكسيد الحديد على التحلل الضوئي في النظام أكسيد الحديد / أكسالات. أظهرت النتائج أن أفضل مردود وجد في درجة حموضة ما بين 2 و 3. تتناسب الفعالية تناسباً طردياً مع تركيز أيونات المتعدد الكربوكسيل. الكتلة الأمثل لأكسيد الحديد المستخدمة المؤدية إلى انقراض جيد للينورون هو  $1\text{g/L}$ . بالإضافة إلى ذلك، الاختلافات في تركيزات الأيونات  $\text{Fe}^{3+}$  و  $\text{Fe}^{2+}$  في التفاعل تعتمد على تركيز الأكسالات و أكسيد الحديد. أظهر استخدام 2 % من الأيزوبروبانول كمثبت لجذور الهيدروكسيل أن عملية التحلل الضوئي لمبيد الحشائش (لينورون) في الغالب تتم بواسطة هذه الأخيرة

**كلمات البحث:** التحلل الضوئي، أكسيد الحديد الطبيعي، لينورون، حمض الأكساليك، الهيدروكسيل

## I- INTRODUCTION

Carboxylic acids have received considerable attention as one of the most common dissolved organic compounds in natural environments [1],[2]. They were also considered to be one of the dominant classes of organic compounds found in the atmosphere in a variety of phases [3] [4]. Among the family of polycarboxylic acids, oxalic acid is one of the most active members. Oxalic acid, mainly secreted by plant roots [5] or formed by incomplete combustion of hydrocarbons [6] [7], is ubiquitous in soil, water and atmosphere.

Iron oxides are natural minerals and geocatalysts widely in the earth's crust and also suspended in aqueous streams, aerosols, clouds and mist of fine particles [8]. Major iron oxides include goethite ( $\alpha$ -FeOOH), hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), lepidocrocite ( $\gamma$ -FeOOH) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) show semiconductor properties with a narrow band gap of 2.0–2.3 eV and could be photoactive under solar irradiation [9].

It is noted that the iron oxides with the polycarboxylic acid may form a system performing a photochemical reaction of photo-Fenton-like with a much higher quantum efficiency than the Fe (OH)<sup>2+</sup>, or photochemical processes of the photocatalytic reaction only iron oxides [10] [11]. In the 1990s several research groups studied the mechanisms of iron (hydr) oxides dissolution in aqueous oxalate solution. [12] [13]. In fact, the complex photochemistry of Fe (III)-oxalate in natural aquatic environment, fog, precipitates, tropospheric aerosols and soil solutions have received considerable attention in recent decades because the complex iron oxide-oxalate shows a strong band transmission load metal-ligand in the UV and visible region.

The photochemical reaction of the complex oxide of iron oxalate involves both mechanisms of the homogeneous reaction in aqueous solution and the heterogeneous reaction on the surface of the iron oxide [14] [15]. The chemical adsorption of oxalic acid first occurs on the surface of iron oxide leading to the formation of Fe-oxalate complexes, and simultaneously the non-reductive/reductive dissolution of iron oxide takes place [16] [17].

Light irradiation can greatly enhance the reductive dissolution of Fe(III)-oxalate complexes, yielding Fe(II) and oxalate radical (C<sub>2</sub>O<sub>4</sub>)<sup>•-</sup> [17] [18].

Herbicides represent the largest group of chemicals used as plant protection agents. One class of herbicides widely used in pre- and post-emergencies is represented by the substituted phenylureas. Linuron, 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea], one of the most important commercial ureas, has good contact activity and it may kill emergent weed seedlings [19] Half-life of linuron in soil ranges from 38 to 67 days [21].

Many methods have been developed to remove Linuron, including adsorption on activated carbon and advanced oxidation processes. These comprised both homogeneous and heterogeneous systems, for example the direct photolysis [22], the UV photolysis of hydrogen peroxide [23] [24], the photolysis in presence of O<sub>3</sub> [25] [26] [27]

[28], the reaction of hydrogen peroxide with ozone [29] by Fenton reaction [24] or photo-Fenton [30] [31] [32] [33], by combined ultrasound photo-Fenton [34], and photolysis by TiO<sub>2</sub> colloidal particles [35] [36] [37] [38]. There was no report that had been published with respect to the photodegradation of Linuron in the Fe(III)-Ox systems.

Until now, the method Fer(III)- oxalic acid was applied to the degradation of dyes [39] [40] of antibiotic [41], of bisphenol and dimethylphenol [42] [43]... etc

## II. Experimental

### II.1. Reagents

Linuron Pestanal was purchased from Sigma Aldrich and was used as received (HPLC grade >99.5%).

NaOH (98%) was provided by Carlo Erba Reagenti. HCl (37%) Merck, ammonium acetate (98%), sodium acetate (99%) and sulfuric acid (98%) provided by Panreac. 1,10 o-phenantroline Fluka (>99%), perchloric acid 98%, and Oxalic acid (99.5%) Prolabo. Isopropanol Scharlau (99,8%). Acetonitrile for HPLC gradient grade (99%) by VWR PROLABO. The natural iron oxide (NIO) was washed several times with distilled water and dried at 45°C. All aqueous solutions were prepared with ultrapure water obtained from a Milli-Q ultrapure water purification system (Millipore, Bedford, MA, USA).

### II.2. Photodegradation procedure

Photodegradation was conducted in a Pyrex glass cell (diameter of 2 cm) with a cooling water jacket placed in an elliptical stainless steel chamber as illustrated in Fig.1.

The reaction mixture inside the cell, consisted of 50 mL of linuron solution and the precise amount of oxalic acid and iron oxide, was continuously stirred with a magnetic bar. The pH of the sample solution of the photochemical reactor was adjusted with HClO<sub>4</sub> and/or NaOH solution. The initial concentration of linuron in all experiments was 10 mg L<sup>-1</sup> (4.0×10<sup>-5</sup> mol L<sup>-1</sup>). In a majority of the experiments, temperatures were kept at 20±1 °C with a water bath.

The sample solution was illuminated with a fluorescent lamp (Philips TLAD 15W/05) which dominantly emits radiation at 365 nm. The beam was parallel and the length between lamp and the reactor wall was 10 cm. The lamp was warmed up for 5 min to reach constant output. The intensity of the light (I = 0.45 mW cm<sup>-2</sup>) was measured by using a radiometer type VLX 3W. The radio meter was set up at the same position as the reactor. The degradation reaction was quenched by adding 1mL of methanol for HPLC. These experiments were conducted in duplicates and the results showed the mean values. The relative standard deviations were between a range of 2–10%. The suspensions of Linuron (4×10<sup>-5</sup> M) and 1 g.L<sup>-1</sup> of iron oxides were stirred in the dark for 30 min before irradiation to establish adsorption/ desorption equilibrium. The particles of iron oxides were removed after

irradiation by filtration through cellulose acetate (Millipore 0.45 μm).

### II.3. Photocatalytic kinetics

At low substrate concentration, the photocatalytic degradation rate of organic pollutants including pesticides can be explained by pseudo-first order kinetics according to the following equation:  $\ln C_0 = C_t k t$ ; where  $k$  (in units of  $\text{time}^{-1}$ ) is the apparent reaction rate constant,  $t$  the reaction time,  $C_0$  the initial concentration of target pesticide in aqueous solution and  $C_t$  is the residual concentration of pesticide at time  $t$ .

### II.4. HPLC analysis

The concentration of Linuron was analyzed by Shimadzu LC-20C HPLC system with Agilent HC-C18 column (5μm, 250 mm× 4.6 mm). The mobile phase was a mixture of acetonitrile and H<sub>2</sub>O with a ratio of 60:40. The flow rate was 1.0 mL/min and the detector wavelength was set at 247 nm.

### II.5. Catalyst characterizaton

The NIO used in this study was obtained from the iron deposits from Chaabet- El-Ballout which is located in North-East Algerian and used without any pretreatment. The NIO morphologically were characterized in precedents works of our group [43], [44]. The analysis of iron deposits revealed that they are mostly composed of hematite.

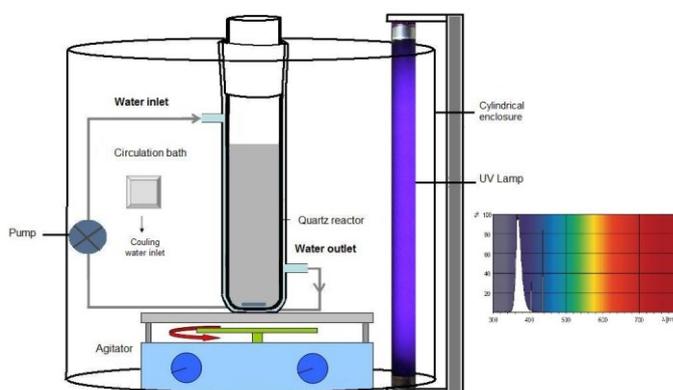


Fig.1 Representative schematic of the photo reactor used in tests

absorption to the light with wavelength above 365 nm. Adsorption of linuron on the NIO was determined by using the batch experiment in the dark. The data indicate that the adsorption of linuron was 19,6 % after 30 min. Under UV irradiation with 1.0 g.L<sup>-1</sup> NIO, in absence of oxalic acid, the removal percentage of linuron after 3 h was 10,1%, and its pseudo-first-order kinetic constant was determined to be  $4 \times 10^{-4} \text{ min}^{-1}$  ( $R^2 = 0.956$ ).

Without iron oxides and only with 10<sup>-3</sup> M oxalic acid under UV illumination the linuron concentration was decreased by 42.2% and  $k$  value was determined to be  $1.1 \times 10^{-2} \text{ min}^{-1}$  ( $R^2 = 0.98$ ).

By contrast, UV illumination of 1.0 g. L<sup>-1</sup> of iron oxides in 10<sup>-3</sup>M oxalate solution from the photo-Fenton-like system, the removal percentage of linuron was considerably increased up to 96,4 % after 60 min only (99% after 90 min) of reaction. The rate constant  $k$  were determined to be  $6 \times 10^{-2} \text{ min}^{-1}$  ( $R^2 = 0.986$ ). It can be seen from Fig.2 that the photodecomposition of linuron in presence of oxalic acid and the NIO is faster because the concentration of dissolved Fe<sup>2+</sup> species was much higher in the suspension of NIO than that in other systems (Fig. 3).

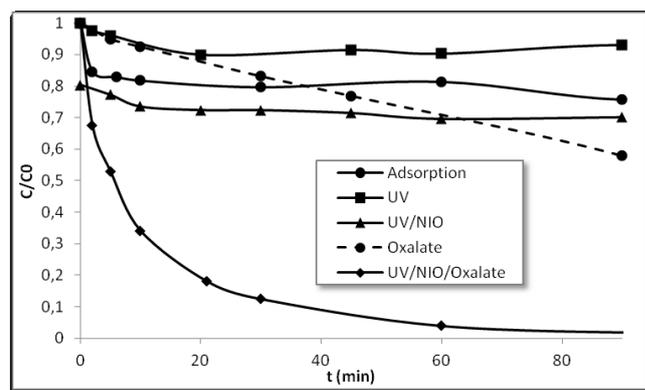


Fig. 2 : Photodegradation of linuron ( $4 \times 10^{-5} \text{ M}$ ) in different systems under UV irradiation ( $[\text{iron oxide}] = 1 \text{ g. L}^{-1}$ ,  $[\text{oxalic acid}] = 10^{-3} \text{ M}$ ).

Table 1. Removal percentage (after 90 min of irradiation, the pseudo- first-order kinetic constant ( $k$ ) and correlation coefficient ( $R^2$ ) of photodegradation of linuron in different systems.

Process	UV	UV/NIO	UV/Ox	UV/NIO/Ox
% Deg	9,7%	10,1 %	42.2%	99%
$k$ ( $\text{min}^{-1}$ )	$3 \times 10^{-4}$	$4 \times 10^{-4}$	$1,1 \times 10^{-2}$	$6 \times 10^{-2}$
$R^2$	0,86	0,956	0.98	0,986

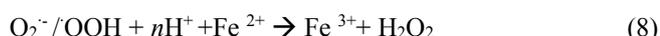
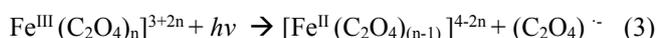
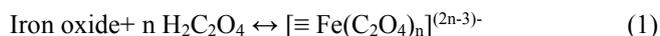
## III. Results and discussion

### III. 1. Photodecomposition of Linuron in different systems

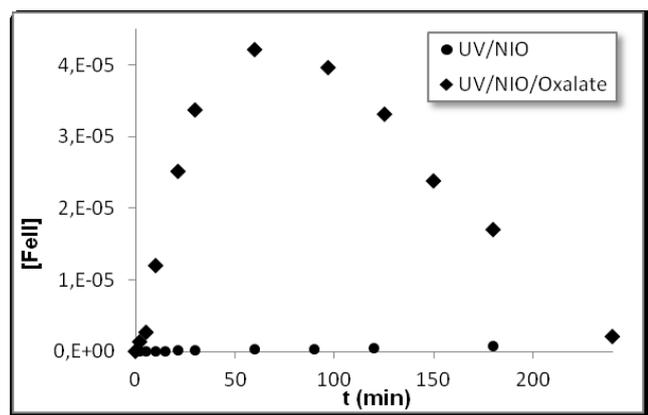
Photodegradation of linuron was followed in different systems (Fig. 2). The results obtained showed that the substrate photolysis in water is very slowly in artificial light ( $\lambda = 365\text{nm}$ ). The removal percentage of linuron was at 9,7 % after 3 h. This is because that linuron in water has no

The addition of oxalic acid ameliorate the degradation of linuron specially with NIO. During the photochemical reaction of Fe(III)–oxalate complexes, dissolved Fe(II) and Fe(III) species, adsorbed Fe(II) and Fe(III) species, the superoxides and hydroperoxyl radicals ( $\text{O}_2^{\cdot-}/\text{OOH}$ ) are the key intermediates formed through the reactions, as shown in Eqs. (1)–(6). H<sub>2</sub>O<sub>2</sub> can be obtained by the dismutation of

$O_2^{\cdot-}/OOH$ , as Eqs. (7) and (8). After  $H_2O_2$  was formed, the classical Fenton reaction happened with Fe (II) species, the photo-reduction products of Fe(III) species, to form  $\cdot OH$ , as Eq. (9).



The aim of this study is to show the efficiency of NIO in presence of oxalate under UV irradiation. So in the experiments below only NIO was used in presence of oxalic acid for the photodegradation of the linuron and an estimation of the kinetic parameters values by means of an optimization procedure was derived.



**Fig. 3 :** The concentration of the dissolved  $Fe^{2+}$  at the presence and absence of  $10^{-3}$  M oxalic acid under UV irradiation.

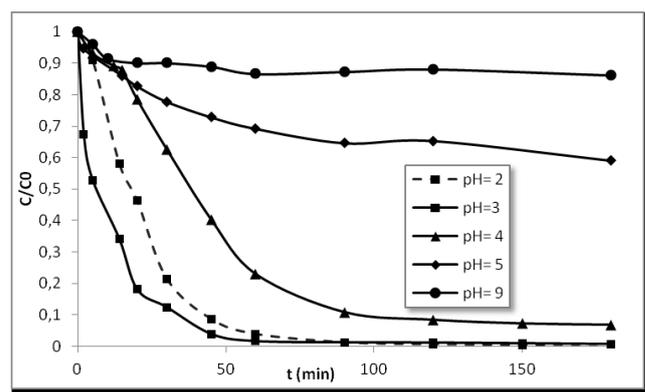
### III.2.1. Effect of initial pH value

Fig. 4 showed the pH effect on the photooxidation of linuron in water at pH values over the range of 3.0-9.0, the experiments were carried out with  $1.0 \text{ g L}^{-1}$  NIO in the presence of linuron ( $4 \times 10^{-5}$  M) and the initial concentration of oxalic acid was the optimal of  $10^{-3}$  M under UV illumination. The experiments indicated that higher photooxidation efficiency at pH values of 2–3, with an optimum pH value of 3,  $k$  value was determined to be  $6 \times 10^{-2} \text{ min}^{-1}$ . The increase of pH values would cause the decrease of photooxidation efficiency. When the pH value was increased to 5.0, photooxidation efficiency hardly changed compared to that at pH 4.0. Higher pH values would also cause unstable ferric ions to produce colloids

and precipitates, so we did not perform experiments at such high pH values.

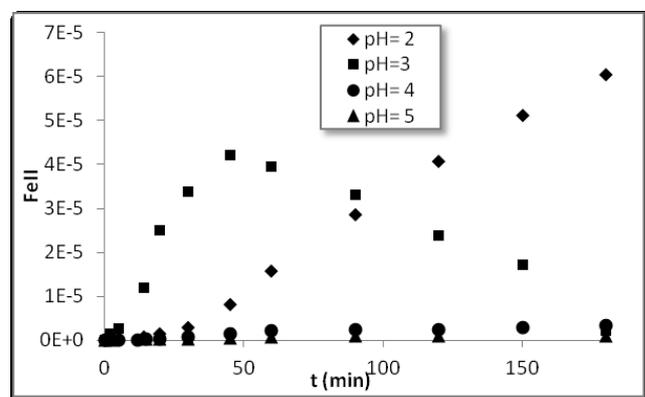
**Table 2.** The pseudo- first-order kinetic constant ( $k$ ) and correlation coefficient ( $R$ ) for photodegradation of linuron in different pH.

pH	2	3	4	5	9
$k \text{ (min}^{-1}\text{)}$	$5,6 \times 10^{-2}$	$6 \times 10^{-2}$	$3 \times 10^{-2}$	$4,8 \times 10^{-3}$	$4 \times 10^{-4}$
$R^2$	0,99	0,98	0,99	0,98	0,956



**Fig. 4.** Photodegradation of linuron ( $4 \times 10^{-5}$  M) in different pH under UV irradiation ( $[iron\ oxide] = 1 \text{ g L}^{-1}$ ,  $[Ox] = 10^{-3}$  M).

The observation that linuron degradation was fastest at pH 3 is likely due to the fact that the pH also controls the speciation of Fe(II) (Fig.5), affecting the rate of the Fenton reaction. Since the fraction of Fe(II)-Ox increases with pH, a larger fraction of Fe(II) was present as  $Fe^{2+}$  at pH 3. The rate constant of reaction of  $H_2O_2$  with  $Fe^{2+}$  is orders of magnitude smaller than that of the Fenton reaction involving Fe(II)-Ox [45]. The observation, on the other hand, that light induced linuron degradation occurred less efficiently at pH 4 and 5 than at pH 3 was possibly due to the fact that part of Fe(III) was present as  $Fe(OH)^{2+}$  at the higher pH values, and  $Fe(OH)^{2+}$  is photolyzed with much lower quantum yields than Fe(III)-oxalate complexes.



**Fig.5.** The concentration of the dissolved  $Fe^{2+}$  in different pH with the dosages of  $1 \text{ g L}^{-1}$  iron oxides at the presence of  $10^{-3}$  M oxalic acid under UV irradiation.

### III.2.2. Effect of oxalic acid concentration

The initial concentration of oxalate ( $C_{0ox}$ ) should be a key factor to affect the photodegradation of linuron in iron oxide–oxalate system. To study the effect of the  $C_{0ox}$  on the photodegradation of linuron, a set of experiments with initial linuron concentration of  $4 \times 10^{-5} M$  and iron oxides dosage of  $1 \text{ g.L}^{-1}$  were carried out under UVA irradiation, followed by the experiments on different  $C_{0ox}$  in the range of  $0-10^{-2} M$ . Fig. 6 shows the dependence of linuron photodegradation on the  $C_{0ox}$  under UVA light irradiation. Obviously, when there was no oxalic acid in the suspension, linuron was only degraded slightly. In the absence of oxalate, iron oxides acted as a photocatalyst and could be excited to generate electron–hole pairs [13], although linuron was degraded at a low  $k$  value of  $3 \times 10^{-4} \text{ min}^{-1}$ . In the presence of oxalate, iron oxide–oxalate complex formed and a photo-Fenton-like system was set up. It was confirmed that the presence of iron oxide and oxalate in cooperation can greatly accelerate the degradation of linuron. The experimental data were well fitted by the first-order kinetic model and the first-order kinetic constant ( $k$ ) for the photodegradation of linuron are listed in Table 3. pH at the beginning which was not favorable to photo-Fenton system [46].

On the other hand excessive oxalate would lead to the formation of a large quantity of  $Fe^{3+}$ , which would reduce the formation of  $H_2O_2$ , as described in Eq. (8). The results in Fig.6 and Table 3 show that the linuron degradation depended strongly on the  $C_{0ox}$ . In the low range, the linuron degradation was increased significantly with the increase of  $C_{0ox}$ . The optimal  $C_{0ox}$  was at  $10^{-3} M$  level and the corresponding  $k$  values were  $6 \times 10^{-2} \text{ min}^{-1}$ .

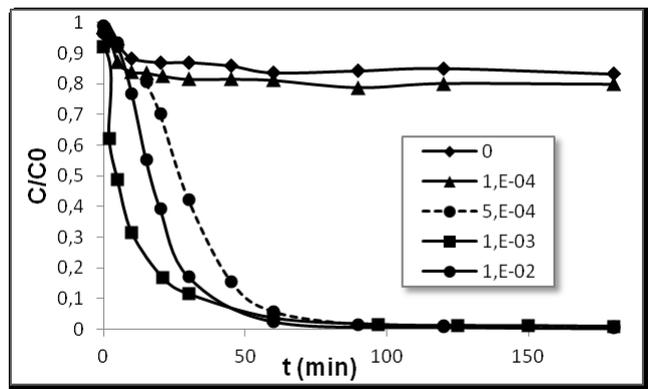


Fig. 6. Photodegradation of linuron ( $4 \times 10^{-5} M$ ) in different oxalate concentration under UV irradiation ( $[iron\ oxide]= 1 \text{ g L}^{-1}$ ).

Table 3. The pseudo- first-order kinetic constant ( $k$ ) and correlation coefficient ( $R^2$ ) for photodegradation of linuron in different oxalate concentration.

Ox (M)	0	$10^{-4}$	$5 \times 10^{-4}$	$10^{-3}$	$10^{-2}$
$k \text{ (min}^{-1}\text{)}$	$3 \times 10^{-4}$	$7 \times 10^{-4}$	$5,4 \times 10^{-2}$	$6 \times 10^{-2}$	$6,7 \times 10^{-2}$
$R^2$	0,9	0,92	0,99	0,98	0,99

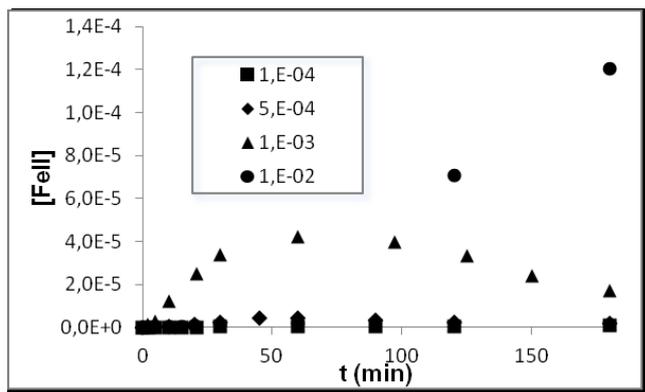


Fig.7. The concentration of the dissolved  $Fe^{2+}$  in different oxalate concentration with the dosages of  $1 \text{ g.L}^{-1}$  iron oxides under UV irradiation.

### III.2.3. Effect of iron oxide contents in the experiments

The influence of the iron oxide dosage on the photodegradation kinetics of linuron in the presence of oxalic acid was investigated using different dosages of NIO varying from 0 to  $2 \text{ g.L}^{-1}$ . It could be seen from (Fig. 8) that there should be an optimal dosage of  $1.0 \text{ g L}^{-1}$ . In fact, excessive dosage of iron oxide will lead to the obstruction in the penetration of UV light in the solid phase.

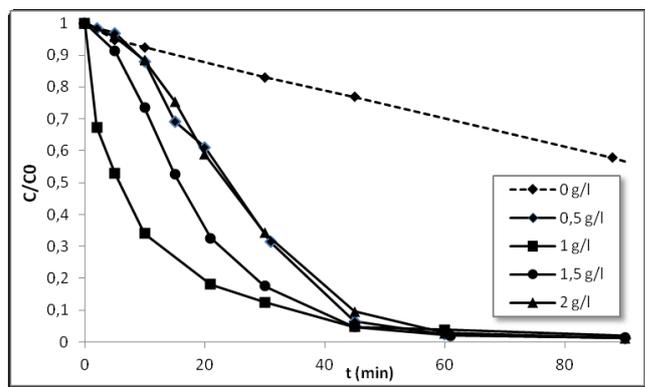


Fig. 8. Photodegradation of linuron ( $4 \times 10^{-5} M$ ) by different quantity of iron oxide under UV irradiation ( $[Ox]= 10^{-3} M$ ).

### III.2.4. The effect of isopropanol

In order to elucidate the formation of  $\bullet OH$  radicals, 2.0% of isopropanol was added to NIO-linuron suspension in the presence of oxalate and under light irradiation. Isopropanol was used as a hydroxyl radicals scavenger. The results showed that the photodegradation of linuron was totally inhibited compared to the photodegradation of linuron in absence of isopropanol (Fig. 9). It can be seen that the kinetic of disappearance of linuron in presence of 2.0% of isopropanol was similar to the kinetic of disappearance obtained from UV direct photolysis of linuron at 365 nm. The  $k$  value was determined to be  $3,1 \times 10^{-4} \text{ min}^{-1}$ ,  $3 \times 10^{-4} \text{ min}^{-1}$  and  $6 \times 10^{-2} \text{ min}^{-1}$  in presence of isopropanol, direct photolysis and in absence of isopropanol respectively. So

the photo-Fenton reaction which used  $\bullet\text{OH}$  for the degradation of organic pollutants, is hindered by the presence of an  $\bullet\text{OH}$  scavenger.

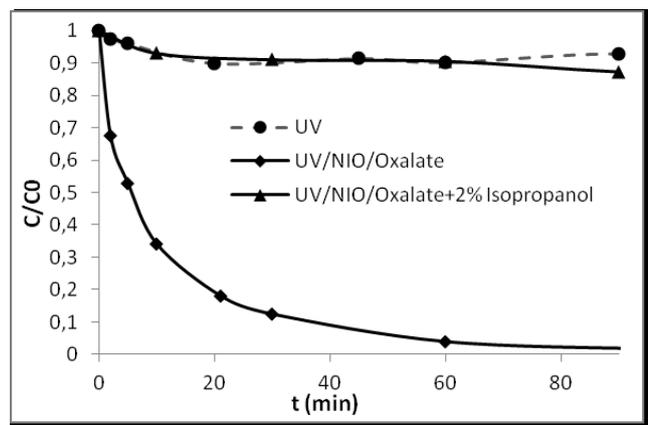


Fig. 9. Effect of isopropanol on the photodegradation of linuron in presence of NIO ( $1\text{g}\cdot\text{L}^{-1}$ ) and Ox ( $10^{-3}\text{ M}$ ).

### CONCLUSION

The experiments confirmed the effectiveness of natural iron oxide used in this study for the degradation of linuron. Degradation significantly depends on various factors, including the dosage of the iron oxide, the initial concentration of the oxalic acid and the initial pH.

Oxalic acid was used to dissolve the iron oxide natural iron, therefore a heterogeneous system of photo-Fenton like complex oxide / iron oxalate was introduced. Fe(III)–Ox complexes induced the photooxidation of linuron in water at pH values over the range of 2.0–9.0 under radiation of a near UV light. The optimum pH value for linuron photooxidation is between 2–3. The optimum concentration of oxalic acid and NIO used a good inducing disappearance of linuron is  $10^{-3}\text{ M}$  and  $1\text{g}\cdot\text{L}^{-1}$  respectively. The contribution  $\bullet\text{OH}$  radicals was proven by the addition of 2% isopropanol as a scavenger of these radicals.

### REFERENCES

- [1] E.M. Thurman, "Organic Geochemistry of Natural Waters," Martinus Nijhoff/Dr. W. Junk Publishers, 1985, p. p. 497.
- [2] E.M. Perdue, E.T. Gjessing (Eds.), Life Sciences Research Report 48: Organic acids in aquatic ecosystems. Report on the Dehlem Workshop on Organic Acids in Aquatic Ecosystems Berlin, 1989, May 7–12, 1990, 345.
- [3] R. W. Talbot, B. W. Mosher, B. G. Heikes, D. J. Jacob, J. W. Munger, B. C. Daube, W. C. Keene, J. R. Maben, and R. S. Artz, "Carboxylic acids in the rural continental atmosphere over the eastern United States during the Shenandoah Cloud and Photochemistry Experiment," *J. Geophys. Res. Atmospheres* 1984–2012, vol. 100, no. D5, pp. 9335–9343, 1995.
- [4] A. Chebbi and P. Carlier, "Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review," *Atmos. Environ.*, vol. 30, no. 24, pp. 4233–4249, 1996.
- [5] M.E. Balmer, B. Sulzberger, *Environmental Science & Technology* 33 (1999) 2418–2424.
- [6] Y.G. Zuo, J. Hoigne, *Science* 260 (1993) 71–73.
- [7] Y.G. Zuo, J. Hoigne, *Environmental Science & Technology* 26 (1992) 1014–1022.
- [8] U. Schwertmann, R.M. Cornell, *Iron Oxides in the Laboratory: Preparation and Characterization*, second ed., Wiley–VCH, 2000.
- [9] J.K. Leland, A.J. Bard, *J. Phys. Chem.* 91 (1981) 5076.
- [10] Y.G. Zuo, Y.W. Deng, *Chemosphere* 35 (1997) 2051.
- [11] B.C. Faust, J. Allen, *Environ. Sci. Technol.* 27 (1993) 2517.
- [12] D. Panias, M. Taxiarchou, I. Douni, I. Paspaliaris, and A. Kontopoulos, "Thermodynamic analysis of the reactions of iron oxides: Dissolution in oxalic acid," *Can. Metall. Q.*, vol. 35, no. 4, pp. 363–373, Oct. 1996.
- [13] B. Sulzberger, H. Laubscher, *Marine Chemistry* 50 (1995) 103–115.
- [14] R.M. Smith, A.E. Martell, *Critical Stability Constants*, vols. 2–3: Inorganic Complexes/Other Organic Ligands, Plenum Press, New York, 1976.
- [15] Q.G. Mulazzani, *J. Phys. Chem.* 90 (1986) 5347.
- [16] P. Mazellier, B. Sulzberger, *Environmental Science & Technology* 35 (2001) 3314–3320.
- [17] Q. Lan, F.B. Li, C.S. Liu, X.Z. Li, *Environmental Science & Technology* 42 (2008) 7918–7923.
- [18] M. I. Litter, E.C. Baumgartner, G.A. Urrutla, M.A. Blesa, *Environmental Science & Technology* 25 (1991) 1907–1913.
- [19] USEPA, Reregistration Eligibility Decision (RED), Linuron, (EPA/NCEPI), 1995.
- [20] O. Cincinati, "NEPIS Document display.
- [21] British Crop Protection Council, *The pesticide manual: a world compendium*, 11th ed. Farnham, Surrey, UK: British Crop Protection Council, 1997.
- [22] V. Faure and P. Boule, "Phototransformation of linuron and chlorbromuron in aqueous solution," *Pestic. Sci.*, vol. 51, no. 4, pp. 413–418, Dec. 1997.
- [23] F. J. Benitez, F. J. Real, J. L. Acero, and C. Garcia, "Photochemical oxidation processes for the elimination of phenyl-urea herbicides in waters," *J. Hazard. Mater.*, vol. 138, no. 2, pp. 278–287, Nov. 2006.
- [24] H. Barlas, Treatment of chlorinated organic materials containing wastewater by oxidation processes, *Fresenius Environ. Bull.* 9 (2000) 590–596.
- [25] F. J. Benitez, F. J. Real, J. L. Acero, and C. Garcia, "Kinetics of the transformation of phenyl-urea herbicides during ozonation of natural waters: Rate constants and model predictions," *Water Res.*, vol. 41, no. 18, pp. 4073–4084, 2007.
- [26] Y. F. Rao and W. Chu, "Reaction mechanism of linuron degradation in TiO<sub>2</sub> suspension under visible light irradiation with the assistance of H<sub>2</sub>O<sub>2</sub>," *Environ. Sci. Technol.*, vol. 43, no. 16, pp. 6183–6189, 2009.
- [27] Y. F. Rao and W. Chu, "Degradation of linuron by UV, ozonation, and UV/O<sub>3</sub> processes—Effect of anions and reaction mechanism," *J. Hazard. Mater.*, vol. 180, no. 1–3, pp. 514–523, Aug. 2010.

- [28] R. Rosal et al. / *Chemical Engineering Journal* 165 (2010) 806–812.
- [29] L. Amir Tahmasseeb, S. Nélieu, L. Kerhoas, and J. Einhorn, “Ozonation of chlorophenylurea pesticides in water: reaction monitoring and degradation pathways,” *Sci. Total Environ.*, vol. 291, no. 1–3, pp. 33–44, May 2002.
- [30] H. Katsumata, S. Kaneco, T. Suzuki, K. Ohta, and Y. Yobiko, “Degradation of linuron in aqueous solution by the photo-Fenton reaction,” *Chem. Eng. J.*, vol. 108, no. 3, pp. 269–276, 2005.
- [31] M. J. Farré, X. Doménech, and J. Peral, “Assessment of photo-Fenton and biological treatment coupling for Diuron and Linuron removal from water,” *Water Res.*, vol. 40, no. 13, pp. 2533–2540, 2006.
- [32] M. J. Farré, X. Doménech, and J. Peral, “Combined photo-Fenton and biological treatment for Diuron and Linuron removal from water containing humic acid,” *J. Hazard. Mater.*, vol. 147, no. 1–2, pp. 167–174, Aug. 2007.
- [33] M. J. Farré, M. I. Maldonado, W. Gernjak, I. Oller, S. Malato, X. Doménech, and J. Peral, “Coupled solar photo-Fenton and biological treatment for the degradation of diuron and linuron herbicides at pilot scale,” *Chemosphere*, vol. 72, no. 4, pp. 622–629, Jun. 2008.
- [34] H. Katsumata, T. Kobayashi, S. Kaneco, T. Suzuki, and K. Ohta, “Degradation of linuron by ultrasound combined with photo-Fenton treatment,” *Chem. Eng. J.*, vol. 166, no. 2, pp. 468–473, Jan. 2011.
- [35] M.C. Lopez, M.I et al. 2005.
- [36] R. Zouaghi, A. Zertal, B. David, and S. Guittonneau, “Photocatalytic degradation of monolinuron and linuron in an aqueous suspension of titanium dioxide under simulated solar irradiation,” *Rev. Sci. Eau/Journal Water Sci.*, vol. 20, no. 2, pp. 163–172, 2007.
- [37] Y. F. Rao and W. Chu, “Linuron decomposition in aqueous semiconductor suspension under visible light irradiation with and without H<sub>2</sub>O<sub>2</sub>,” *Chem. Eng. J.*, vol. 158, no. 2, pp. 181–187, Apr. 2010.
- [38] J. Fenoll, M. Martínez-Menchón, G. Navarro, N. Vela, and S. Navarro, “Photocatalytic degradation of substituted phenylurea herbicides in aqueous semiconductor suspensions exposed to solar energy,” *Chemosphere*, vol. 91, no. 5, pp. 571–578, Apr. 2013.
- [39] F. Gulshan, S. Yanagida, Y. Kameshima, T. Isobe, A. Nakajima, and K. Okada, “Various factors affecting photodecomposition of methylene blue by iron-oxides in an oxalate solution,” *Water Res.*, vol. 44, no. 9, pp. 2876–2884, 2010.
- [40] J. Lei et al. / *Journal of Hazardous Materials B*137 (2006) 1016–1024.
- [41] T. Zhou, X. Wu, Y. Zhang, J. Li, and T.-T. Lim, “Synergistic catalytic degradation of antibiotic sulfamethazine in a heterogeneous sonophotolytic goethite/oxalate Fenton-like system,” *Appl. Catal. B Environ.*, vol. 136–137, pp. 294–301, Jun. 2013.
- [42] F. B. Li, X. Z. Li, X. M. Li, T. X. Liu, and J. Dong, “Heterogeneous photodegradation of bisphenol A with iron oxides and oxalate in aqueous solution,” *J. Colloid Interface Sci.*, vol. 311, no. 2, pp. 481–490, Jul. 2007.
- [43] S. Belaidi, T. Sehili, L. Mammeri, and K. Djebbar, “Photodegradation kinetics of 2,6-dimethylphenol by natural iron oxide and oxalate in aqueous solution,” *J. Photochem. Photobiol. Chem.*, vol. 237, pp. 31–37, Jun. 2012.
- [44] L. Mammeri, T. Sehili, S. Belaidi, and K. Djebbar, “Heterogeneous photodegradation of 1-naphthol with natural iron oxide in water: influence of oxalic acid,” *Desalination Water Treat.*, no. ahead-of-print, pp. 1–10, 2014.
- [45] Sedlak, D.L., Hoigne, J., 1993. The role of copper and oxalate in the redox cycling of iron in atmospheric waters. *Atmos. Environ.* 27, 2173–2185.
- [46] L. Lunar, D. Sicilia, S. Rbio, D. Perez-Bendito, U. Nickel, *Water Research* 34 (2000) 1791.