



Use of natural iron oxide as heterogeneous catalyst in photo-Fenton-like oxidation of chlorophenylurea herbicide in aqueous solution: Reaction monitoring and degradation pathways



H. Mechakra^a, T. Sehili^{a,*}, M.A. Kribeche^a, A.A. Ayachi^b, S. Rossignol^c, C. George^c

^a Laboratoire des Sciences et Technologies de l'Environnement, Université Frères Mentouri, Constantine 1, Algeria

^b Ceramics Laboratory, Faculty of Exact Sciences, Frères Mentouri University, Constantine 1, Algeria

^c Université Lyon1, F-69626, CNRS-UMR5256, IRCELYON Institut de Recherche sur la Catalyse et l'Environnement de Lyon, Villeurbanne, France

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ABSTRACT

The photocatalytic degradation of 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea] (Linuron), which is one of phenylurea herbicides, has been studied using natural iron oxide (NIO) as a heterogeneous catalyst in the presence of H₂O₂ under various conditions. The characterization of this catalyst revealed that NIO has a mixed elemental composition and consists mainly of iron oxide (α-Fe₂O₃). This powder contains hematite as iron source and its dissolution provides Fe³⁺ cations for the Fenton-like reaction in solution. The degradation rate was strongly influenced by pH, initial concentrations of H₂O₂, amount of NIO particles and type of irradiation (artificial or natural sunlight). An initial Linuron concentration of 4.0 × 10⁻⁵ mol L⁻¹ was completely degraded after 45 min under the optimum conditions. The decrease of chemical oxygen demand (COD) as a result of mineralization of the herbicide was observed i.e., 99.99% of the initial concentration of Linuron and over 80% of COD were removed after 6 h under our experimental conditions. The degradation of Linuron is mainly due to the formation of hydroxyl radicals as confirmation by the use of 2.0% of isopropanol as an HO• scavenger. The decomposition of Linuron gave eight main intermediate products, and a degradation mechanism is suggested on the basis of these identified intermediates. The use of NIO is interesting; because in addition to its catalytic effect, its high density enables an easy solid-liquid separation, making it a versatile material for environmental applications.

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1. Introduction

Herbicides are the most widely used types of pesticides in agriculture. These chemicals are generally toxic and non biodegradable. The phenylurea herbicides represent an important group of herbicides applied to the pre and post emergence control of weeds in many agricultural crops. One of the most important widely used members of this group, Linuron (Fig. 1) 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea] is relatively persistent in soil, with half-lives ranges from 38 to 67 days [1]. Its persistence in soil is due to its physicochemical properties such as stability or low solubility in water (estimated as 75 mg L⁻¹ at 25 °C). Like others phenylurea herbicides, linuron was also found in

polluted natural waters, indicating that it is difficult to eliminate by a conventional wastewater treatment process.

In the case of non biodegradable or toxic wastewater sources, alternative treatments have to be used. Advanced oxidation process (AOPs) have been described as effective methods for decontamination of wastewaters. The elimination of Linuron has been developed by different methods, comprising homogeneous and heterogeneous AOPs such as the direct photolysis [2], the UV photolysis of hydrogen peroxide [3], the photolysis by UV/O₃ process [4,5], the combined O₃/H₂O₂ system [6], the Fenton reaction and/or photo-Fenton [7,8], a combined ultrasound photo-Fenton process [9], and photolysis by colloidal particles (TiO₂, ZnO, SnO₂, . . .) [10–14]. The AOPs are characterized by production of hydroxyl radicals (*OH), a powerful oxidizing agent with oxidation potential of 2.8 V, reacting with rate constants usually in the order of 10⁶–10⁹ M⁻¹ s⁻¹ [15].

Oxidation by Fenton (Fe²⁺/H₂O₂) and Fenton-like (Fe³⁺/H₂O₂) processes has been investigated as a viable AOP for the destruction

* Corresponding author.

E-mail address: mechakra_hind@umc.edu.dz (T. Sehili).

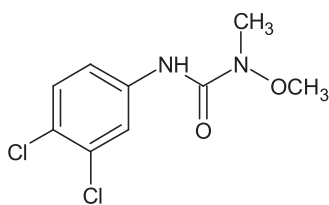
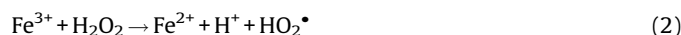


Fig. 1. Chemical structure of Linuron.

of various pollutants in water. HO^\bullet can be produced in this systems as described over 100 years ago by Fenton [16]. UV light irradiation increases the efficiency of the process according to the following mechanism (R is an organic binder):



The HO^\bullet formation rate was increased via the photoreduction of Fe^{3+} to Fe^{2+} and by photochemical reactions of the complexes formed with Fe^{3+} ions (Eq. (3)) because the reduction of Fe^{3+} by H_2O_2 in non-irradiated systems is slow and thus ineffective [17]. An additional reaction of peroxide in the presence of UV light (<320 nm) can occur as follows [18].



Iron oxides can also be used as iron sources in AOPs. Their efficiency in the oxidation of organic compounds has been reported in the literature [19–21]. The use of solid iron oxides is gaining more importance due to their advantages related to the stability under irradiation, possibility to recovering and reuse while no strict control of the pH is required during the reactions [22], their lower cost and non-toxicity.

In the present study, the degradation of Linuron was investigated in water using natural iron oxide in heterogeneous photo-Fenton-like process under UV and solar illumination. The influence of factors, such as pH, quantity of catalyst and initial concentrations of H_2O_2 on the degradation process were evaluated. The progress of mineralization of Linuron was monitored by Chemical Oxygen Demand (COD). Ultra-High Performance Liquid Chromatography coupled to High Resolution Mass Spectrometry (UHPLC–HR/MS) has been used to identify the intermediate products and elucidate the degradation mechanism of Linuron by UV/ H_2O_2 /NIO process.

2. Experimental

2.1. Chemicals

Linuron 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea] (>99.5%) was purchased from Sigma–Aldrich and was used as received. Sodium hydroxide (98%) was provided by Carlo Erba

Reagenti; ammonium acetate (98%), sodium acetate (99%) and sulfuric acid (98%) by Panreac; silver sulfate and 1,10 O-phenanthroline (>99%) by Fluka. Perchloric acid (98%), mercury sulfate, potassium dichromate, hydrogen peroxide (30%) and acetonitrile (99%) for HPLC gradient grade were purchased from Prolabo and isopropanol (99.8%) from Scharlau. All aqueous solutions were prepared with ultrapure water obtained from a Milli-Q ultrapure water purification system (Millipore, Bedford, MA, USA).

2.2. Photodegradation procedure

Photodegradation was conducted in a Pyrex glass cell (diameter of 2 cm and capacity of 50 mL) with a cooling water jacket placed in an elliptical chamber. The reaction mixture was continuously stirred with a magnetic bar. The pH of the sample solution was measured by means of an HANNA Instruments 8521 pH-meter. HClO_4 and/or NaOH were used for adjustment of pH of the solutions. The tests were conducted in an isothermal reaction system ($20 \pm 1^\circ\text{C}$) kept 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 distance 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 ($I=0.45\text{ mW cm}^{-2}$) was measured by using a radiometer type VLX 3W with a 365 nm sensor. The tests under natural solar radiation were carried out during the month of September 2014 during sunny days in Constantine, Algeria (latitude $36^\circ 20' \text{N}$, longitude $6^\circ 37' \text{E}$). Experiences were conducted in a cylindrical Pyrex reactor, placed vertically. Light intensity was 0.98 W/cm^2 measured with a SOLAR LIGHT radiometer PMA2100 positioned to sample height.

The suspensions of Linuron and NIO were stirred in the dark for 30 min before irradiation to establish adsorption/desorption equilibrium. The particles of NIO were removed after irradiation by filtration through cellulose acetate (Millipore $0.45\ \mu\text{m}$). The adsorption rate of Linuron ($4.0 \times 10^{-5}\text{ mol L}^{-1}$) in the presence of 1 g L^{-1} of NIO was 20% after 30 min.

2.3. Analyses

The concentration of Linuron was analyzed by means of a HPLC Shimadzu system, equipped with a photodiode detector (Shimadzu SPD-20A) and a Supelco HC-C18 column ($5\ \mu\text{m}$, $250\text{ mm} \times 4.6\text{ mm}$). The mobile phase was a mixture of acetonitrile and ultrapure water, with a ratio of 60:40 and was pumped at a flow rate of 1.0 mL min^{-1} . The detector wavelength was set at 249 nm. The UV–visible absorption spectra were recorded employing a Thermo scientific spectrophotometer controlled by software «Thermo INSIGHT». Chemical oxygen demand (COD) was obtained according to the method presented by Thomas and Mazas [23], using dichromate as the oxidizer. The sample was digested at 150°C for 2 h in a WTW CR 3200 thermoreactor. Fe(II) concentrations were measured by using complexometric method with 1,10-phenanthroline, the molar coefficient ϵ at 510 nm is equal to $11,430\text{ L mol}^{-1}\text{ cm}^{-1}$.

2.4. UHPLC–HR/MS analysis

The intermediate products during photodegradation of Linuron were extracted with diethyl ether. This solution was concentrated under a nitrogen flow. An Ultra-High Performance Liquid Chromatography (UHPLC, Dionex 3000, Thermo Scientific, USA) equipped with a Waters Acquity HSS T3 column ($1.8\ \mu\text{m}$, $100\ \text{Å} \times 2.1\text{ mm}$) was used for products separation.

The mobile phase was a mixture of (A) 0.1% formic acid in water and (B) 0.1% formic acid in acetonitrile (Optima[®] LC/MS, Ficher

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