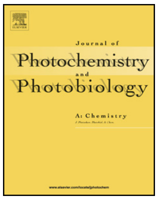
Journal of Photochemistry and Photobiology A: Chemistry 329 (2016) 120–129

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Insight into photochemical oxidation of Fenuron in water using iron oxide and oxalate: The roles of the dissolved oxygen

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ARTICLE INFO

Article history:
Received 11 January 2016
Accepted 11 June 2016
Available online 25 June 2016

Keywords:
Photo-Fenton like
Fenuron
Dissolved oxygen
Iron oxide
Advanced oxidation process

ABSTRACT

The role of dissolved oxygen in the degradation and mineralization of fenuron in the photo-Fenton-like system by using a natural iron oxide and oxalate was studied in detail during this study; the natural iron oxide (NIO) α-Fe_2O_3 was used as an iron source at acidic pH. The dissolved oxygen concentration variation was followed during the process. The dissolved oxygen effect was elucidated by carrying out experiments in the presence and absence of oxygen. It was found that the degradation and mineralization rate were strongly affected by changes in the dissolved oxygen concentration. In the absence of oxygen, we noticed a slight degradation of fenuron (22% in 360 min); this degradation was caused only by the photo-reduction of Fe(III). Ferrous ions were continually generated in this way. Ferrous irons were not oxidized to Fe (III) because of the lack of dissolved oxygen. Moreover, no production of hydrogen peroxide was noticed. The mineralization rate depended strongly on the abundance of dissolved oxygen; fenuron was totally degraded in 120 min in an oxygenated system, in 150 min in a forced aerated system and in 180 min in a free aerated system. Dissolved oxygen permitted the production of species that influenced the degradation efficiency; it improved hydrogen peroxide production under irradiation. The superoxide ion can react with organic radicals leading to an opening ring reaction. The mass balance of the reactive species showed that dissolved oxygen was the main reactive consumed during the process. Acute toxicity of the fenuron degradation by-products was measured by a bioluminescence test on a Microtox 500 analyzer and the results were expressed as the percentage of inhibition of the luminescence emitted by the bacteria *Vibrio fisheri*. Bio-assays showed that the toxicity decreased with irradiation time which proved that the intermediates, generated during photo-oxidation by the photo-Fenton-like system by using NIO, are less toxic than fenuron.

1. Introduction

Pollution from agriculture has largely contributed to the degradation of surface and subterranean water quality. The phytosanitary run off from agricultural fields is very representative of small local sources of pollution. Generally, these discharges consist of mixtures of high concentrations of several pesticides. Phenylurea herbicides are used in large quantities throughout the world [1]. The quantity of pesticides which reaches the target pests is less than 1% of the total applied pesticides [2]. Degradation of Phenylurea pesticides in the environment is very slow. In-streams, herbicide concentrations can be as high as 100 $\mu g\, L^{-1}$ [3]. Because some phenylurea are suspected to be genotoxic [4], conventional biological treatments are in some cases not sufficiently effective. So it is necessary to improve the efficiency of existing wastewater treatment plants. Nowadays, advanced oxidation processes (AOPs) are able to product hydroxyl radicals which are very strong oxidizing species that unselectively react with most bio-refractory or hazardous organic contaminants in water and convert them into small inorganic molecules such as organic acids, CO_2 and H_2O [5]. On the other hand, UV light is widely used in water-disinfection techniques [6]. Moreover, AOPs are environmentally clean technologies since they do not generate secondary waste. These techniques have been successfully employed in wastewater

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http://dx.doi.org/10.1016/j.jphotochem.2016.06.021
1010-6030/

treatment and permit total mineralization of organic contaminants [7].

Many oxidation processes using the metal salt Fe (II), such as Fenton's reagent, have the drawback of producing inorganic sludge that causes a waste disposal problem. To face this drawback, a natural iron oxide was used in this work as an iron catalyst. The photochemical process which occurs with Fe^{3+} and H_2O_2 as reagents and UV as a catalyst is usually called photo-Fenton-like. In the photo-Fenton-like process, Natural Iron Oxide (NIO) can be used as a Fe^{3+} source. During this process, the O^{H} formation is enhanced under UV irradiation via the photo-reduction of Fe^{3+} to Fe^{2+} and the reaction of H_2O_2 with ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron in acidic aqueous solutions, which are among the most common homogeneous systems and potential sources of hydroxyl radical generation [8,9].

Various studies have been carried out on organic pollutant degradation in aqueous solutions by homogenous and heterogeneous photo-Fenton-Like systems [10–14], while other studies have investigated the combination of nano-filtration techniques with solar photo-Fenton like systems [15]. The role of oxalic acid in photo-Fenton-like reaction by using a natural iron oxide was also investigated [16].

It is known that oxygen has very important roles during heterogeneous photocatalysis [17–19]. Dissolved oxygen concentration variations were investigated during the photo-Fenton process using Paracetamol as a model pollutant in 2011 [20]. However, the role of dissolved oxygen and different intermediate species in the photo-Fenton-like process has so far been very poorly studied.

An optimization study using variant experimental conditions (pH, temperature, initial concentrations of NIO and oxalic acid) has already been performed by our group [10]. In this work, the contribution of dissolved oxygen (DO) during the degradation and mineralization of fenuron was elucidated at different reaction times under UV irradiation in the photo-Fenton-like process by using a natural iron oxide (NIO) as an iron source. DO concentration variations were followed during the process and toxicity analyses were conducted to prove the efficiency of the pollutant degradation.

2. Experimental

2.1. Reagents

All solutions were prepared with ultra-pure water (Millipore) with a resistivity of 18.2 mΩ cm. All chemicals used in this study were of analytical grade, fenuron (1,1-dimethyl-3-phenylurea) ($C_9H_{12}N_2O$ 164.2 g mol^{-1}) (Sigma-Aldrich, France), 1,10-phenanthroline (Fluka analytical, France), methanol (Carlo Erba Reagenti, Italy), hydrochloric acid (Sigma-Aldrich, France), oxalic acid (Sigma-Aldrich, France), ammonium acetate and sodium acetate (Sigma-Aldrich, France).

NIO is essentially constituted of hematite, it was used without any treatment; it was only washed and dried at 45 °C. The specific surface area and the total pore volume of NIO measured by the Brunauer–Emmett–Teller method were, respectively, 79.015 (m^2 g^{-1}) and 0.0892 (cm^3 g^{-1}). The initial concentration of Fenuron was 10^{-4} M. The irradiation was carried out under the optimal photo-Fenton-like operating condition determined in our previous study [10]: 0.1 g L^{-1} of NIO, 10^{-3} M of oxalic acid at pH 3. The temperature was kept at 20 ± 0.1 °C during UV irradiation experiments. The high concentration of iron oxide allowed not to be iron limited in the experiments and should be decreased for real applications.

2.2. Materials and irradiation device/photoreactor

All the experiments were repeated at least three times. A Pyrex cylindrical photoreactor equipped with a cooling water jacket was used to conduct all photocatalytic reactions under monochromatic UV irradiation (Fig. 1). A fluorescent lamp (Philips TLAD 15W/05), which mainly emits radiation at 365 nm, was positioned at the center of the photoreactor. The liquid volume exposed to irradiance was 300 mL and the total volume of the reactor was 400 mL. The photoreactor diameter was 8 cm and its annular section was about 2.15 cm long. UV irradiance inside the cell was measured with a VLX 3 W radiometer and was estimated at 0.54 ± 0.01 mW cm^{-2}. The reaction mixture (300 mL) inside the cell was continuously stirred in the dark before irradiation for 30 min to establish an adsorption/desorption equilibrium. The transfer of oxygen into the liquid phase was carried out either by forced aeration, by oxygenation (bubbling) or by free aeration. Forced aeration corresponds to bubbling with air, forced oxygenation corresponds to bubbling with pure oxygen, free aeration corresponds to the transfer of O_2 occurring at the free surface of water of the annular reactor interface (water/air) with a magnetically stirred system ensuring the creation of a vortex. The deoxygenation was performed by injection of pure nitrogen into the solution via the gas diffuser (Fig. 1). The gas flow was controlled by a PERKIN ELMER electronic flowmeter and was set to 12L/h. Temperature, pH and dissolved oxygen measurements were carried out with a CONSORT C831 pH-meter and a WTW Oxi 340i Oxy-meter respectively.

Sampling were taken every 30 min for the first hour and then every 1 h until completion of experiment, NIO particles were removed from the samples by filtration through cellulose acetate syringe filter Millipore (0.45 μm). Every sample was analyzed to determine Total organic carbon (TOC), Fe (II), H_2O_2, fenuron, oxalic acid and fenuron derivative concentrations.

2.3. Analytical methods

Fenuron is highly water-soluble (3850 mg L^{-1}). Its concentration in aqueous solution was determined by HPLC (Waters 600E controller and pump, 717 plus Autosampler) equipped with a UV detector. All HPLC analyzes were done in triplicate. A sample of 20 μL was injected onto a C18 column (Supelco C18, 250 mm × 4.6 mm × 5 μm) and a mobile phase composed of 45/55 (MeOH/H_2O) at a flow rate of 1 mL min^{-1} was used. A maximum absorption

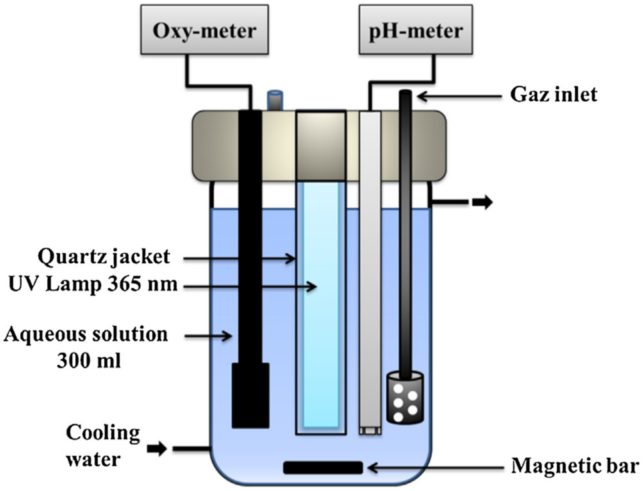

Fig. 1. The experimental setup of the photo-reactor used for UV irradiation.