



# Photo-Fenton degradation of the insecticide esfenvalerate in aqueous medium using a recirculation flow-through UV photoreactor

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## ABSTRACT

The aim of the study was to evaluate the efficiencies of photo-Fenton ( $\text{Fe}^{2+}$ ) and ( $\text{Fe}^{3+}$ ) processes in the degradation of high-concentrations of esfenvalerate (in the form of aqueous emulsion of a commercial formulation) using a recirculation flow-through photoreactor irradiated with UV light from a 15 W lamp (254 nm emission peak). The results obtained using a basic photo-Fenton ( $\text{Fe}^{2+}$ ) reaction (esfenvalerate  $17 \text{ mg L}^{-1}$ ; ferrous sulphate 1 mM; hydrogen peroxide 25 mM; pH 2.5) were compared with those acquired when ferrioxalate (1, 3 or 5 mM) served as the iron source. Degradation of the active component of the commercial formulation was significantly greater, and the rate of oxidation more rapid, using a photo-Fenton ( $\text{Fe}^{3+}$ ) process compared with its  $\text{Fe}^{2+}$  counterpart. The most efficient degradation of the insecticide (75% in 180 min) was achieved with a reaction mixture containing 5 mM ferrioxalate. However, under the same experimental conditions, degradation of pure esfenvalerate preceded much faster (99% in 60 min) and was 100% complete within 180 min reaction time.

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## 1. Introduction

The pyrethroids comprise a class of synthetic compounds whose structures are based on those of the naturally occurring pyrethrin insecticides. Pyrethroids are widely employed in urban areas for the control of pests in residential premises and on industrial sites (both interior and exterior locations), and in rural regions to protect a variety of agricultural crops [1]. The application of synthetic pyrethroid insecticides has increased substantially over the last few decades, concomitant with the decline in use of organophosphate pesticides that are far more toxic to birds and mammals [2,3].

Esfenvalerate [(S)- $\alpha$ -cyano-3-phenoxybenzyl-(S)-2-(4-chlorophenyl)-3-methylbutyrate] is a synthetic pyrethroid that is used against a wide range of pests including flies, moths and beetles. Because of its lipophilic nature, esfenvalerate is considered to be relatively immobile in the soil, showing only a small tendency to leach and, consequently, a low potential to pollute ground water. However, esfenvalerate can bind to particulate matter (clay, soil and sediment) and organic material that may be present in surface water in the form of a suspension [3]. Indeed, the levels of esfenvalerate that have recently been detected in water and sediment samples [4,5] suggest that the insecticide may represent a significant toxic hazard [6]. Furthermore, esfenvalerate has received considerable attention because of its adverse effects

on animal and human reproductive health [7–9]. In this context, esfenvalerate is considered a potential endocrine disruptor and may be capable of interfering with the proper functioning of estrogen, androgen and thyroid hormones in humans and animals [10]. Moreover, the pyrethroid insecticide has been included in the initial list of 58 pesticides to be screened under the Endocrine Disruptor Screening Program (EDSP) organised by the Environmental Protection Agency (EPA) [11]. The “Final Work Plan” adopted by the EPA in 2010 has also called for a detailed evaluation of esfenvalerate with respect to its potential ecological and human health risks.

There is clearly an urgent need to elaborate efficient technologies for the removal of insecticides from water, sediments and soils. Promising results have been achieved through the application of advanced oxidation processes (AOPs) based on the production of hydroxyl radicals that successively attack organic material in a non-selective manner [12]. Hydroxyl radicals may be generated under atmospheric or subcritical conditions of temperature and pressure using a variety of reacting systems involving homogeneous or heterogeneous phases and in the presence or absence of catalysts and/or reactive energy (electrochemical, UV-vis or ultrasound).

The Fenton reaction is based on the complex redox interaction between  $\text{Fe}^{2+}$  and hydrogen peroxide to generate hydroxyl radicals, and it is believed that the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  complexes so-formed play important catalytic roles in the further degradative processes. The efficiency of the interaction is improved under UV-vis irradiation [12], and the so-called photo-Fenton reaction has become one of the most widely used of AOPs in that it represents an

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environmentally friendly application of solar energy with commercial potential in the degradation of contaminants in effluents. While various photo-Fenton processes have been proposed recently for the degradation of toxic and non-biodegradable pollutants present in both low and high-concentrations [13–16], no publications have focussed on the degradation of esfenvalerate by AOPs. The aim of the present study was, therefore, to investigate the suitability and efficiency of photo-Fenton processes in the degradation of high-concentrations of esfenvalerate in aqueous emulsion using a recirculation flow-through UV photoreactor.

## 2. Experimental

### 2.1. Chemicals

Esfenvalerate (analytical standard; purity 97%) was obtained from Sigma-Aldrich (St. Louis, MO, USA; product number 46277), while a commercial formulation (Sumidan 25 EC®) containing 25 g L<sup>-1</sup> esfenvalerate was purchased from an agricultural store. All other reagents were of analytical grade unless otherwise stated. Methanol, acetonitrile and sulphuric acid were obtained from Mallinckrodt (Xalostoc, Edomex., Mexico), formic acid (reagent grade), sodium sulphite and ammonium molybdate were from Merck (Darmstadt, Germany), sodium oxalate and a 30% (w/w) solution of hydrogen peroxide (reagent grade) were from Ecibra (São Paulo, SP, Brazil), ferric nitrate nonahydrate was from Químis (Diadema, SP, Brazil), and ferrous sulphate heptahydrate was from Synthyl (Diadema, SP, Brazil). Purified water (resistivity 18.2 MΩ cm) was prepared using a Millipore (Eschborn, Germany) Milli-Q water purification system.

### 2.2. Photodegradation procedure

Hydrolysis and photodegradation experiments were carried out on the laboratory scale using a recirculation flow-through UV photoreactor, the cell of which was maintained in a Nova Ética (São Paulo, SP, Brazil) thermostatically controlled bath and irradiated using a Philips (Amsterdam, The Netherlands) 15 W UVC lamp (254 nm emission peak). In each experiment, the reactor was filled with 2 L of test solution and operated at a flow rate of 150 L h<sup>-1</sup> [determined using an Applitech (São Paulo, SP, Brazil) model AP300SS rotameter].

Preliminary experiments were performed in order to establish the kinetics of hydrolytic and photolytic degradation of the esfenvalerate-based commercial formulation. Hydrolysis was carried out in the absence of hydrogen peroxide, ferrous ions and light, and was performed using esfenvalerate emulsion (17 mg L<sup>-1</sup>) at its original pH of 6.3, and after adjustment to pH 2.5 by the addition of sulphuric acid. Photolysis was performed in the absence of hydrogen peroxide and ferrous ions, using an esfenvalerate emulsion (17 mg L<sup>-1</sup>; pH adjusted to 2.5) irradiated with UV light (254 nm). The kinetics of both the hydrolytic and photolytic reactions were established by determining the amounts of esfenvalerate remaining in sample aliquots of the reaction mixture that had been collected at appropriate reaction times within a 180 min reaction period.

In order to evaluate the behaviour of the esfenvalerate formulation during the photo-Fenton (Fe<sup>2+</sup>) procedure, an initial experiment was conducted using an esfenvalerate emulsion (17 mg L<sup>-1</sup>) containing 1 mM ferrous sulphate with pH adjusted to 2.5 by the addition of sulphuric acid. The reaction was performed by gradually adding hydrogen peroxide solution (30 mg mL<sup>-1</sup>) at a flow rate of 1.0 mL min<sup>-1</sup> over a period of 62 min to give a final peroxide concentration of 25 mM. The total reaction time was 180 min, being the period determined in equilibrium experiments for the

observation of a significant decrease in hydrogen peroxide concentration. In kinetic experiments, sample aliquots of the reaction mixture were taken at appropriate reaction times. Sodium sulphite (0.1 g) was added immediately to each sample in order to quench the peroxide and stop the Fenton reaction. The quenched sample was subsequently diluted with methanol, filtered through a 0.45 μm cartridge and immediately analyzed in order to evaluate the levels of esfenvalerate, total organic carbon (TOC) and hydrogen peroxide present.

For comparison purposes, photo-Fenton (Fe<sup>3+</sup>) experiments were performed in the presence of 1, 3 or 5 mM ferrioxalate (prepared by mixing appropriate amounts of ferric nitrate and sodium oxalate) with the pH of the reaction mixtures being adjusted to 2.5 by the addition of sulphuric acid.

### 2.3. Analytical procedures

Esfenvalerate was determined quantitatively by HPLC using a Shimadzu (Kyoto, Japan) Prominence LC 20 AT modular system comprising two CBM-20 A pumps, a CTO-10AS oven, a SIL 20A autosampler, an SPD-20A variable wavelength detector and an LC-10 Workstation Class data processor. Separations were carried out on a Supelco (Bellefonte, PA, USA) Supelcosil C-18 column (250 mm × 4.6 mm i.d.; 5 μm), protected by a Supelcosil C-18 column guard column (20 mm × 4.6 mm i.d.; 5 μm), eluted with mixtures of 0.5% formic acid in water (solvent A) and 0.5% formic acid in acetonitrile (solvent B) according to the program: 0–10 min, 60% B (isocratic); 10–11 min, 60–90% B (linear gradient); 11–30 min, 90% B (isocratic). The chromatographic conditions were: oven temperature 25 °C; flow rate 1.0 mL min<sup>-1</sup>; injection volume 20 μL (Rheodyne loop); and UV detection at 277 nm.

Mineralization of esfenvalerate in the commercial formulation (emulsion) and in the analytical standard (suspension) was evaluated through TOC analysis using a Shimadzu model TOC-V<sub>CPN</sub> analyzer. The TOC concentration included the carbon content of the target compound, the by-products generated during the experiment and (where appropriate) that of the ferrioxalate present in the reaction mixture. The TOC value (mg L<sup>-1</sup>) in the emulsion/suspension analyzed immediately after the addition of hydrogen peroxide (0 min) was set at 100%, and the percentage of mineralization was calculated from the level of residual TOC determined in an aliquot of the reaction mixture collected at final reaction time (180 min).

The amount of hydrogen peroxide consumed was estimated by measuring absorption at 350 nm (Cary-50 Scan UV-VIS spectrophotometer; Varian Inc., Lake Forest, USA) following the addition of ammonium molybdate to a sample of the reaction mixture [17].

## 3. Results and discussion

### 3.1. Preliminary investigation

Since the aim of the study was to evaluate the efficiency of the photo-Fenton degradation of esfenvalerate at high-concentrations, the initial amount of commercial formulation employed was always greater than its maximum solubility (0.002 mg L<sup>-1</sup>) in water at room temperature. Although the reaction mixture was in the form of an emulsion, constant circulation through the photoreactor maintained homogeneity and allowed reaction kinetics to be evaluated and compared under different experimental conditions.

No previous information was available concerning the behaviour of esfenvalerate during photo-Fenton (Fe<sup>2+</sup>) treatment and, hence, an initial study was carried out in which the concentrations of reagents (ferrous sulphate 1 mM; hydrogen peroxide 25 mM) were chosen arbitrarily. The detection limit of

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