



## Application of the response surface and desirability design to the Lambda-cyhalothrin degradation using photo-Fenton reaction

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### ABSTRACT

Lambda-cyhalothrin is a potent pyrethroid insecticide used widely in pest management. Detectable levels of the pyrethroid in agricultural watersheds are potentially toxic to aquatic organisms. There is little information in the scientific literature about degradation in aqueous media of the Lambda-cyhalothrin by Advanced Oxidative Process. A mathematical approach for the degradation of this compound has not yet been fully explored... The Central composite design (CCD) and response surface method (RSM) were applied to evaluate and optimize the interactive effects of two operating variables. The initial dosages of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> on photo-Fenton degradation of an aqueous solution of Lambda-cyhalothrin in a recirculation flow-through UV photoreactor were used. The remaining concentration of Lambda-cyhalothrin ( $y_1$ ) and the percentage removal of total organic carbon ( $y_2$ ) were the monitored factors since they are dependent parameters of  $y_1$  and  $y_2$ . According to analysis of variances (ANOVA) results, two proposed models can be used to navigate the design space with regression coefficient  $R^2 = 0.834$  and  $0.843$  for  $y_1$  and  $y_2$ , respectively. A multi-response optimization procedure, based on the global desirability of the factors, was performed to establish the best concentrations of hydrogen peroxide and ferrous sulfate that would allow the most efficient degradation of Lambda-cyhalothrin concomitant with a maximal removal of total organic carbon. The global desirability surface revealed that  $0.295 \text{ mmol L}^{-1}$  of ferrous sulfate and  $3.85 \text{ mmol L}^{-1}$  of hydrogen peroxide were close to the optimum conditions to satisfy both factors simultaneously using minimal amounts of reagents. These photo-Fenton conditions promoted 100% of Lambda-cyhalothrin degradation and 79.83% TOC removal (mineralization) in 120 min of reaction time.

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### 1. Introduction

In the last few decades the use of pyrethroids, a group of lipophilic analogues of naturally occurring pyrethrin insecticides, has increased substantially worldwide (Gan et al., 2008; Agency for Toxic Substances and Disease Registry, United States Department of Health and Human Services, 2011). While the pyrethroids generally exhibit strong insecticidal activities with relatively low mammalian toxicity, they can be adsorbed onto sediment particles and are, thus, potentially toxic to aquatic organisms including fish and amphipods (Rasmussen et al., 2008).

Lambda-cyhalothrin is a halogenated pyrethroid comprising a 1:1 mixture of two stereoisomers, namely, [(S)- $\alpha$ -cyano-3-phenoxybenzyl-(Z)-(1R,3R)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dime-

thylcyclopropanecarboxylate and (R)- $\alpha$ -cyano-3 phenoxybenzyl-(Z)-(1S,3S)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate]. This potent insecticide is widely employed in insect pest control in agriculture and public health, as well as in gardens and household environments (Amweg and Weston, 2005). Lambda-cyhalothrin is, however, highly lipophilic and binds rapidly and extensively to organic matter and sediment particles, resulting in its rapid dissipation from the water column. Concentrations of the pyrethroid in the range  $0.11\text{--}0.14 \mu\text{g L}^{-1}$  have been detected in water from agricultural watersheds, while levels between 0.003 and  $0.315 \mu\text{g g}^{-1}$  dry weight have been found in sediments (California Department of Pesticide Regulation, 2011). Various ecotoxicological studies conducted in the laboratory and in the field have revealed a well-established pattern of effects of Lambda-cyhalothrin on water quality (Hand et al., 2001; Roessink et al., 2005). Furthermore, potential toxicity toward aquatic organisms of the pyrethroid at concentrations encountered in water courses and sediments has been confirmed (Lawler et al., 2007; Wang et al., 2007), and single-

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species toxicity assays have revealed that insect larvae and macrocrustaceans are particularly sensitive (Schroer et al., 2004; Maund et al., 1988).

The removal of pesticides from the environment remains especially challenging since the technologies associated with conventional treatments are not capable of eliminating the contaminants efficiently. Currently, chemical oxidation appears to represent a key methodology in clean-up treatments for wastewater and effluents. In particular, combinations of chemical oxidants (such as hydrogen peroxide), iron salts, semiconductors and/or UV–visible irradiation can give rise to the formation of hydroxyl radicals ( $\cdot\text{OH}$ ) that are very powerful oxidants with high oxidation potential (2.8 V vs standard hydrogen electrode) (Ikehata and El-Din, 2006). Such advanced oxidation processes (AOPs) have gained considerable popularity over recent years and have been shown to offer viable alternatives to conventional wastewater treatments in that they are relatively cheap to apply and are able to promote the partial or total oxidation of a range of pesticides (Ikehata and El-Din, 2006; Jiménez et al., 2011). However, to the best of our knowledge, no studies have yet been published concerning the elimination of Lambda-cyhalothrin residues from water by an AOP. In addition, the degradation of the Lambda-cyhalothrin in aqueous media using a mathematical approach has not yet been fully explored in the scientific literature.

The aim of the present investigation was to determine the suitability of the photo-Fenton process for the degradation of Lambda-cyhalothrin in aqueous medium, and to optimize the procedure for maximum efficiency in the removal and mineralization of the active ingredient and of other organic constituents present in a commercial formulation of the insecticide. Process optimization is frequently carried out by application of chemometric tools (Rozasa et al., 2010; Arslan-Alaton et al., 2010). Such strategies are generally more efficient and economical than the univariate approach, since they allow interactions between two or more variables to be studied within the context of influence of all other system parameters (Bruns et al., 2006). The central composite design (CCD) and response surface methodology (RSM) were proposed to evaluate the influences of individual factors ( $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentrations) as well as their interactive influences. Two interrelated parameters such as the remaining concentration of Lambda-cyhalothrin and the percentage removal of total organic carbon were the factors evaluated. Moreover, the global desirability of the parameters was developed to provide an optimal region to satisfy the operating specifications. The relative significance of several affecting factors, even in the presence of complex interaction, is simultaneously evaluated when those empirical statistical modeling techniques are employed for multiple regression analysis using quantitative data obtained from properly designed experiments to solve multivariable equations (Montgomery et al., 2001; Vining, 2003; Ahmadi et al., 2005). The suitability of the proposed model was tested by analysis of variance (ANOVA).

## 2. Experimental

### 2.1. Chemicals

All reagents were of analytical grade unless otherwise stated. Methanol, acetonitrile and sulfuric acid were obtained from Mallinckrodt (Ecatepec, MX, Mexico), a 30% (w/w) solution of hydrogen peroxide (reagent grade) was from Ecibra (São Paulo, SP, Brazil) and 1,10-phenanthroline monohydrate was obtained from Sigma–Aldrich (St. Louis, MO, USA). Ammonium acetate and ferrous sulfate heptahydrate were from Synth (Diadema, SP, Brazil). Lambda-cyhalothrin (analytical standard; 97% pure) was obtained from Sigma–Aldrich (St. Louis, MO, USA; product number 31058), while

a commercial formulation (Brasão CS<sup>®</sup>; Helm, São Paulo, SP, Brazil) containing 50 g L<sup>-1</sup> of Lambda-cyhalothrin was purchased from a local agricultural store. Purified water (resistivity 18.2 MΩ) was prepared using a Millipore (Eschborn, Germany) Milli-Q water purification system.

### 2.2. Experimental procedures

The hydrolysis and photodegradation experiments were carried out at laboratory scale using a recirculation flow-through UV photoreactor (Fig. 1), with the cell maintained in a thermostatically controlled bath (Nova Ética, São Paulo, SP, Brazil) and irradiated using the core of a Philips (Amsterdam, The Netherlands) 15 W UVC lamp ( $\lambda_{\text{max}}$  254 nm; maximum incident photon flux  $3.33 \cdot 10^{-13}$  photons s<sup>-1</sup>). 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. The kinetic of the hydrolytic and photolytic degradation reactions of the Lambda-cyhalothrin-based commercial formulation was determined in preliminary experiments. The hydrolysis of an aqueous solution of Lambda-cyhalothrin (10 mg L<sup>-1</sup>; 0.022 mmol L<sup>-1</sup>) at its original pH of 6.2, and after the addition of sulfuric acid to pH 2.5 which is the reported optimum pH value for the photo-Fenton process (Trovó et al., 2011), was performed in the absence of  $\text{Fe}^{2+}$  ions, hydrogen peroxide and light. The photolysis of an aqueous solution of Lambda-cyhalothrin (10 mg L<sup>-1</sup>; pH adjusted to 2.5) irradiated with UV light (254 nm) was carried out in the absence of  $\text{Fe}^{2+}$  ions and hydrogen peroxide. The kinetic of the degradation reactions was established by determining the amounts of Lambda-cyhalothrin remaining in aliquots of the reaction mixtures collected at appropriate reaction times within a 120 min period.

In order to evaluate the behavior of the insecticide during the photo-Fenton ( $\text{Fe}^{2+}/\text{UV}$ ) procedure, ferrous sulfate heptahydrate

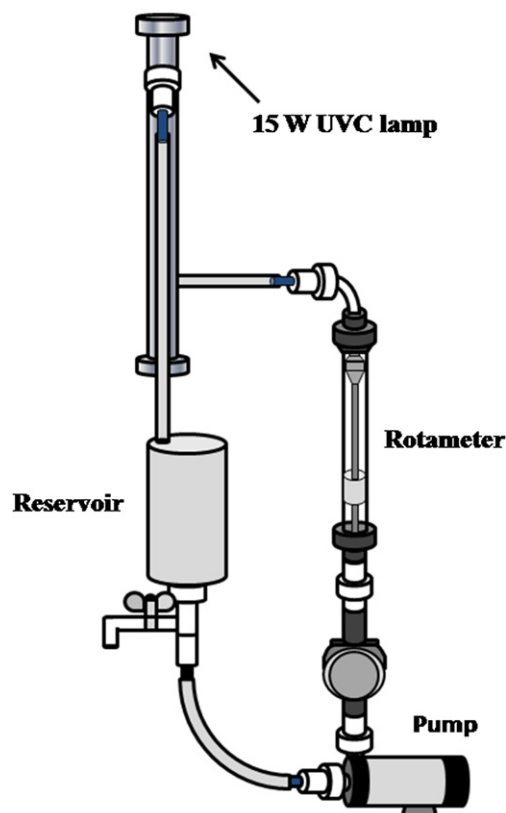


Fig. 1. Scheme of recirculation flow-through UV photoreactor.

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