Bioallethrin degradation by photo-Fenton process in acetonitrile/water and aqueous β-cyclodextrin solutions

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ABSTRACT

Bioallethrin (Bio) is an insecticide that chemically and functionally belongs to the family of the synthetic insecticides named pyrethroids. In this work the degradation of Bio is studied by the photo-Fenton and photo-Fenton-modified processes. The first one produces the complete mineralization of Bio in less than one hour of irradiation. However, due to the low solubility of Bio in water, different modifications of the photo-Fenton process were tested. First, the photo-Fenton process was carried out in mixtures of different acetonitrile/water proportions. Although acetonitrile deactivates the hydroxyl radical, the main oxidizing agent in the photo-Fenton process, a Bio degradation greater than 90% is achieved in 80 min of reaction. Second, degradation of Bio was evaluated by photo-Fenton in a medium with β-cyclodextrin (β-CD), where the Bio solubility could be increased at least thirty-five times. The association constant of Bio to β-CD was measured to be $1933 \pm 300\,M^{-1}$ and molecular simulation results indicate a 1:1 inclusion complex stabilized by the formation of intermolecular H-bonds. The Bio degradation rate in this medium was similar to that observed in aqueous media. The use of β-CD presents a friendly alternative to the environment for the degradation of the pyrethroid insecticide.
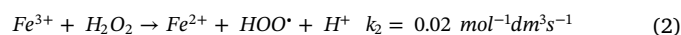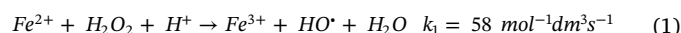
1. Introduction

Pyrethroids (Pyr) are synthetic derivatives of pyrethrins developed in order to maintain the effective insecticidal activity of the pyrethrins while increasing stability to light and residence time in the environment [1]. However, they are more toxic to mammals than natural insecticides and are widely employed in urban areas for the control of pests in residential premises, on industrial sites and in rural regions to protect a variety of agricultural crops. 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 [2–4]. Therefore, the occurrence and potential environmental impact of Pyr have taken considerable attention [4,5]. The intensive use of these Pyr has resulted in environmental contamination of surface and groundwater [4,6]. Bioaccumulation of Pyr in edible river fish samples has also been recently reported [7].

Bio (Fig. 1) is the mixture of two allethrin isomers, [1R,trans;1R] and [1R,trans;1S] in an approximate ratio of 1:1, the first potent synthetic pyrethroid [8,9]. Its chemical structure is composed by the chrysanthemic acid and 2-cyclopenten-1-one moieties.

The presence of these compounds in aqueous media motivates the need of developing methods for their elimination. When no complete removal of certain compounds can be guaranteed, conventional wastewater treatment plants themselves become major sources of water contamination [10,11]. To overcome this issues, Advanced Oxidations Processes (AOPs) are considered a viable alternative due to its ability to oxidize organic pollutants reaching high levels of mineralization [12,13].

The Fenton process is in one of the most reported AOPs and appears as an attractive alternative for removing organic contaminants [14,15]. According to a simplified mechanism, the active species can be generated by the reaction of hydrogen peroxide with ferrous and ferric ions as shown in reactions (1) and (2) [16,17]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO^\bullet + H_2O \quad k_1 = 58\ mol^{-1}dm^3s^{-1} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^\bullet + H^+ \quad k_2 = 0.02\ mol^{-1}dm^3s^{-1} \quad (2)$$

The hydroxyl radical formed in reaction (1) can react with organic compounds by H abstraction or addition to alkenes, alkynes or aromatic rings. However, since the reaction rate constant of reaction (2) is much lower than that of reaction (1), the transformation between the ferric
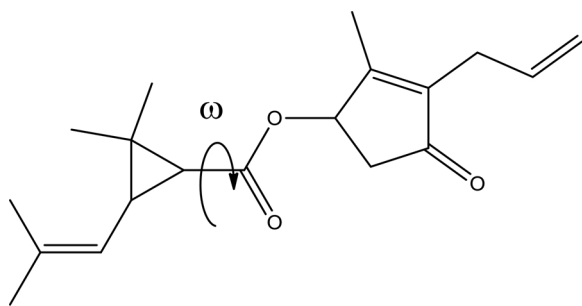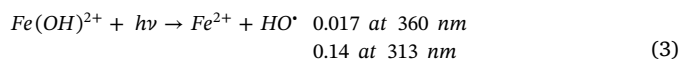
Fig. 1. Chemical structure of Bioallethrin (Bio).

ions and the ferrous ions and the production of active species are limited by reaction (2).

It was found that UV irradiation of the Fenton system enhanced significantly the degradation rate of many organic substances [14,16,18–20] due the direct of HO· radical formation and Fe^{2+} regeneration from photolysis of the complex $[Fe(OH)]^{2+}$ (reaction 3) [10]:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \quad \begin{matrix} 0.017 \; at \; 360 \; nm \\ 0.14 \; at \; 313 \; nm \end{matrix} \quad (3)$$

Furthermore, Fenton and photo-Fenton processes are preferably employed in aqueous media because the hydroxyl radical reacts with a diffusion-controlled rate constant with most organic solvents [21]. This diminishes the efficiency of the process or, worse, it can cause that the process is impracticable in organic solvents. In order to increase the solubility of organic compounds to be degraded, different strategies have been reported: Chen et al. [16] have studied the degradation by photo-Fenton of methyl orange in methanol solution. Lindsey et al. [19] have employed β-cyclodextrin (β-CD) or carboxymethyl-β-cyclodextrin to improve the effectiveness and selectivity of Fenton degradation of hydrophobic organic compounds. While Mousset et.al. [22] have used two solubilizing agents (hydroxypropyl-beta-cyclodextrin and Tween 80) in order to degrade phenanthrene by electro-Fenton. The effectiveness and selectivity of Fenton degradation to organic compounds are attributed to the simultaneous complexation of Fe^{2+} and organic compound with β-CD or derivatized cyclodextrin *via* formation of a ternary pollutant-cyclodextrin-iron complex [19,22].

With regard to the use of the photo-Fenton process for the pyrethroids degradation, the Fenton oxidation of 3-phenoxybenzyl acetate as a model of synthetic pyrethroids was examined in aqueous acetonitrile [23]. Colombo et al. [3] studied the degradation of a synthetic pyrethroid, Esfenvalerate [(S)-α-cyano-3-phenoxybenzyl-(S)-2-(4-chlorophenyl)-3-methylbutyrate], by the classic photo-Fenton process and using ferrioxalate as a source of Fe(II). This latter variant proved to be much more efficient, however, complete mineralization was not achieved due to the formation of recalcitrant organic by-products [3]. However, the pyrethroids studied by Katagi [23] and Colombo [3] have a 3-phenoxybenzyl residue, which is not present in Bio.

Due to the low solubility of bioallethrin, herein a comparative study of the degradation of Bio by photo-Fenton in acetonitrile/water mixtures and in aqueous solutions of β-cyclodextrin was carried out.

2. Materials and methods

2.1. Materials

Bioallethrin 97% (Bio) was purchased from Aldrich. Ferrous sulphate hexahydrate, hydrogen peroxide 30% w/v and acetic acid were from Cicarelli. Perchloric acid 70–72 % was from Merck. All chemicals were used as received. Water was triply distilled. Methanol (MeOH), acetonitrile (ACN) and chloroform, all HPLC quality, were provided by Sintorgan.

Solution pH was adjusted by addition of concentrated perchloric acid.

2.2. Steady-state photolysis

The photo-Fenton experiments were performed in a photochemical reactor chamber (Rayonet RPR-200) containing eight 6-W fluorescent black lamps with emission centred at 354 nm. The lamps were warmed up for 10 min before irradiation to reach constant output.

2.3. Absorption measurements

Ground state absorption spectra were registered employing a Hewlett Packard 8452 A diode array spectrophotometer provided with a ChemStation advanced software for multicomponent analysis (MCA).

2.4. Determination of the association constant (Kas) between Bioallethrin and β-CD

The association constant (*Kas*), was evaluated through the Scoot method [24,25], using Eq. (1).

$$\frac{[Bio_t][\beta - CD_t]L}{\Delta A} = \frac{1}{\Delta\varepsilon}[\beta - CD_t] + \frac{1}{K_{as}\Delta\varepsilon} \quad (1)$$

where ΔA is the difference in absorbance between Bio in the absence and presence of the β-CD at 230 nm, $\Delta\varepsilon$ is the difference in the molar absorptivity between the free and included insecticide and L is the path length.

2.5. Measurement of the solubility of Bio in water and in H₂O:ACN (10:90) system

The solubility of Bio in the different media was measured by UV–vis absorption spectroscopy [26]

2.6. Photo-Fenton reaction in acetonitrile/water system

Since the absorption spectrum of Bio overlaps with the absorption spectra of the Fenton reagents, the MCA method was used to monitor Bio consumption under different reaction conditions.

2.7. Experimental determination of reactive rate constant of Bio with HO· ($k_{OH·}$)

The rate constants for the reaction between Bio and HO· in different media (reaction 4) were determined using competitive kinetics according to Haag et al. [27]

$$Bio + HO^{\bullet} \rightarrow Products \quad k_{HO\cdot} \quad (4)$$

The $k_{OH·}$ value was determined by:

$$k^{HO\cdot} = k_{HO\cdot}^{Phe} \frac{Ln([Bio]_0/[Bio]_t)}{Ln([Phe]_0/[Phe]_t)} \quad (2)$$

$k_{HO\cdot}$ y $k_{HO\cdot}^{Bio}$ are the rate constants for the reference compound an substrate, respectively. Phenol (Phe) was used as reference ($k_{HO\cdot}^{Phe} = 8.41 \times 10^9 \; M^{-1}s^{-1}$) [28].

2.8. CG–MS experiments

The chloroform extract of the aqueous photo-Fenton degradation of Bio was measured by CG-MS. A MS-GC Hewlett Packard 5890 Gas Chromatograph, 5972 Mass Selective detector, Column HP-5 (Crosslinked 5% PH ME Silicone, 30 m × 0.32 mm) was used in chromatography analysis.

The ionization energy was 70 eV. Injector temperature was 200 °C and the oven temperature was programmed as follows: initial