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

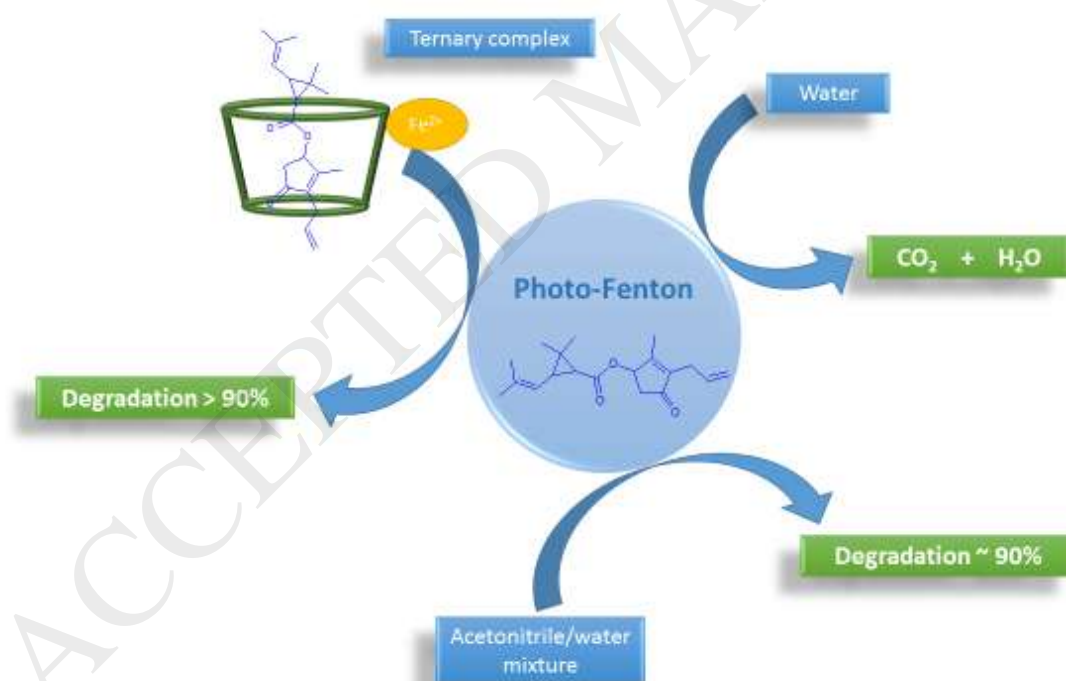
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Graphical abstract



Highlights

- Bioallethrin degradation was studied by photo-Fenton and modified photo-Fenton processes
- Bioallethrin is degraded by photo-Fenton in water, acetonitrile / water mixture and in aqueous solution of β -cyclodextrin
- The association constant of Bioallethrin to β -cyclodextrin was measured to be $1933 \pm 300 \text{ M}^{-1}$
- The degradation rate of Bioallethrin by photo-Fenton is similar in water than in an aqueous solution of β -cyclodextrin

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 $1933 \pm 300 \text{ M}^{-1}$ 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.

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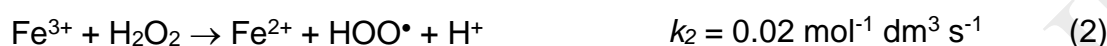
Introduction

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 (Figure 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] [43].

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]:



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 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 Fe²⁺ regeneration from photolysis of the complex [Fe(OH)]²⁺ (reaction 3) [10]:



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.

Materials and Methods

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.

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.

Absorption measurements

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

Determination of the association constant (K_{as}) between Bioallethrin and β -CD

The association constant (K_{as}), was evaluated through the Scoot method [24,25] , using Eq. 1.

$$\frac{[Bio_t][\beta - CD_t]L}{\Delta A} = \frac{1}{\Delta\epsilon}[\beta - CD_t] + \frac{1}{K_{as}\Delta\epsilon} \quad \text{Eq. 1}$$

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

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

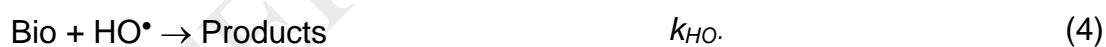
The solubility of Bio in the different media was measured by UV-Vis absorption spectroscopy [26]

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.

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]



The k_{OH} value was determined by:

$$k_{\text{HO}^{\bullet}} = k_{\text{HO}^{\bullet}}^{\text{Phe}} \frac{\text{Ln}([Bio]_0/[Bio]_t)}{\text{Ln}([Phe]_0/[Phe]_t)} \quad \text{Eq. 2}$$

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

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 x 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 temperature 120 °C, final temperature 200 °C, heating rate 10 °C / min. Helium was used as a carrier gas with a constant flow of 0.8 ml / min.

HPLC experiments

The Bio degradation was determined by HPLC analysis employing a Waters 1525 equipment coupled to a UV-Vis detector (Waters 2489). A stainless steel analytical column (Varian SP-C8-IP-5 5 μ m 4 x 150 mm) was used for the chromatographic analysis. The mobile phase consisted of H₂O:ACN (10:90); the aqueous medium used to prepare the mobile phase was an 1% v/v solution of acetic acid. The flow rate was adjusted to 1 mL·min⁻¹. The detection wavelength was 230 nm.

TOC analysis

Total organic carbon (TOC) was determined spectrophotometrically after persulphate oxidation of carbon to carbon dioxide and colour change of a pH indicator (Hach, DR/2500, Method 10129).

Molecular Modeling

A relaxed potential energy surface was calculated at PM6 (Parametric Model 6) level of theory on the molecular geometry of bioallethrin. The scanned parameter was the dihedral angle ω in a 0°-360° range, with a step size of 10° (Figure 1). For β -CD the initial geometry was constructed according to crystallographic data [29]. A previously adopted procedure was followed to simulate the inclusion process, [25] and two possible orientations were considered: the “Head Up” and “Head Down” orientations, in which bioallethrin initially points toward the primary and the secondary hydroxyls of β -CD, respectively. A total of 18 structures for each orientation were calculated, in order to ensure that the guest drug passes completely through the β -CD cavity. The PM6 optimized geometries of minimum energy were further optimized using the DFT B3LYP/6-31G(d) level of theory. In order to quantify the strength of relevant intermolecular interactions in the inclusion complex a NBO analysis was performed on the most stable structure. The stabilization energy (ΔE_{ij}) was calculated using the following equation:

$$\Delta E_{ij} = \frac{q_i F_{ij}}{(\varepsilon_j - \varepsilon_i)} \quad \text{Eq. 3}$$

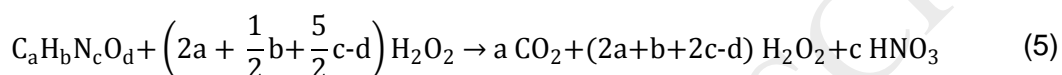
Where q_i is the donor orbital occupancy, ε_i and ε_j are the energies of the interacting orbitals, and F_{ij} is the off-diagonal NBO Fock matrix element [30]. The ΔE_{ij} values are useful to estimate the energy of a donor-acceptor interactions, like H-bonds. All the calculations were performed with GAUSSIAN 09 software packages.

Results and discussion

Photo-Fenton degradation of Bio in H₂O

The objective of this work is to evaluate the degradation of Bio by the process of photo-Fenton in different media. Bio degradation by photo-Fenton in aqueous solution was studied as a first step using typical concentrations ($[\text{Fe}^{2+}] = 5 \times 10^{-5} \text{ M}$; $[\text{H}_2\text{O}_2] = 10^{-2} \text{ M}$ and $\text{pH} = 3$) for the photo-Fenton reagents according to what has been reported for the degradation of different pesticides [3,31] and organics contaminants [32,33].

According to Wang *et al.* [34] several papers have studied a minimum theoretical dose of H_2O_2 to guarantee the complete mineralization of the pollutant. For example for the following reaction:



one mole of $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$ requires $(2a + (1/2)b + (5/2)c - d)$ moles de H_2O_2 . In the case of Bio the minimum dose of H_2O_2 is $2.4 \times 10^{-3} \text{ M}$, whereby the concentration chosen (10^{-2} M) ensure the complete degradation of Bio.

Figure 2 shows the degradation of Bio by the process of photo-Fenton, where it can be observed that after 40 min of irradiation Bio was completely degraded. In the measurements of CG-MS at different reaction times, only the decrease of a peak at 14 minutes corresponding to the Bio was detected (data not shown). By means of HPLC or CG-MS measurements, the appearance of products was not observed. A complete mineralization of Bio is achieved after 60 min of reaction (see TOC, Figure 2 Inset A).

A comparison of Bio photodegradation-rate with those of the archetypal surface-water-contaminant phenol (Inset B, Figure 2) indicates that Bio degradation occurs in a moderately fast fashion than the model contaminants, within a common overall time-scale. The primary

photoprocesses initiating the degradation, *via* HO• involvement, seems to be quite similar for the two compounds. The natural degradation of Bio by reaction with HO• appears as a plausible process, as evaluated under simulated environmental conditions. Additionally, from the competitive method a value of $(1.1 \pm 0.1) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ was determined reaction (4) in aqueous solution (Inset B, Figure 2).

Photodegradation of Bio in ACN/H₂O mixtures

Since no previous information was available concerning the behaviour of Bio during the photo-Fenton treatment in a non-aqueous media, an initial study of the ACN effect on was carried out, for which the concentration of reactants ($[\text{Fe}^{2+}] = 10^{-5} \text{ M}$ and $[\text{H}_2\text{O}_2] = 10^{-3} \text{ M}$) were chosen arbitrarily. The pH value of 3.0 for the reaction mixture was chosen according to a literature report. Although there is not an optimal pH-value, a pH-range from 2.0 to 4.0 is reported as the optimum in Fenton processes. [14,34]

The addition of ACN allows the dissolution of Bio in the Fenton reaction medium. For example, the use of 10% acetonitrile in water allows to increase the solubility from $2.3 \times 10^{-5} \text{ M}$ to $7.3 \times 10^{-5} \text{ M}$ (Inset Figure 3). Figure 3 shows the Bio degradation in different ACN/Water proportions and the following photo-Fenton conditions: $[\text{Fe}^{2+}] = 5 \times 10^{-5} \text{ M}$; $[\text{H}_2\text{O}_2] = 10^{-2} \text{ M}$ and $\text{pH} = 3$. For the irradiation times investigated there is no significant variation in the degradation of Bio for the different proportions of ACN used (10-40%). The decrease in the percentage degradation of Bio with respect an aqueous solution can be attributed to reaction (6):

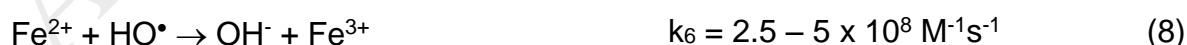


From these results, a 10% ACN / water mixture was chosen as the solvent for further assays. Then, experiments at pH 3 were designed using $[\text{Bio}] = 6 \times 10^{-6} \text{ M}$ and the effect of the two independent variables $[\text{H}_2\text{O}_2]$ (Inset Figure 4) and $[\text{Fe}^{2+}]$ (Figure 4) were evaluated. The photo-Fenton process was carried out using $[\text{Fe}^{2+}]$ in the range from 10^{-5} M to 10^{-4} M and H_2O_2 concentrations from $5 \times 10^{-4} \text{ M}$ to 10^{-2} M . The %Bio degradation at 60 min irradiation and the pseudo-first order rate constants are shown in Table 1.

The results show that for a $[\text{Fe}^{2+}] = 50 \times 10^{-6} \text{ M}$ the variation of the H_2O_2 concentration in a 10 % ACN/water mixture produces changes of 40% in the rate of degradation of Bio. The highest value of Bio degradation is obtained at the lowest concentration of H_2O_2 , probably as a consequence of the reaction:



In contrast, the variation of $[\text{Fe}^{2+}]$ has a more pronounced effect on the degradation rate of Bio, the degradation rate of Bio vary from 8.6 to 39.5 for $[\text{Fe}^{2+}]$ of $10 \times 10^{-6} \text{ M}$ and $50 \times 10^{-6} \text{ M}$ respectively. However, with the increase of $[\text{Fe}^{2+}]$ to 10^{-4} M there is a decrease in the rate and % degradation. This can be attributed to the reaction of Fe^{2+} with HO^\bullet , as reported for the Fenton system in aqueous solution [35]:



Once the photo-Fenton system was characterized in a medium with 10% ACN, we decided to work under the following conditions: $[\text{Fe}^{2+}] = 50 \times 10^{-3} \text{ M}$, $[\text{H}_2\text{O}_2] = 0.01 \text{ M}$ and $\text{pH}=3$. In order to evaluate the effect of ACN under these conditions, the same experiments were performed in the photo-Fenton process without acetonitrile and without light (Fenton reaction). Results are shown in Table 2.

In all cases it was observed that the degradation rate of Bio is much lower in the Fenton process compared to the photo-Fenton system. This is attributed to the lower steady-state concentration of HO^\bullet since the contribution of HO^\bullet from the reaction (3) does not occur. In addition, the percentage of degradation is slightly lower in an ACN/ H_2O medium due to reaction (6). The degradation rate of Bio increases by 35 in the photo-Fenton process performed in water, whereas it is enhanced 17 times when the medium has 10% ACN. It is also noted that the % degradation of Bio is much higher in the photoinduced processes and the addition of ACN causes an increment by factor of two in the degradation time and halves the value of k . This correlates with the value of $(3.1 \pm 0.3) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ obtained for k_{HO^\bullet} (reaction (4) in a medium with 10% ACN (Inset B, Figure 2) which correspond to 30% of the value found in water.

Photo-Fenton in β -cyclodextrin media

As Bio has a low solubility in water, a β -CD solution was used as a means to increase its solubility. From Figure 5, as the β -CD concentration increases there are spectral changes in the Bio spectrum attributable to the formation of an inclusion complex between β -CD and Bio (β -CD-Bio). Using the Scott method, described in the materials and methods

section, the association constant (K_{as}) between Bio and β -CD (Figure 5) was determined obtaining a value of $(1933 \pm 300) \text{ M}^{-1}$.



The β -CD-Bio formation increased the solubility of Bio to $1.1 \times 10^{-4} \text{ M}$ (Figure 3, inset) for a $[\beta\text{-CD}] = 5 \times 10^{-3} \text{ M}$, a typical β -CD concentration used in Bio degradation by photo-Fenton. Moreover, by a simple calculation taking into account the K_{as} and the solubility of Bio in water an increase in 38 times in Bio solubility was estimated.

Results of Bio degradation by Fenton and photo-Fenton processes with and without β -CD under typical conditions for the photo-Fenton process are shown in Figure 6 (Inset) and Table 2. As shown in Figure 6 (Inset), the addition of β -CD practically does not modify the rate of the Fenton reaction, whereas in the case of photo-Fenton the incorporation of β -CD produces a decrease in the rate of the photo-Fenton process, from 0.14 min^{-1} without β -CD to 0.091 min^{-1} with β -CD. But the percentage degradation of Bio achieved does not change.

Regarding the interaction of Fe^{2+} with β -CD, Lindsey *et al.* [19] reported a value of 120 ± 10 for the association constant for the β -CD- Fe^{2+} (reaction (10)) complex, which has been determined by a spectroscopic method [19].



In the typical conditions for the photo-Fenton process ($[\text{H}_2\text{O}_2]=0.01 \text{ M}$, $[\text{Fe(II)}] = 50 \times 10^{-6} \text{ M}$, $[\text{Bio}] = 6 \times 10^{-6} \text{ M}$, $\text{pH}=3$) and $[\beta\text{-CD}] = 10^{-3} \text{ M}$ almost 100 % of Bio is included in the β -CD forming the β -CD-Bio complex and the 99 % of Fe^{2+} is bound to β -CD. However, for

this β -CD concentration, 5 % of the β -CD molecules are forming a β -CD-Bio complex, 0.6 % of the β -CD molecules are bonded to Fe^{2+} and the remainder are free in solution. Therefore, assuming that the β -CD-Bio association processes and the β -CD- Fe^{2+} are independent, there would be only 0.03 % of the β -CD (5 % of Bio) as a ternary complex.

In order to modify these ratios photo-Fenton experiments with different concentrations of Fe (II) were made, the results are shown in Figure 6, where it is observed that in the system with and without β -CD there is an increase in the rate of degradation of Bio with the increase of $[\text{Fe}^{2+}]$. This can be attributed to the increase in the concentration of the ternary complex, for a $[\text{Fe}^{2+}] = 500 \times 10^{-6} \text{ M}$ the probability of formation of the ternary complex is 0.3% which implies that 50% of Bio is forming part of the complex. For all $[\text{Fe(II)}]$ there is a small decrease in the rate of degradation of Bio in presence of β -CD, but always a degradation of 95% of Bio is observed. This small difference can be attributed to a decrease in efficiency due to the reaction of HO^\bullet with β -CD. For the concentration of β -CD (10^{-3} M) used in this experiment, taking a value $4.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ reported for the rate constant between HO^\bullet and β -CD, HO^\bullet is expected to be consumed with a pseudo first order rate constant of $4.2 \times 10^6 \text{ s}^{-1}$. This value is greater than the pseudo-first order constant of $5 \times 10^4 \text{ s}^{-1}$ obtained for Bio under these conditions.

Molecular Modeling

The structure of the β -CD-Bio inclusion complex was also investigated using Quantum Mechanics simulations. The stabilization energy (ΔE) of the inclusion complex formation was calculated at PM6 level of theory with the equation

$$\Delta E = E_{\text{complex}} - (E_{\text{bioallethrin}} + E_{\beta\text{CD}}) \quad \text{Eq. 4}$$

The obtained results for the two possible orientations are reported in Table 3. It is observed that the head down orientation is energetically favorable by almost 14 kJ mol⁻¹. This energy difference is increased at 34.9 kJ/mol when is calculated with the B3LYP/6-31G(d) level of theory. In fact, at this level of theory the head up complex has an unfavorable (positive) ΔE . The DFT optimized structure of the β -CD-Bio complex in head down orientation is illustrated in Figure 7.

It can be observed that the alkyl-cyclopropane moiety of Bio is completely embedded in the CD cavity while the allyl-cyclopentenone remains outside. In addition, the relative position of the carbonyl group favours the interaction with the primary hydroxyls of β -CD. Particularly, two intermolecular hydrogen bonds are formed between the C=O of Bio and OH groups of β -CD. The bond length and angles of these interactions are 1.789 Å and 170 ° for the first one and 1.918 Å and 152 ° for the second one, respectively. According to the NBO analysis, the stabilization energies of the H-bonds (ΔE_{ij} in Eq. 3) were 82.96 and 18.45 kJ mol⁻¹, indicating that these are strong interactions that stabilize the complex formation.

CONCLUSION

In typical conditions of the photo-Fenton process, the mineralization of Bio in aqueous solution in 60 min is achieved. However, the low solubility of Bio makes the use of this technique complicated or impractical for the treatment of large amounts of this insecticide. Although the use of acetonitrile/water solutions allows a higher Bio concentration, the reaction of HO[•] with acetonitrile makes the degradation rate of Bio slower. But at sufficiently

long irradiation times a degradation percentage of Bio similar to that obtained in aqueous medium is achieved. This system has the intrinsic disadvantage that incorporates not environmentally-friendly solvent.

On the other hand, the employment of aqueous β -CD as a solvent presents a friendly system that allows to increase the solubility of Bio and degradation of the insecticide at a similar rate that in water. Molecular simulation results indicate that β -CD forms a 1:1 inclusion complex with bioallethrin, and that this complex is stabilized by the formation of intermolecular H-bonds.

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Figure captions

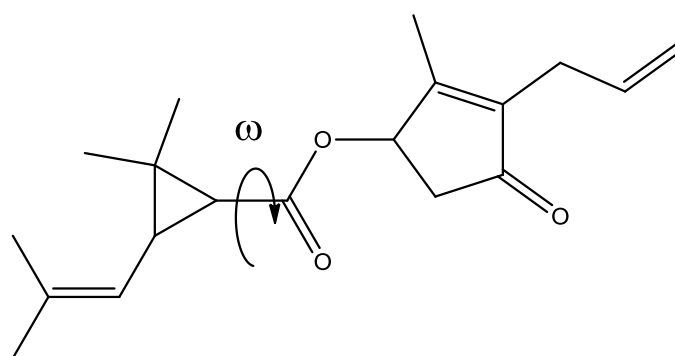


Figure 1: Chemical structure of Bioallethrin (Bio)

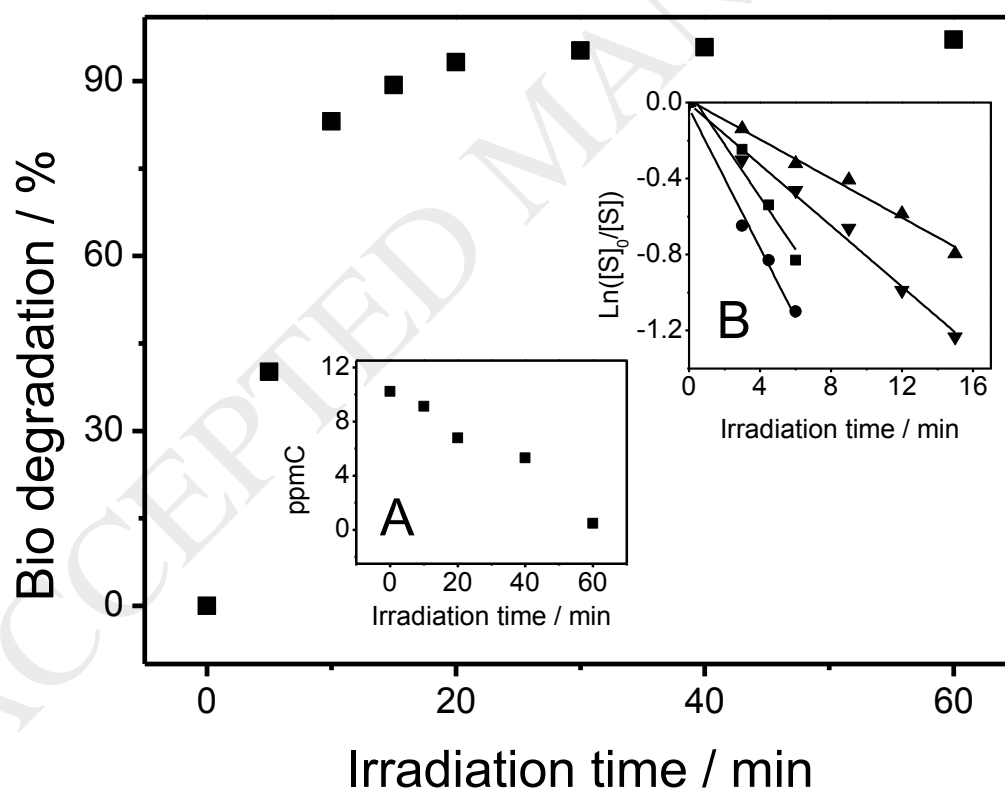


Figure 2: % Degradation of Bioallethrin by photo-Fenton in aqueous media at different irradiation times. $[\text{Bio}]_0 = 6 \times 10^{-6} \text{ M}$ $[\text{Fe}^{2+}] = 5 \times 10^{-5} \text{ M}$, $[\text{H}_2\text{O}_2] = 10^{-2} \text{ M}$ and $\text{pH} = 3$. Inset A: TOC variation of the photo-Fenton process in aqueous media. $[\text{Bio}]_0 = 6 \times 10^{-6} \text{ M}$ $[\text{Fe}^{2+}] = 5 \times 10^{-5} \text{ M}$, $[\text{H}_2\text{O}_2] = 10^{-2} \text{ M}$ and $\text{pH} = 3$. Inset B: k_{HO} determination for Bio in different media: (\blacktriangle) 10% ACN/water, (\blacktriangledown) $[\beta\text{-CD}] = 10^{-3} \text{ M}$, (\bullet) water. (\blacksquare) $[\text{Phenol}] = 10^{-5} \text{ M}$ in water

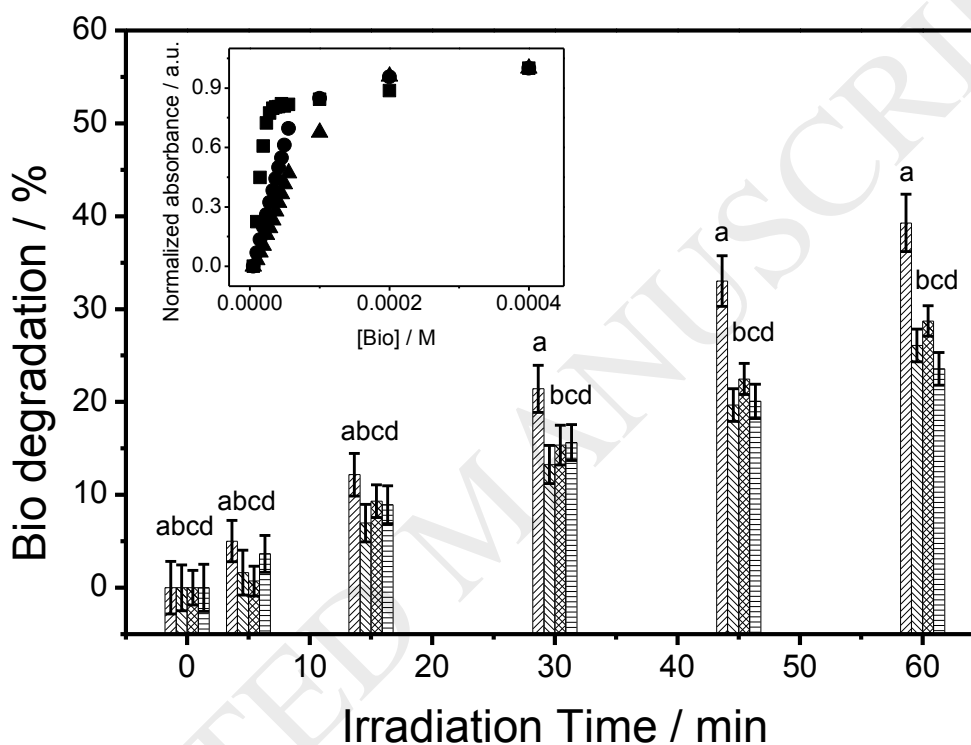


Figure 3: Percent degradation as a function of irradiation time of Bio at different ACN/water mixtures, $[\text{Fe}^{2+}] = 50 \times 10^{-6} \text{ M}$, $[\text{H}_2\text{O}_2] = 10 \times 10^{-3} \text{ M}$, $\text{pH} = 3$; (a) 0 % ACN (b) 10 % ACN (c) 20% ACN (d) 40% ACN. Inset: Normalized absorbance of the supernatants of Bio in : (\blacksquare) Water; (\bullet) 10 % ACN and (\blacktriangle) $5 \times 10^{-3} \text{ M}$ $\beta\text{-CD}$. The error bars are within the dots

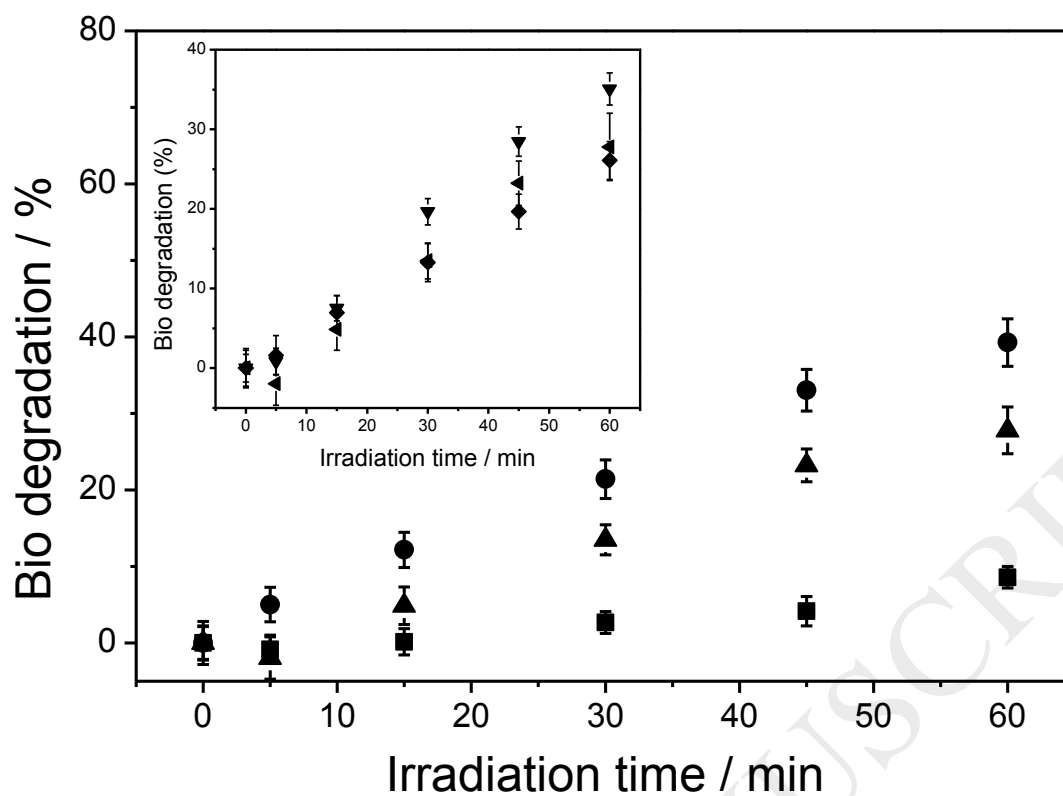


Figure 4: Percent degradation of Bio as a function of irradiation time at different concentrations of Fe (II) in 10% ACN/water. $[\text{H}_2\text{O}_2] = 10^{-2}$ M, pH = 3; (■) $[\text{Fe}^{2+}] = 10 \times 10^{-6}$ M, (●) $[\text{Fe}^{2+}] = 50 \times 10^{-6}$ M, (▲) $[\text{Fe}^{2+}] = 100 \times 10^{-6}$ M. Inset: %Bio degradation at different $[\text{H}_2\text{O}_2]$ in 10% ACN/water, $[\text{Fe}^{2+}] = 50 \times 10^{-6}$ M, pH = 3. (▼) $[\text{H}_2\text{O}_2] = 0.5 \times 10^{-3}$ M, (◆) $[\text{H}_2\text{O}_2] = 5 \times 10^{-3}$ M, (◄) $[\text{H}_2\text{O}_2] = 10 \times 10^{-3}$ M.

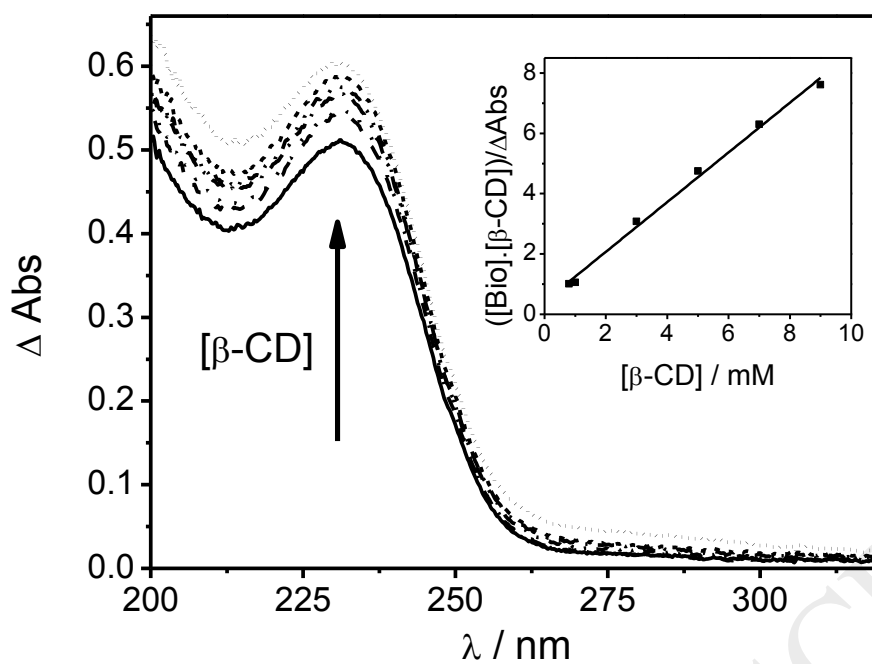


Figure 5: Absorbance spectra of Bio (10×10^{-6} M) at different concentrations of $\beta\text{-CD}$ in water. (—) $[\beta\text{-CD}] = 0.8 \times 10^{-3}$ M, (--) $[\beta\text{-CD}] = 1 \times 10^{-3}$ M, (•••) $[\beta\text{-CD}] = 3 \times 10^{-3}$ M, (-•-) $[\beta\text{-CD}] = 5 \times 10^{-3}$ M, (-••-) $[\beta\text{-CD}] = 7 \times 10^{-3}$ M, (----) $[\beta\text{-CD}] = 9 \times 10^{-3}$ M, (.....) $[\beta\text{-CD}] = 10 \times 10^{-3}$ M. Inset: Plot of $[\text{Bio}][\beta\text{-CD}]/\Delta \text{Abs}$ against $[\beta\text{-CD}]$ obtained with Bio solutions containing $\beta\text{-CD}$.

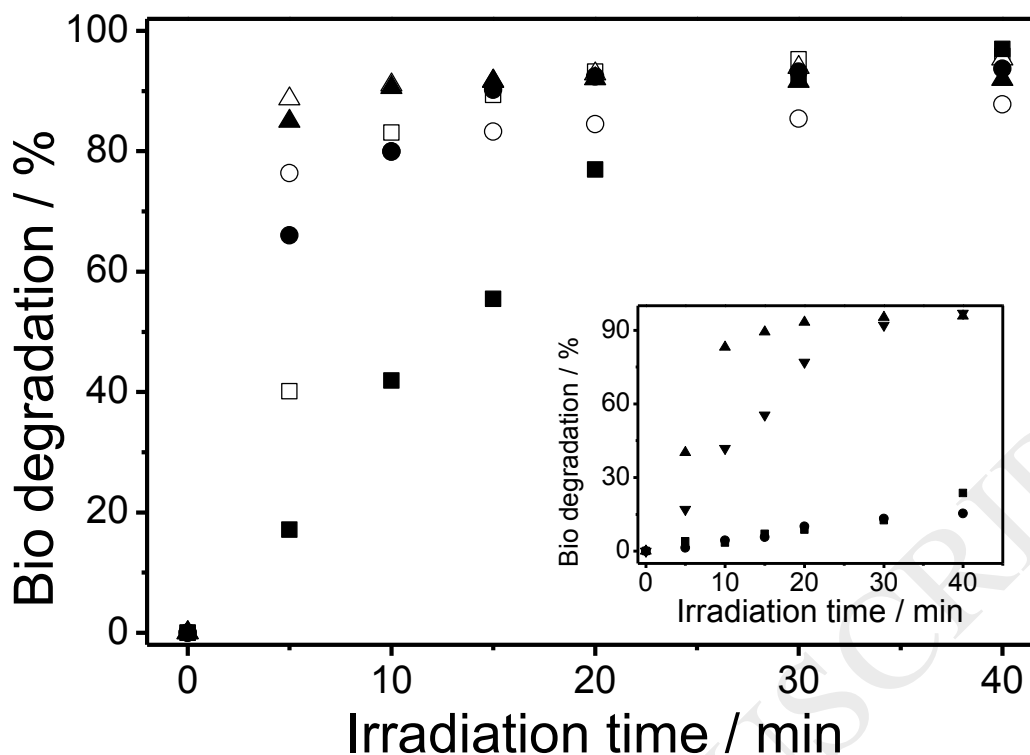


Figure 6: Percent degradation of Bio as a function of irradiation time by photo-Fenton in aqueous solutions (open symbols, [Bio] = 6×10^{-6} M, [H₂O₂] = 10^{-2} M, pH = 3): (□) [Fe²⁺] = 50×10^{-6} M, (○) [Fe²⁺] = 100×10^{-6} M, (△) [Fe²⁺] = 500×10^{-6} M. %Bio degradation as a function of irradiation time in the photo-Fenton system in aqueous β-CD solution (filled symbols, [Bio] = 6×10^{-6} M, [H₂O₂] = 10^{-2} M, [β-CD] = 10^{-3} M, pH = 3): (■) [Fe²⁺] = 50×10^{-6} M, (●) [Fe²⁺] = 100×10^{-6} M, (▲) [Fe²⁺] = 500×10^{-6} M. Inset: Bio degradation by differently different methodologies, for all solutions [Fe²⁺] = 50×10^{-6} M, [Bio] = 6×10^{-6} M, [H₂O₂] = 10^{-2} M, pH = 3: (■) Fenton in aqueous solution, (●) Fenton in β-CD media ([β-CD] = 10^{-3} M) (▲) Photo-Fenton in aqueous solution, (▼) Photo-Fenton in β-CD media ([β-CD] = 10^{-3} M). The error bars are within the dots for the main Figure and the inset.

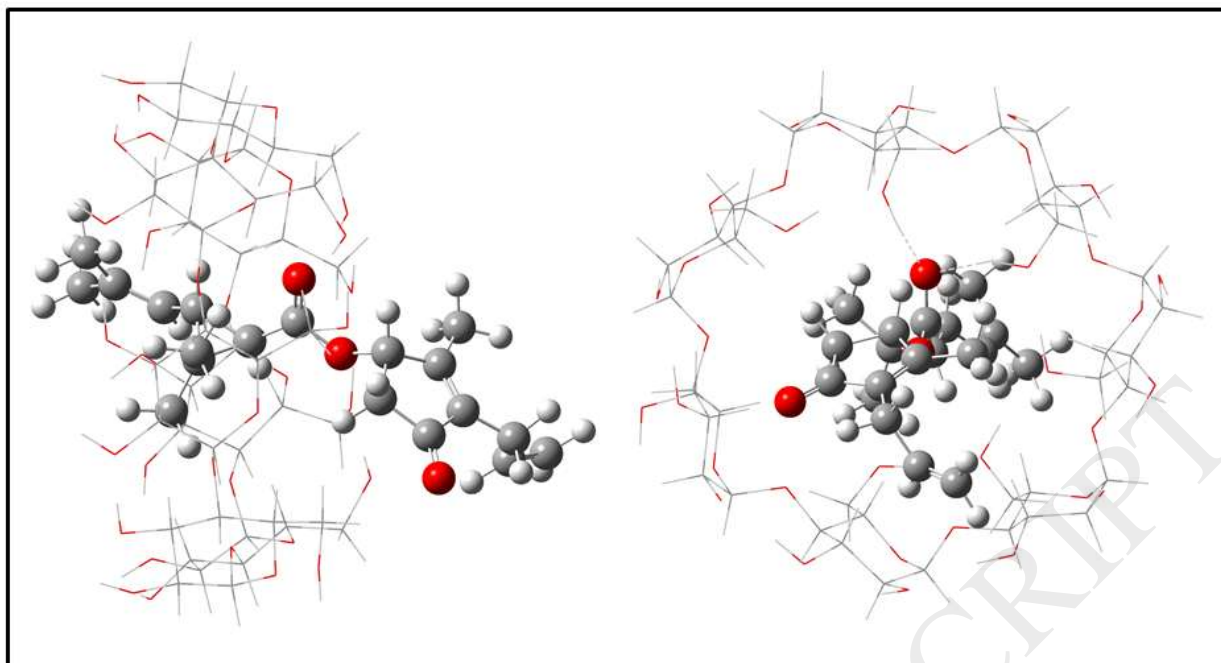


Figure 7: Structure of β -CD-Bio complex in head down orientation calculated at B3LYP/6-31G(d) level of theory. Left view is perpendicular to the cavity axis and right view is along the cavity axis.

Table

Table 1. %Bio degradation at 60 min irradiation and the pseudo-first order rate constants for different photo-Fenton conditions in water and ACN/Water 10%. *The k values have a 10% error.

	Factors		Bio Degradation% at 60 min	First-order reaction kinetics		
	[Fe ²⁺] x 10 ⁻⁶ M	[H ₂ O ₂] x10 ⁻³ M		k (min ⁻¹)*		R ²
				H ₂ O	ACN/Water 10%	
	10	10	9±1	0.0023	0.00171	0.969
	50	10	39±3	0.066	0.00834	0.993
	100	10	28±3	0.029	0.00645	0.989
	50	0.5	35±2		0.0076	0.992
	50	5	26±2		0.0051	0.998
	50	10	28±4		0.0063	0.981

Table 2. [Bio] = [Fe²⁺] = 50 x 10⁻⁶ M, [H₂O₂] = 0.01 M and pH = 3. The k values are expressed in min⁻¹ and have a 10% error.

	H ₂ O		ACN/H ₂ O (10:90)		β-CD (0.001 M)	
	k	%	K	%	k	%
Fenton	0.004	23 % (40 min)	0.004	19% (40 min)	0.004	15 % (40 min)
Photo-Fenton	0.14	> 90 % (40 min)	0.067	90 % (80 min)	0.091	> 90 % (40 min)

Table 3. Energy differences of the bioallethrin inclusion complexes with β -CD in kJ/mol.

β -CD-Bio	ΔE (PM6)	ΔE (B3LYP)
Head Up	-81.93	1.34
Head Down	-96.31	-33.56

ACCEPTED MANUSCRIPT