



# Direct short-wave photolysis of chlorpyrifos-methyl and chlorpyrifos-methyl oxon in the presence of cyclodextrins

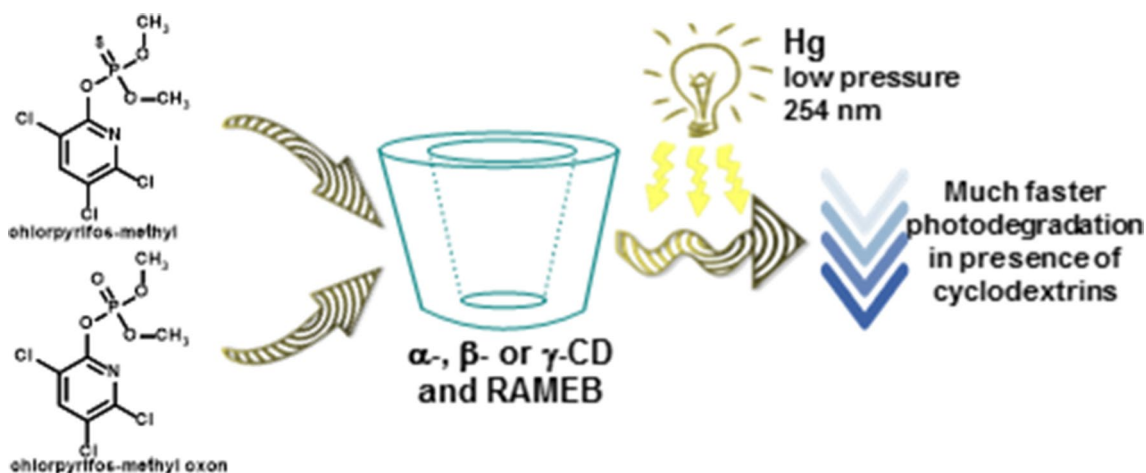
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## Abstract

Direct short-wave photolysis of chlorpyrifos-methyl (**1**) and chlorpyrifos-methyl oxon (**2**) was studied in the presence of native cyclodextrins ( $\alpha$ -,  $\beta$ - and  $\gamma$ -CD) and randomly methylated  $\beta$ -CD (RAMEB). We used for irradiation low pressure Hg lamps emitting at 254 nm and used as solvent 10% acetonitrile (ACN)/H<sub>2</sub>O solutions. The formation of an inclusion complex between **1** and  $\beta$ -CD was evaluated by UV–vis and NMR techniques. We did observe on UV–vis an interaction with  $\beta$ -CD, a feeble one not enough to enable the determination of the association constants. The experiments allowed us to assess that the presence of cyclodextrins produce a more rapid consumption of **1** and **2** compared to the naked molecules. A much faster photodegradation for the two compounds was observed in the presence of  $\gamma$ -CD. The average, at two wavelengths, of calculated ratios for the enhanced photodegradation of **1** were 1.3, 2.9, 25.8 and 2.9 for  $\alpha$ -,  $\beta$ -,  $\gamma$ -CD and RAMEB, while in the case of **2**, they reached 1.4, 3.5, 8.5 and 4.1 respectively. Our results indicate that short-wave photolysis of **1** in the presence of cyclodextrins could become a better plausible detoxification mechanism compared with their absence.

## Graphic abstract



**Keywords** Direct photolysis · Native cyclodextrin · Chlorpyrifos-methyl · Chlorpyrifos-methyl oxon

## Introduction

In natural environments, when pesticides are exposed to sunlight, its influence on their fate and persistence is important. Nevertheless, for many of such molecules, their accumulation—precisely due to their lack of absorption at natural wavelengths—pose a threat and make it necessary to find

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detoxification processes that usually resort to short-wave photolysis [1]. For these reasons, it is important to study the photodegradation of pesticides in aqueous solution systems to find efficient ways to minimize their negative impacts.

Chlorpyrifos-methyl (*O,O*-dimethyl *O*-(3,5,6-trichloro-2-pyridinyl)-phosphoro thioate), **1** (Fig. 1) is a pesticide classified as Class III, slightly hazardous [2], and is one of the most widely used insecticides in the world [3]. It is registered in Argentina for use in the control of insects on stored grains and complementary treatments of storage and transport facilities [4]. One important direct product of **1** is Chlorpyrifos-methyl oxon **2** (Fig. 1), which has a similar lifetime to that of **1** in the absence of CDs [5], so we considered that it was appropriate to include it in this study.

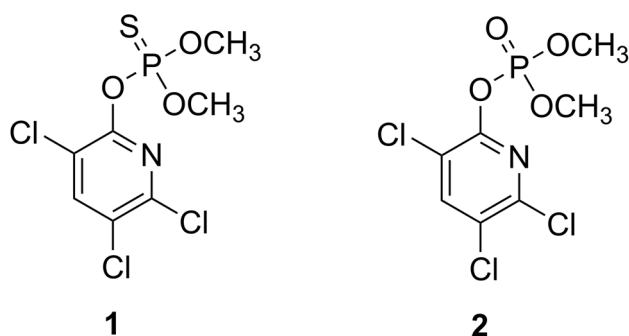
Cyclodextrins (CDs) are cyclic oligosaccharides produced by the microbially induced breakdown of starch [6]. Three types of natural CDs are common, namely  $\alpha$ -,  $\beta$ - and  $\gamma$ -CD, containing six, seven and eight glucopyranose units linked by ( $\alpha$ -1-4) bonds, respectively [7]. The aqueous solubility of the natural CDs is much lower (especially  $\beta$ -cyclodextrin) than modified cyclodextrins with comparable acyclic glucose units [8]. For example, after substitution by methoxy groups, the aqueous solubility of randomly methylated  $\beta$ -CD (RAMEB) is 26.6 times greater than that of  $\beta$ -CD [9]. Cyclodextrins are capable of forming inclusion complexes with various organic molecules in their hydrophobic interior cavity in solution [6]. They have been used to modify the photochemical reactivity of guests in aqueous solution as well as in the solid state [10]. In a photochemical reaction, the presence of CDs in the reaction media might affect the reactant in the ground state, the reactant in the excited state, the intermediates and the products in the ground state. An important factor affecting the reaction in these conditions is the matching of the reactant and product with the size of the cavity of the CDs [11].

There have been many studies that examined degradation of **1** and **2**, as well as of the chlorpyrifos family in the last years. Studies on the atmospheric degradation; [3, 12] the

hydrolysis of chlorpyrifos-methyl oxon (**2**), studied through the use of HPLC-MS/MS methods with detection of its degradation products [13] and studies of **1** with hydroxyl and perhydroxyl ions, as well as the effect of cyclodextrins on these reactions [14], are some examples. Yet, few studies dealt with photodegradation using UV lamps emitting at 200–280 nm as the paper by Nieto et al. [15] and very recently other contribution that focused on the mechanism of photodegradation and identity of the products [5].

When pesticides are included in the cavity of a cyclodextrin, the photolysis rate may show either increase or decrease. Cyclodextrins acted, for example, like photosensitizers in the degradation of the pesticide methyl-parathion [16]. More recently, it was observed that the interaction of norflurazon with CDs in solution form inclusion complexes at 1:1 stoichiometry ratio thus increasing the solubility of the herbicide. For RAMEB, 2-hydroxypropyl- $\beta$ -CD (HPCD) and  $\beta$ -CD increases in photodegradation rate were observed, while photoprotective effects predominated for  $\alpha$ -CD and  $\gamma$ -CD [1]. Also, cyclodextrins promoted the photodegradation of paraoxon, nevertheless, it was observed the inhibition on the photolysis of parathion under sunlight [6]. In the presence of  $\beta$ -CD, Hanna et al. reported an inhibition effect in the photocatalytic degradation of pentachlorophenol in distilled water [17]. Also, the photodegradation of the insecticide cypermethrin by complexation with two methylated CDs (RAMEB and heptakis (2,6-di-*O*-methyl)- $\beta$ -CD -DIMEB-) was reported as inhibition [18]. The irradiation of the herbicide bentazon in aqueous solution in the presence of three cyclodextrins,  $\beta$ -CD, HPCD and sulfobutyl-ether- $\beta$ -CD (SBECD), demonstrated a high photoprotective effect of these cyclodextrins. [19]

In an attempt to find an efficient method for degrading organophosphorus insecticides, we have previously studied in detail direct photodegradation of **1** and **2** in 10% acetonitrile (ACN)/H<sub>2</sub>O [5]. In the present work, we are presenting results on the photodegradation of **1** and **2** (Fig. 1) in the presence of CDs, using low pressure Hg lamps as light source for detoxification processes.



**Fig. 1** Structures of Chlorpyrifos-methyl (**1**) and Chlorpyrifos-methyl oxon (**2**)

## Materials and methods

### Materials

Chlorpyrifos-Methyl PESTANAL® (**1**) (FLUKA) and Chlorpyrifos-Methyl oxon (**2**) (Supelco), were characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR, UV-Vis spectrophotometry, GC-MS and HRMS.

The host compounds  $\alpha$ -CD and  $\beta$ -CD were purchased from Sigma-Aldrich (Argentina);  $\gamma$ -CD was obtained from Cyclolab (Hungary) and randomly methylated  $\beta$ -CD (RAMEB) (substitution percentage 60%) was a sample

generously donated by Prof. Eric Monflier (Université Lille Nord de France, France). All the cyclodextrins were used as received.

Acetonitrile (J.T. Baker) was HPLC grade. Water was purified with a Millipore Milli-Q apparatus.

## UV–vis studies

The UV–vis spectra were measured with a Shimadzu Multi-spec-1501 spectrophotometer using a cuvette of 1 cm optical path (OP).

When the UV–vis spectra were recorded in the presence of CDs, a blank solution containing CD at the same concentration of the sample under study was used in all cases, in order to discount the absorbance due to the CD.

## NMR studies

$^{31}\text{P}$  NMR spectra were obtained in ACN/D<sub>2</sub>O at 121 MHz, respectively, with a Bruker Avance II 400 spectrometer.

## Irradiation methods

Four low-pressure mercury lamps (Philips G6T5, 6 W) emitting at 254 nm, placed inside a metal box were used for irradiation as described in Lobatto et al. [5].

The solutions of **1** and **2** ( $2 \times 10^{-5}$  M) in the presence of CDs in 10% ACN/H<sub>2</sub>O were poured separately in the 1 cm quartz cuvettes sealed with Teflon caps and irradiated at 254 nm. The pH of the resulting solutions was in the range 5.5–6, and they were irradiated for periods of ten minutes, after every one of which irradiation was stopped and each solution analyzed by a new UV–vis spectrum. For compound **2**, the relative changes in absorbance vs. time data were fitted with a simple exponential function that yielded the lifetimes ( $\tau$ ) in all experimental results. In contrast, for compound **1**, the initial velocities method was used since the photodegradation of **1** does produce **2** as was previously reported [5].

Due to the low solubility of the substrates in water and the problems associated with the changes in absorbance that were measured in our UV–Vis spectrometer, we had to use a 10% ACN/H<sub>2</sub>O solution as solvent in order to increase slightly the concentration of the substrates. This modification on the “natural conditions” does not compromise the mechanism of the reactions as has been proved in previous studies by Lobatto et al. [5].

For studying the influence of  $\beta$ - and  $\gamma$ -CD on direct photodegradation of chlorpyrifos-methyl (**1**) and chlorpyrifos-methyl oxon (**2**), samples of **1** or **2** ( $2 \times 10^{-5}$  M) in 10% ACN/H<sub>2</sub>O with increasing concentrations of  $\beta$ -CD ( $1$ – $10 \times 10^{-3}$  M) or  $\gamma$ -CD ( $1$ – $16 \times 10^{-3}$  M) were prepared. A stock solution of  $\beta$ -CD  $10 \times 10^{-3}$  M or  $\gamma$ -CD  $16 \times 10^{-3}$  M in

10% ACN/H<sub>2</sub>O was used to prepare the others. In all cases, the UV–vis spectrum of the solution was taken before irradiation and at different irradiation times in the quartz cuvette of 1 cm path length.

## Results and discussion

### Formation of inclusion complex between chlorpyrifos-methyl and $\beta$ -CD

The complexation of **1** with  $\beta$ -, and  $\gamma$ -CD in 10% ACN/H<sub>2</sub>O and ionic strength 0.6 M was previously studied in our lab by UV–vis spectrophotometry and circular dichroism, but no complexation constant could be calculated [14]. Nevertheless, we recorded the UV–vis spectrum of **1** ( $2 \times 10^{-5}$  M) in the absence and presence of  $\beta$ -CD ( $8 \times 10^{-3}$  M) in 10% ACN/H<sub>2</sub>O.

The spectrum of **1** in 10% ACN/H<sub>2</sub>O shows two absorption bands at 229 nm ( $\epsilon = 9300 \text{ cm}^{-1} \text{ M}^{-1}$ ) and 289 nm ( $\epsilon = 5300 \text{ cm}^{-1} \text{ M}^{-1}$ ). In the presence of  $\beta$ -CD, the maxima are shift to 228 and 288 nm but the changes in absorbance observed were not significant enough to enable the determination of an association constant. (See Supplementary Information Fig. S1).

NMR spectroscopy is a useful method for studying molecular complexes with CDs and their properties in solution [20]. The chemical shift of protons or phosphorus atoms may vary when an interaction is established between the host and the receptor [21, 22]. So we tried to study the formation of a complex between **1** and  $\beta$ -CD by  $^{31}\text{P}$  NMR.

Due to the low sensitivity of this technique, in order to observe any signal, it was necessary to use a higher concentration of **1** than the one used in the photodegradation studies as well as a higher percentage of ACN in order to maintain **1** soluble. Therefore, a solution of **1**  $7.8 \times 10^{-3}$  M in 50% ACN/D<sub>2</sub>O was used. A signal at 64.95 ppm was observed in the absence and the presence of  $\beta$ -CD  $7.8 \times 10^{-3}$  M. (See Supplementary Information Fig. S2).

It is known that ACN forms inclusion complexes with  $\beta$ -CD. [23] Since the percentage of ACN used in our study is high, we should take into account that the solvent act as a competitive species for the cavity of CD. Using the association constants reported by Garcia-Rio et al. [23] for the formation of a 1:1 complex between ACN and  $\beta$ -CD (i.e.  $0.54 \text{ M}^{-1}$ ) and that calculated by kinetic methods by Vico et al. (i.e.  $105 \text{ M}^{-2}$ ) [14] for the complexation of **1** with  $\beta$ -CD in 10% ACN/H<sub>2</sub>O, the concentration of the complexes **1**-CD and ACN-CD in our experimental conditions were calculated. The results indicate that, from the total concentration of  $\beta$ -CD, 11% is complexed with **1**, 75% is complexed with ACN and 14% remains uncomplexed. These values explain why, under the conditions used to perform the

$^{31}\text{P}$  NMR spectrum, only the signal corresponding to free **1** was observed.

### Effect of the presence of different cyclodextrins at constant concentration

The influence of native CDs and RAMEB on the direct photodegradation of chlorpyrifos-methyl (**1**) and chlorpyrifos-methyl oxon (**2**) in 10% ACN/H<sub>2</sub>O was evaluated. For this, solutions of **1** or **2** ( $2 \times 10^{-5}$  M) with CDs ( $\alpha$ -,  $\beta$ - and  $\gamma$ -CD or RAMEB,  $8 \times 10^{-3}$  M) were prepared in 10% ACN/H<sub>2</sub>O. The 1 cm path length quartz cuvette was placed inside the metal box and was irradiated at 254 nm. The UV-vis spectrum of the solution was taken before irradiation and at different irradiation times.

As the temperature inside the box when the lamps are irradiating is 36 °C, we carried out experiments in the presence of the different CDs in the dark at 36 °C, to assess whether the reaction observed could depend on temperature. No reactions were observed by UV-vis spectrophotometry up to 400 min, indicating no thermal contributions.

The insecticide **1** has two absorption bands at 229 and 289 nm that decreased upon irradiation indicating its consumption (Fig. 2a, c, e and g). Compound **2** has two absorption bands at 227 and 288 nm which decreased with time as the solution, in the presence of native cyclodextrins or RAMEB, was irradiated (Fig. 2b, d, f and h).

The plots of A vs. time for the photodegradation of **1** and **2** in the presence of native CDs and RAMEB at one wavelength are shown in Fig. 3. For the other wavelengths, the plots are shown in the supplementary material (See Supplementary Information Fig. S3).

The lifetimes ( $\tau$ ) for **2** in the presence of all the CDs studied at the two wavelength maxima were calculated with a simple exponential function and the results were compared with those obtained in the absence of CDs [5] (Table 1). There, it can be seen that **2** was consumed more rapidly in the presence of CDs. The larger effect was observed in the presence of  $\gamma$ -CD, as is also the case when looking at Fig. 3a for compound **1** since the slope is higher. Curiously, Vico et al. [14] observed inhibition in the basic hydrolysis of **1** in the presence of native cyclodextrins with  $\gamma$ -CD having the largest effect.

The acceleration effect observed in the direct photolysis of **1** and **2** in the presence of native CDs increases in the order  $\alpha$ -CD <  $\beta$ -CD <  $\gamma$ -CD, which is coincident with the increase in the size of the cavities of the native CDs ( $\alpha$ -CD <  $\beta$ -CD <  $\gamma$ -CD).

Vico et al. [14] found that **1** is better included in  $\gamma$ -CD than in  $\beta$ -CD and that  $\gamma$ -CD exhibits the largest effect on the basic hydrolysis of **1**. So, we can assume that the effect observed in the photodegradation of **1** and **2** in the presence

of  $\gamma$ -CD is due to the fact that both compounds are better included in the cavity of  $\gamma$ -CD than in the other CDs.

The photodegradation of **1** or **2** in the presence of RAMEB is similar as that found in the presence of  $\beta$ -CD. Considering that  $\beta$ -CD and RAMEB have the same number of glucose units and cavity volume, we can infer that the presence of the methyl groups in RAMEB has no influence on the rate of degradation and only the size of the cavity is important.

### Effect of the variation in the concentration of $\beta$ - and $\gamma$ -CD

As the effect of  $\beta$ -CD and RAMEB on the photodegradation of **1** and **2** is similar, we decided to study only the effect of the variation of the concentration of  $\beta$ -CD on the photodegradation of the two compounds.

In order to study the influence of the concentration of  $\beta$ -CD on the direct photodegradation of **1** and **2** in 10% ACN/H<sub>2</sub>O, samples of **1** or **2** ( $2 \times 10^{-5}$  M) with increasing concentrations of  $\beta$ -CD in the range of  $1$ – $10 \times 10^{-3}$  M were prepared. The lifetimes at the maximum wavelength were calculated for each  $\beta$ -CD concentration. In the supplementary material (Figs. S4 and S5), are shown the plots for both wavelengths for compounds **1** and **2**.

In general, it can be observed that at both wavelengths there is an increase when comparing the relationship  $\tau_0/\tau^{\text{CD}}$  (lifetime in the absence of CD over the lifetime in the presence of  $\beta$ -CD) of **1** and **2** as the concentration of  $\beta$ -CD increases (Fig. 4). In the case of compound **1**, the maximum value was observed as a plateau at  $\beta$ -CD  $(5$ – $8) \times 10^{-3}$  M, whereas in the case of compound **2** the maximum value was observed at  $\beta$ -CD  $9 \times 10^{-3}$  M.

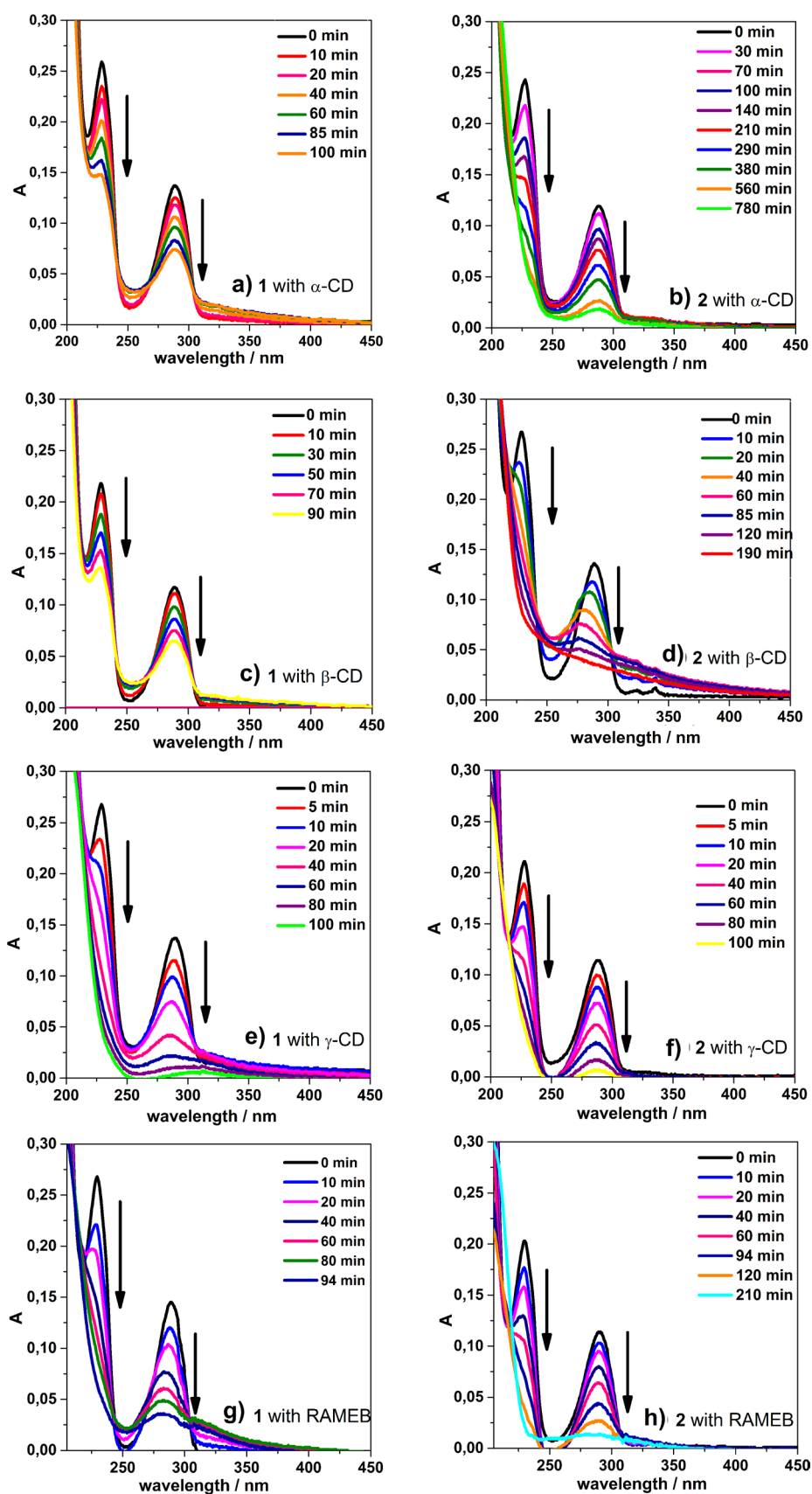
The lifetime of the photodegradation of **2** in the presence of  $\beta$ -CD  $9 \times 10^{-3}$  M, was 0.95 h and the lifetime of the photodegradation of **2** in the absence of CD was 7.2 h at 227 nm. It was possible to perceive clearly that the presence of  $\beta$ -CD accelerates the degradation for **2**. In the case of compound **1**, the maximum value in the relationship  $\tau_0/\tau^{\text{CD}}$  for the photodegradation is in the presence of  $\beta$ -CD  $8 \times 10^{-3}$  M at 229 nm.

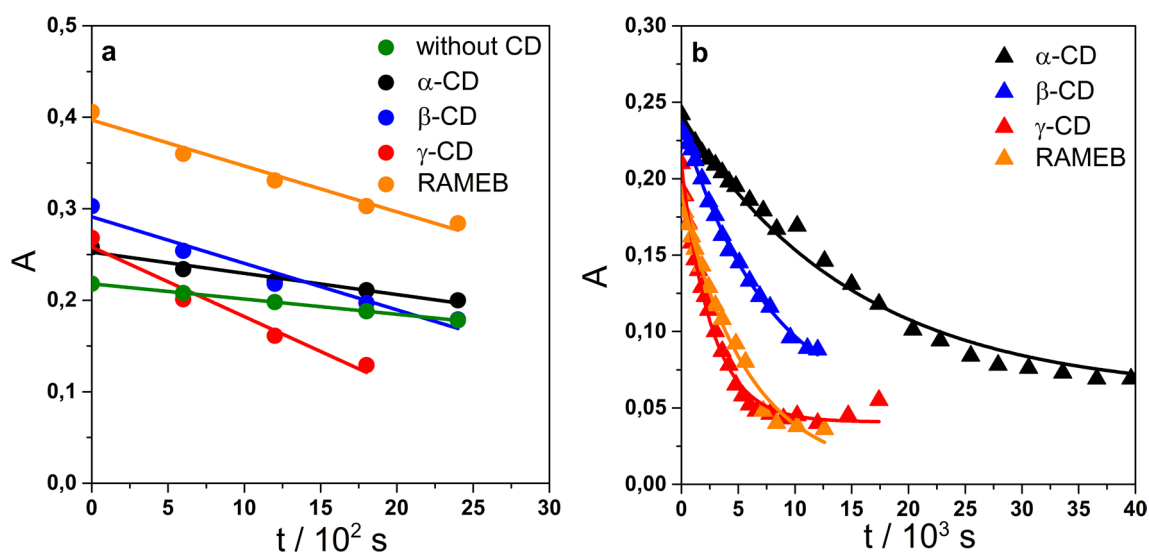
On the other hand, comparing the relationship  $\tau_0/\tau^{\text{CD}}$  at  $[\beta\text{-CD}] = 9 \times 10^{-3}$  M for **1** ( $\tau_0/\tau^{\text{CD}} = 2.7$ ) and **2** ( $\tau_0/\tau^{\text{CD}} = 7.6$ ) it can be noted that  $\beta$ -CD has a greater impact on the disappearance of **2** than that of **1**.

The influence of the concentration of  $\gamma$ -CD ( $1$ – $16 \times 10^{-3}$  M) on the direct photodegradation of **1** ( $2 \times 10^{-5}$  M) in 10% ACN/H<sub>2</sub>O was studied and the lifetimes were calculated. The corresponding plots for both wavelengths are shown in the supplementary material (Fig. S6).

It can be observed that at both wavelengths, there is an increase in the lifetimes of **1** with increasing concentration

**Fig. 2** Spectra of **1** and **2** in 10% ACN/H<sub>2</sub>O at different irradiation times.  $[1]_0 = [2]_0 = 2 \times 10^{-5}$  M;  $[\alpha\text{-CD}]_0 = [\beta\text{-CD}]_0 = [\gamma\text{-CD}]_0 = [\text{RAMEB}]_0 = 8 \times 10^{-3}$  M. **a**, **c**, **e** and **g** correspond to **1** with  $\alpha$ -,  $\beta$ -,  $\gamma$ -CD and RAMEB; while **b**, **d**, **f** and **h** are the analogous for **2**





**Fig. 3** **a** Initial's rate plot for **1** alone and with different CDs at 228 nm; **b** Absorbance vs t for **2** with different CDs fitted with a simple exponential function at 227 nm.  $[1]_0 = [2]_0 = 2 \times 10^{-5}$  M,  $[\alpha\text{-CD}]_0 = [\beta\text{-CD}]_0 = [\gamma\text{-CD}]_0 = 8 \times 10^{-3}$  M in 10% ACN/H<sub>2</sub>O

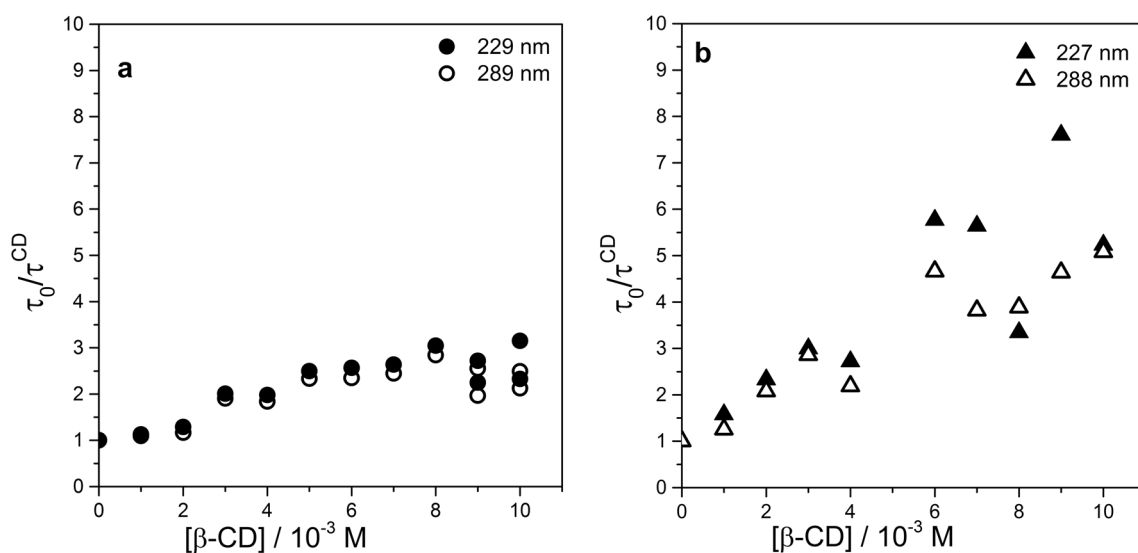
**Table 1** Lifetimes ( $\tau$ , in hours) corresponding to the photodegradation of **2** in the presence of native CDs and RAMEB ( $8 \times 10^{-3}$  M) in 10% ACN/H<sub>2</sub>O

CD	2	
	$\lambda_{227 \text{ nm}}$	$\lambda_{288 \text{ nm}}$
–	7.2 <sup>a</sup>	7.2 <sup>a</sup>
α-CD	4.2	6.8
β-CD	2.2	1.9
γ-CD	0.8	0.9
RAMEB	1.6	1.9

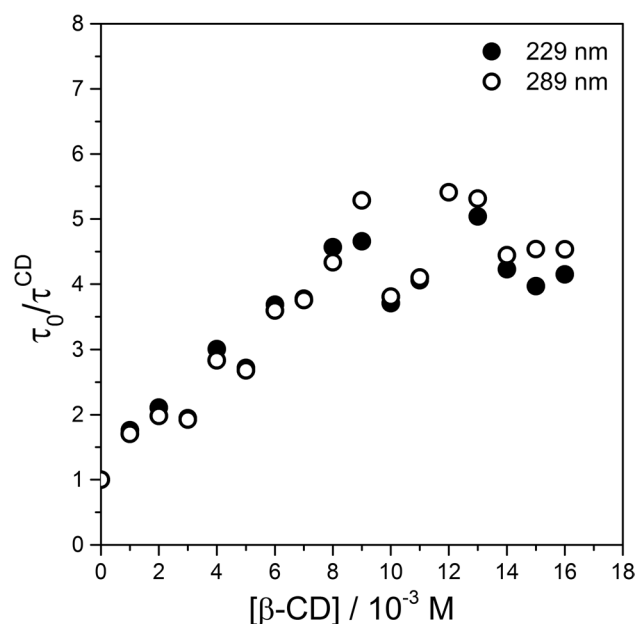
<sup>a</sup>Calculated by Lobatto et al. [5]

of γ-CD up to concentrations of 9 and  $12 \times 10^{-3}$  M where it begins to drop again (Fig. 5).

Comparing the lifetimes calculated for **1** in the presence of β- and γ-CDs, we can observe that **1** degrades more slowly in β-CD. The relationship  $\tau_0/\tau^{\text{CD}}$  for **1** at  $[\beta\text{-CD}] = [\gamma\text{-CD}] = 9 \times 10^{-3}$  M, indicates that the consumption of **1** is two times more rapid in the presence of γ-CD than in the presence of β-CD.



**Fig. 4** The relationship  $\tau_0/\tau^{\text{CD}}$  for **1** (a) and **2** (b) in the absence and the presence of β-CD at the two wavelengths



**Fig. 5** The relationship  $\tau_0/\tau^{CD}$  for **1** in the absence and the presence of  $\beta$ -CD at the two wavelengths

## Conclusion

The photodegradation of **1** and **2** at 254 nm was studied in the presence of native cyclodextrins and RAMEB. We have found that it is beneficial to perform the photolysis of **1** and **2** in the presence of cyclodextrins since they increase the consumption rate, thus decreasing the lifetime when compared with the results reported previously in the absence of CD.

It could be supposed that compounds **1** and **2** are best included within  $\gamma$ -CD that has the largest cavity. It was possible to perceive clearly that the presence of the CDs helps in degrading **1** and **2** faster than in their absence.

The lifetime of **2** in the presence of  $\beta$ -CD  $9 \times 10^{-3}$  M was 0.95 h while in the absence of any CD it was 7.20 h.

It was distinguished that the largest effect observed in the direct photolysis of **1** in the presence of  $\gamma$ -CD was at a concentration of  $12 \times 10^{-3}$  M. In the presence of  $\beta$ -CD, the biggest effect observed in the direct photolysis of **1** and **2** was at a concentration of 8 and  $9 \times 10^{-3}$  M, respectively.

We can conclude that, irradiation with short-wave UV light might be a better method for detoxification of chlorpyrifos-methyl solutions in presence of cyclodextrins compared with the photolysis of the naked substances.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s10847-021-01046-w>.

**Author contributions** VLL: Performed the experiments; Analyzed and interpret the data; Wrote the paper. GAA, EIB: Conceived and designed

the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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## Compliance with ethical standards

**Conflict of interest** The authors declare no conflict of interest.

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