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Research Article

Influence of Hydroxypropyl-β-Cyclodextrin on the Photostability of Fungicide Pyrimethanil

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Pesticides continue to play an important role in pest management. However, the intensive pesticide application has triggered several environment negative effects that cannot be disregarded. In this study, the inclusion complex of pyrimethanil with HP-β-CD has been prepared and characterized by proton nuclear magnetic resonance spectroscopy. The formation of the pyrimethanil/HP-β-CD inclusion complex increased the aqueous solubility of this fungicide around five times. To assess the influence of microencapsulation on the environmental photostability of the fungicide, the photochemical degradation of pyrimethanil and pyrimethanil/HP-β-CD inclusion complex has been investigated in different aqueous media such as ultrapure and river water under simulated solar irradiation. The studies allow concluding that pyrimethanil/HP-β-CD inclusion complex increases significantly the photostability of the fungicide in aqueous solutions, especially in natural water. Actually, the half-life of pyrimethanil/HP-β-CD inclusion complex was increased approximately by a factor of four when compared to the free fungicide. The overall results point out that pyrimethanil can be successfully encapsulated by HP-β-CD, a process that can improve its solubility and photostability properties.

1. Introduction

Farmers use a wide range of chemical compounds to limit damage losses in agriculture upcoming from pests. In fact, nowadays, a large percentage of crops are destroyed before harvest due to the presence of pests for instance of fungus origin [1]. In order to minimize the damage provoked by pests, chemical compounds, such as pesticides, are widely used in the agricultural production. They can prevent or reduce losses and thus increase yield as well as the quality of the product [2]. Scientific research has been intense in pesticides area either with the goal of increasing the efficacy and reducing the nontarget effects or for reducing their environmental risks [3–6].

The increase of pesticides consumption does not necessarily reflect the amount of pesticide that is actually applied to pests, partly because pesticide delivery systems are inefficient [7]. Some estimates concluded that less than 1% of applied pesticides really reach the targets [8]. Sunlight photodegradation is one of the most destructive pathways for pesticides after their release into the environment. In fact, photochemical reactions are one of the most frequently described transformations of pesticides in the environment. Therefore, studies on the photodegradation processes can provide a better knowledge on the transformations processes of pesticides in the environment and consequently on their oxidation/degradation rate [9, 10].

A class of pesticides which presents risks for environment is the fungicides. Actually, the regular use of this type of compounds can potentially pose a risk to the environment, particularly if their residues persist in the soil or migrate off-site and enter waterways causing adverse impacts on the health of terrestrial and aquatic ecosystems. However, the risk to the environment posed by the use of fungicides in

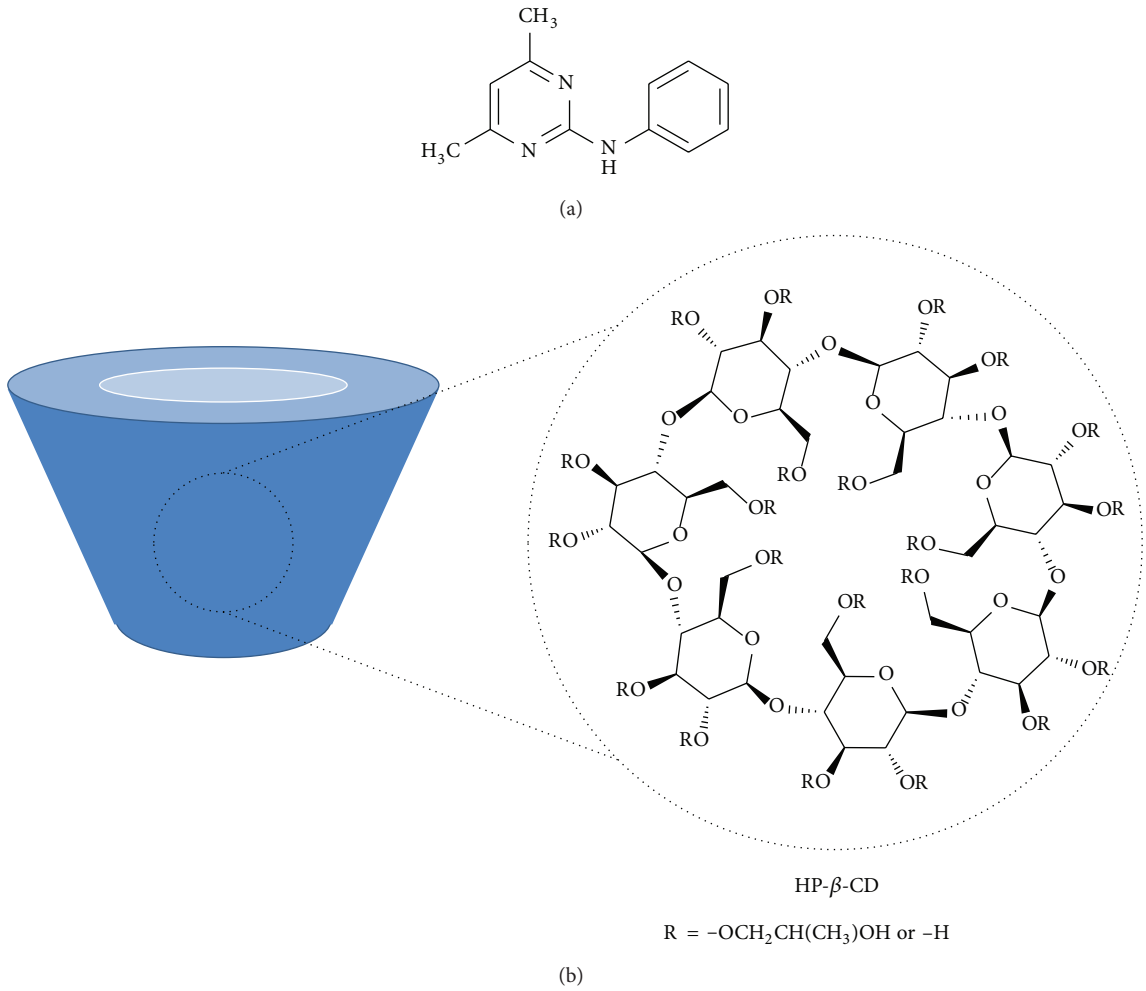


Figure 1: Schematic representation of (a) chemical structure of pyrimethanil and (b) 3D structure of (2-hydroxypropyl)-β-cyclodextrin (HP-β-CD).

horticultural production systems has received relatively little attention when compared to other types of agrochemicals, such as insecticides and herbicides [11].

Pyrimethanil, *N*-(4,6-dimethylpyrimidin-2-yl)aniline (Figure 1(a)), is an anilino-pyrimidine fungicide particularly active against gray mold (*Botrytis cinerea*) and pear scab (*Venturia spp.*) on fruits, vegetables, and ornamental plants. The photodegradation by sunlight plays a significant role in pyrimethanil degradation due to its long half-life (approx. 77 days) in the environment [12]. Although pyrimethanil has no apparent mutagenic, genotoxic, or carcinogenic potential, the concentration of pyrimethanil has been limited in food commodities by the European Commission [13, 14]. It is thus important to increase fungicide efficacy at reduced doses. In this sense, controlled release formulations of pesticides have become a very active research area in recent years. Controlled release formulations of fungicides can allow extended periods of activity, while minimizing the environmental effects of use. Concern over the contamination of soil and water has led to the development of formulations that prevent entry of the pesticides into the groundwater while maintaining effective pest control. In this context, microencapsulation becomes the most appellative industrial process for the production of controlled release agricultural formulations [15, 16].

Cyclodextrins (CDs) are a group of naturally occurring cyclic oligosaccharides derived from starch, with six, seven, or eight glucose residues linked by α (1–4) glycosidic bonds in a cylinder-shaped structure (Figure 1(b)). The CDs structural characteristics, a hydrophobic interior cavity and hydrophilic shell, and their ability to alter the physical, chemical, and biological properties of guest molecules have been regarded as a solution to improve pesticide formulations. When a pesticide is complexed with CD, the interaction of the side groups on the guest pesticide molecule with the hydroxyl or substituted hydroxyl groups of the host can have an effect on the reactivity of the guest molecule [17]. Depending upon the group on the pesticide molecule, this can result in catalysis of the reaction or stabilization of the guest molecule by prevention of chemical reactions [17]. Studies of the catalytic

effects of CDs on the degradation of pesticides are therefore important for an understanding of their persistence and fate in natural environments.

This work was aimed at studying the inclusion effect of (2-hydroxypropyl)-β-cyclodextrin (HP-β-CD) on the chemical and photochemical properties of fungicide pyrimethanil. Ultraviolet spectroscopy and nuclear magnetic resonance (NMR) studies have been carried out to elucidate the strength and binding mode of association of the complex. The influence of microencapsulation of pyrimethanil by HP-β-CD on its rate of photodegradation was also assessed.

2. Experimental

2.1. Reagents and Water Samples. Pyrimethanil, (2-hydroxypropyl)-β-cyclodextrin (HP-β-CD), and MeOD-D_4 (99.96%) were purchased from Sigma-Aldrich Química (Sintra, Portugal). Analytical grade reagents purchased from Sigma-Aldrich Química (Sintra, Portugal) were used without additional purification. The water used was purified with a Millipore system (Milli-Q-50 18 MΩ cm).

HPLC-grade acetonitrile and methanol were obtained from Carlo Erba. Prior to use, the solvents were filtered through a 0.45 μm filter.

Environmental water used in the experiments was collected from Leça river basin located in the north of Portugal. The water samples were obtained from the top metre in 2.5 L brown glass bottles. Immediately after arrival in the laboratory, the samples were filtered through 1 μm glass fibre filters and 0.45 μm cellulose acetate filters, sequentially, to remove suspended particles, and refrigerated at 4°C prior to use.

2.2. Apparatus. The HPLC determinations [18] were performed using a HPLC/DAD system consisting in a Shimadzu instrument (pumps model LC-20AD, Tokyo, Japan), equipped with a commercially prepacked Nucleosil 100-5 C18, analytical column (250 mm × 4.6 mm, 5 μm, Macherey-Nagel, Duren, Germany) and UV detection (SPD-M20A) at the wavelength maximum determined by the analysis of the UV spectrum (268 nm). The mobile phase consisted of methanol/water (75 : 25, v/v). It was delivered isocratically at 1 mL min^{-1} at room temperature.

The chromatographic data was processed in a Samsung computer, fitted with LabSolutions software (Shimadzu, Japan).

^{1}H NMR spectra were obtained at room temperature and recorded on a Bruker Avance III operating at 400 MHz. The NMR experiments were carried out in deuterated methanol (MeOD). Chemical shifts are expressed in δ (ppm) values relative to tetramethylsilane (TMS) as internal reference. Chemical shifts changes ($\Delta\delta$) were calculated according to the formula $\Delta\delta = \delta_{(\text{complex})} - \delta_{(\text{free})}$.

2.3. Phase Solubility Studies. Phase solubility studies were carried out according to the procedure previously reported [5]. Briefly, an excess amount of pyrimethanil (20 mg) was added to 25 mL of aqueous solutions containing increasing concentrations of HP-β-CD (0–35 mM). Then, the suspensions were shaken on an incubator shaker (Ika KS 4000i) at 25 ± 2°C for 2 days. After the equilibrium was reached, suspensions were filtered and properly diluted. The concentrations of pyrimethanil were determined spectrophotometrically (Shimadzu UV-Vis Spectrophotometer, UV-1700 PharmaSpec, Japan) at 268 nm. Each experiment was carried out in triplicate. The apparent stability constant, Ks, was calculated from the phase solubility diagram with the assumption of 1 : 1 stoichiometry, according to (1):

$$K\text{s} = \frac{\text{slope}}{S_0\left(1 - \text{slope}\right)}. \quad (1)$$

S_0 is the solubility of pyrimethanil in the absence of HP-β-CD.

2.4. Preparation of the Pyrimethanil/HP-β-CD Inclusion Complex. The pyrimethanil/HP-β-CD complex was prepared by kneading procedure. Equimolar amounts of pyrimethanil and HP-β-CD were accurately weighed and mixed together using a mortar. The mixture was then triturated and an appropriate amount of ethanol was added till a homogenous paste was formed. The paste was then kneaded for 45 min and dried at 50°C in an oven under vacuum. The dried product was gently ground into a fine powder.

2.5. Irradiation Experiments. Photodegradation rates of pyrimethanil were determined in natural water (Leça river) and in ultrapure water under simulated solar radiation. Photodegradation studies were carried out using a Fitoclima S600PL thermostatic chamber (Aralab, Portugal) equipped with eight Repti Glo (20 W) UV-Vis lamps to simulate solar radiations (UVB 280–315 nm (10%), UVA 320–370 nm (33%), and 400–640 nm (57%)). Considering the emission spectra of the lamps (280–640 nm) all tests were performed using capped pyrex (275 nm cut off) flasks. Aqueous solutions of pyrimethanil (25 mL, 0.05 mmol/L) were maintained at room temperature and exposed (in a 60-degree angle position relative to the radiation source) to UV-Vis irradiation for 42 days at a fixed distance of 30 cm. At this distance the irradiation intensity reaching the sample surface was approximately 1.2 mW·cm^{-2}. Similar experiments were performed in the presence of HP-β-CD at a concentration of 30.0 mM. Control experiments in the dark (blank experiments) under the same conditions and initial concentrations of pyrimethanil samples were carried out in parallel for comparison. At selected time intervals, samples were collected and quantitatively analyzed, after proper dilution, by high performance liquid chromatography (HPLC). The amount of pyrimethanil in the solution after irradiation was calculated based on external calibration. All experiments were carried out in triplicate at 25 ± 1°C.

2.6. Analysis of Data. The disappearance rate of pyrimethanil follows first-order kinetics given by the equation:

$$C_t = C_0 e^{-kt}, \quad (2)$$

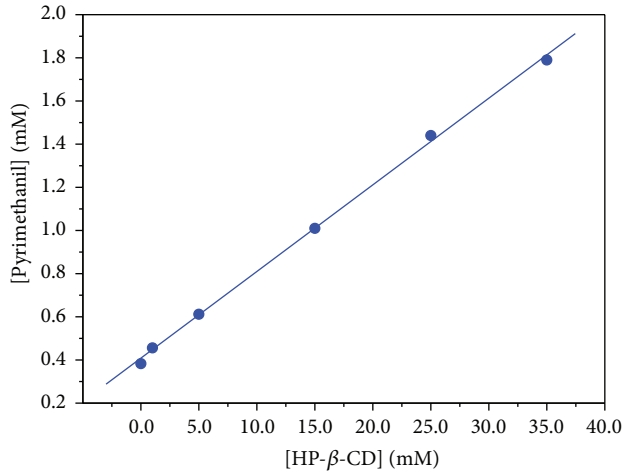


FIGURE 2: Phase solubility diagram obtained for fungicide pyrimethanil and increasing concentrations of HP-β-CD in water at 25°C. Each point represents the mean of three determinations.

where C_0 and C_t are the concentrations at times 0 and t, t is the irradiation time, and k is the first-order rate constant.

The half-life ($t_{1/2}$) of pyrimethanil, time required for its concentration to decrease to half its initial value, is related to the rate constant by the equation: $t_{1/2} = \ln 2/k$.

Results are expressed as mean ± standard error (3 independent samples). Statistically significant difference was determined using the Student's t-test and analysis of variance (Anova) with $P = 0.05$ as a minimal level of significance.

3. Results and Discussion

3.1. Phase Solubility Studies. The stoichiometric ratio and stability constant of the inclusion complex were derived from the changes in the solubility of pyrimethanil in the presence of increasing amounts of HP-β-CD, measured by UV spectrophotometry. Figure 2 presents the phase solubility plot obtained for pyrimethanil and increasing concentrations of HP-β-CD in water at 25°C.

As can be seen, it shows A_L-type solubility diagram as the pyrimethanil solubility increases with increasing HP-β-CD concentrations, according to the classification established by Higuchi and Connors [19]. The linear host-guest correlation ($r^2 = 0.9994$) and the slope of 0.0402 suggest the formation of a 1:1 complex with respect to HP-β-CD concentration [19]. The apparent stability constant, Ks, obtained from the straight-line portion of the phase solubility diagram was $100 \pm 10\ M^{-1}$ (see (1)). Results evidenced that pyrimethanil solubility is enhanced by the HP-β-CD inclusion complexation. Actually, the formation of the inclusion complex has increased the solubility of pyrimethanil in water around 5 times when compared with the free fungicide.

3.2. Nuclear Magnetic Resonance Analysis. Nuclear magnetic resonance (NMR) spectroscopy is a powerful and versatile method for structure elucidation. Thus, it has been widely used for studying inclusion complexes formed by cyclodextrins [17]. NMR spectroscopy provides a superior method to study complexation phenomena, because guest and host molecules are simultaneously observed at the atomic level. Therefore, evidences were acquired by proton nuclear magnetic resonance (^{1}H NMR) to confirm the inclusion of pyrimethanil inside of cavity of HP-β-CD as the formation of inclusion complex will cause a modification on proton chemical shifts in the ^{1}H NMR spectra. The variation of the chemical shift displacements ($\Delta\delta$), defined as the difference in chemical shift in the presence and absence of the host, will reflect the degree of the intermolecular proximity of the protons directly involved in the encapsulation process. The observed changes are intrinsically related to the position of the molecule into the CD cavity.

^{1}H-NMR spectra of pyrimethanil, HP-β-CD, and pyrimethanil/HP-β-CD, synthesized by kneading procedure (see Subsection 2.4) are shown in Figure 3. Due to the low aqueous solubility of pyrimethanil the NMR measurements have been carried out in methanol-d_4. The proton chemical shifts (δ) data found for pyrimethanil, HP-β-CD, and pyrimethanil/HP-β-CD complex are shown in Table 1.

HP-β-CD cyclodextrin consists of seven identical monomers that assume a cone-shaped structure. In consequence, protons H1″, H2″, and H4″ are oriented towards the outside of the cavity whereas the H3″ and H5″ protons are facing the interior of the CD cavity and H6″ protons are located in the narrower end of CD rim (Figures 1 and 3) [20, 21]. The numbering of the hydrogen atoms faced inside and outside of the CD cavities has been ascribed in accordance with the literature [20, 21]. Owing to their inner localization, H3″ and H5″ are frequently the most affected protons upon complexation, which results in a variation of their shifts.

The chemical shift displacements found in the spectra of pyrimethanil/HP-β-CD, when compared with free fungicide (guest), point out the occurrence of a complexation process that can be attributed to the influence of the guest (pyrimethanil) included in CD cavity. In the presence of HP-β-CD pyrimethanil protons exhibit noticeable downfield shifts ($\Delta\delta > 0$) evidencing the occurrence of host-guest interactions. As the higher $\Delta\delta$ values are related to the protons of methyl groups and H5 it is reasonable to speculate that the pyrimidine ring (Table 1) is included in the lipophilic core of HP-β-CD. The smooth variation in chemical shifts and the absence of new peaks that could be assigned to the complex suggest the occurrence of a dynamic process with a fast exchange between free pyrimethanil and included forms. The low shifts deviations observed in the spectra for the H3″ and H5″ signals of HP-β-CD in the inclusion complex can be related to the cyclodextrin nature. Actually, the HP-β-CD protons, especially H3″ and H5″, are difficult to assign as the cyclodextrin contains between 10 and 45% of hydroxypropoxy groups randomly distributed, a reality that is translated in the appearance of broad and overlapped resonance signals in the spectra [21].

In summary, the mentioned displacements are indicative of the presence of host-guest interactions and the formation of the inclusion complex. The stoichiometry of the

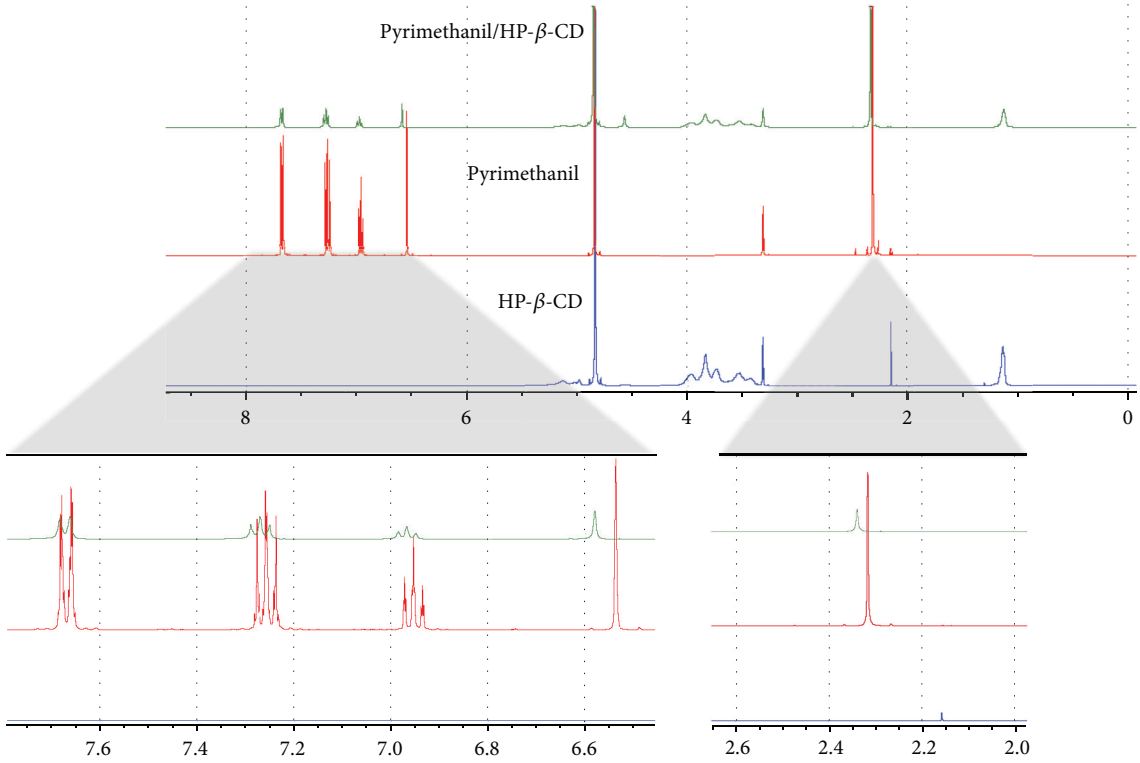
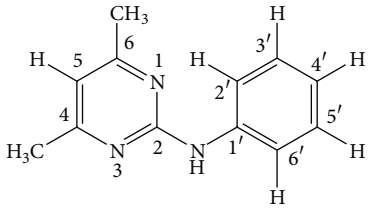


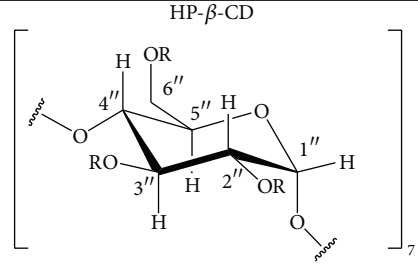
Figure 3: ^{1}H NMR spectra of pyrimethanil, HP-β-CD, and pyrimethanil/HP-β-CD inclusion complex.

Table 1: ^{1}H NMR chemical shift (δ) data of pyrimethanil, HP-β-CD, and pyrimethanil/HP-β-CD inclusion complex.

Pyrimethanil



HP-β-CD



R = H or CH_2CHOCH_3

H assignment	δ pyrimethanil (CH_3OD)	δ HP-β-CD (CH_3OD)	δ pyrimethanil/HP-β-CD (CH_3OD)	$\Delta\delta$
2 × (CH_3)	2.315 (s)	—	2.338	0.023
H5	6.538 (s)	—	6.581	0.043
H4′	6.954 (m)	—	6.967	0.013
H3′/H5′	7.257 (dd)	—	7.271	0.014
H2′/H6′	7.669 (dd)	—	7.671	0.002
H1″	—	5.048 (m)	5.046	−0.002
H3″	—	3.967 (s)	3.950	−0.017
H6″	—	3.831 (s)	3.828	−0.003
H5″	—	3.727 (s)	3.731	0.004
H2″	—	3.528 (m)	3.529	0.001
H4″	—	3.413 (m)	3.417	0.004

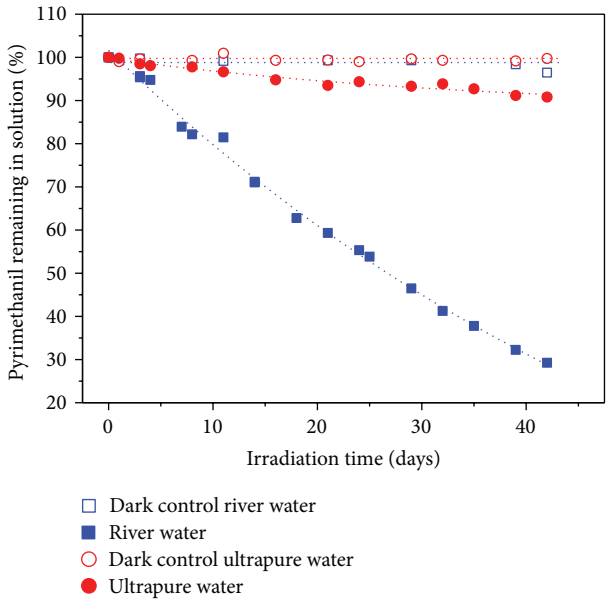


Figure 4: Photodegradation of pyrimethanil in (open red circle, solid red circle) ultrapure and (open blue square, solid blue square) river water under simulated solar irradiation.

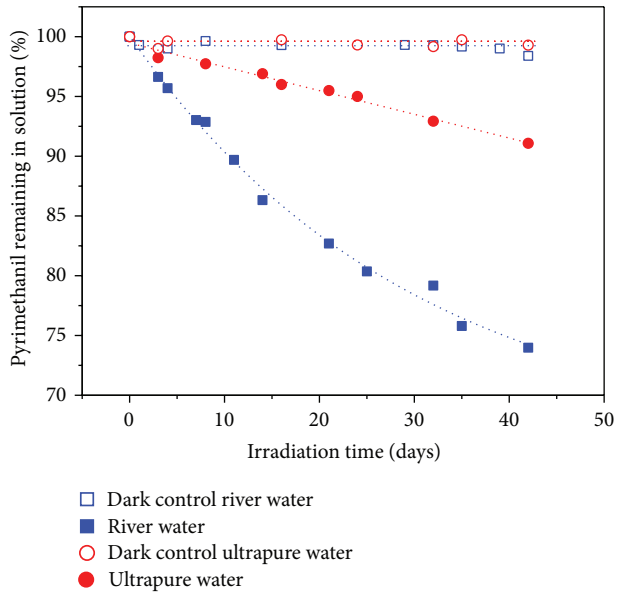


Figure 5: Photodegradation of pyrimethanil/HP-β-CD inclusion complex in (open red circle, solid red circle) ultrapure and (open blue square, solid blue square) river water under simulated solar irradiation.

complex was calculated by integration of the ^{1}H NMR signals at 6.538 and 5.048 ppm, related to the protons of H5 of pyrimethanil and H1$''$ of HP-β-CD, respectively. The ratio of pyrimethanil/HP-β-CD inclusion complex was 1 : 1.

3.3. Photodegradation Studies. Previous studies on the degradation of pyrimethanil were carried out mainly in a waste water treatment context and focused on the photocatalytic degradation using various salts as catalysts [22–24]. Recently, the identification and elucidation of the structures of UV-visible phototransformation products of pyrimethanil in water have been accomplished [12].

In order to comprehend the photodegradation process of the fungicide and to evaluate the effect of its microencapsulation by HP-β-CD on its environmental impact, the rate of photodegradation of pyrimethanil and pyrimethanil/HP-β-CD complex was assessed in ultrapure and in natural water.

The degradation of pyrimethanil was followed by HPLC measurements of the remaining concentration of the fungicide or its HP-β-CD complex in aqueous solution under simulated solar radiation.

The percentage of free and HP-β-CD-complexed pyrimethanil concentrations (obtained by HPLC analysis) was plotted as a function of time, as shown in Figures 4 and 5. The photodegradation kinetics of pyrimethanil disappearance was of first-order in all cases (ultrapure and river water). In fact, pyrimethanil photodegradation profile followed an exponential decay showing that it is affected by photoirradiation in solution. On the contrary, no disappearance of pyrimethanil has been detected in the dark experiments (Figure 4) demonstrating that the disappearance of this fungicide was only due to photodegradation, permitting the exclusion of other phenomena such as microbial degradation. The photodegradation rate of pyrimethanil was much higher in river water than in ultrapure water, showing that there is a relation between the degradation of the fungicide and the constitution of the irradiated media. After 42 days of irradiation, the content of pyrimethanil remaining in ultrapure and in river water was 90.5% and 29.4%, respectively. Actually, the phototransformation of a pollutant in surface water may result from the light absorption by the compound or may be photoinduced by natural organic or inorganic substances, such as organic matter or nitrate ions, present in the water [25, 26].

Table 2 lists the values of the rate constant (k) and half-life ($t_{1/2}$) for the kinetics of the photodegradation of pyrimethanil for simulated solar irradiation.

The irradiation of pyrimethanil in aqueous solution in the presence of HP-β-CD (30 mM) showed a significant decrease in the degradation of fungicide throughout the course of irradiation, more noticeable in the case of river water, demonstrating the photoprotective effect of the cyclodextrin (Figure 5). Actually, cyclodextrin-encapsulated pyrimethanil was more slowly photodegraded in all the waters studied producing first-order rate constants of 2.12 versus 2.08 for ultrapure water and 29.2 versus 7.2 for river water, respectively (Table 2). In river water, the half-lives were increased approximately by a factor of four. After 42 days of irradiation, the content of HP-β-CD-complexed pyrimethanil remaining in ultrapure and in river water was 97.8% and 75.9%, respectively. The microencapsulation in HP-β-CD seems to act as a physical barrier, through which the encapsulated pyrimethanil is protected, against the action of light and/or natural photocatalysts present in the water. This may explain why the residual concentrations of pyrimethanil in river

Table 2: Kinetic parameters of pyrimethanil photodegradation in different aqueous media.

Fungicide	Concentration HP-β-CD (mM)	Water type	k ($10^{-3} \cdot \text{days}^{-1}$)	$t_{1/2}$ (days)
Pyrimethanil	0	Ultrapure	2.12 ± 0.1	327 ± 2.5
		River	29.2 ± 0.6	24 ± 0.5
	30	Ultrapure	2.08 ± 0.1	333 ± 2.9
		River	7.2 ± 0.3	96 ± 1.4

water are much higher in the irradiated samples when fungicide is encapsulated in HP-β-CD than in the free form after 42 days (Figures 4 and 5).

The initiation of the degradation process corresponds, as suggested in literature, to two major routes which continue with a sequence of reactions resulting in a complex and interconnected pathway [22]. One route involves the attack of hydroxyl radicals to the benzene and/or pyrimidine rings with subsequent rings opening, and the other one corresponds to a photoinduced hydrolysis of pyrimethanil molecule by the amine bond [22]. The demonstrated effectiveness of HP-β-CD complexation in improving the photostability of pyrimethanil can therefore be ascribed to the inclusion of the main photoactive centers (as revealed in NMR analysis) of the fungicide in the CD cavity, enabling a deceleration effect of the degradation process, being the reaction rate dependent on the free pyrimethanil concentration arising from dissociation of the complex.

4. Conclusion

The ability of cyclodextrins to alter the physical, chemical, and biological properties of guest molecules has been used to improve the performance of pesticide formulations. The most quoted benefits of CD applications in agriculture include, among others, alterations of the solubility of the pesticide, stabilization against the effects of light or (bio)chemical degradation, and a reduction of volatility.

Owing to the growing interest in cyclodextrins and their ability to improve the stability of drug pesticides, the inclusion complex of pyrimethanil with HP-β-CD has been prepared and characterized. The formation of the inclusion complex increased the solubility of pyrimethanil in water around five times when compared with the free fungicide. Moreover, the formation of pyrimethanil/HP-β-CD inclusion complex increased significantly the photostability of this fungicide in aqueous solutions, presenting a special significance in natural water. Cyclodextrin-encapsulated pyrimethanil was more slowly photodegraded in all the waters studied producing first-order rate constants of 2.12 versus 2.08 for ultrapure water and 29.2 versus 7.2 for river water, respectively. In river water, the fungicide half-lives were increased approximately by a factor of four.

The effectiveness of HP-β-CD complexation in improving the photostability of pyrimethanil was ascribed to the inclusion of the main photoactive centers of the fungicide into the CD cavity. Therefore, it is predictable that the formation of inclusion complexes with CDs may improve the properties of pyrimethanil formulations, increasing the herbicide effectiveness for future applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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