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Dissolved oxygen inhibits the promotion of chlorothalonil photodegradation mediated by humic acid

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ABSTRACT

Chlorothalonil (CT) is widely used to control fungal diseases, and it is commonly detected in the environment. Phototransformation is an important process which removes CT from aquatic environments. The kinetics and mechanisms of CT photodegradation in solutions with and without humic acid (HA) were investigated, and the influence of dissolved oxygen (DO) on the photodegradation process was also considered. The rate constant observed in pure water was only 0.017 h^{-1}, but it increased to 0.083 h^{-1} with 5.0 mgC L^{-1} of HA present. Reactive species generated by HA were shown to play an important role. Moreover, the degradation of CT was promoted at higher HA concentrations. But higher DO concentrations inhibits CT degradation because of the reaction between DO and excited triplet state CT (^{3}CT*) or HA (^{3}HA*). The contributions of the reactive species tested were in the sequence ^{3}HA* > $^1O_2$ > H_2O_2/O_2^- ≈ ·OH in a nitrogen-saturated system, but in an oxygen-saturated system the order was ·OH ≈ $^1O_2$ > H_2O_2/O_2^- > ^{3}HA*. ^{3}CT* was confirmed as the active form of CT during degradation, with 4-hydroxy-chlorothalonil and 2,4,5-trichloroisophthalonitrile as the main products. Compared to direct photodegradation, CT photodegradation mediated by HA can decrease the toxicity of an aquatic environment as demonstrated through tests with *Scenedesmus obliquus*.

1. Introduction

Chlorothalonil (2,4,5,6-tetrachloro-1,3-dicyanobenzene, CT) is a broad-spectrum fungicide applied to control fungal diseases in potatoes, tomatoes, peanuts and other crops. It is also used as an alternative to tributyl-tin in antifouling paints [1,2]. CT has been widely used over the last 30 years with an annual production of more than 8000 tons in China alone [3]. CT is extremely stable in the environment with a long half-life [4,5], and it also has significant cumulative toxicity [6], which could explain CT's performance when it contacts microbes in the soil below the toxic threshold dose over a long period of time. It is reported that CT can inactivate *Daphnia* at concentrations exceeding 1.8 μg L^{-1}, and that the median lethal dose for fish is about 10 μg L^{-1} [7]. Besides its biological toxicity, CT significantly influences the nitrogen cycle in soil by stimulating soil dehydrogenase activity [8], and its long-term use can lead to soil genotoxicity under greenhouse conditions [9]. The half-life of CT in soil is on the order of 1 to 2 months, producing 4-hydroxy-chlorothalonil [10], though it disappears after about 4 weeks in seawater [11]. Owing to its wide use and its persistence in the environment, CT is commonly detected in greenhouse air [12], soil and surface water [13], and in vegetables and fruits [14,15].

Pesticide decomposition in the environment is mainly through biodegradation, hydrolysis and photodegradation. Hydrolysis of CT is significant only at pH > 9 [16], pH values rarely observed in natural aquatic environments. In soil, CT biodegradation is normally insignificant [10]. But amazingly, the half-life of CT decreases to about one hour under irradiation in surface water [17]. A group led by Sakkas has reported that the photodegradation of CT in ground water (a half-life of 0.71 h) was much faster than that in deionized water (36.86 h) with chloro-1,3-dicyanobenzene, dichloro-1,3-dicyanobenzene, trichloro-1,3-dicyanobenzene and benzamide as the products [18]. So in most situations photodegradation is the dominant removal process for CT. In addition, the photolysis of chlorothalonil can be accelerated in the presence of some solutes such as humic substances [18], ferric ion or titanium dioxide [17].

Humic substances (HS) are ubiquitous organic chromophores in most natural waters. They play an important role in the photodegradation of contaminants such as 17α-ethinylestradiol [19], chlorotriazine pesticides [20] and microcystin [21]. HS can mediate photodegradation in three ways. They can absorb a photon to reach an excited singlet state (^{1}HS*) which can return to the ground state through vibrational relaxation, internal conversion or fluorescence. But

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^{1}HS* also can undergo inter-system crossing (isc) to reach an excited triplet state (^{3}HS*). ^{3}HS* may transfer energy to or abstract electrons from ground-state substrates to enhance the photodegradation of contaminants [22,23]. Alternatively, ^{3}HS* may react with oxygen to generate reactive oxygen species (ROS) such as hydroxyl radicals (·OH), singlet oxygen ($^1O_2$) or superoxide ion (O_2^-), all of which can degrade pollutants [24–27]. Or HS themselves may react with ROS to form oxygenated products which can contribute to the degradation of contaminants [28].

The effect of ^{3}HS*on the interaction between CT and ground state HS has been studied. The photodegradation of CT [18] is involved, along with HS accelerating CT's photoreduction and energy transfer [23]. But there have been few reports published about the contribution of ROS to CT degradation, as well as the effect of dissolved oxygen (DO) on CT photodegradation and the degradation pathway. Moreover, many scholars have reported that the main CT photolysis pathway is based on reductive dechlorination. Some have also proposed that ROS might not be involved in CT photolysis [29–31], though there is as yet insufficient evidence to say so definitively.

The aim of this study was to investigate the effects of humic acid (HA) on CT photodegradation in aqueous solution. Xanthone, Fenton solution, Rose Bengal and hydrogen peroxide were used to delineate the role of possible reactive species (RS). The contribution of RS produced from HA on CT degradation was quantified by using sorbic acid, *tert*-butyl alcohol, *β*-carotene and catalase as scavengers. The influence of HA on CT decay with different initial HA and DO concentrations was investigated. *Scenedesmus obliquus* (*S. obliquus*) cell proliferation was used to evaluate the toxicity of CT's photodegradation products.

2. Materials and methods

2.1. Chemicals

Pure (> 99% purity) chlorothalonil, sorbic acid (SA), *tert*-butyl alcohol (TBA), Rose Bengal (RB), *N, N*-dimethyl-*p*-nitrosoaniline (RNO) and sodium perchlorate ($NaClO_4$) were procured from Sigma-Aldrich (USA). *β*-carotene (*β*-car, 96%), catalase (CAT) and xanthone (XT) were purchased from Aladdin (China). The 2,4,6-trimethylphenol (TMP), trifluoroacetic acid, acetonitrile and acetone used were HPLC grade and purchased from Tedia (USA). The other inorganic reagents used in this work were of analytical grade and purchased from Sinopharm Chemical Reagent Co. (China). Ultrapure (UP) water (electric resistance > 18.2 mΩ cm) was produced by using a Millipore (USA) filtration system and used throughout this study. The humic acid was extracted from sediments collected from Dianchi Lake, China (centered around 24°48′2″ N, 102°40′17″ E) following previously-reported methods [32].

2.2. Solution preparation

CT stock solution was prepared by dissolving 3.00 ± 0.05 mg of CT in 1 L of a 5:95 *v/v* mixture of acetonitrile and water. The solution was filtered through a bed of 0.45 μm filter membrane (GF/F, Millipore Corp., USA) which had been baked at 450 °C for 4 h. RNO (3 mM), XT (3 mM), H_2O_2 (5 mM) and CAT (4000 unit/L) stock solutions were prepared with ultrapure water. The SA solution (3 mM) was prepared with a 5 mM solution of NaOH. *β*-car solution was prepared by dissolving 50.30 mg of *β*-car in acetone. All of those solutions were stored in brown reagent bottles at 4 °C. $FeSO_4$ solution was prepared under a N_2 atmosphere at pH 4.

HA stock solution was obtained by dissolving 1.00 g of the Dianchi Lake HA in 500 mL of NaOH solution (0.05 M), stirring over 24 h at room temperature. The solution was then passed through a bed of prebaked 0.45 μm GF/F membrane. Total organic carbon (TOC) content of the HA solution was analyzed using a Micro Cube TOC analyzer (Elementar, USA) with a 0.45 μm glass fiber pre-filter. The prepared HA stock solution was stored in a polyethylene container and kept at 4 °C in the dark, then used within one month.

Table 1
The scheme of experiments.

Additive	Dosage of additive	Role of additive	Reactive species	Reference
SA	20 μM	Quantification and Quencher	Excited triplet state	[33]
TBA	30 mM	Quencher	·OH	[34]
β-car	20 μM	Quencher	$^1O_2$	[35]
CAT	40 unitL^{-1}	Quencher	H_2O_2	[36]
RNO	20 μM	Quantification	·OH	[37]
XT	20 μM	Qualitation	Excited triplet state	[38]
RB	20 μM	Qualitation	$^1O_2$	[19]
Fe^{2+}	2 μM	Qualitation	Blank control	–
Fenton solution	20 μM $FeSO_4$ + 50 μM H_2O_2	Qualitation	H_2O_2	–
H_2O_2	50 μM	Qualitation	H_2O_2	–

2.3. Photodegradation experiments

The CT photodegradation experiments were performed on an XPA-7 merry-go-round photochemical reactor (Xujiang Electromechanical, China). The light source was a 500 W Xe lamp with a 290 nm cutoff filter. The solutions to be irradiated contained 3.0 μM (0.8 mg L^{-1}) of CT with or without HA at 5 mgC L^{-1}. The function and concentration of every additive used in the study is shown in Table 1. SA, TBA, *β*-car and CAT were used as the quenchers for triplet-state HA (or CT) [33], hydroxyl radical [34], singlet oxygen [35], and superoxide ion [36], respectively. RNO was used to quantify ·OH [37], and XT was injected into the CT solution to simulate the reaction of CT with triplet state substances [38]. Fenton reagent was added in the dark to reflect the reaction of CT with ·OH. Rose Bengal was used as a $^1O_2$ generating agent [19]. In order to simulate the photodegradation of CT in natural ground waters, the pH of the solutions was adjusted to 7.8 to 8.2 using 1 M NaOH and 1 M H_2SO_4. The solutions were irradiated in 50 mL cylindrical quartz tubes (D = 15 mm). Samples of 0.60 mL were withdrawn at predetermined time intervals and their CT, SA or RNO content was measured. In the experiment where the Fenton reagent reacted with CT, the pH was adjusted to 3.0 and no irradiation was applied. All of the experiments were carried out in duplicate.

2.4. Analytical methods

The concentrations of CT and SA were quantified using an Agilent 1260 high performance liquid chromatograph (Agilent Technologies, USA) with an ultraviolet detector. Acetonitrile and 0.1% trifluoroacetic acid was used as the mobile phase at a flow rate of 1 mL min^{-1}. The CT was analyzed with a C18 column (Waters, 5 μm, 4.6 × 250 mm) at a detection wavelength of 236 nm. The mobile phase was 85% acetonitrile. SA was determined with a CORTECS™ C18 reversed phase column (Waters, 2.7 μm, 4.6 × 100 mm) at 254 nm. The mobile phase was 17% acetonitrile.

Hydroxyl radical (·OH) analysis involved measuring the solution's absorbance at 440 nm using a Shimadzu UV2600 spectrophotometer. RNO has a yellow color and it absorbs at 440 nm. Its absorption decreases as it reacts with ·OH [37].

The products of CT photolysis were analyzed on a Thermo Ultimate 3000 ultra-high performance liquid chromatograph with a Phenomenex cosmosil 5 PYE column (5.0 μm, 4.6 × 150 mm) coupled with a Bruker AmaZon ion trap mass spectrometer. The mobile phases were acetonitrile (A) and ultrapure water with 0.5% acetic acid (B). The gradient elution program was 0 − 7.0 min 50% A + 50% B, 7.1 − 9.0 min 90%