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Photodegradation of chlorpyrifos with humic acid-bound suspended matter

A.A.D. Amarathunga*,[1], F. Kazama

Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-3-11, Takeda, Kofu, Yamanashi 400-8511, Japan

HIGHLIGHTS

- Photodegradation of chlorpyrifos is more efficient with liquid humic acid (LHA) than without HA.
- Adsorption takes place within a very short time; immediately after photodegradation in the HABSM phase starts.
- Photodegradation of chlorpyrifos is more efficient with HABSM than with LHA and adsorption.
- No effects of HA concentration with LHA or HABSM on the chlorpyrifos photodegradation.
- HABSM is a potentially suitable catalyst for pesticide photodegradation under sunlight.

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ABSTRACT

Land exploitation in several developing countries, including tropical areas, has caused a rapid change of the landscape, from forest to farms. This has led to an increase of pesticide use and concentration of suspended matter in river waters, which may cause soil erosion of these areas. Humic acid (HA), one of the main components in the soil particulate organic matter, has a positive effect on the photodegradation of organic matter in water; however, the efficiency of HA-bound suspended matter (HABSM) for pesticide photodegradation is not known. The aim of this study is to clarify the effect of HABSM on the photodegradation of chlorpyrifos employed in artificial soil particulate covered with HA. Experiments were carried out in liquid HA phase, with/without HABSM phase and HABSM with additional LHA phase under light. The adsorption procedure of the pesticide on HABSM was also studied. Our results reveal that adsorption takes place within a short time period on HABSM and that photodegradation is successfully achieved. The additional LHA + HABSM phase have not demonstrated any significant effect of HA concentration to photodegradation of chlorpyrifos. For instance, when 2.0 mg/L chlorpyrifos was used in the experiments, concentration reductions caused by adsorption, photodegradation under suspended matter and HABSM were found to be 19.3, 17.7, and 61.7% respectively. This finding suggests that HABSM can be considered as a potential catalyst for pesticide photodegradation under sunlight.

1. Introduction

Tropical areas that are characterized by intensive farming in the river basins are subject to a greater amount of precipitations. If runoff surface water is contaminated by pesticides from farming fields, a poor soil management may trigger soil erosion, leading to a large amount of suspended sediments in water. In recent years, with the advent of modern agricultural technologies in developing countries, there has been a steady increase in the use of pesticides. Environmental issues related to soil and water arising from the massive use of pesticides in irrigated rice and other crops in developing countries of the tropics are becoming of great concern. In addition, only a limited amount of pesticide reaches the target; the remaining causes pollution of soil and water, including ground water [1–6]. Among the pesticides

Abbreviations: DEAEC, diethylaminoethyl cellulose; FPD, flame photometric detector; GC, gas chromatography; HA, humic acid; HABSM, humic acid-bound suspended matter; HA-C, carbon in HA; HRM, heated rocking shaker; HSs, humic substances; ICC, initial chlorpyrifos concentration; LHA, liquid humic acid; SM, suspended matter; SPE, solid-phase extraction; TiO_2, titanium dioxide; TOC, total organic carbon; UV, ultraviolet.

* Corresponding author. Tel.: +81 055 222 8193; fax: +81 055 222 8193.
E-mail addresses: deeptha.amarathunga@gmail.com, deeptha@nara.ac.lk (A.A.D. Amarathunga).
[1] Permanent address: Environmental Studies Division, National Aquatic Resource Research & Development Agency, Crow Island, Colombo 15, Sri Lanka. Tel.: +94 112521009; fax: +94 112521009.

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used worldwide, organophosphorus pesticides play a major role in the agricultural industry and are employed to target insects and other pests in farms. Chlorpyrifos (O,O-diethyl-O-(3,5,6-trichloro-2-pyrpyridinyl) phosphorothioate) is one of the most widely used chlorinated organophosphate insecticides across the world [7–10], because of its short persistence after application and acute toxicity to insects. The solubility of chlorpyrifos is 2.0 mg/L at 25 °C in water, $\log K_{ow}$ and $\log K_{oc}$ being 4.82 and 3.73, respectively [9,11]. Previous studies mainly focused on adsorption, photodegradation, and microbial degradation of these compounds [12–15]. It is established that sunlight is crucial for the degradation of various pesticides [16–19], photodegradation being one of the most destructive pathways for pesticides after their release into the environment. However, most pesticides are resistant to chemical and/or photochemical degradation under standard environmental conditions [20]. Several studies have been conducted on chlorpyrifos photodegradation under artificial solar sources of irradiation or ultraviolet (UV) light in combination with catalysts, such as TiO_2, metals ions, hydrogen peroxide, and humic substances (HSs) [16,18,21]. Furthermore, direct and indirect degradation may cause for different transformation products which are more or less toxic product or completely mineralization. Several studies have been conducted on toxicological effect of these transformation products [22–24].

Depending on the source of organic materials involved in the humification process, HSs may include a variety of molecular structures; having different origins [25], they can be categorized into three groups of substances: humin, the insoluble humus fraction; fulvic acid, soluble at all pH values; and humic acid (HA), soluble at pH values larger than 2 [26]. The binding of biocides to HSs has been investigated with a diverse range of experimental methods [27,28]. HSs aggregate via weak hydrogen and π–π bonds or hydrophobic interactions. Moreover, HA, which contains both hydrophilic and hydrophobic domains, can attract a virtually unlimited amount of substances with poor water solubility, and form a shell of molecules around these, which can protect them from the interaction with highly polar water molecules [29]. It was shown that higher pH values promote the formation of HA micelles in solution [30], since the acidic groups can break large molecules into a number of small structures. Hence, membrane-like micelles structures can bind organic substances in their hydrophobic domains [31]; thus, HA can effectively bind chlorpyrifos.

Thirumavalavan et al. [32] reported that a high suspended matter (SM) concentration can cause a decrease of the photodegradation rate of microcystin. In addition, the presence of HA acts as a photosensitizer, accelerating the rate of photodegradation. The inorganic detritic core of clay minerals is surrounded by a layer of amorphous aluminum or ferric oxide, which is partly covered by a humic coating. The humic-coated particles may then interact with organic pollutants [33], due to the high surface area associated to their small size [34]. Aquatic HSs (such as HA and fulvic acid) exist in large and/or small aggregates [26]. The binding between HSs and particles is particularly strong, and the formation of colloidal HSs is the main factor that controls the aqueous concentration and transportation of hydrophobic organic compounds in the environment [33]. In addition, HSs absorb UV as well as visible light in the wavelength range of 290–600 nm, while promoting a chain reaction, which leads to a stimulus-electron promotion of π-electrons from binding orbitals to antibonding orbitals [35]; the transfer energy associated with this process leads to the formation of radicals [26]. Then, the release of a complex mixture of reactive-oxygen species generated in different ways [27,28,36] promotes photodegradation. Several factors influence the rate of degradation, such as the chemical structure of the pollutants, pH, iron concentration, hydrogen peroxide, and the organic load [37]. Earlier studies on abiotic-pesticides investigated separately adsorption and photodegradation, and only a few focused on the chlorpyrifos photodegradation promoted by HSs [38–41].

While HA is known to have positive effect on photodegradation, the efficiency of HABSM is unknown. Thus, the purpose of this work is to study the efficiency of chlorpyrifos photodegradation by HABSM under sunlight.

2. Methodology

2.1. Materials

Chlorpyrifos (reference grade standard, 99.6% purity) was used for all the experiments; high purity (analytical grade 99.9%) acetone (Wako pure Chemical Industries, Ltd., Japan) was used as a solvent for the preparation of the chlorpyrifos solutions and for the extraction procedure. Chlorpyrifos solutions were prepared at a concentration of 100 mg/L and protected from light. Ultrapure water (Milli-Q type-1 – TOC – ≤5 μg/L, resistivity of 18.2 MΩ cm) was obtained for the preparation of solutions and suspensions. LHA was prepared by solving of 1 g humic acid (Wako Pure Chemical Industries, Ltd., Japan) to 100 mL of NaOH (0.1 M) during 24 h agitation followed by filtration with omnipore membrane filter (ø 0.45 μm, MERCK Co.) after adjusting the pH to 6.5 using HCl (0.1 N) and diluting to 1.0 L. The TOC concentration of the sample was 313 mg/L. Diethylaminoethyl cellulose (DEAEC) was used as a model suspended matter; a mixture of HA-bound DEAEC was prepared using 30 g of activated DEAEC (Whatman DE52) with 500 mL of HA. A reactor (100 mL volume, round shaped, flat quarts bottle) was used for the adsorption and photodegradation experiments (Scheme 1) with a heated rocking shaker. Each experimental procedure is described in Section 2.2 in detail. Artificial sun lighting (SOLAX-XC 100W series lighting lamps, about 80% of ultraviolet rays cut) was used within a wavelength range of 370–780 nm at a distance of 20 cm from the reactor; light intensity was 0.8×10^5 lx. Shaking was performed with a heated rocking shaker (HRM-1 from AS ONE company). Solid-phase extraction (SPE) cartridges (GL science, size 230 mg) were used to extract pesticide from water samples. The determination of chlorpyrifos was carried out with gas chromatography (GC, Shimadzu G3000) on a capillary column (length of 30 m, internal diameter of 0.53 mm, film thickness of 1.5 μm) with a flame photometric detector (FPD).

2.2. Experimental procedure

Scheme 1 shows a schematic diagram of the three experimental set-ups.

2.2.1. Photodegradation conduct with liquid humic acid

The photodegradation experiments were carried out in a controlled room temperature with an artificial solar irradiation, with a light wavelength similar to that of sunlight. The pH was kept at 7.0 (7.0 ± 0.2); 10 mL (2.5 mM) of phosphate buffer (pH = 7.1) was added to a reactor; Millipore water was added to fill the bottle completely. Temperature was maintained at 30 ± 5 °C in all the experiments. Experiments were conducted under sunlight in liquid phase without HA to examine the influence of LHA on the degradation of systems with an ICC of 0.5 mg/L, 1.0 mg/L, and 2.0 mg/L. A 4 h irradiation (photodegradation test, Scheme 1) was conducted while shaking. Then, 20 mL samples were used for analysis. Different experiments were conducted without HA; then 3.13 mg/L, 6.26 mg/L, and 9.39 mg/L solutions containing a different concentration of LHA (0.31 mg of carbon in HA (HA-C)/100 mL, 0.62 mg of HA-C/100 mL, and 0.93 mg of HA-C/100 mL) were added into the systems with the above ICC.