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Degradation of chlorpyrifos, an organophosphorus insecticide in aqueous solution with gamma irradiation and natural sunlight

M.S. Hossain [a], A.N.M. Fakhruddin [a,*], M. Alamgir Zaman Chowdhury [b], M. Khorshed Alam [b]

[a] Department of Environmental Sciences, Jahangirnagar University, Dhaka 1342, Bangladesh
[b] Agrochemical and Environmental Research Division, Institute of Food and Radiation Biology, Atomic Energy Research Establishment, Savar, Dhaka 1349, Bangladesh

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ABSTRACT

The radiation induced degradation of chlorpyrifos, an organophosphorus insecticide, was studied using gamma irradiation and sunlight. Chlorpyrifos was analysed by High Performance Liquid Chromatography (HPLC) with Photo Diode Array (PDA) detector. The effect of various doses (1–10 kGy) of gamma irradiation on the degradation of different concentrations (5, 10 and 20 mg/l) of chlorpyrifos insecticide in distilled water was investigated. The lowest tested concentration (5 mg/l) indicated higher removal compare to higher concentration (10–20 mg/l) and irrespective of the absorbed doses (1–10 kGy) and the study revealed a direct relation between absorbed dose and percent of pesticides removal. The degradation of chlorpyrifos by sunlight in distilled water was 39.5% in 12 days, whereas 51.95% was degraded in lake water under same period and same light intensity. The highest degradation rate was recorded in distilled water in 9 days (4.2% per day) at the light intensity of 43,400 lx and in lake water highest degradation was found in 1st day (7.4% per day) at the light intensity of 42,200 lx. Chlorpyrifos degradation using gamma irradiation had the potential to clean up environmental samples contaminated with the organophosphate pesticide, chlorpyrifos.

Introduction

In the last century the development and use of pesticides have played an important role in the increase of agricultural productivity, because of their effectiveness, low cost and acute toxicity [1]. Organophosphorus insecticide, Chlorpyrifos, has significant importance because of its wide distribution, extensive use, and persistence. The most commonly used formulations include the emulsified concentrate, granule, wet powder, and dispersible granule [2,3]. Chlorpyrifos acts by interfering with cholinesterase, an enzyme that is essential for the proper working of the nervous system of both humans and insects [4]. Large-scale manufacture and handling of the organophosphate insecticide chlorpyrifos have led to contamination of soil, air, surface, and groundwater by this pesticide in many parts of the world, which in turn has resulted in disabilities and deaths of mammals including humans. The widespread use of chlorpyrifos in agriculture has raised public concerns about the potential human health risks that can be caused by the ingestion of chlorpyrifos contaminated foods [5].

For the treatment of water, sediments and soils polluted with pesticides, many technologies have been evaluated including physico-chemical and biological treatments. They are generally referred to as advanced oxidation processes (AOPs), which include UV photolysis, photo-catalysis (hydrogen peroxide and ozone), Fenton reagent and radiolysis of water [6] and biodegradation [7–9]. Radiation process is one of the most powerful AOPs, where irradiation with a beam of accelerated electrons or gamma radiation is employed for decomposition of various pollutants. Numerous publications were devoted to the degradation of organic compounds by ionizing radiation [10–12]. The radiolytic degradation of pollutants was employed in recent years for treatment of natural waters and wastes of different origins and it was also used for drinking water treatment [11–13]. The aim of this study is to degrade organophosphorus insecticide chlorpyrifos by gamma irradiation and natural sunlight in aqueous solutions.

Materials and methods

Chemicals and reagents

Reference grade standards for chlorpyrifos (99.5%) were purchased from GmbH (D-86199 Augsburg, Germany). The organic solvent was acetone of HPLC grade. Sample solutions were

* Corresponding author. Tel.: +880 2 7791045 51x1370; fax: +880 2 7791052.
E-mail addresses: a.fakhruddin2@mail.dcu.ie, kazal_f@yahoo.com (A.N.M. Fakhruddin).

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prepared in doubly distilled water further purified by Barnstead E-pure system (USA).

Irradiation source

A Cobalt-60 gamma irradiation source and natural sunlight was used for all irradiation studies. A Gamma cell 220 from MDS Nordion, Canada was calibrated using aqueous ferrous sulfate (Fricke dosimetry) solution [14]. The dose rate was 5.59 kGy h^{-1}. All of the irradiations were conducted at room temperature, 30 °C. The prepared solutions were irradiated at the absorbed dose of 1, 2, 5, 8 and 10 kGy.

Experimental setup

The stock solution of chlorpyrifos was prepared in acetone and stored in glass stoppered flasks at −18 °C. The stock solution of chlorpyrifos was diluted in distilled water (pH 6.8) to prepare the desired concentrations 5, 10 and 20 mg/l and then the chlorpyrifos solutions were placed in 20 ml vials having airtight caps. Moreover, the prepared solutions were irradiated in these vials at tested doses using gamma-ray irradiation and immediately after irradiation; the solution was taken into eppendorf. Then the eppendorf were labeled and kept in a refrigerator prior to their analysis for chlorpyrifos degradation by ^{60}Co gamma irradiation. All the experiments in this study were carried out in triplicate; the average was calculated to describe the removal of chlorpyrifos in tested aqueous solution.

For the degradation of chlorpyrifos by sunlight, the stock solution of chlorpyrifos was diluted by adding in both 2 L distilled and 2 L lake water (pH adjusted to 6.8 using 2 M HCl) to prepare the desired concentration 20 mg/l in both distilled and lake water. Then the chlorpyrifos solutions were placed in 4 L beakers and sealed with transparent polyethylene sheet. Then beakers were kept under direct sunlight for 6 h in everyday on the roof of the building of Institute of Food and Radiation Biology, Atomic Energy Research Establishment. Incident solar intensity was measured with a lux-meter (lx) at the beginning, middle and end of the day. The dark control for both distilled and lake water were kept in the dark condition by sealing with black carbon paper. A portion (approximately 10 ml) of water from distilled and lake water beaker was taken aseptically in centrifuge tube and centrifuge at 8000 rpm for 10 min. After that the supernatant was taken and allowed to centrifuge again at the same condition. The final supernatant (approximately 1 ml) was taken into eppendorf. The contents were thoroughly mixed every time before taking the experimental portion of water. The new level was marked after each sampling and kept in refrigerator prior to their analysis using HPLC. All the samples were thawed and mixed thoroughly prior to analysis. pH was measured everyday in both distilled and lake water. All the experiments were performed in triplicate. The study period for this experiment was up to 12 days.

Analysis of irradiated chlorpyrifos solutions by HPLC

Analysis of irradiated chlorpyrifos solutions was carried out using High Performance liquid Chromatography (HPLC) system (SHIMADZU LC-10 Avp-Series) Automated with LC Solution Software LabSolutions (LC solution Release 1.11SP1) that was equipped with a SPD-M 10 Avp outfitted with a photodiode array (PDA) detector. A C_{18} Reverse Phase Alltech analytical column (5 μm, 250 mm × 9 mm × 4.6 mm) was used and maintained at 30 °C in a column oven. Prior to the HPLC analysis, the samples were passed through 0.45 μm nylon (Alltech Assoc) syringe filters and were manually injected (20 μl) into the HPLC system each time. These conditions were selected after experimental studies. The undegraded chlorpyrifos after irradiation was obtained by comparing peak retention times in samples to those of peaks in the pure analytical standard. Quantification was performed using the method described by Chowdhury et al. [15]. A typical chromatogram from the analysis is shown in Fig. 1.

The percentage recoveries were calculated using the equation: percentage of recovery = [$C_E/C_M \times 100$], where C_E is the experimental concentration determined from the calibration curve and C_M is the spiked concentration. The mean percentage recoveries of all tested pesticides were more than 85% which was satisfactory. These values were quite satisfactory and meet the requirements of the European Commission [16], indicating that the method can be considered accurate and precise when the accuracy of data is between 70 and 110%.

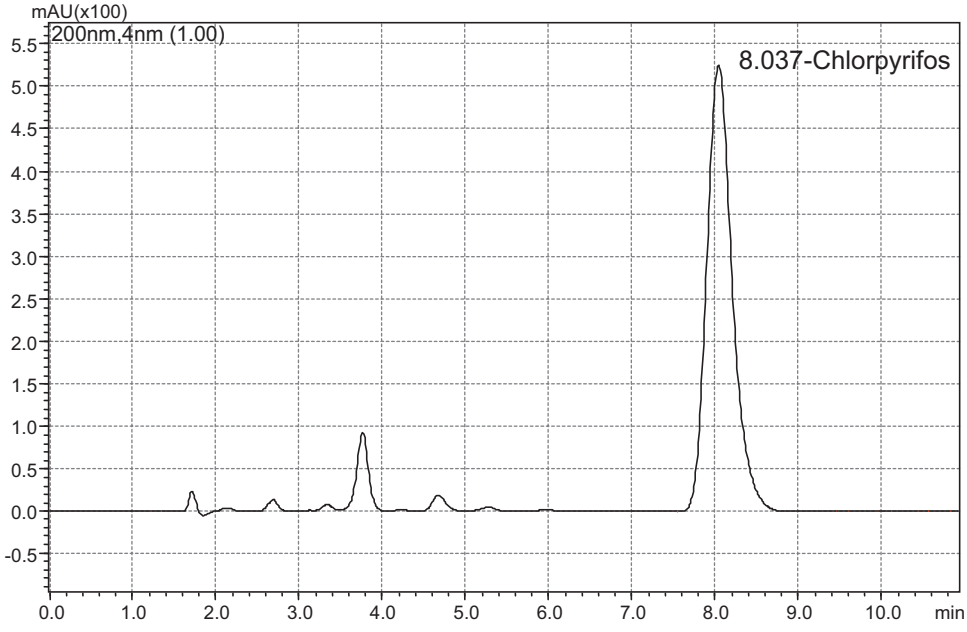

Fig. 1. A typical chromatogram showing chlorpyrifos standard peak (RT = 8.037 min.).