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Photocatalytic degradation of monocrotophos and chlorpyrifos in aqueous solution using TiO_2 under UV radiation

Augustine Amalraj, Anitha Pius *

Department of Chemistry, The Gandhigram Rural Institute – Deemed University, Gandhigram, Dindigul 624 302, Tamil Nadu, India

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ABSTRACT

Monocrotophos (MCP) and chlorpyrifos (CPS) are most popular and broadly used organophosphorous pesticides owing to its low cost and high efficiency in controlling pests in agriculture. Presence of pesticides in aquatic environments causes serious problems to human beings and other organisms. Photocatalytic degradation has been proved to be a promising method for the treatment of water. In view of this, TiO_2 photocatalyst was prepared by sol–gel method and characterized by SEM with EDAX, XRD, BET and FTIR. The photocatalytic degradation of MCP and CPS was carried out using prepared TiO_2 photocatalyst irradiated with 16 W UV light source. The effect of various parameters, i.e., photocatalyst concentration, pesticide concentration and pH of the solution on the percentage of degradation of selected pesticides had been examined. The kinetic analysis of photodegradation of MCP and CPS under different initial concentration followed the Langmuir–Hinshelwood model. TiO_2 found to be an excellent photocatalyst for the degradation of MCP and CPS under UV light irradiation.

1. Introduction

Safe and potable drinking water availability for the Indians, particularly rural population is found to be a mission not accomplished, as the economics associated with the cleanup of the contaminated water is complicated. The presence of pesticide contaminants in surface and ground water has increased many folds in recent years due to their significant use in demanding agricultural field for plant and crop protection. The sources of this contamination may be direct applications of insecticides, rain water runoff from agricultural fields, disposal of outdated stocks and discharge of wastewater from industries are some of the major sources of pesticide contamination in water bodies [1,2]. Rigorous developments of new chemicals for this purpose have significantly increased the variety and quantities of agrochemicals present in the environment. Organophosphorus (OP) pesticides represent the most applied group of insecticides for the last two decades. OPs are comprised within the 10 most widely used pesticides all over the world. They have been used as an alternative to organochlorine compounds for pest control. However, they are considered as extremely toxic compounds. Organophosphorous pesticides like monocrotophos (MCP) and chlorpyrifos (CPS) are commonly used in India and they are noticed in various environmental segments, such as soil, water and air because of their extensive use [2,3]. The chemical structure of MCP and CPS are shown in Fig. 1.

Monocrotophos is one of the most popular and broadly used OP pesticides owing to its low cost and high efficiency in controlling pests mainly on cotton crop, rice and sugarcane, and active against heavy diversity of insects in India. World Health Organization (WHO) and Environmental Protection Agency (EPA) classified MCP in class I – highly toxic compound, which is identified as endocrine disrupting chemicals. As an exogenous agent present in the environment, it disrupts the endocrine functions, such as growth, development and reproduction of humans and animals. Several research reports [4,5] have highlighted the existence of these chemicals in surface and ground water via point and non-point sources. A few adverse effects of endocrine disrupting chemicals are early maturing, defect in child birth and impotence [5,6]. Hence, treatment of wastewater containing endocrine disrupting chemicals is imperative. However, monocrotophos is continually used for the control of major pests in agriculture in developing countries like India primarily due to lack of alternative replacements [7,8].

Chlorpyrifos is another widely used organophosphorus pesticides in agriculture. Exposure to CPS and its metabolites has been related to a variety of nerve disorders in humans. CPS shows a wide spectrum of biological activity and is used to control a range

* Corresponding author. Fax: +91 451 2454466.
E-mail address: dranithapius@gmail.com (A. Pius).

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of insects, pests as well as soil dwelling grubs, rootworms, borers and subterranean termites. The contamination has been found up to about 24 km from the site of application. Symptoms of acute poisoning include headache, nausea, muscle twitching and convulsions and in some extreme cases even death. Human birth defects have also been associated with exposure to CPS and its products. It also affects male reproductive system. CPS is toxic to a variety of beneficial arthropods, including bees, ladybird beetles and parasitic wasps. It kills fish at concentrations as low as a few parts per trillion [9–11].

India is currently the second largest producer of pesticides in Asia, after China. It ranks as the fourth largest pesticide producing nation in the world after the USA, Japan and China. India has more than 139,000 MT pesticide production capacities annually, with more than 219 technical grade and manufacturing units, and over 4000 formulation units. A steady growth in the production of technical grade pesticides was observed during the period 1958 (total production 5000 MT) to 1997 (total production 102,600 MT). Consumption patterns of pesticides in India are different from that of the rest of the world. It is highly inconsistent and varies from one state to another. The state of Tamil Nadu, with an area of 130,000 km^2 uses 12,500 MT of pesticides annually. Pesticides in Tamil Nadu with the highest consumption rates include monocrotophos, endosulfan, phorate, chlorpyriphos, methyl parathion, quinalphos, mancozeb, paraquat, butachlor, isoproturon and phosphamidon [12].

Presence of selected pesticides as contaminants in aquatic environments may cause serious problems to human beings and other organisms. Increased awareness about selected potential pesticide movement into the drinking water sources has forced the researchers to identify ways to prevent such contamination. Currently available water treatment technologies, such as adsorption or coagulation merely concentrate the pollutants present by transferring them to other phases, but still remain and not being completely "eliminated" or "destroyed" [13]. Photocatalytic degradation has been proved to be a promising method for the treatment of wastewater contaminated with organic and inorganic pollutants. In recent years, advanced oxidation processes (AOPs) have been proposed as innovative water treatment technologies. The motivation of these AOPs is based on the in situ generation of active species (i.e., H_2O_2, $HO^{\bullet}$, $O_2^{-\bullet}$, and O_3) for the mineralization of refractory organic compounds, water pathogens and disinfection by-products [13–19]. Heterogeneous photocatalysis, which is the acceleration of a photoreaction by a catalyst, an attractive and efficient method for the degradation of environmental pollutants or non-biodegradable toxics present in aqueous domestic, industrial or agricultural effluents. Titanium dioxide (TiO_2) is one of the most appropriate semiconductor materials to be employed as a photocatalyst, because of its stability under harsh conditions, commercial availability, possibility of coating as a thin film on solid support, ease of preparation in the laboratory, etc. A number of important features of the heterogeneous photocatalysis have extended their feasible applications in water treatment. The fact that the highly reactive oxygen species generated as a result of the photo-induced charge separation on TiO_2 surfaces for microbial inactivation and organic mineralization without creating any secondary pollution is well-documented [13–15].

The aim of this research is to study the photocatalytic degradation of MCP and CPS in the presence of TiO_2. Comparative study of the photocatalytic degradation of MCP and CPS in the presence of TiO_2 has been scarcely reported. The effect of important parameters such illumination time, catalyst dose, initial MCP and CPS concentrations and pH was examined. Kinetic photochemical behavior of MCP and CPS using titanium dioxide as a photocatalyst was also studied.

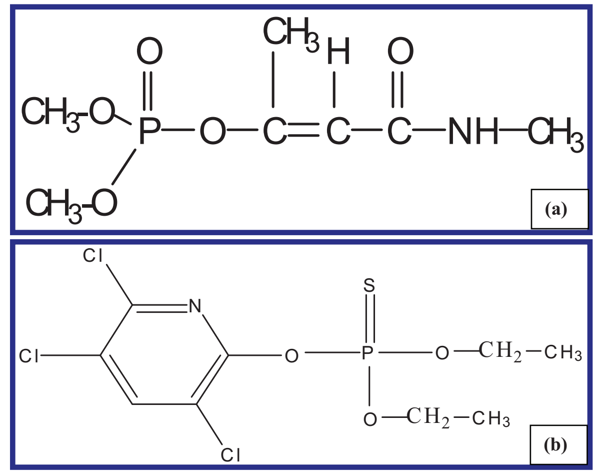

Fig. 1. Chemical structures of (a) MCP and (b) CPS.

2. Materials and methods

2.1. Selection of the study area

Oddanchatram block of Dindigul district in Tamil Nadu was selected for this study taking into consideration of many factors. Dindigul district constituted approximately eight per cent of the total vegetable area in the state and Oddanchatram has the second largest wholesale vegetable market in Tamil Nadu and all the left over vegetables are dumped around the market. The pesticide contents of vegetables dumped over the years find their way to the ground water and surface water. This area has close proximity to the institution where the study was carried out. Oddanchatram is located at the base of the Western Ghats in South India (10°29′16″N latitude, 77°45′9″E longitude).

2.2. Materials

Chemicals, such as tetrabutyl titanate, ethanol absolute AR (99.9%), hydrochloric acid and sodium hydroxide and glacial acetic acid were purchased from Sigma–Aldrich, India, were used for the study. Monocrotophos and chlorpyrifos of commercial grade were purchased from local markets. All solutions and reaction mixtures were prepared using Milli-Q water.

2.3. Preparation of TiO_2 catalyst

Preparation of TiO_2 nanophotocatalysts was carried out by sol–gel method. In this method, 20 mL tetrabutyl titanate and 4 mL acetic acid were added into 26 mL of absolute ethanol under continuous stirring condition to obtain solution A. 8 mL deionized water, 12 mL absolute ethanol and 12 mL acetic acid were mixed together to obtain solution B. Then, solution B was added drop wise into solution A under stirring. The obtained solution was sealed and stirring was continued for another 30 min at room temperature. The resultant gel was aged at room temperature for 24 h and dried in an oven at 100 °C for 36 h. After grinding, the gel was heat-treated in a furnace at 300 °C for 3 h and white crystalline TiO_2 nanoparticles were obtained at the end of the process [18,20].

2.4. Characterization

The synthesized photocatalyst was characterized using scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX) (Vega3Tescan, Brucker) and X-ray diffraction