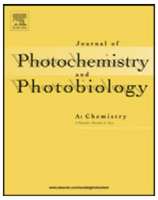
Journal of Photochemistry and Photobiology A: Chemistry 251 (2013) 33–40

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Degradation intermediates and reaction pathway of carbofuran in leaching water using TiO_2 and ZnO as photocatalyst under natural sunlight

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ARTICLE INFO

Article history:
Received 26 June 2012
Received in revised form
28 September 2012
Accepted 12 October 2012
Available online 23 October 2012

Keywords:
Water remediation
Carbofuran
Photocatalytic oxidation
Semiconductor materials

ABSTRACT

In this work the solar-photocatalytical degradation of carbofuran in leaching water has been studied using zinc oxide (ZnO) and different mixed-phase (rutile/anatase) titanium dioxide (TiO_2) at pilot plant scale. Comparison of catalysts showed that ZnO is the most efficient for catalyzing the removal of carbofuran and their main organic intermediates. The residual levels of carbofuran at the end of the experiment (240 min) were 0.1, 22.4, 62.8, 68.4 $\mu g\,L^{-1}$ for ZnO, TiO_2 P25 Degussa (70A/30R), TiO_2 rutile (25A/75R) and TiO_2 anatase (90A/10R), respectively. The primary degradation of carbofuran followed pseudo-first order kinetics. The analysis and evolution of the intermediates suggest that oxidation of the C—O bond on the carbamate group and 3C position of the furan ring as the main metabolic pathway.

1. Introduction

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is a broad-spectrum carbamate insecticide and nematicide widely used to control several soil-borne insects and nematodes found in potatoes, corn, rice, alfalfa, grapes and other agricultural crops. This pesticide is directly sprayed onto soil and plants immediately after emergence. It is an inhibitor of acetylcholinesterase and highly toxic to fish and mammals. This carbamate pesticide is highly soluble in water (351 $mg\,L^{-1}$) [1]; therefore, it is susceptible to leaching through the soil profile. Thus, residues of these compounds were found in surface and groundwater [2,3]. Therefore, the application of effective techniques for carbofuran degradation is a need. Advanced oxidation processes (AOPs), like H_2O_2/UV, O_3/UV and H_2O_2/O_3/UV, heterogeneous photocatalysis, homogeneous photo-Fenton, etc., have been successfully tested for the elimination of pesticides [4,5].

Due to their high effectiveness and low cost, heterogeneous photocatalysis has been widely used by numerous authors [4–6]. This technique uses light with wavelengths energy $h\nu \geq E_g$ (band gap energy) to excite the semiconductor particles, usually titanium dioxide (TiO_2) [7], and to produce an electron–hole pair. The hole can react with hydroxyl groups on the surface of the semiconductor forming $OH^{\bullet}$ radicals with an $E^{\circ} = 2.8$ V, which can lead to complete mineralization of organic pollutants [8]. Similar oxidation pathways to those of TiO_2 are confirmed in ZnO photocatalyst (Fig. 1). ZnO is reported to be as reactive as TiO_2 under concentrated sunlight, since the band gap energy of ZnO is similar to that of TiO_2, i.e., 3.2 eV.

In recent years, the photocatalytic degradation of carbofuran in aqueous solution has been studied using TiO_2 Degussa P25 as the semiconductor catalyst [9–11]. However, the effect of ZnO, TiO_2 rutile and TiO_2 anatase for the removal of this carbamate from water has received little attention [10]. Thus, to contribute to the actual application of this technology, the main goal of this work was to investigate the photocatalytic degradation of carbofuran (CF) using zinc oxide (ZnO) and different mixed-phase titanium dioxide (TiO_2) as catalysts in leaching water under solar irradiation at pilot scale. In order to investigate the degradation pathway, the generated intermediates were also determined.

2. Experimental

2.1. Pesticides and reagents

Analytical standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany): Carbofuran (99.5% purity), 7-phenolcarbofuran (99.0% purity), 3-hydroxycarbofuran (96.0% purity), 3-hydroxy-7-phenolcarbofuran (95.5% purity), 3-keto-7-phenolcarbofuran (99.0% purity) and 3-ketocarbofuran (96.0% purity). Zinc oxide (99.9%, 10 $m^2\,g^{-1}$ BET specific surface area, <70 μm particle size), and titanium dioxide anatase (99.9%,

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http://dx.doi.org/10.1016/j.jphotochem.2012.10.012

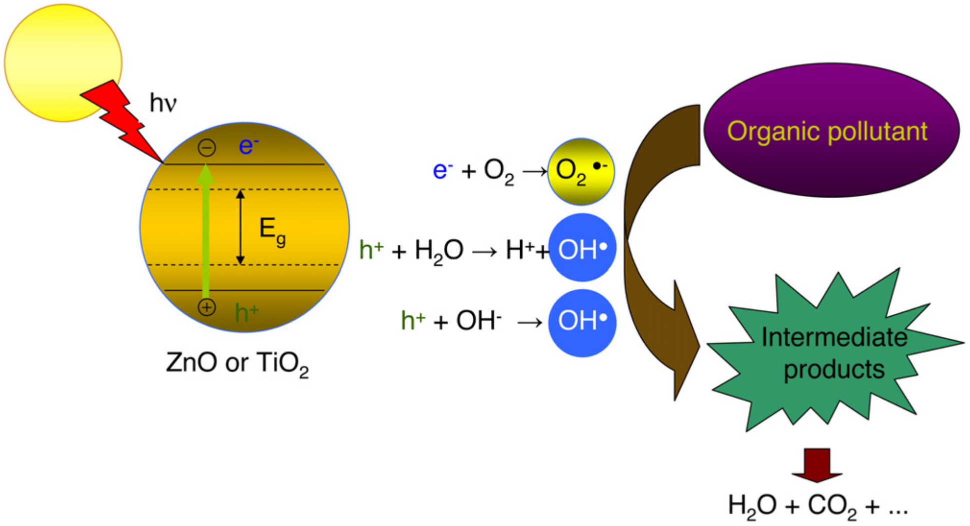

Fig. 1. Scheme for the heterogeneous photocatalysis (TiO_2 or ZnO).

45 $m^2 g^{-1}$ BET specific surface area, 32 nm particle size) were purchased from Alfa Aesar (Karlsruhe, Germany). Titanium dioxide mixture of rutile and anatase (99.5%, <100 nm particle size) was supplied from Sigma–Aldrich Química S.A. (Madrid, Spain). Titanium dioxide P25 Degussa (99.5%, 50 $m^2 g^{-1}$ BET specific surface area, <21 nm particle size) was supplied from Nippon Aerosil Co. Ltd. (Osaka, Japan). The titanium dioxide solid phases were characterized by means of powder X-Ray Diffractometry (XRD), on a Philips PW 1700. The samples were measured at 40 kV and 24 mA using Cu-Kα radiation at a scanning speed of 1° (2θ). The contents of anatase (A) and rutile (R) phases in the powders were 70A:30R for TiO_2 P25 Degussa, 25A:75R for TiO_2 rutile and 90A:10R for TiO_2 anatase. The point of zero charge (pzc) of TiO_2 and ZnO is about 6.0 and 9.0, respectively. Thus, the average pzc of titanium dioxide anatase and rutile reported in the literature was 5.9 ± 1.0 and 5.4 ± 0.8, respectively [12]. Sodium peroxydisulfate (98%) was purchased from Panreac Química (Barcelone, Spain). Deionized water (18 MΩ cm resistivity) was obtained from a Milli-Q ultrapure water purification system (Millipore, Bedford, MA, USA).

2.2. Photoreaction setup

The experiment was carried out in a pilot plant in Murcia, SE Spain (latitude 37°59′N, longitude 1°08′W) using natural sunlight irradiation during summer, 2010. The values (mean ± SD) of visible plus near-infrared (400–1100 nm), UVA (315–400 nm), UVB (280–315 nm) and UVC (200–280 nm) radiation were taken with a portable photoradiometer Delta Ohm HD 2102.2 (Caseelle di Selvazzano, Italy). Fig. 2 shows the mean values (n = 15) recorded from UV radiation during the sampling.

The solar pilot plant used in this experiment is based on compound parabolic collector (CPC) technology (Fig. 3). This small prototype consists of one photoreactor module (1.27 m^2) with five borosilicate tubes (200 cm length × 4 cm i.d.) mounted on curved polished aluminum reflectors (0.9 cm radius of curvature) running in east–west line. The water flows directly from tube one to another connected in series and finally to the reservoir tank (250 L) and a centrifugal pump (0.55 kw) before returning (45 L min^{-1}) to the collector tubes in a closed circuit. The reservoir tank was continuously stirred to achieve a homogeneous suspension and thermostated by circulating water to keep the temperature at 25 ± 2 °C. The illuminated volume was 12.55 L and the dead volume in the PVC tubes was 6.5 L. Storage tank, flowmeter, sensors (pH, O_2 and T), pipes, and fittings completed the installation.

The water used in the photodegradation studies was obtained from several lysimeters (3.5 m × 4 m × 1 m) from an experimental greenhouse located in Campo de Cartagena (SE Spain). The lysimeters were filled with clay-loam soil, pH 8.7 and OM = 0.22%. The soil was irrigated every four days by three dripperlines (60 min per day and 50 mL min^{-1} per emitter). About 7–8 L per day were collected from each lysimeter. The leaching water was collected and transported to the storage tank and stored in dark at ambient temperature for one week. The leaching water had the following composition: pH 8.4, EC = 3.96 dS m^{-1}, TOC = 133 mg L^{-1}, Ca^{2+} = 297 mg L^{-1}, Mg^{2+} = 140 mg L^{-1}, Na^+ = 418 mg L^{-1}, K^+ = 82 mg L^{-1}, SO_4^{2-} = 879 mg L^{-1}, Cl^- = 537 mg L^{-1}, HCO_3^- = 300 mg L^{-1}, NO_3^- = 301 mg L^{-1}, and NO_2^- = 0.06 mg L^{-1}.

At the beginning of each experiment, 150 L of leaching water were mixed with the commercial product (CURATERR, Bayer CropScience) to reach a spiking level of about 0.1 mg L^{-1} of carbofuran (CF). The mixture was homogenized for 20 min in the dark with collectors covered by a black awning. Finally, the photosensitizer (150 mg L^{-1} of ZnO and 100 mg L^{-1} of TiO_2) were added and the cover was removed after 20 min when 100 mg L^{-1} of $Na_2S_2O_8$ were added. Samples were collected at 0, 5, 10, 20, 45, 60, 120 and 240 min from 10 a.m. to 14.00 p.m. Air was injected into the tank

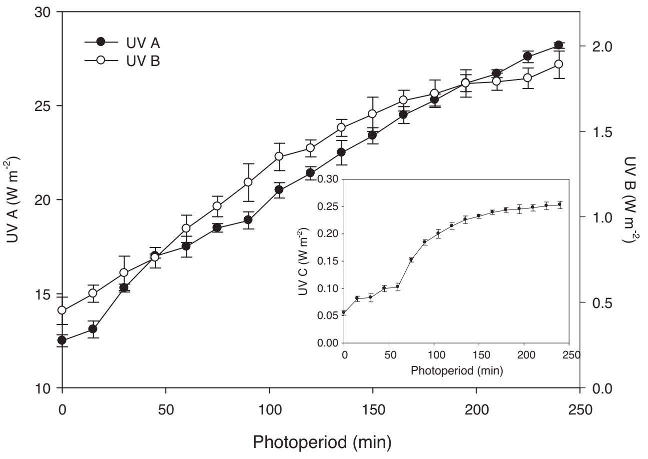

Fig. 2. Mean values (n = 15) for UV-A and UV-B radiation recorded in the different sample points of the photoperiod. Insert graphic shows UV-C radiation. Error bars denote standard deviation.