



Semiconductor oxides-sensitized photodegradation of fenamiphos in leaching water under natural sunlight

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ARTICLE INFO

Article history:

Received 20 October 2011

Received in revised form

13 December 2011

Accepted 15 December 2011

Available online 23 December 2011

Keywords:

Water detoxification

Fenamiphos

Fenamiphos sulfoxide

Fenamiphos sulfone

Photocatalytic oxidation

Semiconductor materials

ABSTRACT

The photocatalytic degradation of fenamiphos in leaching water has been studied using zinc oxide (ZnO), different mixed-phase titanium dioxide (TiO₂), tungsten(VI) oxide (WO₃), and tin(IV) oxide (SnO₂) at pilot plant scale under natural sunlight. Photocatalytic experiments showed that the addition of semiconductors in tandem with the oxidant (Na₂S₂O₈) strongly enhances the degradation rate of fenamiphos in comparisons carried out with photolytic tests. The primary degradation of fenamiphos followed a pseudo-first order kinetics. The time required for 50% degradation was in the range 1–3 min for ZnO and TiO₂. The main photocatalytic intermediates (fenamiphos-sulfoxide and fenamiphos sulfone) detected during the degradation of fenamiphos were identified. Comparison of catalysts showed that ZnO is the most efficient for catalyzing the removal of fenamiphos and their metabolites. Thus, complete disappearance of all the compounds studied achieved after 240 min of illumination in the ZnO/Na₂S₂O₈ system.

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1. Introduction

Fenamiphos (ethyl 4-methylthio-m-tolyl isopropylphosphoramidate), an organophosphorus pesticide, is primarily used to control nematodes in a wide range of horticultural crops and in turf. This systemic nematicide is an inhibitor of acetylcholinesterase. Fenamiphos quickly oxidizes to fenamiphos sulfoxide, which in turn, slowly oxidizes to fenamiphos sulfone [1]. The molecular structures of these chemicals are illustrated in Fig. 1. Due to their high solubility, fenamiphos and their metabolites may leach through the soil profile. Thus, residues of these compounds were found in surface and groundwaters [2,3]. Similar to fenamiphos, their metabolites are of a potential concern with regards to their fate and toxicity to water bodies. Consequently, it is of primary importance to apply remediation strategies to polluted waters or leachates in order to protect water resources. Advanced oxidation processes (AOPs), like H₂O₂/UV, O₃/UV and H₂O₂/O₃/UV, heterogeneous photocatalysis, homogeneous photo-Fenton, etc., have been proposed for treatment of polluted water by pesticides [4].

In particular, heterogeneous photocatalysis is an efficient technique to eliminate organic pollutants in water [5,6]. Semiconductors (TiO₂, ZnO, Fe₂O₃, ZnS, etc.) can act as sensitizers for

light induced redox processes due to their electronic structure which is characterized by a filled valence band and an empty conduction band. This technique is based on the irradiation of semiconductor particles, usually titanium dioxide (TiO₂) because of its relatively high activity, its stability under operation conditions and its low cost [7]. Among the three main TiO₂ crystallographic forms (anatase, rutile and brookite), anatase and rutile forms have been investigated extensively as photocatalysts. Rutile generally exhibits lower catalytic activity than anatase [8]. The photocatalytic activity of TiO₂ is dependent on surface and structural properties of semiconductor. The commercial photocatalyst titanium dioxide Degussa P25 has been widely used and it is considered as the standard photocatalyst [9]. Degussa P25 consists of anatase and rutile in an approximately 3:1 proportion and is obtained by hydrolysis of TiCl₄ in a hot flame with a relatively short residence time [10].

When TiO₂ is irradiated with photons with wavelengths energy $h\nu \geq E_g$ (band gap energy), electrons (e⁻) are promoted to the conduction band, leaving a positive hole (h⁺) in the valence band. Holes can react with hydroxyl groups on the surface of the semiconductor to produce strongly oxidizing OH• radicals. The hydroxyl radicals are extremely reactive ($E^\circ = 2.8\text{ V}$), non-selective and readily attack pesticides. As a result, these organic contaminants are sequentially transformed to simpler organic molecules that are eventually mineralized to CO₂, H₂O and inorganic salts [11]. On the other hand, electrons are trapped at surface sites and removed by reactions with adsorbed molecular O₂ to form superoxide anion radical O₂•⁻. Similar oxidation pathways to those of TiO₂ are confirmed in

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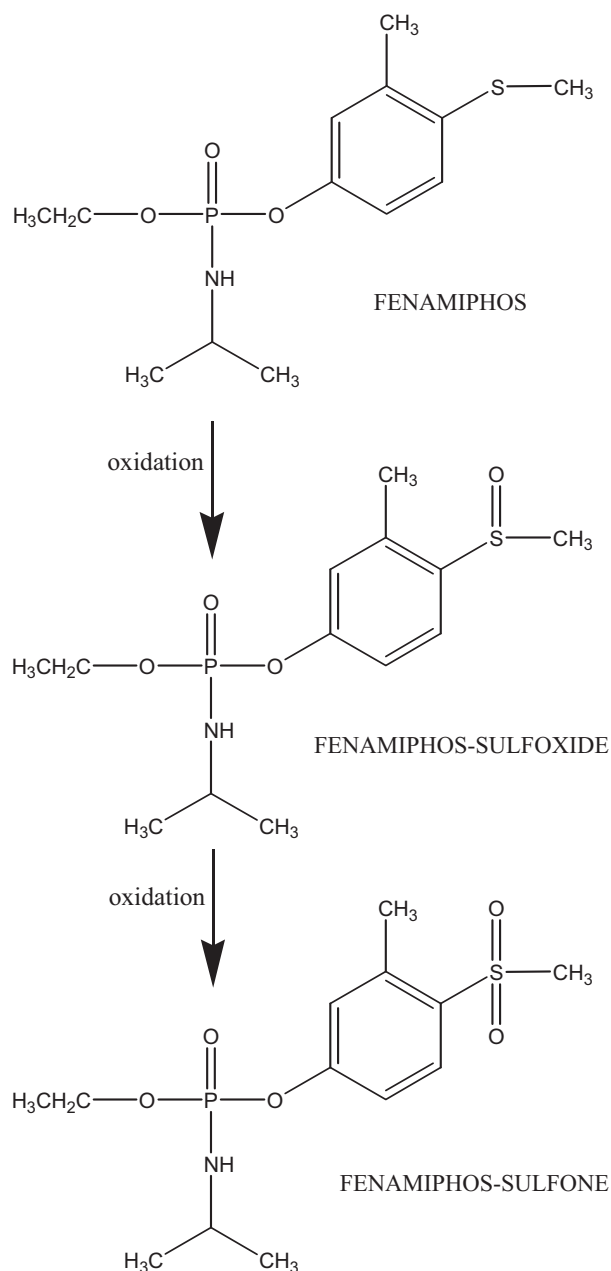


Fig. 1. Scheme for fenamiphos oxidation.

ZnO photocatalyst. ZnO is reported to be as reactive as TiO₂ under concentrated sunlight, since the band gap energy of ZnO is equal to that of TiO₂, i.e., 3.2 eV. No significant effort has been made in evaluating the photocatalytic efficiency of ZnO and TiO₂ on fenamiphos's oxidation. For this reason, in this study, the photocatalytic degradation of fenamiphos and their two main metabolites in leaching water has been investigated using zinc oxide (ZnO) and different mixed-phase titanium dioxide (TiO₂) as catalysts.

2. Experimental

2.1. Pesticides, metabolites and reagents

Fenamiphos, fenamiphos-sulfoxide, fenamiphos-sulfone were purchased from Dr. Ehrenstorfer (Augsburg, Germany): The commercial formulation used (NEMACUR 40 LE, fenamiphos 40%) was purchased from Fitodolores SL (Murcia, Spain). Zinc oxide (99.9%,

10 m² g⁻¹, <70 μm), titanium dioxide anatase (99.9%, 45 m² g⁻¹, 32 nm) and tungsten(VI) oxide (99.8%, powder <20 μm) were purchased from Alfa Aesar (Karlsruhe, Germany). Titanium dioxide mixture of rutile and anatase (99.5%, <100 nm) and tin(IV) oxide (99.9%, powder <44 μm) were supplied from Sigma-Aldrich Química S.A. (Madrid, Spain). Titanium dioxide P25 Degussa (99.5%, 50 m² g⁻¹, <21 nm) 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 diffractogram of the X-ray of TiO₂ types are given in Fig. 2. The contents of anatase (A) and rutile (R) phases in the powders were 70A:30R for TiO₂ P25 Degussa, 25A:75R for TiO₂ mixture of rutile:anatase and 90A:10R for TiO₂ anatase. Sodium peroxydisulfate (98%) was purchased from Panreac Química (Barcelona, Spain). Acetonitrile was supplied by Scharlau (Barcelona, Spain).

2.2. Preparation of solutions

Stocks solutions (1000 μg mL⁻¹) of each pesticide standard were prepared in acetonitrile, protected from light and stored at 5 °C. A pesticide intermediate standard solution was prepared by dilution in the same solvent to obtain a concentration of 10 μg mL⁻¹. Several standard solutions, with concentrations of 0.5–200 μg L⁻¹, were injected to obtain the linearity of detector response.

2.3. Leaching experiment

The soil selected for the study was taken from Campo de Cartagena (Murcia, SE Spain), air dried, ground, sieved through 2 mm mesh sieve and stored at 4 °C. The characteristics of the soil were as follows: pH 8.70; organic matter content 0.22%, electrical conductivity 3.54 dS m⁻¹ and clay loam texture (33% clay, 30% silt, 37% sand).

All experiments were performed according to the OECD guidelines [12]. Downward movement of the fungicides was studied in polyvinyl chloride (PVC) columns of 30 cm (length) × 4 cm (i.d.) packed with 200 g of soil (bulk density, 1.34 g cm⁻³). The top 3 cm of the columns were filled with sea sand and the bottom 3 cm with sea sand plus nylon mesh with an effective pore diameter of 60 μm to minimize the dead-end volume and prevent losses of soil during the experiment. Before the application of the compound, the columns were conditioned with 0.01 M CaCl₂ in distilled water to their maximal water holding capacity and then allowed to drain for 24 h. The pore volume (PV) of the packed columns was estimated by the weight difference of water-saturated columns versus dry columns. The calculated PV of the soil columns after saturation was 66 ± 3 mL. Afterwards, 2 mL of a methanol/water solution (10/90, v/v) containing 25 μg of fenamiphos were added to the top of each column. Twenty-four hours after pesticide application (when solvent was completely evaporated), the compounds were leached using a peristaltic pump with 0.01 M CaCl₂ at a rate of 50 mL day⁻¹ (equivalent to 21 mm) for 22 days. CaCl₂ instead of water was used in order to minimize soil mineral balance disruption. After this time, the columns were opened and the soil was separated into two segments of approximately 10 cm each. Five replications were run at room temperature (21 ± 2 °C), avoiding direct light.

2.4. Solar photocatalysis experiment

The water used in the photodegradation studies was obtained from 8 lysimeters (3.5 m × 4 m × 1 m) from an experimental greenhouse located in Campo de Cartagena (SE Spain). A clay loam soil (pH 8.7 and OM=0.22%) was used. The soil was irrigated every four days by three dripperlines (45 min/day and

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