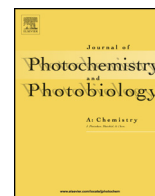




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Photocatalytic oxidation of pirimicarb in aqueous slurries containing binary and ternary oxides of zinc and titanium



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ABSTRACT

The photocatalytic degradation of pirimicarb in pure water has been studied using zinc oxide (ZnO), titanium dioxide (TiO₂) and zinc titanates (Zn₂TiO₄ and ZnTiO₃) under artificial light (300–460 nm) irradiation. Comparison of catalysts showed that TiO₂ is the most efficient for the removal of pirimicarb and their transformation products. To obtain a better understanding of the mechanistic details of these ZnO–TiO₂-assisted photodegradation of pirimicarb, the transformation products of the processes were identified by liquid chromatography tandem mass spectrometry (LC–MS²) and liquid chromatography time of flight mass spectrometry (LC–TOF/MS) techniques. The probable photodegradation pathways are proposed and discussed. The main steps involved: N-dealkylation of the 2-dimethylamino group to form the carbamate and decarbamylation of the carbamate moiety with further N-dealkylation of the 2-dimethylamino group to have the hydroxypyrimidines.

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1. Introduction

Carbamate pesticides have been extensively used in pest control owing to their high effectiveness and low persistence. Pirimicarb (2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate) is an *N,N*-dimethylcarbamate insecticide that is widely employed against aphids in fruit and vegetable. Pirimicarb exerts its toxic effects by inhibiting the enzyme acetylcholinesterase [1]. This systemic insecticide is suspected carcinogen and mutagen [2]. In addition, their high solubility, pirimicarb may leach through the soil profile [3,4]. Consequently, it is of primary importance to apply remediation strategies to polluted waters in order to protect hydric resources.

In this context, the degradation of organic pollutants in water by photocatalysis, using semiconductors such as TiO₂ and ZnO, has been widely used by numerous authors in the past two decades [5–9]. Solar radiation, a renewable source of energy, inexhaustible and pollution-free, can be widely utilized in the photocatalytic degradation of the dyes, pesticides and detergents [10–13]. The

photocatalytic process is based on the generation of electron–hole pairs by irradiation of semiconductor particles with energy $h\nu \geq E_g$ (band gap energy). These electron–hole pairs are capable of initiating a series of chemical reactions that eventually mineralize the pollutants [14].

These semiconductors have many advantages such as a low price, high photocatalytic activity, simple preparation, etc. However, ZnO has a low stability at high pH, while TiO₂ can only absorb a small portion of solar spectra in the UV region [15]. Thus, the photocatalytic activity of ZnO–TiO₂ systems (Zn₂TiO₄ with cubic spinel crystal structure, Zn₂Ti₃O₈ with cubic defect spinel structure and ZnTiO₃ with cubic or hexagonal structure) is being investigated with the purpose of looking for more efficient materials for photocatalytic applications [16–18]. Although the photocatalytic degradation of pirimicarb using ZnO and TiO₂ has been studied from previous researchers [5,19], the effect of ZnO–TiO₂ system for the removal of pirimicarb from water has not been studied. The main goal of this work was to assess the effectiveness of the photocatalytic process for the decontamination of water polluted by pirimicarb, to evaluate the kinetics aspects of the process and the reaction intermediates for understanding the mechanistic details of the photodegradation in the ZnO–TiO₂ systems (ZnO, TiO₂, Zn₂TiO₄ and ZnTiO₃).

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2. Experimental

2.1. Pirimicarb, transformation products and reagents

Analytical reagents were purchased from Dr. Ehrenstorfer (Augsburg, Germany) with purity >99%. Pirimicarb and their main organic transformation products are listed in Table 1. Zinc oxide (ZnO) and zinc titanium oxide (Zn_2TiO_4) were purchased from Alfa Aesar (Karlsruhe, Germany), zinc titanate ($ZnTiO_3$) was purchased from Sigma–Aldrich Química S.A. (Madrid, Spain). Titanium dioxide P25 Degussa (TiO_2) was supplied from Nippon Aerosil Co., Ltd. (Osaka, Japan). Acetonitrile was supplied by Scharlau (Barcelona, Spain).

2.2. Photocatalyst characterization

The photocatalysts were characterized by a PerkinElmer Lambda 750S UV/VIS spectrophotometer equipped with 60 mm integrating sphere accessory for diffuse reflectance spectra. Software: UV WinLab DPV 1.0 (Shelton, USA). A $BaSO_4$ standard was used as the reference spectrum. The crystalline structure of the photocatalysts was 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-K α radiation at a scanning speed of 1° (2θ). The morphology of the solids was examined by field emission scanning electron microscopy (FE-SEM) using a Carl Zeiss MERLIN VP Compact microscope (Oberkochen, Germany) with high resolution imaging up to 0.8 nm @15 KV, acceleration voltage of 0.02–30 kV and energy dispersive X-ray (EDX) attached to SEM. The surface area (S_{BET}) of the semiconductors was measured according to the BET method by nitrogen adsorption–desorption isotherms at 77 K on a Micromeritics Tristar 3000 instrument (Micromeritics Instruments Co., USA).

2.3. Photoreactor setup

The photocatalytic and photolytic experiments were performed in a photochemical reactor [20]. The reactant solution containing different amounts of the semiconductor powder (100–400 mg L^{-1}) was circulated at a flow rate of 600 mL min^{-1} .

Initially, 2000 mL of type II analytical-grade water (pH 7.1, ORP 212 mV, resistivity $>5 M\Omega cm$ (25 °C); conductivity $<1 \mu S cm^{-1}$, TOC $<30 \mu g L^{-1}$; microorganisms $<10 cfu mL^{-1}$) was mixed with commercial product (APHOX, Syngenta) to reach a spiking level of about 0.1 mg L^{-1} of pirimicarb, homogenizing the mixture for 20 min to constant concentration in the dark. After this time the appropriate amount of catalyst (200 mg L^{-1}) was added to the reaction solution. The respective mixtures were maintained for 30 min in the dark, prior to illumination, in order to achieve the maximum adsorption of pirimicarb onto semiconductor surface. Several samples from 0 to 60 min were taken during the illumination period. In all cases, assays were replicated three times.

2.4. Analytical determinations

The extraction procedure involves a pre-concentration of pirimicarb from water samples (50 mL) step based on solid-phase extraction with a silica-based bonded C_{18} cartridge (Sep-Pak Plus 500 mg, 6 mL, Waters). The SPE cartridge was first conditioned with 5 mL of acetonitrile, followed by 5 mL of deionised water. Extraction of water samples was carried out at a 8 mL min^{-1} flow rate. The samples were loaded onto the cartridges, and washed with deionised water and dried for 15 min under a vacuum. The analytes retained were eluted with 5 mL of acetonitrile. The solution was filtered through a 0.45 μm filter and analyzed by LC-MS² according to the procedure described by Fenoll et al. [21]

Analysis of pirimicarb and their transformed products: 2-[(methylformyl) amino]-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (Metabolite I), 2-(dimethylamino)-5,6-dimethyl-4-hydroxypyrimidine (Metabolite II), 2-(methylamino)-5,6-dimethyl-4-hydroxypyrimidine (Metabolite III) and 2-(methylamino)-5,6 dimethylpyrimidin-4-yl dimethylcarbamate (Metabolite V) was achieved by comparison with commercially available standards using an HPLC system (Agilent Series 1100, Agilent Technologies, Santa Clara, CA, USA) equipped with a G6410A triple quadrupole mass spectrometer. A preliminary study of the optimal single reaction monitoring (SRM) transitions for each compound was carried out by injecting individual analytes at a concentration level of 10 $\mu g mL^{-1}$. Various fragmentor voltages (FV) and collision energies (CE) were applied to

Table 1
Analytical conditions of pirimicarb and their transformation products by HPLC-MS² and HPLC-TOF/MS.

Compounds	MF ^a	t_r^b (min)	HPLC-MS ²						HPLC-TOF/MS					
			SRM ₁ ^c		F ₁ ^d (V)		CE ₁ ^e (V)		SRM ₂ ^c		F ₂ ^d (V)		CE ₂ ^e (V)	
			Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	Error (ppm)	DBE
Pirimicarb(2-(dimethylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate)	$C_{11}H_{18}N_4O_2$	13.7	239	→ 72	90	20	239	→ 182	90	15	239.1503	239.1504	−0.77	5
Metabolite I(2-[(methylformyl) amino]-5,6-dimethylpyrimidin-4-yl dimethylcarbamate)	$C_{11}H_{16}N_4O_3$	18.9	253	→ 72	110	10	253	→ 225	110	5	253.1295	253.1294	0.31	6
Metabolite II(2-(dimethylamino)-5,6-dimethyl-4-hydroxypyrimidine)	$C_8H_{13}N_3O$	3.25	168	→ 98	110	20	168	→ 71	110	30	168.1131	168.1132	−0.41	4
Metabolite III(2-(methylamino)-5,6-dimethyl-4-hydroxypyrimidine)	$C_7H_{11}N_3O$	3.1	154	→ 98	110	20	154	→ 137	110	10	154.0975	154.0967	4.81	4
Metabolite IV(2-(formylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate)	$C_{10}H_{14}N_4O_3$	16.0	239	→ 166	90	10	239	→ 72	90	20	239.1139	239.1136	0.93	6
Metabolite V(2-(methylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate)	$C_{10}H_{16}N_4O_2$	11.2	225	→ 168	110	10	225	→ 72	110	20	225.1346	225.1348	−1.06	5

^a Molecular formula.

^b Retention time.

^c Transitions (m/z).

^d Fragmentor.

^e Collision energy.

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