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Photooxidation of three spirocyclic acid derivative insecticides in aqueous suspensions as catalyzed by titanium and zinc oxides

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ABSTRACT

The photocatalyzed degradation of tetramic (spirotetramat) and tetronic (spirodiclofen and spiromesifen) spirocyclic acid (ketoenol) derivative insecticides has been studied in aqueous suspensions using different semiconductor oxides. The photodegradation was studied by monitoring the change in compound concentration using HPLC-MS analysis and by the decrease in the dissolved organic carbon (DOC) content as a function of irradiation time. Laboratory scale experiments under UVA irradiation were performed to investigate the kinetics degradation of these compounds using different binary (ZnO, TiO_2 and TiO_2 Kronos vlp 7000) and ternary oxides (Zn_2TiO_4 and $ZnTiO_3$) of zinc and titanium. Highest degradation rates were observed for ZnO and TiO_2 P25 Degussa while with ternary oxides smaller photodecomposition rates were assessed, especially with $ZnTiO_3$. New photocatalytic experiments were then performed under natural sunlight using ZnO, TiO_2 P25 Degussa and TiO_2 Kronos vlp 7000 leading nearly complete degradation of the studied insecticides when ZnO and TiO_2 P25 Degussa were used. The photodegradation processes followed first-order reaction kinetics. Comparison of these catalysts showed that ZnO is the most efficient for the removal of these insecticides at constant volumetric rate of photon absorption in the photoreactor. The main photocatalytic intermediates (enol-derivatives) were detected during the degradation in all cases as a consequence of the cleavage of alkyl-oxygen bond of the parent compounds.

1. Introduction

Spirocyclic tetronic/tetramic acid (ketoenol) derivatives (SADs) such as spirotetramat, spirodiclofen and spiromesifen are one of the most recently developed and used acaricide/insecticide classes for the control of a wide spectrum of sucking insects in numerous agricultural crops. These compounds affect juvenile stages with additional effects on adult fecundity. This new insecticide family interferes with lipid biosynthesis and are thought to act as inhibitors of acetyl-coenzyme A carboxylase (ACCase) [1–3]. Despite their low leachability [4], these compounds may leach through the soil profile. In addition, some of their transformation products, more mobiles as compared to the parent compounds, can be present in the commercial formulations due to degradation process and can be found in surface and groundwater [5,6]. Consequently, it is of primary importance to apply remediation strategies such as heterogeneous photocatalysis to polluted waters in order to protect hydric resources.

In recent years, the role of semiconductor oxides in organic degradation of pollutants in water has been more and more important due to their high effectiveness and low cost in comparison with other materials [7]. Among these materials, titanium dioxide (TiO_2) and zinc oxide (ZnO) are the most widely photocatalysts studied due to their properties [8,9]. The irradiation of TiO_2 or ZnO with photons energy $h\nu \geq E_g$ (band gap) produces electron-hole pair (e^-/h^+). The h^+ can react with hydroxyl groups on the semiconductor surface to generate hydroxyl radicals ($^\bullet OH$). On the other hand, e^- are trapped at surface sites and removed by reactions with adsorbed molecular O_2 to form superoxide anion radical $O_2^{\bullet-}$. Subsequent reactions of these radicals between themselves and with adsorbed molecules can lead to complete mineralization of organic pollutants [10]. Anatase and rutile crystal structures are the most common forms of TiO_2. The most common

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commercial photocatalyst is the TiO_2 P25 Degussa, a powder consisting of both rutile and anatase crystallites. TiO_2 and ZnO have the similar band gap energy and the same mechanism of photodegradation. However, TiO_2 has high recombination rate of the photo-induced e^-/h^+ at or near its surface [11], while ZnO has also the disadvantage of undergoing photodissolution (induced by self-oxidation) [12]. In addition, the major disadvantage of anatase phase photocatalyst is its wide band gap (3.2 eV), which make it a good photocatalyst only under UV-light ($\lambda \leq 387.5$ nm). The smaller band gap of rutile (3.0 eV, 410 nm) extends slightly the photoactivity range into the visible region. The improved performance of Degussa P25 can be also attributed to the slower recombination of electron-hole pairs through stabilization of charge separation by electron transfer from rutile to anatase and to the small size of rutile crystallites facilitating this transfer, making catalytic hot spots at the rutile/anatase interface [13]. Therefore, it is desirable to improve the photocatalytic efficiency of TiO_2 by extending its activities into visible light range and enhancing the charge carrier separation for more useful applications. For this reason, a modified photocatalyst (Kronos vlp 7000) is used in this research. Kronos vlp 7000 is a C-doped visible light activated TiO_2 based material. C-doping involves substitution of oxygen by carbon atoms producing new energy states deep in the TiO_2 band gap, which is responsible for the visible light absorption [14]. Also, ZnO doped with Ag has been effective for the degradation of pesticides with visible light [15]. No study for abatement of spirodiclofen, spiromesifen and spirotetramat and their transformation products residues in water by heterogeneous photocatalysis under irradiation by artificial or natural light was reported up to date. The main goal of this work was to assess and compare the effectiveness of the photocatalytic process for the decontamination of water polluted by these insecticides and their transformation products present in the commercial formulations using several catalytic systems. Preliminary experiments using as catalysts, different binary and ternary oxides of zinc and titanium were performed at laboratory scale under artificial UVA irradiation, while selected catalysts were then assayed under natural sunlight. In contrast with other studies published in the scientific literature, the photoactivity of the most effective systems was evaluated at constant volumetric rate of photon absorption.

2. Material and methods

2.1. Insecticides, transformation products and reagents

Three commercial insecticides spirodiclofen (SD), spiromesifen (SM), and spirotetramat (ST) were used for the photodegradation experiments. Pure ingredients were purchased from Dr. Ehrenstorfer (Augsburg, Germany) with purity > 98%. Structures of these insecticides and their main transformation products are listed in Table 1. The binary and ternary oxides of zinc and titanium used were ZnO and Zn_2TiO_4 (Alfa Aesar, Karlsruhe, Germany), $ZnTiO_3$ (Sigma-Aldrich, Madrid, Spain), TiO_2 P25 Degussa (Nippon Aerosil Co Ltd, Osaka, Japan) and TiO_2 Kronos vlp 7000 (Kronos Titan Gmbh, Leverkusen, Germany). Acetonitrile for residue analysis was supplied by Scharlau (Barcelone, Spain).

2.2. Photocatalyst characterization

The photocatalysts were characterized by a PerkinElmer Lambda 750 S 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 direct band gaps energy was calculated by plotting $[F(R)hv]^{1/2}$ vs. $[hv-E_g]$, where $F(R) = (1-R)^2/(2R)$, h is Plank's constant, E_g is the band gap energy, v is the frequency of light and R is diffuse reflectance based on the Kubelka–Monk theory of diffuse reflectance. The indirect band gap estimated from the intercept of the tangents to the plots were 3.0, 2.4, 3.1, 3.3 and 2.8 eV for the samples of TiO_2 P25 Degussa, TiO_2 Kronos vlp 7000, ZnO, Zn_2TiO_4 and $ZnTiO_3$, respectively The crystalline structure of the photacatalysts 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-Kα radiation at a scanning speed of 1° (2θ). The X-ray diffractograms of ZnO–TiO_2 systems are given in Supplementary Fig. 1. The morphology of the solids was examined by field emission scanning electron microscopy (FE-SEM) using a Carl Zeiss MERLIN VP Compact microscope (Oberkochem, 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 (Supplementary Fig. 2). 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). The main characteristics of photocatalysts are summarized in Table 2.

2.3. Photocatalysis Experiments

Preliminary experiments were conducted at laboratory scale using a cylindrical glass (250 mm long, 100 mm diameter) photochemical reactor (SBS, Barcelona, Spain) equipped with a magnetic stirring bar, and a 8 W medium pressure mercury lamp as previously described by Fenoll et al. [16]. The photochemical reactor was loaded with 2000 mL of water spiked at 0.1 mg L^{-1} of each active ingredient. The irradiated volume of suspension ($V_{reactor}$) was 1660 mL. The intensity of the light was approximately 8.5 mW cm^{-2} with major emission output at 366 nm. The photon irradiance at the wall of the lamp (UVA) was approximately 24 W m^{-2}. The photon flux from the lamp was controlled using a portable photoradiometer Delta Ohm HD 2102.2 (Caseelle di Selvazzano, Italy) fitted with a 366 nm UVA sensor (range 315–400 nm). The study was carried out in a batch recirculation mode. The reactant solution was slurred containing appropriate amounts of semiconductor and circulated at a flow rate of 600 mL min^{-1}. The reaction system was periodically bubbled with air, continuously stirred and thermostated by circulating water to maintain a constant temperature of 23 ± 1 °C during photocatalytic experiments.

On the other hand, selected photocatalysts were assayed using in a pyrex glass vessels (110 mm long, 80 mm diameter) containing 500 ml of water spiked at 0.1 mg L^{-1} of each active ingredient using natural sunlight irradiation during July, 2015. All photodegradation experiments were carried out in Murcia, SE Spain (latitude 37°59′N, longitude 1°08′W). The reaction system was continuously stirred to achieve a homogeneous suspension. The values (mean ± SD) of visible plus near infrared (400–1100 nm), UVA (315–400 nm) and UVB (280–315 nm) irradiation were measured with the same photoradiometer previously mentioned. Several samples were taken during the photoperiod (120 min), from 12–14 h. The mean values of visible plus near infrared (all in W m^{-2}), UVA and UVB at 13 h were 1075.8 ± 66.2 (1.54 cal min^{-1} cm^{-2}), 31.6 ± 4.1 (0.045 cal min^{-1} cm^{-2}) and 2.2 ± 0.3 (3×10^{-3} cal min^{-1} cm^{-2}), respectively.

For both experiments, initially, 2000 mL (experiment using artificial light) or 500 mL (experiment using sunlight) of type II analytical-grade water (pH 7.1, ORP 215 mV, resistivity >5 MΩ cm (25 °C); conductivity < 1 μS cm^{-1}, TOC < 30 μg L^{-1}; microorganisms < 10 cfu mL^{-1}) were mixed with commercial formulations of ENVIDOR, 24% w/v (SD), OBERON, 24% w/v (SM), and MOVENTO, 15% w/v (ST), all supplied by Bayer CropScience SL (Valencia, Spain)