



Photometabolic pathways of chlorantraniliprole in aqueous slurries containing binary and ternary oxides of Zn and Ti



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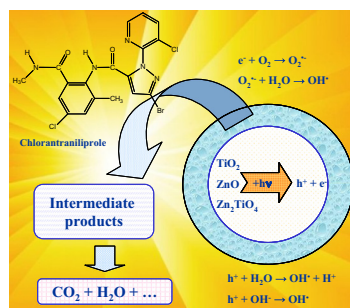
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HIGHLIGHTS

- The photocatalytic oxidation of chlorantraniliprole (CL) in water was studied.
- ZnO, TiO₂ and Zn₂TiO₄ were used as photocatalyst under artificial irradiation.
- The addition of Na₂S₂O₈ enhanced the photodegradation rate of CL in all cases.
- The efficiency in the photodegradation of CL was in the order: ZnO > TiO₂ ≫ Zn₂TiO₄.
- The photodegradation pathways proceed mostly *via* hydroxylation.

GRAPHICAL ABSTRACT



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ABSTRACT

The photocatalytic degradation of a new insecticide, chlorantraniliprole (CL) was studied in aqueous suspensions of binary (ZnO and TiO₂) and ternary (Zn₂TiO₄) oxides of Zn and Ti under artificial light irradiation (300–460 nm). Photocatalytic experiments showed that the addition of semiconductors, paired with Na₂S₂O₈ as electron acceptor, greatly improved the elimination of CL in aqueous slurries compared with ZnO and TiO₂ alone, and photolytic tests. The reaction rates significantly increased, especially for ZnO/Na₂S₂O₈ and TiO₂/Na₂S₂O₈ systems with half-lives of 53 and 71 min, respectively. Zn₂TiO₄/Na₂S₂O₈ appears to be less effective than ZnO/Na₂S₂O₈ and TiO₂/Na₂S₂O₈, although it can be used as photocatalyst for CL oxidation (*t*_{1/2} = 462 min). Seven phototransformation products were identified by liquid chromatography tandem mass spectrometry (LC–MS²) and liquid chromatography time of flight mass spectrometry (LC–TOF/MS) techniques while its mineralization was followed using dissolved organic carbon (DOC) analysis. The probable photooxidation pathways are proposed and discussed, being hydroxylation and N-demethylation the major routes of phototransformation observed.

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1. Introduction

Chlorantraniliprole (CL), 3-bromo-N-[4-chloro-2-methyl-6-[(methylamino)carbonyl] phenyl]-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-carboxamide, one of a new class of anthranilic diamide

insecticides, was developed by DuPont Crop Protection and launched commercially in 2007. It has a novel mode of action as an activator of insect ryanodine receptors via stimulation of the release and depletion of intracellular calcium stores, causing the rapid cessation of feeding, lethargy, regurgitation and muscle paralysis and ultimately death of sensitive species. It is used to control numerous insects in agricultural varieties crops and turf [1–3]. Due to their high leachability with a GUS leaching potential index

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of 4.22 [4], CL and some of its metabolites may leach through the soil profile. In addition, CL is considered persistent and mobile in surface water and displays relatively high aquatic toxicity [5]. Therefore, effective, low-cost and robust methods to decontaminate waters polluted with CL residues are needed, as long as they do not further stress the environment or endanger human health.

Particularly, advanced oxidation processes (AOPs) constitute a collection of established methods for removing organic pollutants like pesticides from water [6–8]. Among AOPs, heterogeneous photocatalysis using different semiconductor oxides has been extensively studied due to its efficiency in the removal of pollutants at ambient temperatures and pressures, without the formation of harmful by-products [9–11]. The basis of this technique is the irradiation of semiconductor particles. Thus, when a semiconductor is illuminated by photons with energy higher than its band gap, electrons (e^-) are excited from the valence to the conduction bands, while holes (h^+) are formed in the valence band. These holes can react with hydroxyl groups on the semiconductor surface to generate hydroxyl radicals ($\cdot OH$), highly oxidant species, to degrade pesticides. Meanwhile, e^- are retained on the surface points and removed via superoxide anion radical O_2^- as a consequence of reactions with the adsorbed O_2 [12].

ZnO and TiO_2 are metal oxides widely used for the detoxification of water polluted with organic compounds due to their chemical and optical properties [13–17]. As a general rule, TiO_2 is considered the best photocatalyst because of its high photochemical stability, high efficiency, non-toxic nature and low cost [18], although ZnO shows similar features and versatility to TiO_2 . ZnO has similar band gap energy as TiO_2 and both follow an identical photodegradation mechanism. In comparison to TiO_2 , ZnO shows a greater capacity to absorb solar spectrum and light quanta. However, it is photocorroded in acidic aqueous suspensions [19–21]. Toxicity in the illuminated ZnO system may be magnified by the release of Zn^{2+} into water as a consequence of the attack of Zn–O bonds by the photo-generated holes. Several authors have reported the photocatalytic degradation of organic pollutants in aqueous media using both photocatalysts, finding that ZnO is a more efficient than TiO_2 and can be considered a suitable alternative to it [22–24].

On the other hand, Zn_2TiO_4 is a fascinating candidate for the photodegradation of pesticides and other xenobiotics in water due to its band gap, ca. 3.1 eV [25]. However, little work has been done on the photocatalytic activity of zinc titanate particles. Moreover, no study on the abatement of CL residues in water by heterogeneous photocatalysis under irradiation by artificial light has been reported to date. Thus, the main objectives of this work were as follows: (a) to evaluate the efficacy of ZnO, TiO_2 and Zn_2TiO_4 as photocatalysts on the photodegradation of CL in water, (b) to assess the kinetics aspects of different treatments and the influence of various parameters like catalyst loading, $Na_2S_2O_8$ concentration and initial pH, and (c) the identification of the reaction intermediates to advance our knowledge of the mechanistic aspects during the photooxidation process.

2. Experimental

2.1. Chlorantraniliprole and reagents

CL standard with purity >99% was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Zinc oxide (ZnO, 99.99%) and zinc titanate (Zn_2TiO_4 , 99.9%) were purchased from Alfa Aesar (Karlsruhe, Germany). Titanium dioxide P25 Degussa (TiO_2 , 99.5%) was supplied by Nippon Aerosil Co., Ltd. (Osaka, Japan). Sodium peroxydisulfate ($Na_2S_2O_8$, 98%) was supplied by Panreac Química (Barcelona, Spain). Acetonitrile was purchased from Scharlab (Barcelona, Spain).

2.2. Photocatalyst characterization

The used photocatalysts were characterized for diffuse reflectance (DR-UV/vis spectroscopy), crystalline structure (X-ray diffraction, XRD), morphology (field emission scanning electron microscopy, FE-SEM), and surface area (BET method by nitrogen adsorption–desorption isotherms) according to the previous paper [26].

2.3. Photocatalysis experiment using artificial light

For the photocatalytic and photolytic experiments a cylindrical glass photochemical reactor (2.0 L volume, 0.25 m long, 0.10 m diameter) equipped with a magnetic stirring bar and a 8 W medium pressure mercury lamp (Philips) (300–460 nm, UVB/UVA ratio less than 0.1%) with major emission output at 366 nm as light source was used as previously described by Fenoll et al. [24]. Typical radiation of ca. 10 mW cm^{-2} was measured using a radiometer Delta Ohm HD 2102.2 (Caselle di Selvazzano, Italy). The reactant solution containing different amounts of the semiconductor powder (0–500 mg L^{-1}) was circulated at a flow rate of 600 mL min^{-1} .

Initially, a commercial formulation (Rynaxypyr[®], 20% SC, DuPont) at ca. 0.1 mg L^{-1} of CL was added to 2 L of analytical-grade water (type II, pH 7.1) and the mixture was homogenized for 20 min in the dark. Later, an appropriate concentration of ZnO (200 mg L^{-1}), TiO_2 (300 mg L^{-1}) or Zn_2TiO_4 (200 mg L^{-1}) and $Na_2S_2O_8$ (250 mg L^{-1}), used as electron acceptor, were added to the aqueous media. Finally, the slurries were kept for 30 min in the dark before irradiation. Two parallel blank assays were carried out, one without semiconductor and oxidant (photolytic test) and one with only oxidant. In each case, the assays were replicated three times and several samples were taken during irradiation time.

2.4. Analytical determinations

The extraction of water samples was performed according to the method published by Fenoll et al. [27]. The identification of CL and its transformation products was carried out using an HPLC system (Agilent Series 1100, Agilent Technologies, Santa Clara, CA, USA) equipped with a reversed phase C8 analytical column of $150 \text{ mm} \times 4.6 \text{ mm}$ and $5 \mu\text{m}$ particle size (Zorbax Eclipse XDB-C8). The HPLC system was connected to a TOF/MS (Agilent Technologies) with an electrospray interface. Mobile phases A and B were acetonitrile and 0.1% formic acid, respectively. The gradient program started with 10% A, constant for 5 min, followed by a linear gradient to 100% A in 35 min. After this 35 min run time, 10 min of post-run time followed using initial 10% of A. The flow rate was held constant (0.6 mL min^{-1}) throughout the process and $20 \mu\text{L}$ of samples were injected in every case.

Confirmation and quantification of CL and its transformation products was achieved using an HPLC system consisting of vacuum degasser, autosampler and a binary pump (Agilent Series 1100, Agilent Technologies, Santa Clara, CA, USA) equipped with a reversed phase C8 analytical column of $150 \text{ mm} \times 4.6 \text{ mm}$ and $5 \mu\text{m}$ particle size (Zorbax Eclipse XDB-C8) and an G6410A triple quadrupole mass spectrometer from Agilent equipped with an electrospray ionization (ESI) interface operating in positive ion mode. Liquid chromatography was performed under the same conditions as used in TOF/MS. A preliminary study of the optimal single reaction monitoring (SRM) transitions for CL was carried out by injecting individual analytes at a concentration of $10 \mu\text{g mL}^{-1}$. Various fragmentor voltages (FV) and collision energies (CE) were applied to the compounds under study. Table 1 lists the compounds along with their retention times and their optimized SRM transitions with a dwell time of 40 ms.

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