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Fipronil decomposition in aqueous semiconductor suspensions using UV light and solar energy

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ABSTRACT

The photocatalytic degradation of fipronil in drinking water was studied using zinc oxide (ZnO) and titanium dioxide (TiO_2) as photocatalyst under irradiation by solar and artificial light. Photocatalytic experiments showed that the addition of semiconductors in tandem with the oxidant ($Na_2S_2O_8$) strongly enhances the degradation rate of fipronil in comparisons carried out with photolytic experiments under artificial light. However, under solar irradiation, the photocatalytic decomposition of fipronil occurs very slowly. The residual levels of fipronil for $ZnO/Na_2S_2O_8$ and $TiO_2/Na_2S_2O_8$ after 60 min of illumination at a constant volumetric rate of photon absorption in the photoreactor were 0.8 and 1.5 μg/L, respectively. The main intermediates (fipronil-sulfone, fipronil-sulfide, fipronil-desulfinyl and fipronil-carboxamide) detected during the degradation of fipronil in water were identified.

1. Introduction

Fipronil ((±)-5-amino-1-(2,6-dichloro-α,α,α-trifluoro-*p*-tolyl)-4-trifluoromethylsulfinylpyrazole-3-carbonitrile) is a broad-spectrum phenylpyrazole insecticide discovered by Rhône-Poulenc Agrochemie Company (now Bayer CropScience) in 1987 and introduced in 1993 [1]. It is used to control ants, beetles, cockroaches, fleas, ticks, termites, mole crickets, thrips, rootworms, weevils, and other insects. Fipronil acts as a potent blocker of the γ-aminobutyric acid (GABA)-regulated chloride channels in the central nervous system. Several studies have examined the behaviour of fipronil in soil and water [2–6], finding that fipronil shows low to moderate sorption and relative mobility in soil, and low to moderate solubility in water. Fipronil and some of its degradation products have been detected in several water bodies in urban and agricultural areas [7,8]. Consequently, it is of primary importance to apply remediation strategies to polluted waters in order to protect water resources.

Photocatalytic degradation processes, using semiconductors, have been widely investigated as techniques to eliminate organic pollutants such as detergents, dyes, and pesticides in water [9–13]. Pesticides are especially prone to contaminate the aquatic environment because they are directly applied to plants or soil and may then leach into surface and groundwater. The photocatalytic process is based on the formation of an electron hole pair through UV light absorption, with an energy equal to or greater than the band gap of the semiconductor. Hydroxyl (•OH) radical can be formed by the reaction between an electron/hole pair and oxygen and hydrogen in water [14–16]. These radicals are able to react with organic molecules to produce CO_2, H_2O and mineral acids.

The optimization of these processes requires, among other aspects, a study of the degradation mechanisms involved and of the effect of different semiconductors and types of irradiation. No significant effort has been made to evaluate the photocatalytic efficiency of ZnO and TiO_2 on fipronil oxidation. Thus, in this work, the photocatalytic degradation of fipronil and its generated intermediates in drinking water under different types of irradiation was investigated using zinc oxide (ZnO) and titanium dioxide (TiO_2) as catalysts. In contrast with other studies mentioned in the literature, the photoactivity of these semiconductors was evaluated at a constant volumetric rate of photon absorption in the photoreactor.

2. Experimental

2.1. Fipronil, metabolites and reagents

Fipronil, fipronil-sulfone, fipronil-sulfide, fipronil-desulfinyl and fipronil-carboxamide with a purity higher than 97.5% were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The

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commercial formulation used (REGENT TS, fipronil 50%) was purchased from Fitodolores SL (Murcia, Spain). Zinc oxide (99.9%, BET 10 m^2/g, <70 μm) was purchased from Alfa Aesar (Karlsruhe, Germany). Titanium dioxide P25 Degussa (99.5%, BET 50 m^2/g, <21 nm) was supplied by Nippon Aerosil Co. Ltd. (Osaka, Japon). Sodium peroxydisulfate (98%) was purchased from Panreac Química (Barcelone, Spain). Acetonitrile was supplied by Scharlau (Barcelona, Spain).

2.2. Preparation of solutions

Several standard solutions (0.5–200 μg/L) were prepared in acetonitrile, protected from light and stored at 5 °C, before being injected to obtain the linearity of the detector response.

2.3. Photocatalyst characterization

Absorption and scattering coefficients (κ_λ and σ_λ) were measured from the UV–vis spectra using a HITACHI U-3200 UV-VIS spectrophotometer (Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra acquisition. A $BaSO_4$ standard was used as the reference spectrum. The semiconductor suspensions (ZnO, 200 mg/L and TiO_2, 53 mg/L) were placed in the reflectance cell and measured at 366 and 400 nm according to the procedure described by Cabrera et al. [17]. The absorption coefficients obtained for ZnO and TiO_2 were 8932 and 20,703 cm^2/g, respectively, at 366 nm and 4152 and 8463 cm^2/g at 400 nm, while the scattering coefficients obtained for ZnO and TiO_2 were 4599 and 35,641 cm^2/g, respectively, at 366 nm and 10,817 and 33,450 cm^2/g at 400 nm.

2.4. Photocatalysis experiment using artificial light

The photocatalytic and photolytic experiments were performed in a 2000 mL cylindrical glass (250 mm long, 100 mm diameter) photochemical reactor (SBS, Barcelona, Spain) equipped with a magnetic stirring bar, and one or two 8 W low pressure mercury lamps. The volume of irradiated suspension ($V_{reactor}$) was 1660 mL. The intensity of the light for each lamp was approximately 8.5 mW/cm^2 at 366 nm (based on manufacturer's data). The photon flux from the lamp was controlled using a portable photoradiometer Delta Ohm HD 2102.2 (Caselle di Selvazzano, Italy) fitted with a 366 nm UVA sensor (range 315–400 nm). The study was carried out in batch recirculation mode. The reactant solution was circulated at a flow rate of 600 mL/min. The reaction system was periodically bubbled with air, continuously stirred to achieve a homogeneous suspension and thermostated by circulating water to keep the temperature at 23 ± 1 °C during irradiation (1 h). The diagram of the experimental system used is shown in Fig. 1A.

2.5. Solar photocatalysis experiment

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 July, 2012. 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 a portable photoradiometer Delta Ohm HD 2102.2 (Caselle di Selvazzano, Italy). Several samples were taken during the photoperiod (60 min), from 12 to 13 h. The mean values of visible plus near infrared, UVA and UVB at 13 h were 975.3 ± 42.1, 25.2 ± 2.4 and 1.46 ± 0.20 (all in W/m^2), respectively, while 98,131 ± 5063 lx were recorded.

The solar pilot plant used in this experiment is based on compound parabolic collector (CPC) technology. 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 aluminium reflectors (0.9 cm radius of curvature) running east–west. The water flows directly from one tube to another connected in series and finally to the reservoir tank (250 L) before a centrifugal pump (0.55 kw) returns the water (45 L/min) to the collector tubes in a closed circuit. The reaction system 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 12.6 L and the dead volume of the PVC tubes was about 6.5 L. Storage tank, flowmeter, sensors

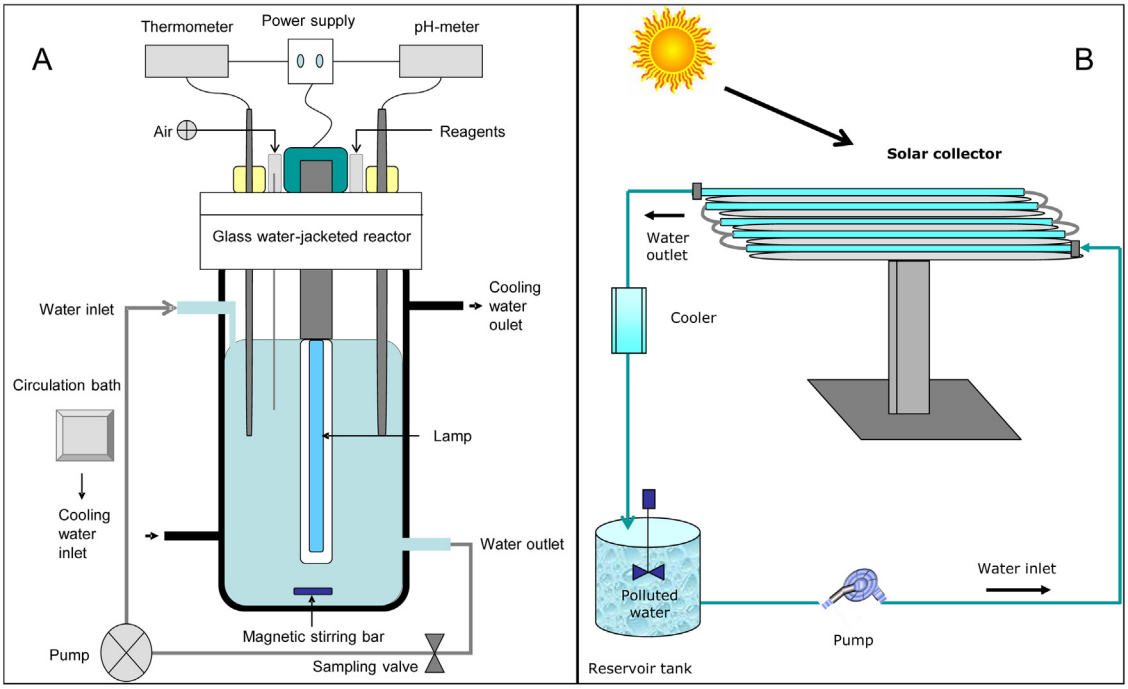

Fig. 1. Schematic drawing of the photochemical reactor (A) and pilot plant (B).