Introduction and Objectives

Pesticides are widely used as a result of intensive agricultural practices. Industrial effluents, agricultural runoff and chemical spills have led to widespread contamination of the environment with these bio-recalcitrant organic compounds. Pesticides are often toxic and non-biodegradable; they accumulate in the environment through the trophic network with unpredictable consequences for the mid-term future [1].

Thiacloprid ([(2Z)-3-(6-Chloropyridin-3-yl)-1,3-thiazolidin-2-ylidene] cyanamide) is an insecticide of the neonicotinoid class, used on agricultural crops to control a variety of sucking and chewing insects, primarily aphids and whiteflies. Thiacloprid is highly soluble in water and has been detected in drinking water [2].

Heterogeneous photocatalytic oxidation (TiO₂/UV-A) in the presence of artificial or solar light, has been effective for the degradation of a variety of toxic agrochemical substances, such as pesticides and insecticides [3]. Our study investigates the effect of various operating conditions of heterogeneous photocatalytic decomposition and mineralization of thiacloprid.

Materials and Methods

The catalysts used during photocatalytic oxidation were TiO₂ P-25 (Degussa, anatase/rutile =3:6/1, BET: 50 m²g⁻¹, nonporous), TiO₂ UV 100 (Hombikat, 100% anatase, BET: 300 m²g⁻³), TiO₂ Kronos 7000, TiO₂ A, TiO₂ Kronos 7500 (Kronos Worldwide, Inc., 100% anatase, BET: 250 m²g⁻¹) and ZnO (Merk, BET 10 m²g⁻¹).

Experiments were performed in a closed Pyrex cell of 600 ml capacity. The cell was fitted with a central 9 W lamp and had inlet and outlet ports for bubbling CO₂ free air during the photocatalytic process. The spectral response of the UV-A irradiation source ranged between 350-400 (max: 366 nm), while that of the visible irradiation source ranged between 400-520 nm (max 450 nm). Experiments were conducted at a working volume of 500 ml, under constant magnetic stirring. The catalyst/thiacloprid suspension was left for 30 minutes in the dark, to achieve maximum adsorption of the insecticide onto the semiconductor’s surface. Samples were filtered through a 0.45 µm filter. Photocatalytic experiments were carried out at the pH value of 5.0±0.2. The reaction temperature was kept constant at 25°C.

Discussion and Conclusions

• TiO₂ P-25 and ZnO followed by UV-100 are the most efficient photocatalysts, since after 120 min of illumination the degradation rates were 96%, 79% and 48%, respectively. In the presence of Kronos 7000 and 7500 under visible irradiation, practically no degradation of the herbicide was observed for the same illumination times. No remarkable differences were observed in the case of initial mineralization rates for the aforementioned catalysts.

• Release of chloride ions was complete in the presence of 0.5 g L⁻¹ TiO₂ P-25 and UV-A during photocatalytic mineralization of chlorpyrid. By using UV-100, the release of Cl⁻ was 60% for the same illumination times. The efficiencies of both catalysts was enhanced in the presence of H₂O₂.

• After 180 min of UV-A illumination in the presence of 0.5 g L⁻¹ TiO₂ P-25, complete elimination of ecotoxicity was observed, as monitored by the bioluminescence of V. Fischeri. The determination of major intermediate by-products is currently in progress, aiming to the determination of possible photocatalytic degradation pathways.

References


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