Heterogeneous Photocatalytic Degradation Of The Herbicide Clopyralid In Aqueous Media

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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 [1]. These contaminants are often toxic and non-biodegradable, they accumulate in the environment through the trophic network with unpredictable consequences for the mid-term future [2].

Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid, CAS No. 1702-17-6, Mr: 192 g mol\(^{-1}\)) is a systemic herbicide, used to control annual and perennial broadleaf weeds in certain crops and turf and provides control of certain brush species on rangeland and pastures. Its chemical stability along with its mobility enables this herbicide to penetrate through the soil, causing long-term contamination of ground water and surface water supplies [3].

Heterogeneous photocatalytic oxidation (TiO\(_2\)/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 insecticides and pesticides [4]. Our current study investigates the effect of various operating conditions of heterogeneous photocatalytic decomposition and mineralization of clopyralid.

Materials and Methods

- **Materials**
  The catalysts used during heterogeneous photocatalytic oxidation were TiO\(_2\), P-25 (Degussa, anatase/rutile=3.6/1, BET: 50 m\(^2\) g\(^{-1}\)), TiO\(_2\), UV 100 (Hombikat, 100% anatase, BET: 300 m\(^2\) g\(^{-1}\)), TiO\(_2\), Kronsos 7000, TiO\(_2\), Kronsos 7001, TiO\(_2\), Kronos 7500 (Kronsos Worldwide, Inc., 100% anatase, BET: 250 m\(^2\) g\(^{-1}\)) and ZnO (Merck, BET 10 m\(^2\) g\(^{-1}\)).

- **Photocatalytic experiments**
  Experiments were performed in a closed Pyrex cell of 600 ml capacity. The reaction vessel was fitted with a central 9 W lamp and had inlet and outlet ports for bubbling CO\(_2\)-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/herbicide suspension was left for 30 minutes in the dark, to achieve maximum adsorption of the herbicide onto the semiconductor surface. Samples were filtered through a 0.45 \(\mu\)m filter. Heterogeneous photocatalytic experiments were carried out at the pH value of 5.0±0.2. The reaction temperature was kept constant at 25°C.

Results

- **Figure 1**: Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid, CAS: 1702-17-6, Mr: 192 g mol\(^{-1}\))
- **Figure 2**: Sketch of the photocatalytic reactor employed for the photocatalytic oxidation of clopyralid: 1. reaction vessel, 2. irrigation source, 3. borosilicate glass, 4. air inlet, 5. air outlet 6. stirrer. B: Photograph of the experimental setup: 1 photocatalytic reactor equipped with a black light irradiation source, 2. voltage regulator, 3. lamp power supply 4. stirrer.

Discussion and Conclusions

- **•TiO\(_2\), P-25 and ZnO followed by UV-100 are the most efficient photocatalysts, since after 120 min of illumination the degradation rates were 99%, 87% and 67% respectively. In the presence of Kronsos 7000 and visible irradiation no degradation of the herbicide was observed even after 210 min of illumination.**
- **Release of chlorine ions was higher in the presence of 0.5 g L\(^{-1}\) TiO\(_2\), P-25 in comparison to UV-100 during heterogeneous photocatalytic mineralization of clopyralid (100% vs. 60% respectively). In both cases, the efficiency of the photocatalysts was enhanced in the presence of H\(_2\)O\(_2\).**
- **After 180 min of UV-A illumination in the presence of 0.5 g L\(^{-1}\) TiO\(_2\), P-25 no inhibition of the bioluminescence of V. Fischeri was observed. This finding is in agreement with the results of mineralization of the herbicide, which was complete, under the same experimental conditions.**
- **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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