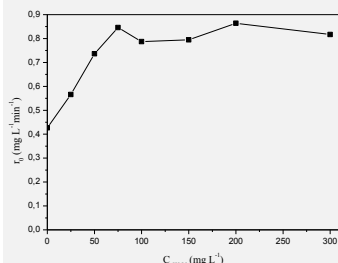


Heterogenous Photocatalytic Degradation Of The Herbicide Clopyralid In Aqueous Media

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C. Berberidou¹, V. Kitsiou¹, S. Karahanidou¹, D. Lambropoulou¹, A. Kouras¹, I. Poullos¹. (1) Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece, cberber@chem.auth.gr.



The effect of the addition of H₂O₂ to the initial degradation rate of clopyralid in the presence of 0,5 g L⁻¹ TiO₂ P25.

Degradation and mineralization of clopyralid, a systemic herbicide often reported to occur in drinking water, by heterogeneous photocatalytic oxidation in the presence of UV-A and visible light has been studied. The effect of various operating conditions such as different commercial TiO₂ products, the addition of H₂O₂, the effect of initial pH on the degradation and the organic content reduction (DOC) of the wastewater was examined. The addition of H₂O₂ resulted in all cases in higher initial degradation rates of the herbicide, while the use of TiO₂ P25 in the presence of UV-A, led to higher initial degradation rates in comparison to other commercial photocatalysts.

Agrochemical compounds including 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]. As these contaminants are in many cases toxic and non-biodegradable, they have the ability to accumulate in the environment and to magnify through the global trophic network with unpredictable consequences for the mid-term future [2, 3].

Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid, CAS No. 1702-17-6, Mr: 192 g mol⁻¹) is a systemic herbicide from the chemical class of pyridine compounds, often reported to occur in drinking water [4]. It is used to control annual and perennial broadleaf weeds in certain crops and turf and provides control of certain brush species on rangeland and pastures. Clopyralid presents high solubility in water and is particularly stable against hydrolysis and photolysis. Its chemical stability along with its mobility enables this herbicide to penetrate through the soil, causing a long term contamination of ground water and surface water supplies [5].

Treatment methods currently employed for agrochemical degradation include advanced chemical oxidation, adsorption on granular activated carbon and incineration. Among the advanced oxidation processes (AOPs), heterogeneous photocatalytic oxidation (TiO₂/UV-A) in the presence of artificial or solar light, has been effective for the degradation of various contaminants found in industrial or domestic wastewaters. A variety of toxic agrochemical substances, such as insecticides and pesticides has

been studied in regard to their photocatalytic degradation, in the presence of artificial or solar illumination, with very encouraging results, while studies dealing with real or simulated wastewater have revealed that their complete or partial degradation is possible via the above mentioned method [6]. Our current study investigates the heterogeneous photocatalytic decomposition and mineralization of clopyralid, in order to assess the effect of various operating conditions on pesticide degradation and mineralization.

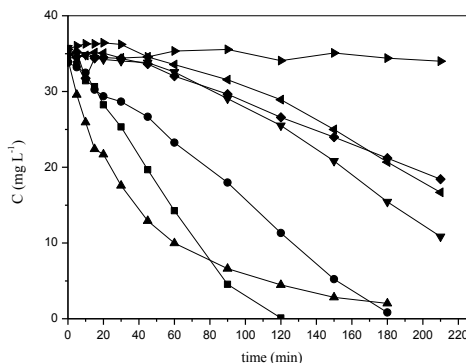


Figure 1. Photocatalytic degradation of 40 mg L⁻¹ clopyralid in the presence of various commercial photocatalysts at an initial concentration of 0,5 g L⁻¹. [■] TiO₂ P25, (●) UV 100, (▲) ZnO, (▼) Kronos 7500 και UVA, (◄) Kronos 7000 και UVA, (►) Kronos 7000 και Visible, (◆) Kronos 7001 και UVA.

Photocatalytic degradation of clopyralid in the presence of TiO₂ P25 (Degussa) and UV-A irradiation was enhanced by the addition of H₂O₂, resulting in all cases in higher initial degradation

rates of the herbicide (Graphical Illustration).

Among the various photocatalysts employed in the study, TiO₂ P25, UV-100 (Hombikat) and ZnO (Merck) in the presence of UV-A, resulted in higher initial degradation rates of the herbicide. In contrast, Kronos 7000 or 7500 (Kronos Worldwide, Inc) in the presence of either UV-A or

visible light, led to low initial degradation rates.

The determination of ecotoxicity and of major intermediate by-products is currently in progress, aiming to the determination of possible photocatalytic degradation pathways.

Acknowledgements

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