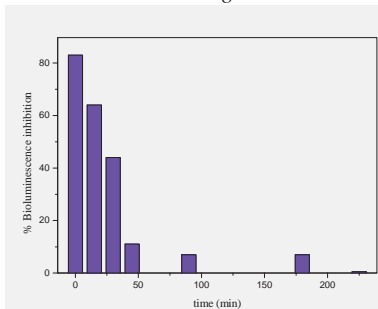


Homogenous Photocatalytic Degradation Of The Herbicide Clopyralid In Aqueous Media: Kinetics, mineralization and toxicity

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Variation of ecotoxicity of 40 mg L⁻¹ clopyralid solution using the photo-Fenton reagent (7 mg L⁻¹ Fe³⁺, 100 mg L⁻¹ H₂O₂, UV-A.

Degradation and mineralization of clopyralid, a systemic herbicide often reported to occur in drinking water, by the photo-Fenton and Ferrioxalate reagents in the presence of UV-A and visible light has been studied. The effect of various operating conditions such as Fe³⁺, oxalate and H₂O₂ concentrations in the photodegradation kinetics was investigated. Mineralization via the organic content reduction (DOC) and inorganic nitrogen evolution of the insecticide was examined. The use of UV-A irradiation resulted in all cases in higher initial degradation and mineralization rates, while ecotoxicity in the presence of 7 mg L⁻¹ Fe³⁺, 100 mg L⁻¹ H₂O₂ and UV-A was completely removed within 240 min of illumination.

Among the various organic substances that are known as water pollutants, pesticides are a major pollution source for both ground and surface waters. [1]. In highly industrialized countries the problem of pesticide wastes is mainly related to wastewater, recycling, elimination of packaging and the remediation of contaminated soils. For developing countries, the main problem is the elimination of unused (forbidden), obsolete and unusable pesticide stocks. As these xenobiotics 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]. Alternative treatment methods currently employed for the degradation of agrochemicals in water and wastewater include Advanced Oxidation Processes (AOPs). Among them, homogenous photocatalytic oxidation 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 heterogenous photocatalytic decomposition and mineralization of clopyralid mediated either by the photo-Fenton or the Ferrioxalate reagent, in order to assess the effect of various operating conditions on pesticide degradation and mineralization.

Bench scale photocatalytic experiments were performed in a closed Pyrex cell of 600 ml capacity, fitted with a central 9 W lamp, under constant magnetic stirring. The spectral response of the UV-A irradiation source, ranged between 350-400 nm (max: 366 nm), while that of the visible irradiation source ranged between 400-520 nm. Changes in the concentration of clopyralid were monitored via its characteristic absorption band at 280 nm using a UV-Visible spectrophotometer (UV-1700, Shimadzu). Determination of dissolved organic carbon (DOC) was conducted according to standard methods by a TOC analyzer (Shimadzu VCSH 5000). Ions were determined by a Shimadzu system equipped with a CDD-6A conductometric detector. Ecotoxicity was determined by a Microtox M500 analyzer using marine bacteria *Vibrio fischeri*.

In the case of UV-A irradiation, photo-Fenton degradation of aqueous clopyralid solutions of 40 mg L⁻¹ initial concentration, using 7 mg L⁻¹ Fe³⁺ and increasing H₂O₂ concentrations up to about

100 mg L⁻¹ led to increase of the initial degradation rates; nonetheless, increasing the concentration to 200 mg L⁻¹ has no further beneficial effect. Similar results were obtained in the case of photo-Fenton degradation of thiacloprid under visible light. The ferrioxalate reagent (7 mg L⁻¹ Fe³⁺, 33 mg L⁻¹ C₂O₄²⁻, 100 mg L⁻¹) led to higher degradation and mineralization rates in both UV-A and visible light experiments. Evolution of inorganic sulphur and nitrogen during photocatalysis using the photo-Fenton reagent,

reached almost 90% in both cases, within 180 min of UV-A illumination under optimum conditions. Ecotoxicity was completely removed within 240 min of UV-A illumination, under the same conditions (Graphical Illustration). Phytotoxicity experiments are in progress, aiming to provide data concerning the potential of homogenous photocatalysis to purify wastewater containing pesticides and to provide water suitable for irrigation.

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