

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

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## Introduction and Objectives

Among the various water pollutants, pesticides are a major pollution source for ground and surface waters [1]. These xenobiotics are often toxic and non-biodegradable, they accumulate in the environment and magnify through the global trophic network with unpredictable consequences [2].

Clopyralid is a systemic herbicide from the chemical class of pyridinecarboxylic acids, often than reported to occur in drinking water [3]. It is used to control annual, perennial broadleaf weeds and certain brush species on rangeland and pastures. Clopyralid is highly soluble in water and particularly stable against hydrolysis and photolysis. Its chemical stability along with its mobility enables penetration through soil, causing a long term contamination of ground water and surface water supplies [4].

Homogenous photocatalytic oxidation mediated by the photo-Fenton reagent ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV-A}$  or Visible) has been effective for the degradation of toxic agrochemical substances, such as insecticides and herbicides [5]. Here, we investigate the potential of the photo-Fenton and the Ferrioxalate reagents to degrade clopyralid under various operating conditions, as well as mineralization and reduction of ecotoxicity.

## Materials and Methods

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  $\text{CO}_2$  free air during the photocatalytic process. 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 (max: 450 nm). Experiments were conducted at a working volume of 500 mL, under constant magnetic stirring, at the pH value of  $3.0 \pm 0.1$ . The reaction temperature was kept constant at  $25^\circ\text{C}$ .

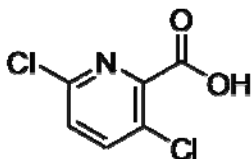


Figure 1: Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid, CAS No. 1702-17-6, Mr:  $192 \text{ g mol}^{-1}$ )

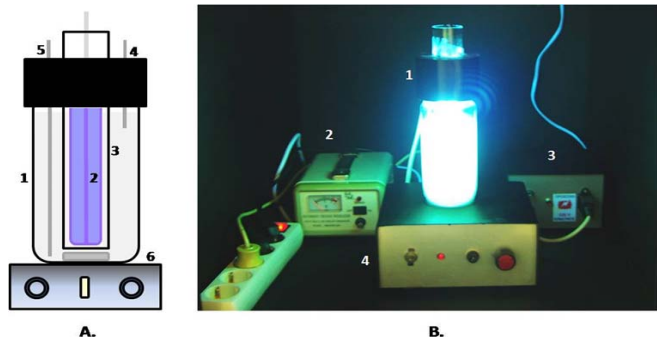


Figure 2: A: Sketch of the photocatalytic reactor employed in the homogenous oxidation of clopyralid: 1. reaction vessel, 2. irradiation source, 3. borosilicate glass, 4. air inlet, 5. air outlet 6. stirrer. B: Photograph of the experimental setup: 1 photocatalytic reactor equipped with a black light irradiation source, 2. voltage regulator, 3. lamp power supply 4. stirrer.

## Results and Discussion

• During photo-Fenton oxidation of aqueous solutions of thiacloprid at an initial concentration of  $20 \text{ mg L}^{-1}$ ,  $3.5 \text{ mg L}^{-1} \text{ Fe}^{3+}$  and UV-A irradiation, increase of the amount of  $\text{H}_2\text{O}_2$  from 0-100  $\text{mg L}^{-1}$  results to increase of the reaction rate. Further increase of  $\text{H}_2\text{O}_2$  to 200  $\text{mg L}^{-1}$  has no further beneficial effect on  $r_0$  values (Fig. 3). Optimal concentration of  $\text{H}_2\text{O}_2$  was also 100  $\text{mg L}^{-1}$  in the case of visible light experiments, however,  $r_0$  was in all cases lower than the ones under UV-A.

• Photo-Fenton mineralization of thiacloprid under UV-A reached almost 70% within 180 min of illumination, while mineralization under visible light was a slow process (Fig. 4).

• Release of inorganic nitrogen and sulphur under optimal experimental conditions reached in both cases almost 90% within 180 min of illumination (Fig. 5).

• Ecotoxicity determined by *V. Fischeri* marine bacteria was completely removed within 300 min of illumination under optimal experimental conditions (Fig. 6).

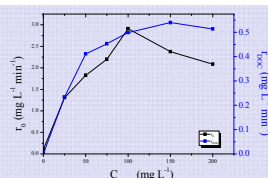


Figure 3: Effect of  $\text{H}_2\text{O}_2$  concentration on the initial degradation and mineralization rates of  $40 \text{ mg L}^{-1}$  CLPR in the presence of the photo-Fenton reagent ( $7 \text{ mg L}^{-1} \text{ Fe}^{3+}$ ,  $100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ ) and UV-A irradiation: (■)  $r_0$ , (●)  $r_{\text{DOC}}$

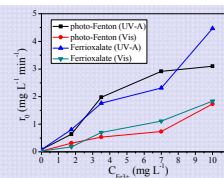


Figure 4: Effect of  $\text{Fe}^{3+}$  concentration on the initial degradation rates of  $40 \text{ mg L}^{-1}$  CLPR in the presence of  $100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$  and (■) photo-Fenton + UV-A, (●) photo-Fenton + visible, (▲) Ferrioxalate + UV-A, (▼) Ferrioxalate + visible irradiation.

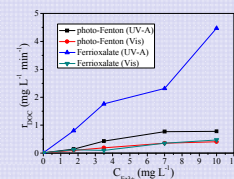


Figure 5: Effect of  $\text{Fe}^{3+}$  concentration on the initial mineralization rates of  $40 \text{ mg L}^{-1}$  CLPR in the presence of  $100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$  and (■) photo-Fenton + UV-A, (●) photo-Fenton + visible, (▲) Ferrioxalate + UV-A, (▼) Ferrioxalate + visible irradiation.

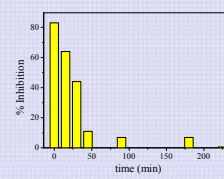


Figure 6: Inhibition of bioluminescence of *V. Fischeri* during photocatalytic oxidation of  $40 \text{ mg L}^{-1}$  CLPR in the presence of the photo-Fenton reagent ( $7 \text{ mg L}^{-1} \text{ Fe}^{3+}$ ,  $100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ ) and UV-A irradiation.

## References

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