

C. Berberidou*, V. Kitsiou, S. Karahanidou, D. Lambropoulou, A. Kouras, I. Poullos

Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

* Correspondence: cberber@chem.auth.gr

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 a long term contamination of ground water and surface water supplies [3].

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 insecticides and pesticides [4]. Our current study investigates the effect of various operating conditions of heterogenous photocatalytic decomposition and mineralization of clopyralid.

Materials and Methods

Materials

The catalysts used during heterogenous photocatalytic oxidation were TiO₂ P-25 (Degussa, anatase/rutile=3.6/1, BET: 50 m² g⁻¹, nonporous), TiO₂ UV 100 (Hombikat, 100% anatase, BET: 300 m² g⁻¹), TiO₂ Kronos 7000, TiO₂ Kronos 7001, TiO₂ Kronos 7500 (Kronos Worldwide, Inc., 100% anatase, BET: 250 m² g⁻¹) and ZnO (Merck, BET 10 m² g⁻¹).

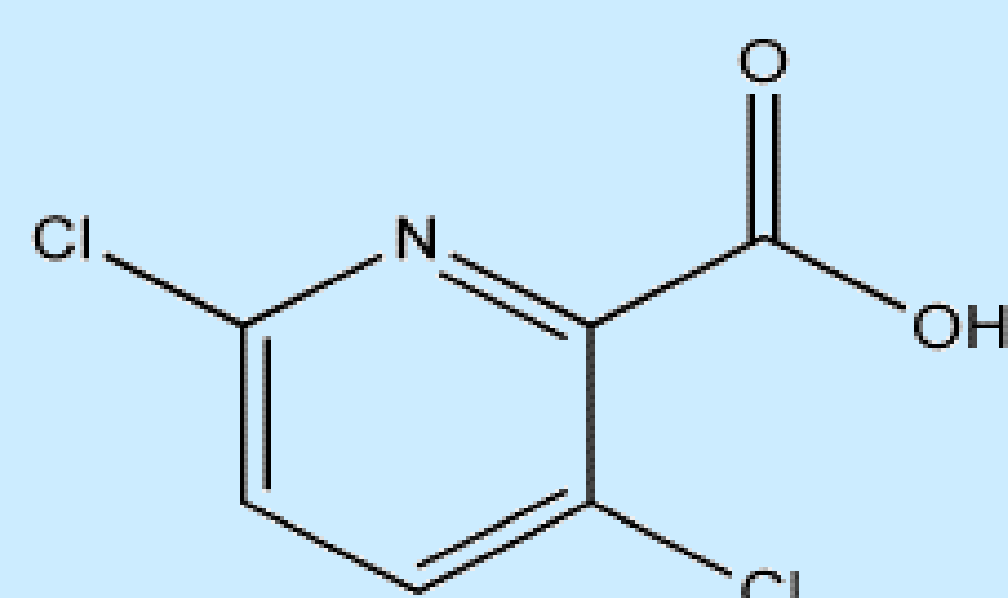


Figure 1: Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid, CAS: 1702-17-6, Mr: 192 g mol⁻¹)

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 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/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 μm 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.

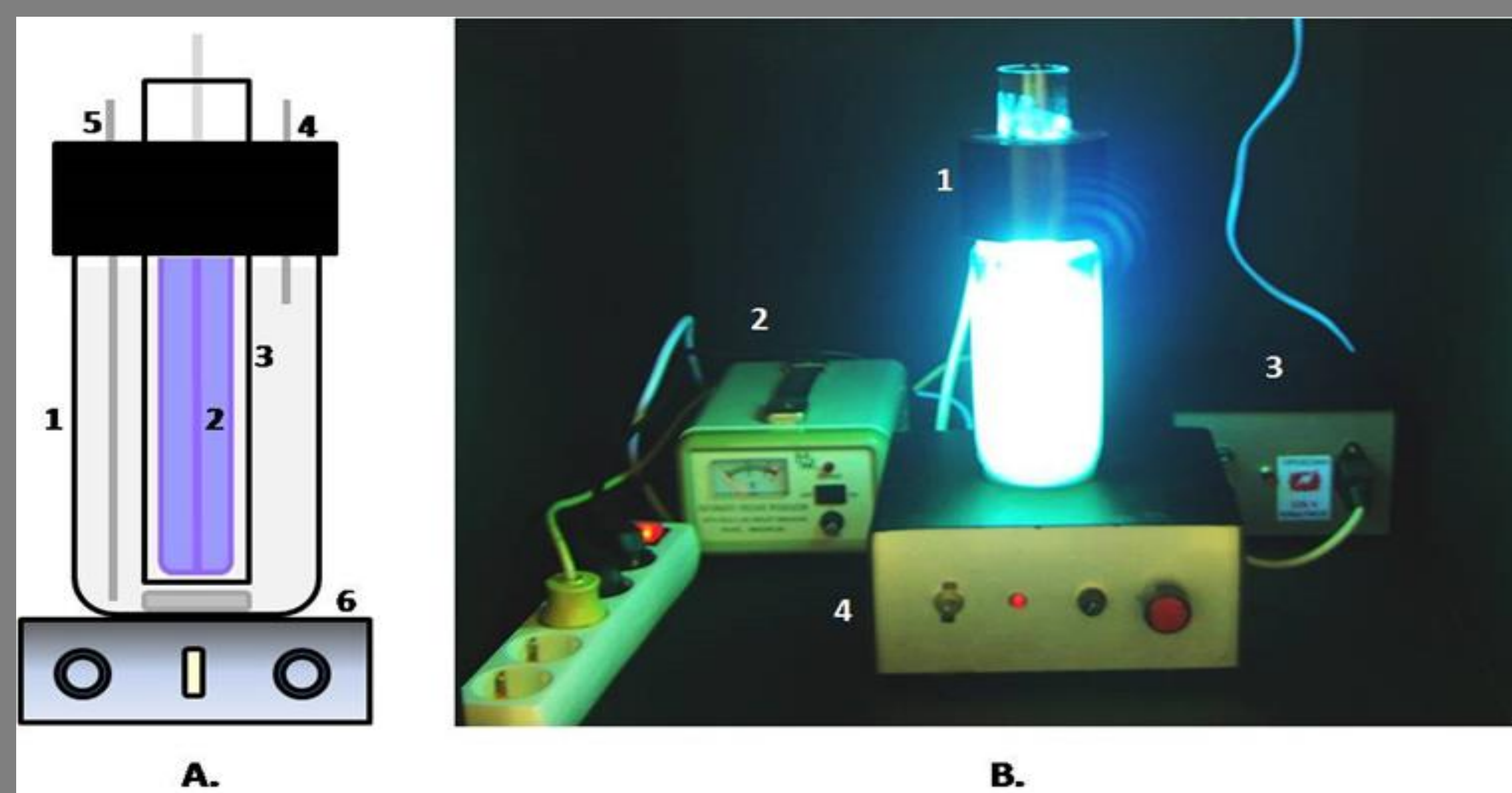


Figure 2: A: Sketch of the photocatalytic reactor employed in the photocatalytic oxidation of clopyralid: 1. reaction vessel, 2. irradiation source, 3. borosilicate glass, 4. air inlet, 5. air outlet 6. stirrer. B: Photograph of the experimental setup: 1 photocatalytic reactor equipped with a black light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

Results

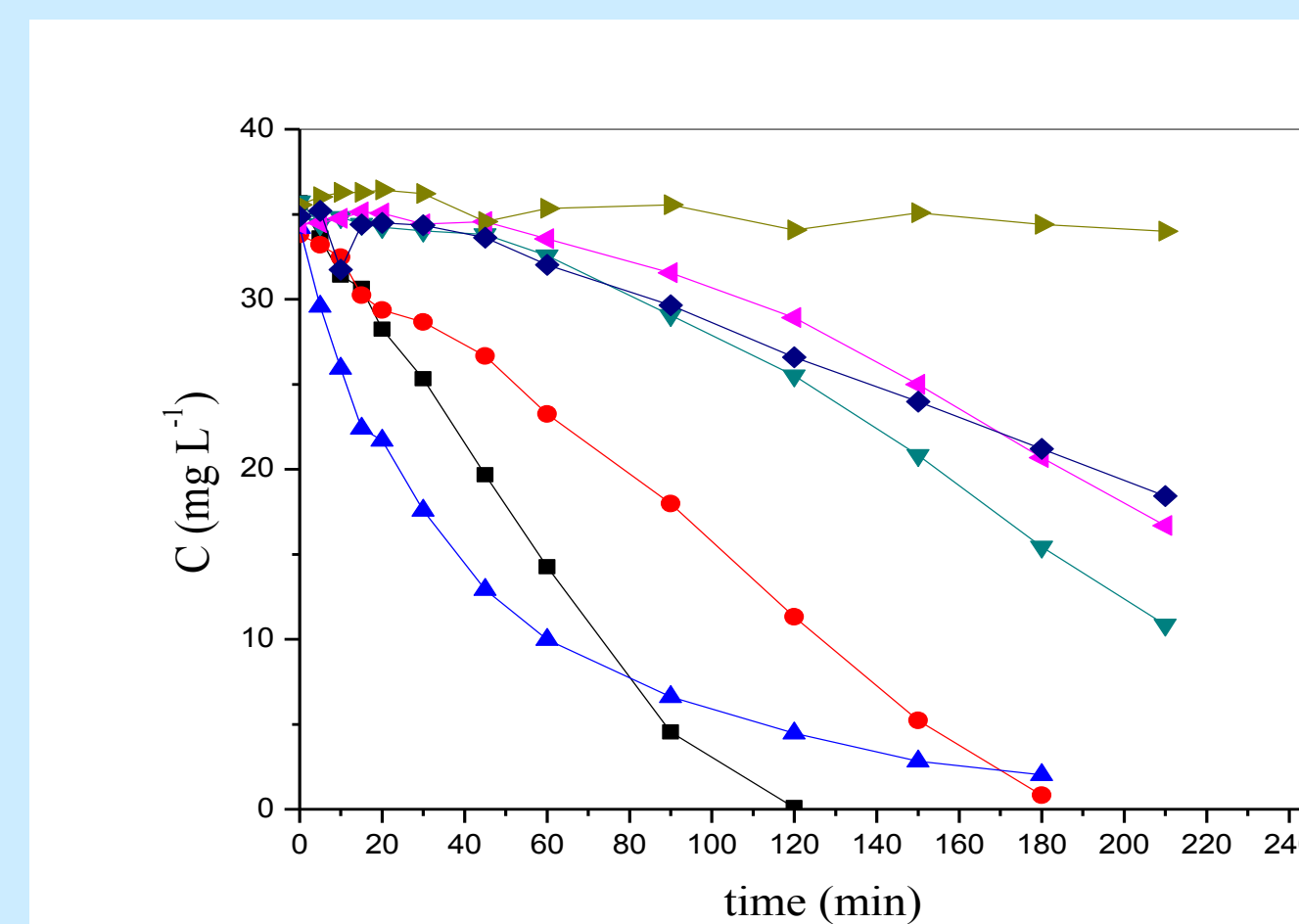


Figure 3: Photocatalytic degradation of 40 mg L⁻¹ CLPR in the presence of various commercial catalysts at an initial concentration of 0,5 g L⁻¹: (■) TiO₂ P25, (●) UV-100, (▲) ZnO, (▼) Kronos 7500 and UV-A, (◄) Kronos 7000 and UV-A, (►) Kronos 7000 and Visible, (◆) Kronos 7001 and UV-A.

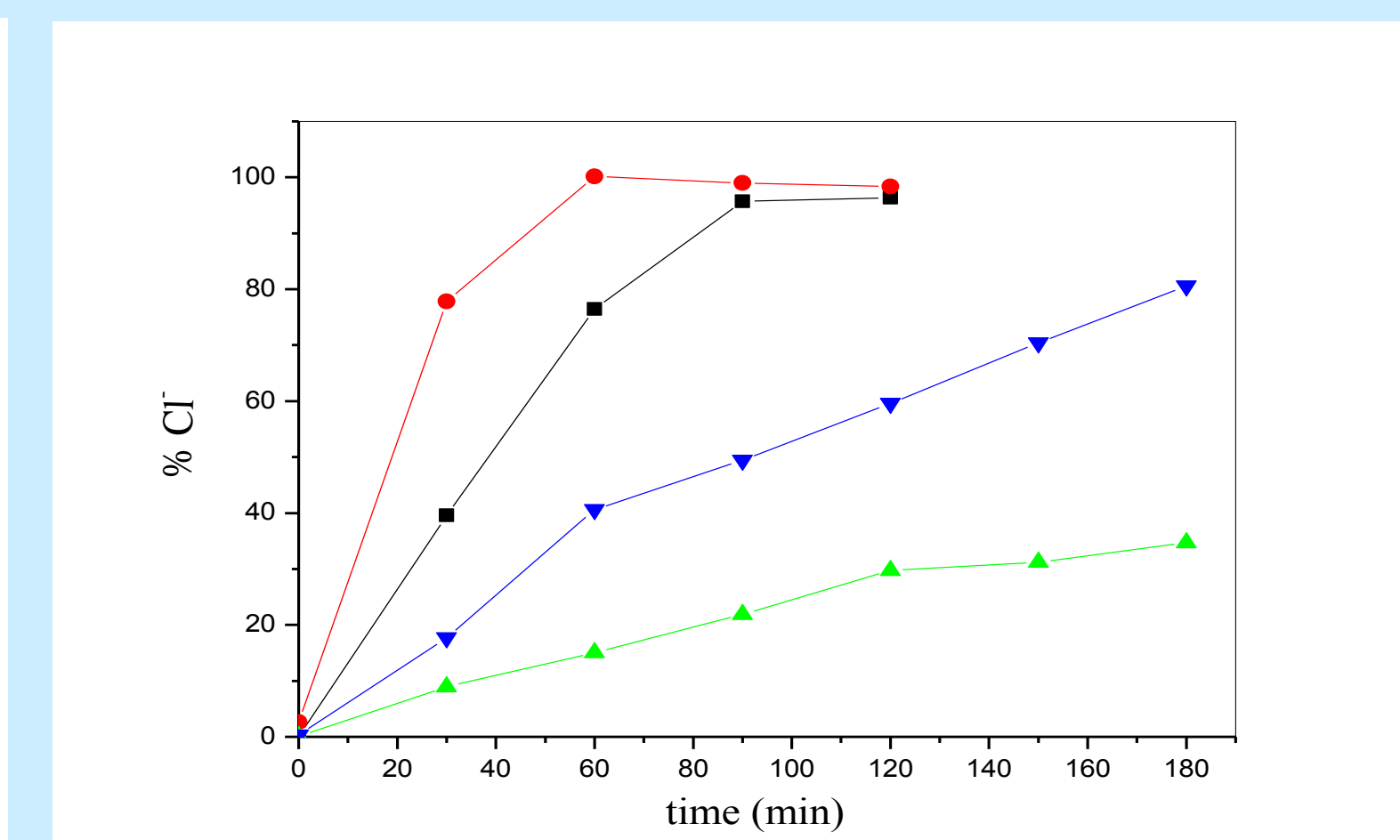


Figure 4: Release of chloride ions during heterogenous photocatalytic mineralization of 40 mg L⁻¹ CLPR and UV-A irradiation: (■) 0,5 g L⁻¹ TiO₂ P25, (●) 0,5 g L⁻¹ TiO₂ P25, 100 mg L⁻¹ H₂O₂, (▲) 0,5 g L⁻¹ TiO₂ UV-100, (▼) 0,5 g L⁻¹ TiO₂ UV-100, 100 mg L⁻¹ H₂O₂.

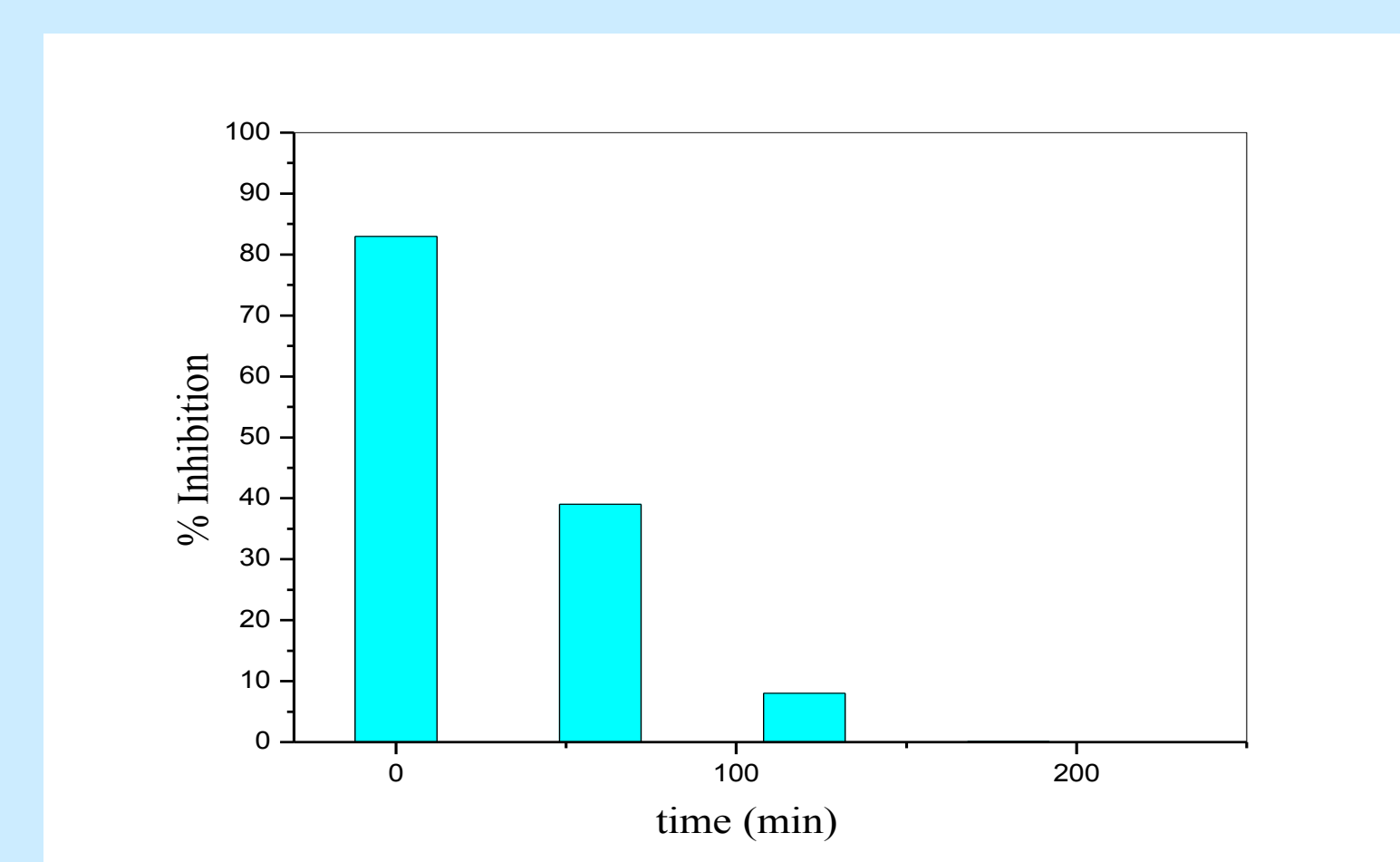


Figure 5: Inhibition of bioluminescence of *V. Fischeri* during heterogeneous photocatalytic oxidation of CLPR in the presence of 0,5 g L⁻¹ TiO₂ P-25 and UV-A irradiation.

Discussion and Conclusions

- TiO₂ P25 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 Kronos 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 TiO₂ P25 in comparison to UV-100 during heterogenous photocatalytic mineralization of clopyralid (100% vs. 60% respectively). In both cases, the efficiency of the photocatalysts was enhanced in the presence of H₂O₂
- After 180 min of UV-A illumination in the presence of 0,5 g L⁻¹ TiO₂ P25 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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