



Heterogenous Photocatalytic Degradation and Mineralization of

The Herbicide Thiachloprid

C. Berberidou*, V. Kitsiou, D. Michailidou, 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. Pesticides are often toxic and non-biodegradable, they accumulate in the environment through the trophic network with unpredictable consequences for the mid-term future [1].

Thiachloprid ((2Z)-3-[(6-Chloropyridin-3-yl) methyl]-1,3-thiazolidin-2-ylidene) cyanamide) is an insecticide of the neonicotinoid class, used on agricultural crops to control a variety of sucking and chewing insects, primarily aphids and whiteflies. Thiachloprid is highly soluble in water and has been detected in drinking water [2].

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 pesticides and insecticides [3]. Our study investigates the effect of various operating conditions of heterogenous photocatalytic decomposition and mineralization of thiachloprid.

Materials and Methods

The catalysts used during 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, TiO₂ Kronos 7500 (Kronos Worldwide, Inc., 100% anatase, BET: 250 m² g⁻¹) and ZnO (Merck, BET 10 m² g⁻¹).

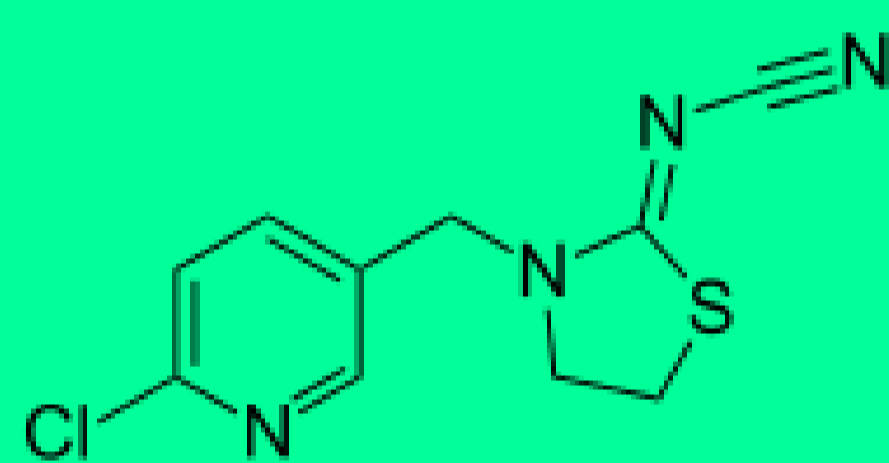


Figure 1: Thiachloprid ((2Z)-3-[(6-Chloropyridin-3-yl) methyl]-1,3-thiazolidin-2-ylidene) cyanamide), Mr: 252.72 g mol⁻¹

Experiments were performed in a closed Pyrex cell of 600 ml capacity. The cell 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/thiachloprid suspension was left for 30 minutes in the dark, to achieve maximum adsorption of the insecticide onto the semiconductor's surface. Samples were filtered through a 0.45 μm filter. Photocatalytic experiments were carried out at the pH value of 5.0±0.2. The reaction temperature was kept constant at 25°C.

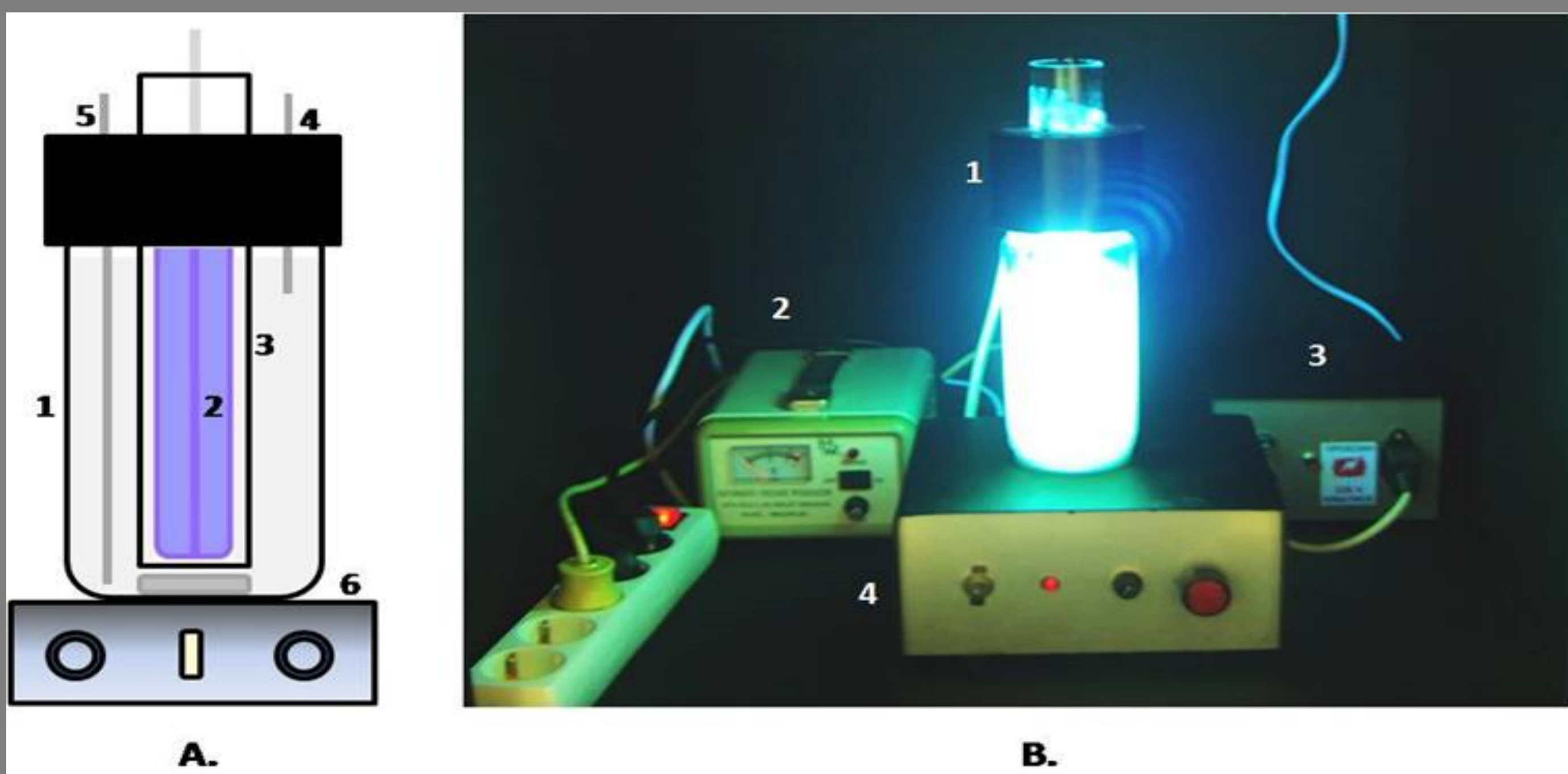


Figure 2: A: Sketch of the photocatalytic reactor employed in the photocatalytic oxidation of thiachloprid: 1. reaction vessel, 2. irradiation source, 3. borosilicate glass, 4. air inlet, 5. air outlet 6. stirrer. B: Photograph of the experimental setup: 1 photocatalytic reactor equipped with a black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

Results

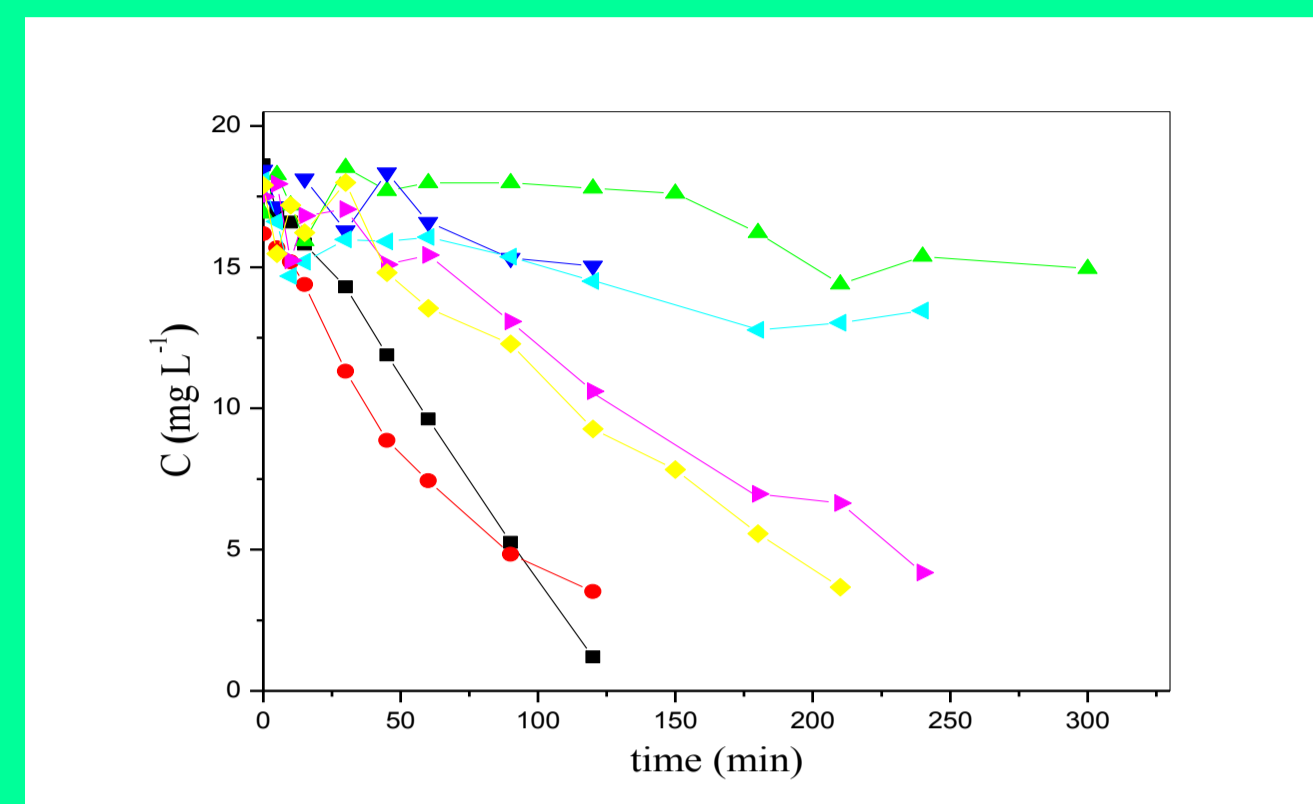


Figure 3: Photocatalytic degradation of 20 mg L⁻¹ TCD in the presence of various commercial catalysts at an initial concentration of 0,5 g L⁻¹: (■) TiO₂ P25 and UV-A, (●) ZnO and UV-A UV-100, (▲) Kronos 7000 and Visible, (▼) Kronos 7000 and UV-A, (◀) Kronos 7500 and Visible, (▶) Kronos 7500 and UV-A, (◆) UV-100 and UV-A

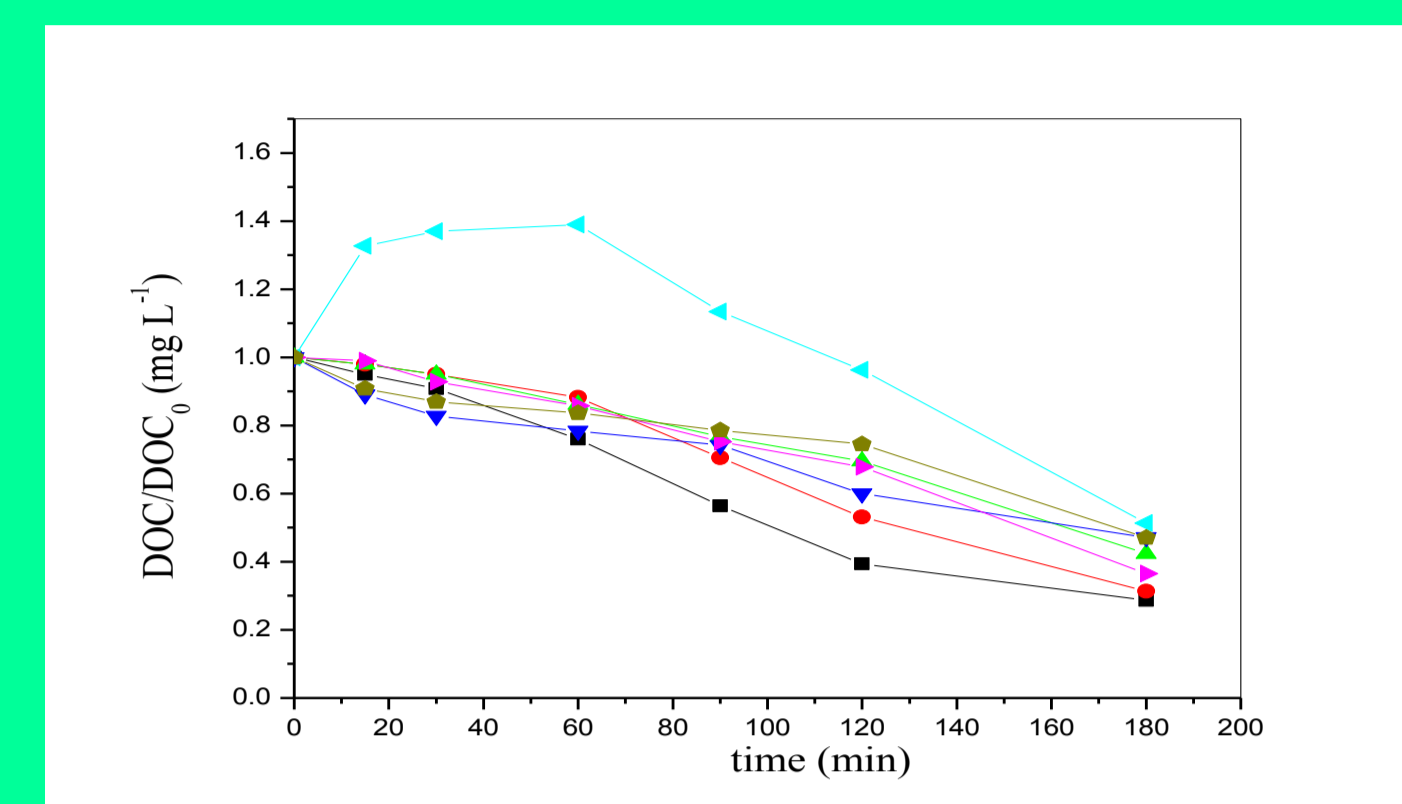


Figure 4: Photocatalytic mineralization of 20 mg L⁻¹ TCD in the presence of various commercial catalysts at an initial concentration of 0,5 g L⁻¹ and UV-A irradiation: (■) TiO₂ P25 and UV-A, (●) TiO₂ P25 and 100 mg L⁻¹ H₂O₂, (▲) UV-100, (▼) UV-100 and 100 mg L⁻¹ H₂O₂, (◀) Kronos 7000, (▶) Kronos 7500, (◆) ZnO.

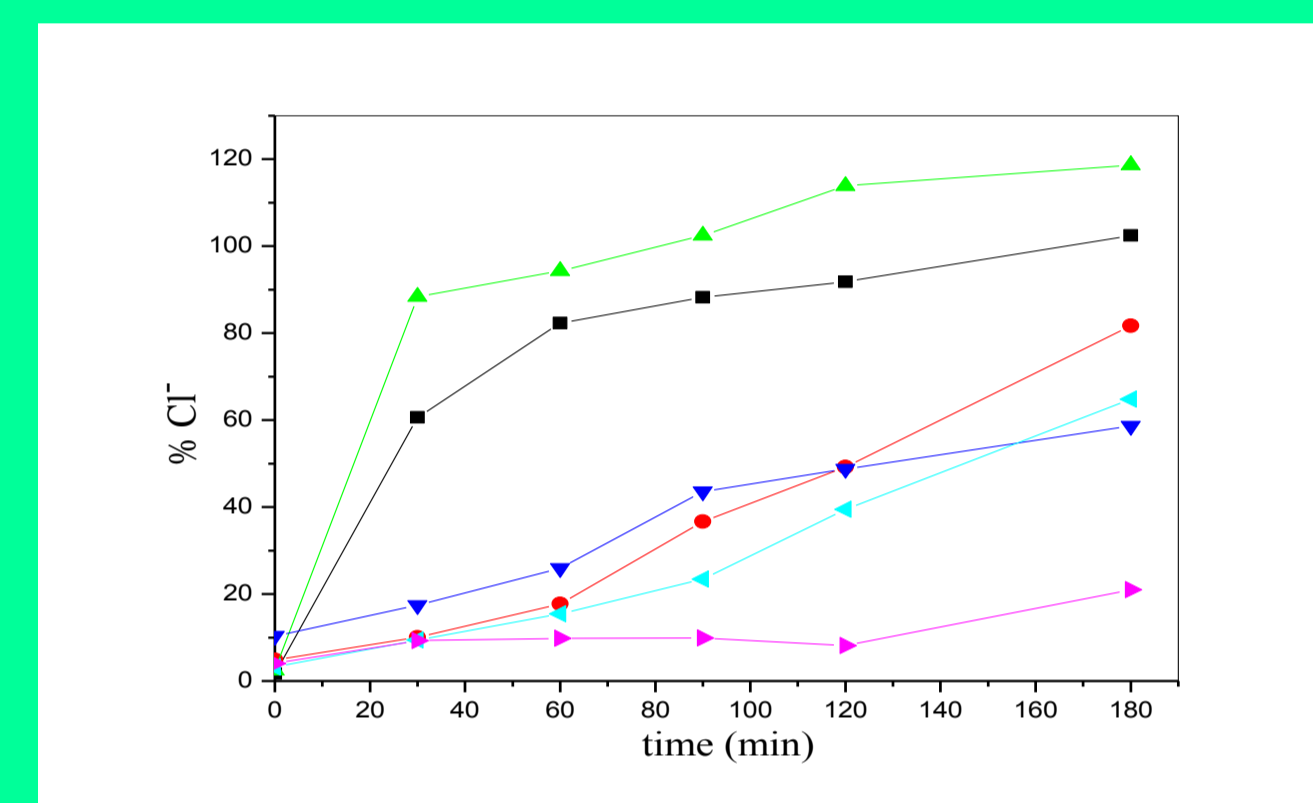


Figure 5: Release of chloride ions during photocatalytic mineralization of 20 mg L⁻¹ TCD and UV-A irradiation: (■) 0,5 g L⁻¹ TiO₂ P25, (●) 0,5 g L⁻¹ TiO₂ UV-100, (▲) 0,5 g L⁻¹ TiO₂ P25 and 100 mg L⁻¹ H₂O₂, (▼) 0,5 g L⁻¹ TiO₂ Kronos 7500, (◀) 0,5 g L⁻¹ TiO₂ UV-100 and 100 mg L⁻¹ H₂O₂, (▶) 0,5 g L⁻¹ Kronos 7500 and 100 mg L⁻¹ H₂O₂.

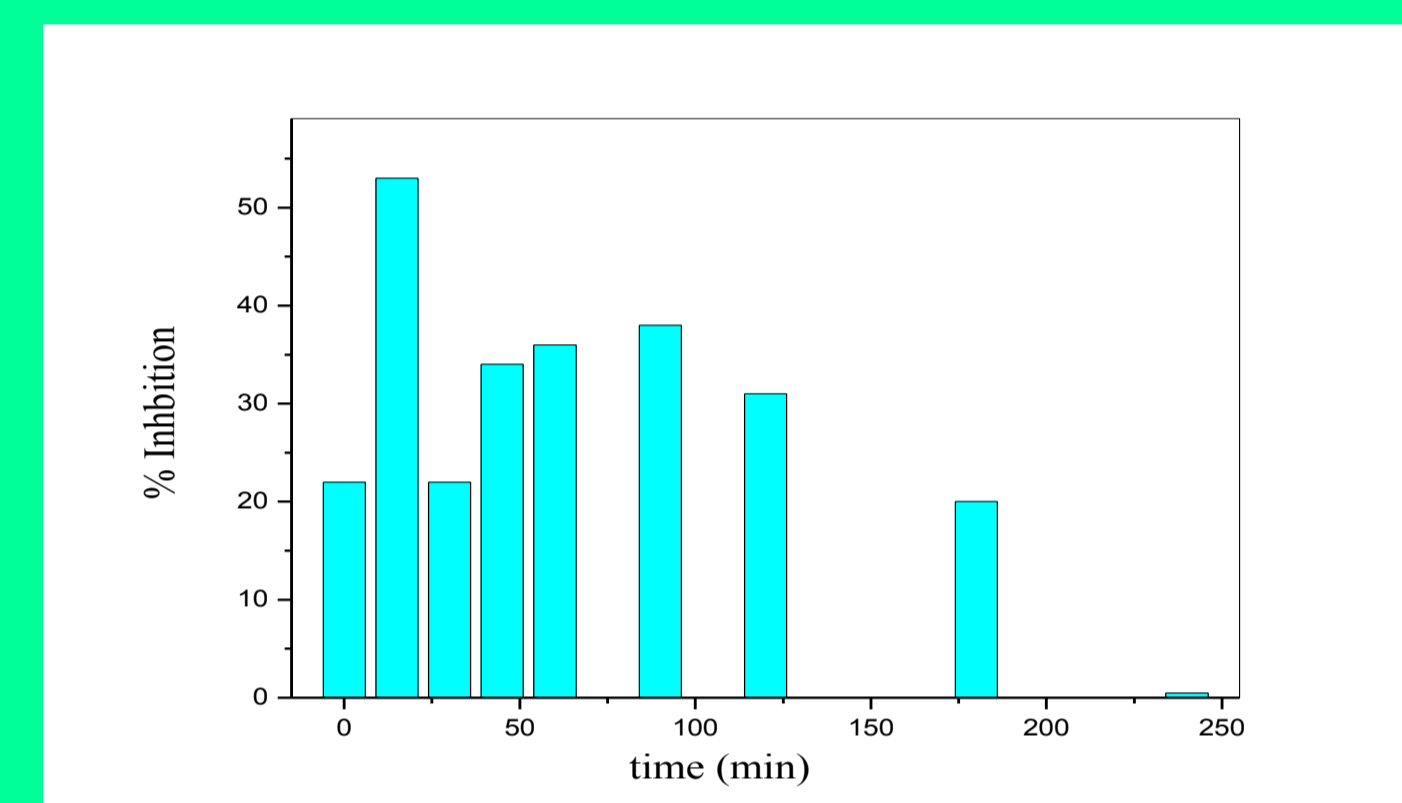


Figure 6: Inhibition of bioluminescence of *V. Fischeri* during photocatalytic oxidation of TCD in the presence of 0,5 g L⁻¹ TiO₂ P-25 and UV-A irradiation.

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 96%, 79% and 48%, respectively. In the presence of Kronos 7000 and 7500 under visible irradiation, practically no degradation of the herbicide was observed for the same illumination times. No remarkable differences were observed in the case of initial mineralization rates for the aforementioned catalysts.
- Release of chlorine ions was complete in the presence of 0,5 g L⁻¹ TiO₂ P25 and UV-A during photocatalytic mineralization of clopyralid. By using UV-100, the release of Cl⁻ was 60% for the same illumination times. The efficiencies of both catalysts 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, complete elimination of ecotoxicity was observed, as monitored by the bioluminescence of *V. Fischeri*.
- The determination of major intermediate by-products is currently in progress, aiming to the determination of possible photocatalytic degradation pathways

References

- [1] M. Arias-Estevéz, E. Lopez-Periago, E. Martínez-Carballo, J. Simal-Gandara, J.C. Mejuto, L. Garcia-Rio, *Agr Ecosyst Environ* 123 (2008) 247-260.
- [2] Seccia, S., et al., Multiresidue determination of neonicotinoid insecticide residues in drinking water by liquid chromatography with electrospray ionization mass spectrometry. *Analytica Chimica Acta*, 2005. 553(1-2): p. 21-26.
- [3] I.K. Konstantinou, T.A. Albanis, *Appl Catal B-Environ* 42 (2003) 319-335.

Acknowledgements

The present study is implemented within the framework of the research project entitled "A novel method for detoxification and reuse of wastewater containing pesticides by solar photocatalysis and constructed wetlands" (project No: 957) of the Action ARISTEIA of the Operational Program "Education and Lifelong Learning" (Action's Beneficiary: General Secretariat for Research and Technology), and is co-financed by the European Social Fund (ESF) and the Greek State.



Co-financed by Greece and the European Union