

# HETEROGENOUS PHOTOCATALYTIC DEGRADATION AND MINERALIZATION OF THE HERBICIDE THIAACLOPRID

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*

## Summary

Degradation and mineralization of thiacloprid, a neonicotinoid insecticide 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 TiO<sub>2</sub> products, the addition of H<sub>2</sub>O<sub>2</sub>, the effect of initial pH on the degradation and the organic content reduction (DOC) of the insecticide was examined. The addition of H<sub>2</sub>O<sub>2</sub> resulted in all cases in higher initial degradation rates, while the use of TiO<sub>2</sub> P25 in the presence of UV-A, led to higher initial degradation and mineralization rates in comparison to other commercial TiO<sub>2</sub> photocatalysts.

## Introduction

Agrochemical compounds including pesticides are widely used as a result of intensive agricultural practices [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]. Thiacloprid (*trans*-1,3-bis(6-chloropyridin-3-yl)propan-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. Thiacloprid is highly soluble in water and has been detected in drinking water [3]. Alternative treatment methods currently employed for the degradation of agrochemicals in water and wastewater include Advanced Oxidation Processes (AOPs). Among them, heterogeneous photocatalytic oxidation (TiO<sub>2</sub>/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 [4]. Our current study investigates the heterogenous photocatalytic decomposition and mineralization of thiacloprid, in order to assess the effect of various operating conditions on pesticide degradation and mineralization.

## Materials and Methods

Photocatalytic experiments were performed in a closed Pyrex cell of 600 ml capacity, under constant magnetic stirring. The reaction vessel was fitted with a central 9 W lamp. 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. Prior to heterogeneous photocatalysis, the catalyst suspension was left for 30 minutes in the dark, to achieve maximum adsorption of the insecticide onto the semiconductor surface. During photocatalysis samples were withdrawn and filtered through a 0.45 µm

filter. The catalysts employed in the study were TiO<sub>2</sub> P-25 (Degussa, anatase/rutile=3.6/1, BET: 50 m<sup>2</sup>g<sup>-1</sup>, nonporous), TiO<sub>2</sub> UV 100 (Hombikat, 100% anatase, BET: 300 m<sup>2</sup>g<sup>-1</sup>), TiO<sub>2</sub> Kronos 7000, TiO<sub>2</sub> Kronos 7500 (Kronos Worldwide, Inc., 100% anatase, BET: 250 m<sup>2</sup>g<sup>-1</sup>) and ZnO (Merck, BET 10 m<sup>2</sup> g<sup>-1</sup>). Changes in the concentration of thiacloprid were monitored via its characteristic absorption band at 280 nm using a UV-Visible spectrophotometer (UV-1700, Shimadzu). Determination of the dissolved organic carbon (DOC) was conducted according to standard methods by a TOC analyzer (Shimadzu VCSH 5000).

## Results and Discussion

Photocatalytic degradation of thiacloprid in the presence of TiO<sub>2</sub> P25 and UV-A irradiation was enhanced by the addition of H<sub>2</sub>O<sub>2</sub>, resulting in all cases in higher initial degradation rates of the insecticide. Among the various photocatalysts employed in the study, TiO<sub>2</sub> P25, ZnO and UV-100 in the presence of UV-A, resulted in higher initial degradation rates of the insecticide. In contrast, Kronos 7000 in the presence of either UV-A or visible light, led to low initial degradation rates. Moreover, mineralization of carbon was faster in the case of TiO<sub>2</sub> P25 in comparison to other photocatalysts. The determination of inorganic chlorine, nitrogen and sulfur produced during the oxidation of thiacloprid, of ecotoxicity and of major intermediate by-products is currently in progress, aiming to the determination of possible photocatalytic degradation pathways.

## Acknowledgments

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.

## References

1. Wei, L., et al., *Titanium dioxide mediated photocatalytic degradation of methamidophos in aqueous phase*. Journal of Hazardous Materials, 2009. **164**(1): p. 154-160.
2. Arias-Estevéz, M., et al., *The mobility and degradation of pesticides in soils and the pollution of groundwater resources*. Agriculture Ecosystems & Environment, 2008. **123**(4): p. 247-260.
3. Seccia, S., et al., *Multiresidue determination of nicotinoid insecticide residues in drinking water by liquid chromatography with electrospray ionization mass spectrometry*. Analytica Chimica Acta, 2005. **553**(1-2): p. 21-26.
4. Konstantinou, I.K. and T.A. Albanis, *Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways*. Applied Catalysis B-Environmental, 2003. **42**(4): p. 319-335.