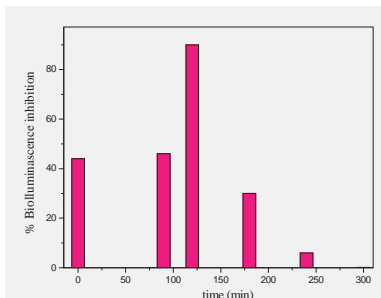


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Variation of ecotoxicity of 20 mg L⁻¹ thiacloprid solution using the photo-Fenton reagent (7 mg L⁻¹ Fe³⁺, 100 mg L⁻¹ H₂O₂, UV-A.

Degradation and mineralization of thiacloprid, a neonicotinoid insecticide often present in drinking water, by homogenous photocatalytic oxidation in the presence of UV-A and visible light has been studied. The effect of various operating conditions such as Fe³⁺ and H₂O₂ concentrations in the photodegradation kinetics was investigated. Mineralization via the organic content reduction (DOC) and inorganic sulphur and 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 300 min of illumination.

Pesticides are widely used as a result of intensive agricultural practices [1]. As these contaminants are in many cases toxic and non-biodegradable, they tend to accumulate in the environment and to magnify through the global trophic network with unpredictable consequences [2]. Thiacloprid ((2Z)-3-[(6-Chloropyridin-3-yl) methyl]-1,3-thiazolidin-2-ylidene) cyanamide) is an insecticide of the neonicotinoid class, with high water solubility, used on agricultural crops to control a variety of insects, primarily aphids and whiteflies [3]. Studies of the environmental behavior of TCL have shown that the molecule is resistant for 6 and more months to the degradation in water by hydrolysis in acidic or neutral media. Alternative treatment methods currently employed for the degradation of agrochemicals in water and wastewater include Advanced Oxidation Processes (AOPs). Among them, homogenous photocatalytic oxidation mediated by the photo-Fenton reagent (Fe³⁺/H₂O₂/UV-A or Visible) has been effective for the degradation of various contaminants found in industrial or domestic wastewaters, including toxic agrochemical substances, such as insecticides and herbicides [4]. Our current study investigates the potential of the photo-Fenton reagent to degrade thiacloprid under various operating conditions, as well as mineralization and reduction of ecotoxicity under optimal conditions.

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 thiacloprid 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 thiacloprid solutions of 20 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 from 100 to 200 mg L⁻¹ had no further beneficial effect since greater peroxide dosages may be responsible for hydroxyl radical scavenging. Similar results were obtained in the case of photo-Fenton degradation of thiacloprid under visible light. Moreover, mineralization of carbon was faster under UV-A in comparison to visible light. Evolution of inorganic sulphur and nitrogen during photocatalysis, reached almost 90% in both cases, within 180 min of UV-A illumination under optimum conditions. Ecotoxicity was completely removed within 300 min of UV-A illumination, under the same conditions. This fact highlights the potential of the photo-Fenton reagent to purify water or wastewater containing pesticides, which are characterized for their high toxicity and resistance to biodegradation. Determination of major intermediate by-products is currently in progress,

aiming to the determination of possible photocatalytic degradation pathways.

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