

Photo-Fenton mediated degradation, mineralization and detoxification of the insecticide thiacloprid in aqueous media

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Introduction and Objectives

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 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. Studies have shown that the molecule is resistant for six and more months to degradation in water by hydrolysis in acidic or neutral media and it has been detected in drinking water [3].

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 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.

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 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 ± 0.1 . The reaction temperature was kept constant at 25°C .

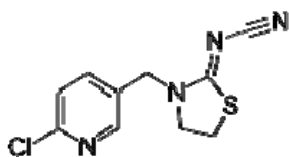


Figure 1: Thiacloprid ((2Z)-3-[(6-Chloropyridin-3-yl) methyl]-1,3-thiazolidin-2-ylidene) cyanamide), CAS No: 111988-49-9, Mr: 252.72 g mol⁻¹)

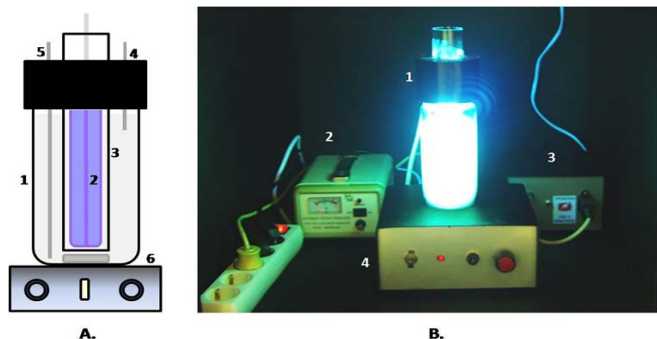


Figure 2: A: Sketch of the photocatalytic reactor employed in the homogenous oxidation of thiacloprid: 1. reaction vessel, 2. irradiation source, 3. borosilicate glass, 4. air inlet, 5. air outlet 6. stirrer. B: Photograph of the experimental setup: 1 photocatalytic reactor equipped with a black light 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 mg L^{-1} , $3.5 \text{ mg L}^{-1} \text{ Fe}^{3+}$ and UV-A irradiation, increase of the amount of H_2O_2 from 0-100 mg L^{-1} results to increase of the reaction rate. Further increase of H_2O_2 to 200 mg L^{-1} has no further beneficial effect on r_0 values (Fig. 3). Optimal concentration of H_2O_2 was also 100 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).

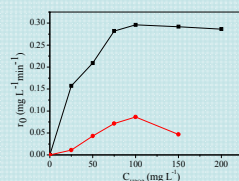


Figure 3: Effect of H_2O_2 concentration on the initial degradation rate of 20 mg L^{-1} TCD in the presence of the photo-Fenton reagent ($3.5 \text{ mg L}^{-1} \text{ Fe}^{3+}$, $100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$) and (■) UV-A or (●) visible irradiation.

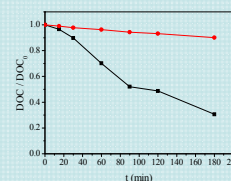


Figure 4: Mineralization of 20 mg L^{-1} TCD in the presence of the photo-Fenton reagent ($3.5 \text{ mg L}^{-1} \text{ Fe}^{3+}$, $100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$) and (■) UV-A or (●) visible irradiation.

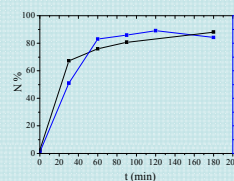


Figure 5: Release of inorganic nitrogen and sulphur during photo-Fenton mineralization ($3.5 \text{ mg L}^{-1} \text{ Fe}^{3+}$, $100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$) of 20 mg L^{-1} TCD and UV-A irradiation.

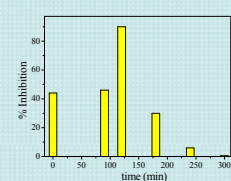


Figure 6: Inhibition of bioluminescence of *V. Fischeri* during photocatalytic oxidation of 20 mg L^{-1} TCD in the presence of the photo-Fenton reagent ($3.5 \text{ mg L}^{-1} \text{ Fe}^{3+}$, $100 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$) and UV-A irradiation.

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