



Efficiency of neonicotinoids photocatalytic degradation by using annular slurry reactor

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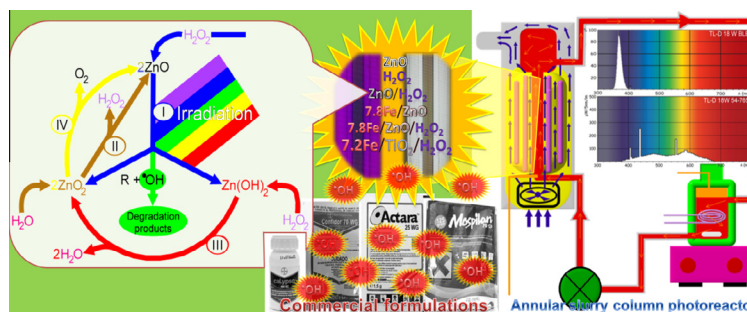
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HIGHLIGHTS

- Annular slurry reactor (ASR) for photodegradation of commercial pesticides was tested.
- Different AOPs were investigated in the presence of UVA and visible light irradiation.
- 7.2Fe/TiO₂/H₂O₂ system using both type of irradiation was the most efficient.
- ASR design showed the highest photodegradation efficiency for pesticide removal.
- For ZnO/H₂O₂ system general reaction mechanism was assumed.

GRAPHICAL ABSTRACT



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ABSTRACT

This article is concerned with the kinetics of the photocatalytic degradation of four neonicotinoids insecticides as active ingredients (AIs) in their commercial formulations by using the annular slurry reactor (ASR). For all AIs, more effective photodegradation was achieved by UVA than by visible light irradiation. The most efficient degradation was observed in the case of thiacloprid, which degraded completely after two hours of irradiation using UVA, and 59% using visible light irradiation. On the other hand, the most stable appeared to be acetamiprid, whereby during the same time of irradiation it was degraded 42% using UVA, and only 4% using visible light irradiation. Because of that the efficiency of a number of advanced oxidation processes was examined in the case of acetamiprid. It was found that the presence of H₂O₂ in ZnO, 7.8Fe/ZnO, and 7.2Fe/TiO₂ systems using UVA did not bring significant changes in the efficiency of degradation. However, using visible light irradiation the presence of H₂O₂ in ZnO and 7.8Fe/ZnO systems significantly increases efficiency of acetamiprid degradation. Also, by adjusting pH to 2.80 in the system 7.2Fe/TiO₂/H₂O₂ using both type of irradiation resulted in a significant increase of the degradation efficiency. For the first time, for ZnO/H₂O₂ system a general reaction mechanism in the dark, as well as in the presence of visible light irradiation was proposed. The electrical energy consumption of ASR was estimated for the most efficient visible light irradiation system using the figure-of-merit electrical energy per order and compared with batch and laminar falling film slurry reactor.

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1. Introduction

Neonicotinoids are a relatively new type of insecticides, used in the last 20 years to control a variety of pests, especially whiteflies, sucking insect pests such as aphids, leafhoppers and planthoppers, some micro-Lepidoptera, thrips, and a number of coleopteran pests. This class of insecticides (registered in more than 120 countries) has reached an enormous economic value and represents one of the most important groups of insecticides on the current market of plant protection products [1]. On the other hand, the treatment of water contaminated with traces of toxic organic compounds is a common problem throughout the world [2]. During the last few decades, attention has been focused on chemical methods that could be used to achieve efficient removal of persistent organic pollutants from wastewater. Conventional systems for wastewater treatment which include activated carbon adsorption, membrane filtration, chemical coagulation, ion exchange on synthetic adsorbent resins, and other, also produce wastes that require additional steps and costs [3]. Processes based on aqueous phase hydroxyl radical chemistry [4,5] are becoming powerful oxidation methods that can completely remove almost all toxic organic compounds in water.

Oxidative procedures targeting total mineralization of organic pollutants into harmless final products, so-called advanced oxidative processes (AOPs) have particularly attracted attention [6,7]. In treating pollutants in water, TiO₂ slurry is the most commonly applied method [8]. Because of its high specific surface area and dispersion, TiO₂ slurry has been demonstrated to be more effective than immobilized TiO₂ [9]. However, widespread use of TiO₂ is uneconomical for large scale water treatment, thereby interest has been drawn towards the search for suitable alternatives to TiO₂ [10]. Therefore, many studies have been conducted to examine photocatalytic activity of different semiconductors such as SnO₂, ZrO₂, WO₃, CdS [11,12], SnO₂, ZnS [12] and ZnO [12–15]. Another approach for producing ·OH radicals is photo-Fenton process which is the most prone of all AOPs for the utilization of solar irradiation, because soluble iron–hydroxyls and especially iron–organic acid complexes, not only absorb UVA irradiation,

but even part of the visible light spectrum. The photo-Fenton system is therefore a very efficient reaction system for the generation of radicals for oxidative processes [16], especially at pH 2.8 [17], where approximately one half of the Fe(III) is present as Fe³⁺ ion and the other half as Fe(OH)²⁺ ion – a photo-active species. The main advantage of the photo-Fenton system is light sensitivity up to a wavelength of 600 nm [18].

Among the most attractive configurations for photocatalytic applications, the tubular, cylindrical reactor has often been used in solar trough collectors. On the other hand, if artificial light is to be used in combination with continuous-flow reactors, the cylindrical geometry of an annular reactor is perhaps the simplest and most efficient configuration [19].

In the present work we studied two photodegradation processes, UVA/ZnO and Vis/ZnO, for the removal of four neonicotinoid active ingredients (AIs) contained in their commercial formulations (CFs) from water by using the annular slurry reactor (ASR). Degradation efficiency of the most stable acetamiprid in Mospilan[®] was also studied by other AOPs (H₂O₂; ZnO/H₂O₂; 7.8Fe/ZnO; 7.8Fe/ZnO/H₂O₂; 7.2Fe/TiO₂/H₂O₂) using UVA and visible light irradiation. For the first time, it was assumed general reaction mechanism for ZnO/H₂O₂ system in the dark, as well as in the presence of visible light irradiation.

2. Materials and methods

2.1. Materials

Commercial formulations, Confidor[®] 70-WG, containing 70% (w/w) of imidacloprid (IMID); Calypso[®] 480-SC, containing 480 g/L (40.4%) of thiacloprid (TCL); and Mospilan[®] 20-SP, containing 20% of acetamiprid (ACET), were obtained from Bayer. Actara[®] 25-WG, containing 25% (w/w) of thiamethoxam (THIA), was supplied by Syngenta. All these chemicals were used as received.

The initial concentration of AIs in their CFs in all experiments was always 0.38 mM. Thirty percent H₂O₂ and 99.8% acetonitrile (ACN, HPLC gradient grade), were purchased from Sigma–Aldrich; 85% H₃PO₄ was a product of Lachema (Neratovice, Czech Republic); NaOH was a product of Zorka Pharm (Šabac, Serbia), and H₂SO₄ was purchased from Merck. All solutions were made using doubly distilled water.

Fe/TiO₂ and Fe/ZnO with 7.24% and 7.80% of Fe, respectively (w/w, denoted as 7.2Fe/TiO₂ and 7.8Fe/ZnO), were synthesized by a simple deposition–precipitation method [20] and used as a photocatalysts. In addition to these, commercial ZnO (>99% p.a.) obtained from Kemika (Zagreb, Croatia) whose structure was defined in our previous work [21] was also used.

2.2. Photocatalytic study

Photodegradation experiments were carried out using a laboratory-scale ASR (Fig. 1), which was operated in a circular ‘closed-loop’ mode.

The reactor glass column (length 525 mm, inner diameter 31 mm, Fig. 1(1)) was surrounded by a set of six low-pressure mercury vapor fluorescent lamps (TL-D 18 W BLB) in the case of degradation using UVA irradiation, and six fluorescent lamps (TL-D 18 W 54-765) in the case of degradation using visible light irradiation (Fig. 1(4)). All lamps had length 604 mm, external diameter 28 mm and were purchased by Philips. The spectra of the mentioned lamps are shown in Fig. 1(12) and (13), respectively. The intensity of UVA and visible light irradiation was 1.75 and 6.96 mW/cm², respectively. The lamps are placed in a symmetrical way around the centered glass column, forming a hexagon (Fig. 1(4)). The lamps and the column are placed in a cylindrical metal

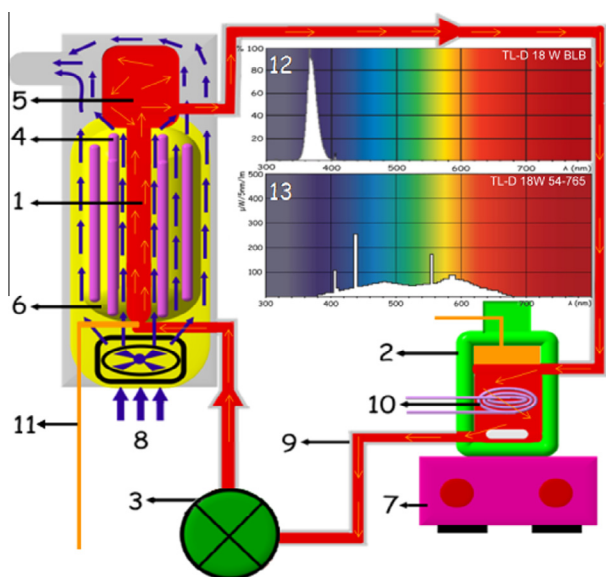


Fig. 1. Schematic view of the laboratory-scale ASR: (1) Pyrex glass column; (2) feed tank; (3) pump; (4) fluorescent lamps; (5) overflow vessel; (6) reflective insert; (7) magnetic stirrer; (8) ventilator; (9) pipe jacket; (10) heater connected to the thermostat and (11) gas supply. Emission spectrum of (12) TL-D 18 W BLB and (13) TL-D 18 W 54–765 lamp.

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