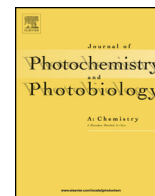




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photocatalytic treatment of metribuzin herbicide over TiO₂ aqueous suspensions: Removal efficiency, identification of transformation products, reaction pathways and ecotoxicity evaluation



M. Antonopoulou, I. Konstantinou*

Department of Environmental and Natural Resources Management, University of Patras, 30100 Agrinio, Greece

ARTICLE INFO

Article history:

Received 7 May 2014

Received in revised form 17 August 2014

Accepted 20 August 2014

Available online 27 August 2014

Keywords:

Metribuzin

TiO₂ photocatalysis

Transformation products

Scavengers

Ecotoxicity

ABSTRACT

The present study describes the detailed transformation and mineralization of metribuzin, a widely used herbicide, by TiO₂ mediated photocatalysis under simulated solar irradiation. Transformation of MET by heterogeneous photocatalysis with TiO₂ ([metribuzin] = 10 mg L⁻¹, [TiO₂] = 100 mg L⁻¹ and I = 750 W m⁻²) was completed within 40 min irradiation, whereas 80% of mineralization was achieved within 300 min irradiation. The degradation for both metribuzin and total organic carbon (TOC) followed pseudo-first order kinetics. Rate constants of $k_{app(MET)} = 10.85 \times 10^{-1} \text{ min}^{-1}$ and $k_{app(TOC)} = 5.2 \times 10^{-3} \text{ min}^{-1}$ and half-lives ($t_{1/2}$) of 6.4 min and 133.3 min were recorded for metribuzin and TOC respectively. High resolution accurate mass spectrometry coupled with liquid chromatography (HR-LC-MS) and gas chromatography–mass spectrometry (GC-MS) techniques were used to identify the degradation products. The main metribuzin phototransformation pathways were observed to be the cleavage of –NH₂ and –SCH₃ groups, hydroxylation and dealkylation of *tert*-butyl chain. The investigation of the role of the reactive species suggests that HO•, h⁺ and O₂^{•-} play the principal role in the degradation mechanism of metribuzin. Substrate decomposition is accompanied by the formation of intermediates compounds more toxic than the parent molecule, as evidenced by the measurement of acute toxicity using the *Vibrio fischeri* bacteria test.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Pesticide contamination of surface water and groundwater has been recognized as a major environmental issue all over the world [1]. The increasing production and application of pesticides for agricultural and non-agricultural purposes along with their resistance to natural decomposition, biodegradation, chemical and photochemical degradation under typical environmental conditions have resulted in the presence of their residues, their metabolites and/or transformation products in various environmental matrices [2,3]. The occurrence of these contaminants in aquatic environment is considered to be a potential threat both to the environment and human health due to their toxicity and widespread use [4].

Abbreviations: MET, metribuzin; HR-LC-MS, high resolution accurate liquid chromatography mass spectrometry; GC-MS, gas chromatography–mass spectrometry; DA, deaminated metribuzin; DK, diketo-metribuzin; DADK, deaminated diketo-metribuzin.

* Corresponding author. Tel.: +30 2641074186; fax: +30 2641074176.

E-mail addresses: iokonst@upatras.gr, iokonst@cc.uoi.gr (I. Konstantinou).

<http://dx.doi.org/10.1016/j.jphotochem.2014.08.008>

1010-6030/© 2014 Elsevier B.V. All rights reserved.

Herbicides, used in agriculture as the principal protection against pests, disease and weed infestation, are among the most widely encountered pesticides present in water supplies in the vicinity of agricultural areas [4]. Metribuzin (4-amino-6-*tert*-butyl-3-methylthio-1,2,4-triazin-5(4H)-one), one of the most important selective triazinone herbicides, is used for pre-emergence and post emergence control of grass and broadleaved weed in a variety of agricultural crops [5]. Its mode of action is based on the inhibition of photosynthesis, blocking the electron transport in the Hill reaction of photosystem II [6]. This selective herbicide has high water solubility (1200 mg L⁻¹, 20 °C), sorption coefficient in soil varying from 0.56 in a sandy loam soil to 31.7 in a soil containing 60% organic matter and logK_{ow} equal to 1.60 [5,7]. Based on the above physicochemical properties, metribuzin (MET) possesses an increased potential for runoff, leaching and thus for surface and groundwater pollution [5]. Residue levels up to 25.15 μg L⁻¹ of MET have been reported in environmental waters by many authors [8–11]. However, modeling studies have concluded that MET can reach concentrations as high as 390 μg L⁻¹ in surface water runoff [12].

Like other pesticides, MET can contaminate natural aquatic systems by various means: spray and vapor drift, surface water

runoff or leaching from treated land or from accidental spills [6]. As regards its environmental fate, MET undergoes degradation through photochemical, chemical and biochemical processes. In the environment, it may break down into three primary transformation products (TPs): deaminated metribuzin (DA), diketo-metribuzin (DK), and deaminated diketo-metribuzin (DADK) [5,9]. DA, DK and DADK have been detected in the environment in concentrations ranging from 0.1 to 1.9 $\mu\text{g L}^{-1}$ and in some cases they have been detected even when metribuzin was absent [13]. MET undergoes rapid photolysis in natural pond water with a half-life of <7 days. Biodegradation in soil showed half-lives from 1.5 to 4 months. In soil surface photodecomposition of MET proceeds with a half-life of 14–25 days [6]. Under environmental conditions, MET was proven to be hydrolytically stable in the pH range from 4 to 9 under 25 °C [14].

This selective herbicide is moderate toxic to fish and invertebrates; however, it has been recognized to be extremely toxic at freshwater macrophytes and algae and to be generally more toxic to aquatic plants than other widely used herbicides such as atrazine, alachlor, or metolachlor [6]. Due to its properties, the removal of MET is of special interest since its dispersion in soils and the hydrosphere, constitutes an outstanding long-term environmental problem. Therefore, the development of an effective treatment technology for elimination of MET is of great scientific, regulatory and public interest.

In the last decade advanced oxidation processes have been considered as promising detoxification methods for pesticide contaminated water [15,16]. Among them, TiO_2 photocatalytic oxidation is an advantageous technology as it can be carried out under ambient conditions and usually lead to complete mineralization of pollutants to CO_2 , water and inorganic ions [17,18].

To the best of our knowledge there is only one study dealing with the photocatalytic degradation of MET focusing only on the effect of different parameters on the process efficiency [19]. As a consequence, an in-depth photocatalytic degradation study of MET in the presence of TiO_2 under simulated solar light was performed focusing on the detailed mechanistic investigation, mineralization and toxicity evaluation. Thus, the aims of the present study were to investigate the following aspects which have not previously been studied: (i) to evaluate the total mineralization of MET by a combination of analytical techniques; (ii) to identify the TPs by using powerful mass spectrometric techniques such as accurate mass HR-MS and GC-MS; (iii) to clarify the dominant reactive species involved in the reaction mechanism using different scavengers; (iv) to study the degradation pathways followed and (v) to evaluate the ecotoxicity along the photocatalytic reactions by means of luminescence bioassays using *Vibrio fischeri* bacteria. A comparison between the TPs found by TiO_2 photocatalysis and those reported in previous biotic or abiotic degradation studies is also presented.

2. Experimental

2.1. Reagents and materials

Metribuzin analytical grade (>98%) standard was purchased from Sigma Aldrich. TiO_2 -P25 from Degussa (Germany) was used as photocatalyst. HPLC grade solvents (acetonitrile, isopropanol and methanol) were supplied by Merck (Darmstadt, Germany). Sodium azide (NaN_3), potassium iodide (KI) and *p*-benzoquinone (BQ) were obtained from Sigma-Aldrich. Ultrapure water was obtained from a Millipore Waters Milli-Q water purification system.

2.2. Photocatalytic degradation experiments

Irradiation experiments were performed on stirred aqueous solutions using a double-wall pyrex glass (Duran®) reactor

containing 250 mL of MET aqueous solution (10 mg L^{-1}) and 100 mg L^{-1} of TiO_2 . Photocatalytic degradation experiments were performed at inherent pH (pH=6.8) in order to simulate a cost-effective photocatalytic treatment (no use of additional reagents) and natural water conditions prior to and during treatment. However, it should be mentioned that only a slight decrease of pH value was observed after 300 min of irradiation time. A higher initial concentration of MET (10 mg L^{-1}) than the typical values found in aquatic matrices was selected in order to facilitate the process of the identification and structural elucidation of transformation products. Before irradiation, separate dark adsorption experiments were conducted for 30 min under stirring in order to reach adsorption equilibrium onto TiO_2 surface. Aliquots were collected and filtered (0.45 μm membrane filters, Millipore) at different time intervals. Finally, photolysis experiments in the absence of TiO_2 were performed under the same irradiation conditions. All the experiments were run in triplicate and mean values are quoted as results with standard deviation never exceeding 1.1%.

Irradiation was performed using a Suntest XLS+ photo-simulator from Atlas (Germany) equipped with a xenon arc lamp (2200 W) and special glass filters to prevent the transmission of wavelengths below 290 nm. The radiation intensity was 750 W m^{-2} according to previous publications [20–22] in order to ensure the activation of all catalyst particles [23]. The corresponding light dose for 10 min of irradiation was 450 kJ m^{-2} . Suntest apparatus is equipped with a black standard thermometer (BST) to regulate air temperature conditions in the exposure chamber by air-cooling circuit. The temperature of samples did not exceed 25 °C using also tap-water cooling circuit for the UV-reactor.

2.3. Analytical procedures

2.3.1. Kinetic study

MET concentrations were determined by a Dionex P680 HPLC equipped with a Dionex PDA-100 photodiode array detector. The analysis was performed by means of a Discovery C₁₈, (250 mm length \times 4.6 mm ID, 5 μm particle size) analytical column from Supelco (Bellefonte, PA, USA) thermostated at 40 °C, that was fitted with a guard column of the same static phase. The HPLC mobile phase was a mixture of LC-grade water pH 3 (70%) and acetonitrile (30%) with a flow rate of 1 mL min^{-1} . Under these conditions, MET retention time was 4.17 min and the quantitation limit was 0.1 mg L^{-1} . For the determination of MET the detector was set at 211 nm.

2.3.2. Mineralization studies

The mineralization of MET during the photocatalytic process, was evaluated by measuring the decrease of the total organic carbon (TOC) after filtration (Millipore 0.45 μm membrane filter), using a Shimadzu TOC V-csh Analyzer equipped with a non-dispersive infrared detector. NO_3^- and NO_2^- ions, released during the process, were determined by a Dionex ICS-1500 equipped with ASRS Ultra II self-regenerating suppressor. The elution was isocratic with Na_2CO_3 (9 mM) at a flow rate of 1.2 mL min^{-1} . NH_4^+ ions were analyzed by the colometric method based on indophenol blue formation [24] using an UV-Vis spectrophotometer Hitachi, U-2000.

2.3.3. Scavenging experiments for reactive species

The contribution of HO^\bullet , $\text{O}_2^{\bullet-}$, h^+ and $^1\text{O}_2$ in the reaction mechanism was evaluated with the addition of isopropanol (1000 mg L^{-1}), *p*-benzoquinone (20 mg L^{-1}), oxalic acid (100 mg L^{-1}) and azide (10 mg L^{-1}) to the solutions containing 10 mg L^{-1} MET, respectively. The concentrations of selected scavengers were enough to inhibit the majority of the reactive species, according to literature data [21,25].

Download English Version:

<https://daneshyari.com/en/article/26143>

Download Persian Version:

<https://daneshyari.com/article/26143>

[Daneshyari.com](https://daneshyari.com)