Applied Catalysis B: Environmental 192 (2016) 152–160

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Kinetic and mechanistic study of photocatalytic degradation of flame retardant Tris (1-chloro-2-propyl) phosphate (TCPP)

M. Antonopoulou [a,b], P. Karagianni [a], I.K. Konstantinou [b,*]

[a] *Department of Environmental and Natural Resources Management, University of Patras, 30100, Agrinio, Greece*
[b] *Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece*

ARTICLE INFO

Article history:
Received 11 October 2015
Received in revised form 11 March 2016
Accepted 16 March 2016
Available online 18 March 2016

Keywords:
Flame retardants
TCPP
Photocatalysis
Scavengers
Transformation products

ABSTRACT

In the present work, a comprehensive study on the application of TiO_2 photocatalysis for the removal of the flame retardant tris (1-chloro-2-propyl) phosphate (TCPP) from both ultrapure water (UW) and real wastewater (WW) is presented. All the photocatalytic experiments were conducted using environmental relevant concentrations of TCPP, inherent pH and simulated solar irradiation with the view to simulate real environmental conditions. Degradation followed apparent first-order kinetics with rate constants varying from $k_{app} = 14.2 \times 10^{-2}\ min^{-1}$ to $k_{app} = 1.41 \times 10^{-2}\ min^{-1}$ for initial TCPP concentrations in the range of 25–500 μgL^{-1} while mineralization was accomplished in prolonged irradiation times as monitored by the release of chlorine and phosphate ions. Scavenging studies were carried out in UW, indicating that photogenerated $HO^{\bullet}$ in the catalyst surface are the main species participating in the photocatalytic mechanism. Experiments using secondary treated wastewater showed a significant retardation of TCPP photocatalytic degradation mainly due scavenging effects and competitive adsorption of aromatic and phenolic compounds and inorganic ions, such as HCO_3^{-}, contained in the wastewater matrix. The transformation products were elucidated by UPLC-TOF-MS instrumentation and hydroxylation, oxidation, dechlorination and dealkylation have been identified as the principal photocatalytic transformation routes before complete mineralization. Toxicity assays in UW and WW were also conducted using *Vibrio fischeri* as tested organism showing a progressive toxicity decrease along the treatment till low values. Measurements showed a higher initial toxicity and a slower decrease in WW that is attributed to the more complex matrix regarding chemical pollutants and their transformation products formed during the treatment as well as scavenging effects.

1. Introduction

The efficiency of heterogeneous photocatalysis for the removal of a great number of organic contaminants from aqueous phase is well-documented in the literature [1–3]. An increasing number of scientific works are focused on the photocatalytic removal of aquatic pollutants such as personal care products, pharmaceuticals, pesticides, taste and odor compounds, veterinary products and food additives, among others, demonstrating promising results [1–7]. The efficiency of the process has been associated with the generation of various oxidizing and reductive species when the photocatalyst is illuminated with energy greater than its bang gap [1–3,7]. Although heterogeneous photocatalysis has become a field of extensive research during the last decades, the photocatalytic removal of aquatic pollutants belonging to the category of flame retardants is scarce.

Flame retardants (FRs) constitute a class of emerging contaminants as their heavy use in consumer and building products, has led to their presence in air, water and sediments at various concentration levels [8–12]. FRs are considered to be environmentally persistent and exert ecotoxicological effects at relatively low concentrations [9,10,12]. In recognition of their adverse effects on aquatic ecosystem and human health, various FRs are under evaluation in the framework of Toxic Substances Control Act from U.S. Environmental Protection Agency (USEPA) [9].

Among FRs, we have focused on the aliphatic halogenated phosphate ester, tris (1-chloro-2-propyl) phosphate (TCPP), a compound included in the European Commission fourth priority list [10]. Due its heavy production and major application, TCPP has also been categorized as an EU high production volume (HPV) chemical [10]. Recent studies have reported the occurrence of TCPP in natural water bodies and effluents as a result of incomplete removal by

---

* Corresponding author.
E-mail address: iokonst@cc.uoi.gr (I.K. Konstantinou).

http://dx.doi.org/10.1016/j.apcatb.2016.03.039

conventional wastewater treatment plants (WWTPs) [10,12]. TCPP has been detected in effluent and surface water samples at concentrations as high as 24 μg L^{-1} and 200 ng L^{-1}, respectively [10,12].

The main focus of the present work is to provide novel knowledge in relation to the applicability of heterogeneous TiO_2 photocatalysis to remove TCPP, a representative flame retardant pollutant, from water matrices that is studied for the first time. For this purpose, the photocatalytic transformation of TCPP was investigated using concentrations similar to those detected in real effluents and two different aqueous matrices, ultrapure water (UW) and municipal wastewater secondary treatment effluent (WW). More specifically, the photocatalytic transformation of TCPP in UW and WW, in terms of pollutant abatement and mineralization and the effect of the matrix on the transformation process were evaluated. The contribution of oxidative and reductive species generated during the process was studied in detail using various well-established scavengers. Emphasis was also placed on the identification of the transformation products using ultra pressure liquid chromatography coupled to time-of-flight mass spectrometry (UPLC-TOF-MS). Finally, the study focused also on the integrated evaluation of the treatment process by assessing the evolution of ecotoxicity during the treatment.

2. Experimental

2.1. Chemicals

TCPP (mixtures of isomers), analytical standard was obtained by Sigma-Aldrich (USA). TiO_2 P25 (Evonik, Germany; particle size 20–30 nm; crystal structure, 80% anatase and 20% rutile; surface area, 56 m^2 g^{-1}, zero point of charge ≈6.3–6.8) was employed as the semiconductor catalyst in the photocatalytic experiments. All reagents used (sodium azide (NaN_3), KI, *p*-benzoquinone (BQ), NaF, $K_2Cr_2O_7$ and Folin Ciocalteu) were obtained from Sigma-Aldrich. LC–MS-grade solvents (acetonitrile, isopropanol, methanol and water) were supplied by Merck and used for UPLC-TOF-MS analyses. In order to remove the TiO_2 particles of the solution samples during the experiments, HA 0.45 μm filters were supplied by Millipore (Bedford, USA). Oasis HLB (divinylbenzene/N-vinylpyrrolidone copolymer) cartridges (60 mg, 3 mL) from Waters (Mildford, MA, USA) were used for the extraction of water samples and the identification of transformation products. TCPP solutions were prepared both in ultrapure water (Milli-Q) and secondary (conventional activated sludge) treated municipal wastewater samples (WW). Samples of WW were collected directly from the treatment plant of Patras University, West Greece. After collection, the samples were transferred to the laboratory immediately and filtered to remove particulate matter. Mean values of physicochemical parameters of the WW were: pH 7.85 ± 0.04; conductivity = 310.51 ± 25.3 μS cm^{-1}; Total suspended solids = 1.07 ± 0.013 mg L^{-1}; Chemical oxygen demand = 18.9 ± 1.82 mg L^{-1}; Total organic carbon = 6.2 ± 0.18 mg L^{-1}; TPh = 1.03 ± 0.015 mg L^{-1}; PO_4^{3-} = 1.85± 0.017 mg L^{-1}; SO_4^{2-} = 30 ± 0.96 mg L^{-1}; NO_3^- = 20.5± 0.48 mg L^{-1}.

2.2. Photocatalytic experiments

Photocatalytic experiments were carried out in a solar simulator Suntest XLS+ apparatus (Atlas, Germany) equipped with a 2.2 kWatt xenon lamp jacked and special glass filters cutting the irradiation with wavelengths below 290 nm. In each experiment 250 mL of aqueous solutions with the desired concentration of TCPP and the appropriate amount of catalyst (50 mg L^{-1}) were loaded in Pyrex glass UV-reactor at ambient conditions (temperature = 23 °C and pH 6.5) under continuous stirring. The catalyst loading level (50 mg L^{-1}) was selected based on the low environmental relevant concentration levels used in the irradiation experiments in order to not obtain very fast kinetics and to facilitate the study on the degradation kinetics, mechanisms and identification of transformation products. Prior to exposure to simulated solar irradiation, the suspension was magnetically stirred for 30 min in the dark to ensure adsorption equilibrium of TCPP onto the TiO_2 surface. The radiation intensity was fixed at 250 W m^{-2} for all experiments and the incident irradiance dose for 10 min of irradiation was 150 kJ m^{-2} as provided by an internal radiometer of Suntest instrument. Samples of about 2 mL were periodically withdrawn from the reactor and filtered for further analysis.

2.3. Analytical determinations

TCPP quantification and identification of transformation products was performed by means of UPLC coupled to a time of flight mass spectrometry (UPLC-TOF-MS) system in positive ionization mode. Samples (20 mL) were pre-concentrated by means of solid phase extraction (SPE) as reported in our previous study to a final volume of 0.2 mL [5]. The UPLC-TOF-MS system consisted of an Ultra-High Performance LC pump (Dionex Ultimate 3000, Thermo) equipped with a C18 Acclaim™ RSLC 120 column, 100 mm x 2.1 mm, 2.2 μm particle size (Thermo Fisher Scientific, San Jose, USA), thermostated at 30 °C and a microTOF Focus II – time of flight mass spectrometer (Brüker Daltonics, Germany). A and B mobile phases were methanol and water with 5 mM ammonium formate respectively, at a flow rate of 0.4 mL min^{-1}. The following program was adopted: 1% A/99% B at 0 min to 99% A/1% B in 10 min and back to the initial ratio in 13 min. The injection volume was 10 μL. The TOF mass analyzer with an electrospray interface was operated under the following conditions: dry gas flow rate 8 L min^{-1} (nitrogen), nebulizer pressure 2.4 bar, capillary voltage at 4500 V, end plate offset at 500 V, hexapole RF 100.0 Vpp, dry temperature at 200 °C using otof control software. The mass accuracy (±5 ppm) of the TOF mass analyzer was ensured by an externally calibration using sodium formate, in the scan range *m*/*z* 50–1000, prior to analysis. Under the adopted chromatographic conditions, TCPP retention time was 8.1 min The limit of detection (LOD) and limit of quantitation (LOQ) was 50 and 165 ng L^{-1}, respectively.

Aromatic compounds content in WW sample was evaluated by means of the absorbance at 254 nm that was monitored using a UV–vis spectrophotometer (Hitachi, U-2000). The total phenols were determined by the Folin–Ciocalteau method. The phenolic content (TPh) was expressed as mg L^{-1} of equivalent phenol, using a calibration curve based on standard solutions of phenol. Cl^- and PO_4^{3-} ions, released during the oxidation of TCPP, were determined by a Dionex ICS-1500 Ion Chromatography system incorporated with an ASRS Ultra II suppressor. Analysis was performed on an IonPac AS9-HC using an aqueous sodium carbonate (9 mM) solution as mobile phase was at a flow rate of 1 mL min^{-1}.

2.4. Scavenging experiments

The role of $HO^\bullet$, h^+, e^-_{aq} and $O_2^{\bullet -}$ in the degradation mechanism was assessed by the addition of 1×10^{-3} M isopropanol (i-PrOH), 1×10^{-3} M I^-, 50×10^{-3} μM $K_2Cr_2O_{7,}$ 1×10^{-3} M *p*-BQ and 1×10^{-3} M N_3^-, respectively. Photocatalytic experiments with the addition of 1×10^{-3} M methanol as well as using MeCN as reaction media were also conducted for discrimination between the oxidation by $HO^\bullet$ and h^+. To wash $HO^\bullet_{ads}$ into solution as bulk $HO^\bullet_{bulk}$, NaF at 0.1×10^{-3} mM was used. Finally, aqueous solutions of TCPP degassed with high-purity N_2 were also subjected to photocatalytic treatment [13,14].