Ozonation, photocatalysis and photocatalytic ozonation of diuron. Intermediates identification

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HIGHLIGHTS

- ·OH radical plays an important role in diuron photocatalytic ozonation (>99%).
- $O_3/TiO_2/UVA$ enhances TOC removal (83% synergism) if compared to simpler systems.
- By-products derive from ·OH attack to the alkyl side chain and/or Cl substitution.
- $O_3/TiO_2/UVA$ is capable of mineralize small oxygenated species.
- Diuron toxicity to *Vibrio fischeri* shows a maximum at initial stages of oxidation.

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ABSTRACT

Aqueous 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) has been oxidized by ozonation, photocatalysis and photocatalytic ozonation. Diuron degradation takes place via radical pathway through hydroxyl radicals in those systems involving ozone. Diuron elimination in photocatalytic ozonation is not enhanced if compared to single ozonation; however, TOC removal was significantly improved. Specifically, 80% TOC removal in 2 h was reached in photocatalytic ozonation while single ozonation just led to 25% TOC reduction. Photocatalysis required 9 h to reach 25% TOC reduction. Ten transformation by-products generated during the application of the three technologies were tentatively identified by liquid chromatography–quadrupole time-of-flight mass spectrometry (LC–QTOF–MS/MS). Single ozonation and photocatalytic ozonation led to the formation and complete elimination of all by-products. Low weight carboxylic acids evolution suggests that high TOC removal in photocatalytic ozonation is linked to its capacity to oxidize small oxygenated compounds and release of inorganic chloride and nitrate. Toxicity evolution to *Vibrio fischeri* in photocatalytic ozonation displayed an increase in inhibition at the initial stages (>90% of inhibition), followed by a decrease of this parameter as the reaction progressed. The final treated sample shows a lower toxicity than the initial one (55% *vs* 20%).

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1. Introduction

Intensive agriculture involves a high herbicide demand. The presence of these substances in the environment is alarmingly increasing all over the world. Since herbicides are usually persistent in soil and water, their presence supposes a potential harmful risk in natural ecosystems.

Water resources scarcity is an increasingly problem in many areas of the Earth. Recycling aqueous effluents by new treatment methods is a challenge for the scientific community. Although treating organic/inorganic pollutants by means of different technologies (usually biodegradation) is quite often viable, a variety of them, such as some pesticides, are recalcitrant to conventional biological treatments [1]. For this reason, more powerful oxidizing technologies are required.

Organochlorides are some of the most popular and widely used pesticides. They derive from chlorinated hydrocarbons. The high physical and chemical stability favor their persistence and slow biodegradability in the environment. Diuron ($C_9H_{10}Cl_2N_2O$, 3-(3,4-dichlorophenyl)-1,1-dimethylurea) works by inhibiting the photosynthesis process. Diuron is an organochloride phenylurea herbicide commonly used as pre and post emergent herbicide of a huge variety of both, crop and non-crop areas. Diuron's use is currently

approved in the European Union until 2018 [2]. This herbicide, whose presence has been reported in 70% of 100 rives of 27 European Countries with a maximum concentration of 0.826 μg L^{-1} [3], appears to be moderately persistent and relatively immobile in water [4]. Moreover, because of its high toxicity, pollution due to this substance is considered as a real environmental hazard. This is evidenced by a recently launched European Directive which includes diuron in the list of priority pollutants in water treatment policy [5].

The harmful presence of phenylurea herbicides in aqueous environments has initiated a considerable research production, including ozone and advanced oxidation processes such as Fenton-based systems, photocatalysis and, ozone combined with UV radiation, catalysts or H$_2$O$_2$ [6]. Diuron ozonation has been reported in the literature as an effective technology [7]. Nevertheless, to the author's knowledge, individual diuron photocatalytic ozonation focused on the generated transformation products has not yet been reported.

Photocatalytic ozonation consists in the simultaneous application of ozone and photocatalysis. The process is presented as a promising chemical technology which reaches high mineralization rates. The combination of ozone in photocatalytic systems allows for a synergistic effect based on the high efficient electron trapping by ozone. Additionally higher amounts of hydroxyl radicals are generated if compared to photocatalysis in the presence of oxygen alone [8]. In spite of being an effective technology, separation of catalyst from the media and energy requirements must be considered at the time of scaling up. In any case, the synergistic effect frequently observed considerably reduces the costs if compared to photocatalysis or ozonation alone [9].

In the last years, photocatalytic efforts have been focused on developing more reliable and efficient photocatalysts which can take benefit of the solar spectrum more effectively [10]. Amongst the main proposed strategies, TiO$_2$ metal and non-metal doping [11], coupling of oxides to TiO$_2$ [12], photocatalysts alternative to TiO$_2$ and supported or easily removable solids [9,13] can be listed. In this work, a lab manufactured N-doped titania has been used. N doping improvements on photoactivity and characterization of the solid have previously been studied in-depth in a mixture of three pyridine based herbicides, under photocatalysis and photocatalytic ozonation processes [14]. Moreover, N-doping may be considered as a starting point in catalyst recovering due to the increase in particle size. A higher particle diameter, if compared to commercial formulas, makes easier the recovering process from the effluent. Ozonation and photocatalysis of diuron have been compared to photocatalytic ozonation under UVA radiation when required (maximum of emission at 365 nm).

The aim of the present work has been focused on the identification of the main transformation byproducts formed in photocatalytic ozonation and comparison to those generated under single ozonation or photocatalysis. Final oxidation organic acids evolution has also been monitored in order to explain TOC removal extents. Toxicity evolution to bacteria Vibrio fischeri has been studied for the three processes and compared to results of intermediates, organic acids released and TOC evolution.

2. Materials and methods

2.1. Chemicals

Analytical standard diuron was acquired from Sigma–Aldrich (>98%) and used as received in all experiments. HPLC-grade acetonitrile from VWR Chemicals was used in the HPLC system. Ionic chromatography solutions were prepared from Sigma–Aldrich reagents. Titanium isopropoxide (Sigma–Aldrich, >97%), trimethy-lamine (Panreac, 99.5%) and HCl (Fischer Scientific, 37%) were used in N doped titania photocatalyst synthesis. Potassium indigo trisulfonate, used in dissolved ozone monitoring, was purchased from Sigma–Aldrich (99%). Ultrapure water used in all trials was produced in a Mili-Q® academic (Millipore) system.

Chemicals for mobile phase in LC–QTOF–MS analysis (water, >99.9% and acetonitrile, >99.9%) were LC–MS CROMASOLV® from Fluka. Formic acid was used (98%, LC–MS from Fluka) to acidify water.

2.2. Experimental setup and procedure

Photoreaction installation was equipped with a 1.0 L volume cylindrical reactor made of borosilicate glass. The reactor was placed into a cylinder pipe (54 cm of height and 31 cm of external diameter) equipped with four black light lamps of 41 cm of length (LAMP15TBL HQPOWER™ 15 W emitting in the range 350–400 nm, maximum at 365 nm). The inner surface was covered with aluminum foil in order to enhance photons reflection. UVA photon flow entering the reaction system was calculated in a previous work by means of ferrioxalate actinometry. Values of 1.77, 3.26, 5.13 and 6.86 × 10^{-5} Einstein min^{-1} L^{-1} when 1, 2, 3 and 4 lamps, were reported [15]. Additionally, when the aluminum foil covering the internal walls of the installation was substituted by a black surface, the intensity (4 lamps switched on) decreased to 3.60 × 10^{-5} Einstein min^{-1} L^{-1}.

In a typical experiment, 30 L h^{-1} gas flow rate of oxygen, or an oxygen–ozone mixture, was fed to the photoreactor system through a stainless steel diffuser. Solid photocatalyst was added 30 min before starting the reaction, in order to reach the possible adsorption equilibria onto its surface. Samples at different times were extracted and filtered by means of Millex-HA filters (Millipore, 0.45 μm) before analysis.

Ozone was continuously generated by electrical discharges of pure oxygen in a Sander Laboratory Ozone Generator. An Anseros Ozomat ozone analyzer, the measurement based on 254 nm absorbance, was used to monitor ozone gas phase concentration.

2.3. Photocatalyst synthesis

N doped titania photocatalyst was prepared applying a sol–gel method followed by thermal treatment and calcination according to literature and previous works [16,14]. Briefly, 12 mL of titanium (IV) isopropoxide were dissolved in 100 mL of ethanol. Next, 9 mL of trimethylamine was added. Afterwards, titania was precipitated using 100 mL of HCl 0.1 M. The suspension was thermally treated at 80 °C for 12 h. The final residue was dried overnight at 100 °C and calcined at 500 °C for 4 h (initial ramp of 10 °C min^{-1}).

2.4. Analytical methods

Diuron was analyzed by an Agilent 1100 (Hewlett-Packard) high performance liquid chromatography with UV detection (HPLC-UV). The column used was a Kromasil 100 5C18 (5 μm, 2.1 × 150 mm). 0.1% H$_3$PO$_4$ acidified water (A) and acetonitrile (B) were the mobile phases used. An elution gradient from 50% to 65% of B in 6 min was applied. UV detection was conducted at 243 nm.

Liquid chromatography coupled to a quadrupole time-of-flight mass spectrometer (LC–QTOF–MS) was used to identify and monitor transformation products generated in single ozonation, photocatalytic oxidation and photocatalytic ozonation processes. Chromatographic separation was carried out in an Agilent 1260 Infinity system equipped with a Poroshell 120 EC-C18 (2.7 μm, 4.6 × 50 mm) column. Pure MiliQ water (phase A) or acidified water with 0.1% formic acid (for negative and positive ionization