



Photocatalytic diphenhydramine degradation under different radiation sources: Kinetic studies and energetic comparison

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ABSTRACT

The degradation of diphenhydramine hydrochloride (DPH) by TiO₂ photocatalysis was studied under different radiation sources: UVC, black blue lamps (BLB), simulated solar radiation (SB, Solarbox) and solar radiation (CPCs, Compound Parabolic Concentrators) at lab and pilot plant scales. Results indicated that photolysis showed an important role in the DPH abatement under UVC radiation (32.5% of DPH conversion), being negligible in all other cases. Different TiO₂ concentrations (0.05, 0.1 and 0.4 g/L) were used in SB device and the best results were obtained for 0.4 g/L: 35.7% of DPH conversion, after 60 min of irradiation. For comparison purposes, concentration of 0.4 g/L TiO₂ was used in all the devices. The best results obtained after 60 min of irradiation using only TiO₂ were 44.8% of DPH degradation in BLB and 9.0% of mineralization in SB. The addition of H₂O₂ improves the photocatalytic process (without H₂O₂) and the best results obtained were when UVC was used obtaining 100% DPH degradation and 28.6% TOC reduction. Concerning the removal efficiencies to the energy used, the best results were obtained for UVC with H₂O₂ (4492 mg DPH/kWh and 2246 ppm DPH/kWh), being also the corresponding cheapest costs (2.89×10^{-5} €/mg DPH and 5.79×10^{-5} €/ppm DPH). In terms of efficiency between 380 and 400 nm (absorption range for TiO₂), BLB presents the best results. Kinetic constants were also estimated referred to the irradiation time (h⁻¹) or the accumulated energy (kJ⁻¹), the highest values correspond to UVC with hydrogen peroxide (7.64 h⁻¹ and 0.493 kJ⁻¹). Finally, toxicity and reaction intermediates were identified and DPH photo-degradation pathway was proposed.

1. Introduction

In the last years, water scarcity and quality have become a worldwide concern [1]. Every day large amounts of water are contaminated by different pollutants coming from domestic or industrial uses. Pollution of water, regulated by Directive (2013/39/EU) [2] as regards priority substances in the field of water policy, is generally decreasing. However, organic substances with harmful properties such as pharmaceuticals and personal care products are increasingly detected in the environment [3,4]. Spain is ranked as one of the world's largest consumer of pharmaceuticals [5]. These compounds are recalcitrant and with bioaccumulation problems [6–8]. They are also resistant to conventional wastewater treatments and are found in effluents at concentrations ranging 0.1–20.0 µg/L [9–11].

Among those pollutants, there is a special group of pharmaceuticals, antihistaminic drugs, easily found in waters. Between them, diphenhydramine hydrochloride (DPH) is the classic H₁ receptor antagonist used in pregnancy for the treatment of allergies and nausea, as well as an analgesic adjuvant in cancer pain. This kind of drugs can be

achieved in wastewaters coming from some pharmaceutical industries in concentrations between 1300–1400 µg/L and some antibiotics can reach concentrations between 28,000–31,000 µg/L [12]. DPH has relatively low molecular weight and high lipid solubility, allowing easy blood–brain barrier and placental passage [13]. Unfortunately, information on the environmental fate and toxicity to aquatic species is scarce for most pharmaceuticals [14]. Due to the growing demand of society for the decontamination of water, regulations are increasingly strict in recent years, raising the research on methods to eliminate pharmaceuticals from water and wastewater, and this is the case of advanced oxidation processes (AOPs) [15,16].

AOPs are environmental friendly methods based on in situ production of hydroxyl radical (·OH) as main oxidant, which is able to react non-selectively with most organic compounds [17]. Different studies have been reported related to the photocatalytic treatment of DPH [18,19]. However, studies about DPH removal under different radiation sources and at low catalyst concentrations have not yet been reported.

The present work is focused on the degradation and mineralization

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of DPH by photocatalytic treatment in different experimental devices. Experiments were performed in three laboratory scale photoreactors under artificial irradiation sources: UVC lamps (monochromatic radiation, maximum at 254 nm), black blue lamps (emission ranging from 300 to 410 nm, maximum at 365 nm) and simulated solar radiation (Solarbox with Xe lamp, spectrum similar to the solar one in the UV range). Moreover, a solar reactor has been used, at pilot plant scale, based on CPC configuration capable to collect the direct and diffuse radiation [20]. The energetic and economic efficiencies of the different tested devices were evaluated and compared. The most important intermediates have been also proposed.

2. Materials and experimental set-ups

2.1. Chemicals and reagents

The solution of 50 mg/L of DPH ($C_{17}H_{21}NO \cdot HCl$, HPLC grade, purity $\geq 98\%$ from Sigma-Aldrich) was prepared using deionized water. This high concentration (50 mg/L) was selected to assure accurate measurements of concentrations and to follow TOC. Moreover, this concentration was chosen to represent the conditions of wastewater coming from some pharmaceutical industries [21]. Acetonitrile (analytical reagent grade from Fischer Chemical) and orthophosphoric acid (85% from Panreac Quimica) were used for HPLC analysis. H_2O_2 (30% w/w, from Merck), $NaHSO_3$ and MeOH (PAI from Panreac) reagents were used without further purification. Heterogeneous photocatalysis was performed using TiO_2 P-25 (Evonik, Germany).

2.2. Techniques and analytical instruments

DPH concentration was monitored by HPLC from Waters using a SEA18 Teknokroma column (250×4.6 mm i.d.; $5 \mu m$ particle size) and a Waters 996 photodiode array detector. The mobile phase was composed by water (pH 3) and acetonitrile (70:30), injected with a flow-rate of 0.85 mL/min. DPH concentration was followed at UV maximum absorbance (220 nm). TOC was analyzed with a Shimadzu TOC-V CNS analyzer. H_2O_2 consumption was followed using the metavanadate spectrophotometric method at 450 nm [22]. H_2O_2 contained in samples was quenched with sodium hydrogen sulfite or the same volume of methanol, to avoid further reactions depending on the analysis to be done. For the intermediates identification, samples were analyzed by the electrospray ionization/mass spectrometry using an electrospray (ion spray) ESI-MS and a LC/MSD-TOF (Agilent Technologies) mass spectrometer. With the purpose to evaluate the acute toxicity depending of the different conditions Microtox[®] bioassays were performed. This method measures the inhibition of light emission of bioluminescent bacteria *vibrio fischeri* caused by the presence of toxic compounds in the aqueous media. All the tests were carried out in a Microtox[®] M500 toxicity analyzer (Modern Water, UK). All samples were filtered with a polyethersulfone membrane filter (0.45 μm , Chemlab) to remove the catalyst before analytical procedures.

2.3. Experimental devices

All the experimental devices described below have already been used in other investigations of the group and extensively described in other publications [23–25].

2.3.1. Artificial irradiation: UVC reactor

The experiments with UVC lamps were performed in a thermostatic Pyrex-jacketed 2 L vessel (inner diameter 11 cm, height 23 cm), equipped with three low pressure mercury lamps (Phillips TUV 8W, G8T5) located at the center of reactor. Lamps emit monochromatic radiation (254 nm). The effective radiation power was measured by ferrioxalate actinometry [26] and the obtained value was 4.31 J/s at 254 nm. A solution of DPH (50 mg/L) was introduced in the reactor

with TiO_2 (0.4 g/L), and immediately the lamps were switched on. Next H_2O_2 (15, 75 or 150 mg/L) was added depending on the experiment to be carried out. Magnetic stirring was used to ensure a good mixing. The temperature of the solution was maintained constant at 25 °C with the recirculated water by the jacket connected to an ultra-thermostatic bath (P Selecta).

2.3.2. Artificial irradiation: black blue lamps (BLB) reactor

BLB reactor consists on a 2 L Pyrex-jacketed thermostatic vessel (inner diameter 11 cm, height 23 cm), equipped with three 8 W BLB lamps (Phillips TL 8W-08 FAM) located at the center of reactor. The radiative power was 1.55 J/s between 300 and 410 nm, measured by o-nitrobenzaldehyde actinometry [22]. The used actinometry changes according to the wavelength range of lamp emission. The tank was fed with DPH solution (50 mg/L) and TiO_2 (0.4 g/L). H_2O_2 (15, 75 or 150 mg/L) was added depending on the experiment to be carried out. The solution was maintained at constant temperature (25 °C) by controlling the jacket temperature with an ultra-thermostatic bath (P Selecta).

2.3.3. Artificial solar irradiation: Solarbox (SB)

A Solarbox (CO.FO.ME.GRA, 220V, 50 Hz) was used with a Xenon lamp (Phillips 1 kW), located at the top of the device. The effective radiation power was 0.97 J/s between 300 and 410 nm, measured also by o-nitrobenzaldehyde actinometry [22]. The tubular photoreactor (24 cm length, 2.11 cm diameter, Duran glass material) was placed at the bottom of the Solarbox on the axis of a parabolic mirror made of reflective aluminum. A filter cutting off wavelengths under 280 nm was placed between the lamp and the reactor. The DPH solution (50 mg/L) was prepared in a batch jacketed feeding tank (total volume 1L), connected to an ultra-thermostatic bath (Haake K10) to assure constant temperature during the process. H_2O_2 (15, 75 or 150 mg/L) and TiO_2 (0.05, 0.1, 0.4 g/L) were added depending on the experiment to be carried out. The solution to be treated was pumped to solarbox by a peristaltic pump (Ecoline VC-280 II, Ismatec) from the feeding tank with a flow-rate of 0.71 L/min. All connections employed were made of Teflon to avoid losses. A preliminary sample was collected before irradiation, representing initial concentration at time 0.

2.3.4. Solar irradiation: CPC reactor

Photocatalytic experiments were also carried out in a solar pilot plant based on compound parabolic collectors (CPC), at the University of Barcelona (latitude 41.4 N, longitude 2.1 W). The CPC consists in a module, 41° inclined, with a mirror made of polished aluminum, with 6 parallel tubular quartz reactors (length 56 cm, inner diameter 1.75 cm, wall thickness 0.15 cm). The total volume irradiated was 0.95 L. The total mirrors area for solar irradiation capture-reflection was 0.228 m². Experiments were done between 12:00 and 18:00 h in summer and temperature was 30 ± 5 °C. The exposure time was enough to reach the total hydrogen peroxide consumption. The aqueous suspension of DPH was pumped, with a peristaltic pump with a flow-rate 2.6 L/min, from the stirred (RW 16 basic agitator IKA) reservoir tank (5 L) to irradiated quartz tubes and continuously recirculated. The specific solar radiation was measured in each sample time ranging 12.45 W/m² to 49.78 W/m², by a spectroradiometer Bentham DMc300. The reservoir tank was fed with DPH solution (50 mg/L) and 0.4 g/L of TiO_2 , with or without H_2O_2 (0 or 150 mg/L).

3. Results and discussions

DPH degradation by photocatalysis was evaluated during one hour based on previous experiments performed, in each experimental device. Different concentrations of H_2O_2 (15, 75 and 150 mg/L) and TiO_2 (0.05, 0.1 and 0.4 g/L) were used depending on the experiment to be carried out. These TiO_2 and H_2O_2 concentrations can be broadly found in literature and they were also selected based on the previous

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