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Treatment of Diphenhydramine with different AOPs including photo-Fenton at circumneutral pH

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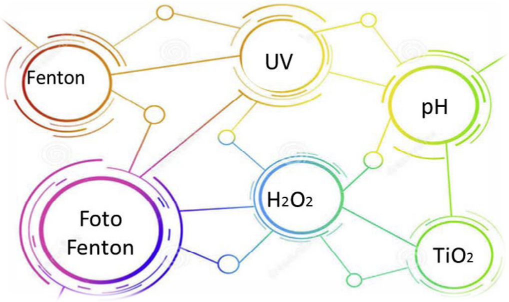
HIGHLIGHTS

- Diphenhydramine degradation by different AOPs is compared.
- Power and wavelengths of lamps are important in the contaminant degradation.
- Fenton and photo-Fenton can work at initial circumneutral pH.
- Black blue lamps gave the best results in diphenhydramine abatement.
- Acidification of the solution is avoided by the addition of Resorcinol.

GRAPHICAL ABSTRACT



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ABSTRACT

The degradation of diphenhydramine hydrochloride (DPH), via UV–vis/H_2O_2, Fenton, photo-Fenton and photocatalysis processes, was studied under different radiation sources. In addition, the Fenton and photo-Fenton processes at acid pH and circumneutral pH have been compared. The importance of the source of irradiation, UV-C ($\lambda = 254$ nm), black blue lamps (BLB, $\lambda = 365$ nm) and simulated solar radiation (SB, SolarBox), was investigated at lab-scale. Moreover, compound parabolic collectors (CPC), at pilot plant scale with sunlight, have been also applied in photocatalytic treatments. Photo-Fenton process employing black blue lamps gave the best DPH abatement (100% of DPH conversion at 10 min for acid pH and 20 min for circumneutral pH), using the highest Fe^{2+} (5 mg/L) and H_2O_2 (150 mg/L) concentrations at 50 mg/L of initial DPH concentration. Using Fenton, 100% of DPH conversion was reached at 30 min for both pHs tested. In the case of UV-C/H_2O_2, 100% of DPH elimination was achieved in 20 min using 150 mg/L of H_2O_2. In the photocatalytic process, using 0.4 g TiO_2/L, after 60 min of irradiation, only 35.7% and 8.7% of DPH conversion have been obtained in SB and CPC, respectively. The DPH degradation in the photocatalytic process was greatly enhanced adding H_2O_2. In all the cases, increasing the H_2O_2 dose enhances the reaction rate due to higher $OH^{\cdot}$ production. However, not significant mineralization was obtained. The highest DPH mineralization was 36.8% and 38.5% of TOC reduction with photo-Fenton in BLB lamps using 150 mg/L of H_2O_2 and 2.5 mg/L of Fe^{2+}, for acid pH and circumneutral pH, respectively. The major reaction intermediates these processes were identified by ionization/mass spectrometry and a DPH photo-degradation structures was proposed.

1. Introduction

Water is fundamental to survival on earth. In the last years, water scarcity and water quality have become a worldwide concern. Every day large amounts of water are contaminated by differ-

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ent pollutants coming from domestic or industrial uses. Although pollution of rivers by heavy metals and other compounds, strictly regulated by Dangerous Substances Directive (2006/11/EEC), is generally decreasing, organic substances with harmful properties such as pharmaceuticals and personal care products are increasingly detected in the environment [1]. Spain is ranked as one of the world's largest consumer of pharmaceuticals [2]. According to Miranda [3] these compounds are also recalcitrant and present properties of bioaccumulation in the environment. They are also resistant to conventional wastewater treatments and are found in effluents at concentrations ranging from 0.1–20.0 μg/L [3–5].

Among those pollutants, there is a special group of pharmaceuticals, antihistaminic drugs, found in water. Diphenhydramine hydrochloride is the classic H1 receptor antagonist that has been used in pregnancy for the treatment of allergies, nausea and vomiting as well as an analgesic adjuvant in cancer pain. DPH has relatively low molecular weight and high lipid solubility, allowing easy blood–brain barrier and placental passage [6]. Unfortunately, information on the environmental fate and toxicity to aquatic species is scarce for most pharmaceuticals [7]. The growing demand of society for the decontamination of water from various sources, materialized in regulations increasingly strict, has caused, in recent years, increasing research on methods to eliminate pharmaceuticals from wastewater, and this is the case of advanced oxidation processes (AOPs).

Advanced oxidation processes (AOPs) are environmental friendly methods based on in situ production of hydroxyl radical ($^{\cdot}OH$) as main oxidant. Hydroxyl radical is able to react non-selectively with most organic compounds [8].

The focus of this work is to evaluate the efficiency of UV–vis/H_2O_2, Fenton, photo-Fenton and photocatalysis in the degradation of Diphenhydramine under different radiation sources. Moreover, it has been studied the DPH conversion by Fenton and photo-Fenton at initial circumneutral pH. The acidification of the solution is avoided by the addition of resorcinol (RES, di-hydroxy benzene isomer) [9–11], which in addition is used to simulate organic matrix in water. RES addition also generates ferricarboxylates complexes and avoids the precipitation of Fe^{3+} hydroxy complexes at neutral pH. The efficiency of this process was also compared with the classical Fenton and photo-Fenton process at acid pH.

2. Chemicals and experimental set-ups

2.1. Chemicals and reagents

The solution of 50 mg/L of Diphenhydramine hydrochloride ($C_{17}H_{21}NO \cdot HCl$, HPLC grade, purity $\geqslant$98% from Sigma-Aldrich) was prepared using deionized water. This high concentration (50 ppm) was selected to assure accurate measurements of concentrations and to follow TOC levels. Moreover this quite high concentration value was chosen to represent the concentrations in wastewaters coming from pharmaceutical companies (10–100 mg/L) [12,13]. Acetonitrile (analytical reagent grade from Fischer Chemical) and orthophosporic acid (85% from Panreac Quimica) were used for HPLC analysis. H_2O_2 (30% w/w, from Merck), $FeSO_4.7H_2O$ (PA from Panreac), $NaHSO_3$ and MeOH (PAI from Panreac) reagents were used without further purification. Heterogeneous photocatalysis was performed using TiO_2 P-25 (EvoniK, Germany). Sulphuric acid (H_2SO_4, 96% purity from Panreac) was used for initial pH adjustment. Resorcinol (RES, CAS number 108-46-3) was purchased from Sigma-Aldrich.

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 μm 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. Reproducible TOC values, with an accuracy of ±1%, were obtained by injecting 50 μL samples into the analyzer. H_2O_2 consumption was followed using the metavanadate spectrophotometric method at 450 nm [14]. 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. All samples were filtered with a polyethersulfone membrane filter (0.45 μm, Chemlab) to remove the catalyst before analytical procedures except for iron measures. The iron (II) content was determined by o-phenontraleine standardized procedure (ISO 6332).

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.

2.3. Experimental devices

2.3.1. Artificial irradiation: UV-C reactor

The experiments with UVC lamps were performed in a thermostated Pyrex-jacketed 2 L vessel (inner diameter 11 cm, height 23 cm), equipped with three low pressure mercury lamps (Phillips TUV 8 W, G8T5) located at the center of reactor. Lamps emit monochromatic 254 nm radiation. The radiation inside the photoreactor was assessed by uranyl oxalate actinometry [15] and the obtained value was 8.01 J/s at 254 nm. A solution of DPH (50 mg/L) was introduced in the reactor and Fe^{2+} (2.5 or 5 mg/L), H_2O_2 (15, 75 or 150 mg/L), RES (50 mg/L) and TiO_2 (0.4 g/L) were added, depending on the AOPs studied, and immediately the lamps were switched on. Magnetic stirring was used to ensure sufficient mixing. The temperature of the solution was maintained constant at 25 °C by the jacket connected to an ultra-thermostat bath.

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 (Philips TL 8 W-08 FAM) located at the center of reactor. The lamps emit radiation between 350 and 400 nm, with a maximum at 365 nm. The radiation entering to the photoreactor was 1.97 J/s, measured by o-nitrobenzaldehyde actinometry [16]. This batch tank was fed with DPH solution (50 mg/L). Next Fe^{2+} (2.5 or 5 mg/L), H_2O_2 (15, 75 or 150 mg/L), RES (50 mg/L) and TiO_2 (0.4 g/L) were added depending on the advanced oxidation process. The solution was maintained at constant temperature of 25 °C; the jacket temperature of the stirred tank was controlled with an ultra-thermostat bath.

2.3.3. Artificial solar irradiation: Solarbox (SB)

A Solarbox (CO.FO.ME.GRA 220V 50 Hz) with a Xenon lamp (Phillips 1 kW), located at the top of the device was used. The irradiation entering the photoreactor was 3.59 J/s measured also by o-nitrobenzaldehyde actinometry [16]. 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). Next Fe^{2+} (2.5 or 5 mg/L), H_2O_2 (15, 75 or 150 mg/L), RES (50 mg/L) and TiO_2 (0.05, 0.1, 0.4 g/L) were added depending on the advanced oxidation process. The solution to be treated was pumped to solarbox by peristaltic pump (Ecoline VC-280 II, Ismatec) from a stirred double jacket reservoir batch tank