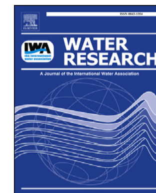
Water Research 88 (2016) 681–690

Contents lists available at ScienceDirect

Water Research

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



# Time-of-flight mass spectrometry assessment of fluconazole and climbazole UV and UV/$H_2O_2$ degradability: Kinetics study and transformation products elucidation

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A R T I C L E I N F O

*Article history:*
Received 16 July 2015
Received in revised form
22 October 2015
Accepted 27 October 2015
Available online 2 November 2015

*Keywords:*
Fluconazole
Climbazole
UV degradation
Transformation products
Liquid chromatography
Time-of-flight mass spectrometry

A B S T R A C T

The efficiency of UV irradiation for the removal of the antimycotic drugs fluconazole (FCZ) and climbazole (CBZ) from water samples is evaluated. Degradation experiments, at laboratory scale, were carried out with spiked aliquots of ultrapure water solutions and treated wastewater samples using low-pressure mercury lamps emitting at 254 nm. Time course of precursor pollutants and identification of arising transformation products (TPs) was performed by injection of different reaction time aliquots in a liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) system. Chemical structures of identified TPs were proposed from their full-product ion spectra, acquired using different collision energies. During UV irradiation experiments, the half-lives ($t_{1/2}$) of FCZ and CBZ were similar in ultrapure water solutions and wastewater samples; however, the first species was more recalcitrant than the second one. Four TPs were identified in case of FCZ resulting from substitution of fluorine atoms by hydroxyl moieties and intramolecular cyclization with fluorine removal. CBZ interacted with UV radiation through reductive dechlorination, hydroxylation and cleavage of the ether bond; moreover, five additional primary TPs, with the same empirical formula as CBZ, were also noticed. Given the relatively long $t_{1/2}$ of FCZ under direct photolysis (ca. 42 min), UV irradiation was combined with $H_2O_2$ addition to promote formation of reactive hydroxyl radicals. Under such conditions, the degradation rate of FCZ was enhanced significantly and no TPs were detected. These latter conditions allowed also the effective removal of CBZ TPs.

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## 1. Introduction

Antimycotics are a group of pharmaceuticals with increasing consumption rates. Azoles (triazoles and imidazoles) constitute the most important class of antimycotic drugs applied to the treatment of topic and systemic fungal infections. Wastewater, particularly domestic wastewater, is the main input of these pollutants in the aquatic media. After arrival at sewage treatment plants (STPs), antimycotic drugs are distributed between aqueous and solid (sludge) phases on the basis of their polarities, with poor removal efficiencies during primary and biological (activated sludge) treatments. Fluconazole (FCZ, CAS number 86386-73-4), with a log $K_{ow}$ 0.45, is one of the most polar antimycotic drugs. The active ingredient is mainly administrated through oral and intravenous routes and excreted as conjugated or unmodified drug. Mass balances performed at STPs point out to poor accumulation in sludge, with similar concentrations, or even slightly higher, in the outlet of the plants versus those found in raw wastewater reaching STPs (Lindberg et al., 2014; Casado et al., 2014). These data suggest a poor/null biodegradation and possible de-conjugation of the glucorinated form of FCZ, excreted in urine (Brammer et al., 1991), during biological treatments. Batch experiments, at laboratory scale, confirmed the null biodegradability of FCZ (Bergheim et al., 2014). In agreement with such behaviour, FCZ was detected in the 98% of 90 treated wastewater samples collected in different points of Europe with an average concentration of 108 ng $L^{-1}$ (Loos et al., 2013); moreover, it is present in surface water samples heavily impacted by the discharge of urban STPs (Qi et al., 2014) and groundwater affected by septic systems (Phillips et al., 2015).

The stability of FCZ during advanced oxidative treatments has

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http://dx.doi.org/10.1016/j.watres.2015.10.053
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also been studied; although, in most of the cases, the potential formation of transformation products (TPs) was not evaluated. As regards ozonization of treated wastewater, FCZ has been classified as a recalcitrant pollutant requiring large amounts of ozone ($O_3$/dissolved organic carbon ratios higher than 2) for 90% removal after 10 h of contact time (Antoniou et al., 2013). Addition of $H_2O_2$ (ratios up to 0.5 g per g of $O_3$) scarcely affected the removal efficiency of FCZ during ozonization (Lee et al., 2014). As regards UV degradation tests, controversial results have been reported. Chen and co-workers (Chen et al., 2014) have identified three TPs generated after exposure of FCZ ultrapure water solutions to low-pressure mercury lamps emitting at 254 nm. On the other hand, another study reported negligible removal of FCZ when exposed to UV light from mercury and xenon lamps for longer than 2 h (Bergheim et al., 2014).

Climbazole (CBZ, CAS number 38083-17-9) is an imidazole fungicide incorporated in the formulation of personal care products as anti-dandruff agent. Its structure is close to that of some agriculture fungicides, such as triadimefon with the difference that the triazolic ring of the former is replaced by an imidazole one in CBZ. Thus, it displays a similar ecotoxicity to other azolic phytochemicals and antimycotic pharmaceuticals towards aquatic organisms (Richter et al., 2013). Despite its high consumption rates, the environmental fate of CBZ has received less attention than that of other antimycotic pharmaceuticals. Recently, it has been found in treated wastewater (up to 600 ng $L^{-1}$) (Qi et al., 2015), surface water (Zhang et al., 2015) and also in sludge (Chen et al., 2013; Casado et al., 2015a). The presence of CBZ in liquid and solid phases at STPs can be explained considering a limited biodegradability and its medium polarity (log $K_{ow}$ 3.49). To the best of our knowledge, the behaviour of CBZ during oxidative treatments, susceptible to be implemented at STPs, remains unexplored.

The aim of this research was to assess the stability of FCZ and CBZ under direct-photolysis, using UV light from low-pressure mercury lamps, and indirect-photolysis in presence of $H_2O_2$. Under UV irradiation (wavelengths below 300 nm), $H_2O_2$ is known to be decomposed generating high reactive hydroxyl radicals (•OH). Experiments were carried out on model solutions of ultrapure water and real samples of wastewater, after biological treatment, spiked with individual solutions of the precursor pharmaceuticals. Liquid chromatography (LC) time-of-flight (TOF) mass spectrometry (MS) was applied to follow the time-course of both antimycotic drugs and to identify the potential formation of TPs under the investigated experimental conditions. The proposed structures for the detected TPs were based on their accurate full-product ion spectra. In some cases, gas chromatography mass spectrometry (GC-MS) was also used in order to obtain additional information about the structures of TPs, not detected by LC-QTOF-MS but suspected to be formed on the basis of proposed degradation routes. Degradation kinetics and transformation routes of both species were compared for the two tested matrices: ultrapure and wastewater.

## 2. Experimental

### 2.1. Standards, solvents, reagents and samples

FCZ (98%), CBZ (100%) and 4-chlorophenol (100%) were acquired from Sigma (Milwaukee, WI, USA). Individual stock solutions of the above compounds were prepared in methanol and stored at 4 °C. Further dilutions were made in the same solvent (FCZ and CBZ) and in ethyl acetate for 4-chlorophenol.

Methanol, HPLC-grade quality and ammonium acetate (99%) were provided by Merck (Darmstadt, Germany). Ethyl acetate for trace analysis was also purchased from Merck. Ultrapure water (pH 6) was obtained from a Milli-Q system provided by Millipore (Billerica, MA, USA). Hydrogen peroxide ($H_2O_2$, 30% v:v) and the silylation reagent *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide (MTBSTFA) were obtained from Sigma. The exact concentration of the stock solution of $H_2O_2$ was weekly checked by titration with potassium permanganate. Diluted solutions were prepared when needed in ultrapure water. Solid-phase extraction (SPE) cartridges OASIS HLB, 60 mg sorbent, were purchased from Waters.

Treated wastewater samples were collected at the outlet stream of an urban STP serving a population of 100,000 inhabitants and equipped with primary and biological (activated sludge) treatment units. After reception, wastewater samples were sequentially passed through glass fibre and cellulose (0.45 μm pore size) filters, allowed to equilibrate at room temperature (20 ± 2 °C) and used in degradation experiments. Filtered wastewater samples were characterized in terms of total carbon (TC) and organic carbon (TOC) contents. The obtained values ranged between 29 and 32 μg $mL^{-1}$ for TC, and 5.0–5.5 μg $mL^{-1}$ in case of TOC. The pH of wastewater samples varied between 7.1 and 7.3 units depending on the sampling date. The UV–vis spectrum for a representative sample of treated wastewater, acquired with a variable wavelength spectrometer furnished with 1-cm light path quartz cells, is provided as supplementary material, Fig. S1.

### 2.2. Degradation experiments

Degradation of FCZ and CBZ was investigated in ultrapure water model solutions and real wastewater samples spiked with individual solutions of each antimycotic drug at 500 and 200 ng $mL^{-1}$ levels, respectively. The addition of precursor pollutants to the samples was done directly in the quartz tubes (o.d. 30 mm, 200 mm length, Afora, Barcelona, Spain) employed in photodegradation experiments. To this end, an aliquot (0.05–0.1 mL) of the corresponding methanolic standard was poured in an empty tube and the organic solvent was evaporated with a gentle stream of nitrogen at room temperature. Thereafter, 10 mL of sample were added and the tube was soaked for 5 min to guarantee solubilisation of the precursor drug.

Photolysis experiments were performed using an in-house developed photoreactor equipped with a pair of 8 W low pressure mercury lamps (Philips reference G8T5) emitting at 254 nm. The photoreactor also incorporates a fan to dissipate the heat released by the lamps and an orifice, to introduce the quartz photoreaction vessel, situated between both lamps. The distance from the lamps to the quartz vessel, which remained uncovered during irradiation assays, was 3 cm. Lamps were equilibrated during 30 min before inserting the quartz vessel, with the spiked water sample, in the photoreactor. UV-exposed water aliquots (0.2 mL volume) were withdrawn at different times, with an automated micropipette without switching off the lamps, transferred to 0.4 mL inserts, within autosampler vessels, and stored at −20 °C for a maximum of 3 days before analysis. Zero-time aliquots were taken before introducing the spiked sample into the photoreactor. Dark control assays were performed wrapping the quartz vessel with aluminium foil.

The UV/$H_2O_2$ experiments were carried out with small changes in the aforedescribed procedure. In this case, the selected volume of $H_2O_2$ was added to the spiked water samples just before introducing the vessel into the photoreactor. UV-exposed water aliquots (0.2 mL) were withdrawn at different reaction times and transferred to glass inserts containing 0.02 mL of methanol to quench hydroxyl (•OH) radicals (Li, 2013). Zero-time experiments and dark controls, in presence of $H_2O_2$, were performed in the same way as for UV direct-photolysis assays.

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