Water Research 100 (2016) 413–420

Contents lists available at ScienceDirect

Water Research

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

Removal of carbamazepine in aqueous solutions through solar photolysis of free available chlorine

Bin Yang*, Rai S. Kookana, Mike Williams, Jun Du, Hai Doan, Anupama Kumar

CSIRO Land and Water, Waite Campus, PMB 2, Glen Osmond, South Australia 5064, Australia

ARTICLE INFO

Article history:
Received 16 February 2016
Received in revised form
12 May 2016
Accepted 14 May 2016
Available online 17 May 2016

Keywords:
Carbamazepine
Sunlight
Free available chlorine
Photolysis

ABSTRACT

Removal of a persistent antiepileptic drug carbamazepine (CBZ) in aqueous solutions was investigated by using solar photolysis combined with free available chlorine (FAC). The combination of chlorination with simulated or natural sunlight markedly enhanced removal of CBZ in 10 mM phosphate buffer solution (pH 7.0) and river water (pH 7.0) compared with sunlight or FAC alone. Further analysis indicated that the observed enhancements in CBZ removal can be attributed to the *in situ* hydroxyl radical (HO•) and ozone (O_3) production during FAC photolysis. During 70 min simulated sunlight photolysis combined with FAC treatment, HO• reaction contributed to 35.8% removal of CBZ and O_3 reaction contributed to 40.6% removal, while only 5.3% of CBZ was removed by HOCl reaction. The oxidation products of CBZ, epoxide CBZ, 10,11-dihydro-10,11-dihydroxy CBZ, 1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one (BQM), 1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione (BQD) and 4-aldehyde-9-acridone, were mainly formed from the HO• and O_3 attack at the double bond on the central heterocyclic ring of CBZ. Formation of these oxidation products did not cause any increase or decrease in toxicity to microbial species tested through Microbial Assay for Toxicity Risk Assessment (MARA). The initial FAC concentration and pH had a major influence on the removal process of CBZ during FAC photolysis, while temperature had a minor effect only. The combination of chlorination with natural sunlight could provide an effective approach for removal of CBZ and other contaminants during water treatment.

1. Introduction

Carbamazepine (CBZ), an antiepileptic drug, is a dibenzazepine derivative with an olefinic double bond on the central heterocyclic ring. CBZ is one of the most persistent pharmaceutical compounds in aquatic environment due to its resistance to biodegradation and photodegradation (Ternes et al., 2002; Tixier et al., 2003). CBZ is also found to be highly persistent during chlorination processes commonly employed in water treatment systems. Soufan et al. (2013) reported a half-life in the range of 52–69 days for CBZ chlorination with 1 mg L^{-1} free available chlorine (FAC) and 1–10 mg L^{-1} chloride solutions at pH 7. While ozone (O_3) has been reported to react rapidly with the double bond in CBZ, with a second order rate constant (k) of 3.0×10^5 M^{-1} s^{-1}; rates of hydroxyl radical (HO•) reactivity with CBZ is nearly that of a diffusion limited reaction ($k = 8.8 \times 10^9$ M^{-1} s^{-1}) (Huber et al., 2003). Photolysis of FAC by sunlight and/or artificial UV light can generate HO• and atomic oxygen ($O(^3P)$) – a precursor to O_3 *in situ* (Eqs (1)–(3)) (Klaning et al., 1984; Nowell and Hoigné, 1992). Therefore, solar-driven UV photolysis of FAC appears to be a promising tool for the removal of CBZ in water.

$$HOCl/OCl^- + h\nu \rightarrow HO^{\bullet}/O^{\bullet -} + Cl^{\bullet} \quad (1)$$

$$OCl^- + h\nu \rightarrow O(^3P) + Cl^- \quad (2)$$

$$O(^3P) + O_2 \rightarrow O_3 \; k = 4.0 \times 10^9 \; M^{-1} \; s^{-1} \quad (3)$$

The UV/chlorination process has been extensively investigated as an advanced oxidation process (AOP) for the removal of emerging organic contaminants (Watts and Linden, 2007; Jin et al., 2011; Sichel et al., 2011; Wang et al., 2012; Fang et al., 2014; Qin et al., 2014). However, only a limited degree of solar-driven UV photolysis of FAC has been studied so far. For example, Forsyth et al. (2013) indicated that solar photolysis of FAC dramatically enhances inactivation of *Bacillus subtilis* endospores compared to FAC or sunlight alone. The observed enhancements in spore inactivation

* Corresponding author.
E-mail addresses: Bin.Yang@csiro.au, ppyangbin@163.com (B. Yang).

http://dx.doi.org/10.1016/j.watres.2016.05.048
0043-1354/

can be attributed to the concomitant attack of spores by HO• and O_3. Similar enhancement effect on inactivation of *Cryptosporidium parvum* oocysts was also observed by Zhou et al. (2014) during solar photolysis of FAC. Photodegradation of methylene blue and cyclohexanoic acid has been reported by Chan et al. (2012) by using a solar-driven UV/chlorine process. The solar/chlorine process can also effectively remove naphthenic acids and fluorophore organic compounds in oil sands process-affected water (Shu et al., 2014).

The feasibility of UV/chlorine for CBZ removal in water and wastewater was examined by Sichel et al. (2011) at a technical scale. However, complete mineralization of CBZ is not always achievable and the ecotoxicity of its transformation products can be a potential concern (Donner et al., 2013). The objectives of the present study were (i) to assess the potential of removal of CBZ in aqueous solutions through simulated and natural sunlight photolysis of FAC and (ii) to investigate the role of reactive oxygen species (ROS) by analysis of HO• and O_3 in irradiated FAC solutions. A high-resolution accurate-mass Orbitrap mass analyzer and a tandem mass spectrometer were used to tentatively identify the reaction products of CBZ during simulated sunlight photolysis of FAC. Changes in toxicity of CBZ solutions during FAC photolysis was also examined using the Microbial Assay for Toxicity Risk Assessment (MARA) bioassay based on a range of microbial strains.

2. Experimental section

2.1. Chemicals and materials

Chemical standards carbamazepine (CBZ, 99%), *para*-chlorobenzoic acid (*p*CBA, 99%), *tert*-butanol (*t*BuOH, 99.5%), *trans*-cinnamic acid (97%), benzaldehyde (99%), *p*-nitroanisole (97%), pyridine (99.8%) and *N*,*N*-Diethyl-*p*-Phenylenediamine (DPD, 97%) were purchased from Sigma-Aldrich (Sydney, Australia). Sodium hypochlorite solution (NaOCl, 12.5% w/v) was purchased from Ajax Finechem. Buffer chemicals and all other reagents used in the experiments were of analytical grade. All reaction solutions were prepared with Milli-Q water (≥18.2 MΩ cm) from a Millipore Water Purification System. A stock solution of free available chlorine (FAC, 6.0–10.0 mM) was freshly prepared by dilution of NaOCl solution in Milli-Q water and then characterized spectrophotometrically at 292 nm ($\varepsilon = 350\ M^{-1}\ cm^{-1}$) (Johnson and Margerum, 1991). A stock solution of CBZ was prepared in Milli-Q water assisted by 50% (v/v) acetonitrile at the concentration of 500 mg L^{-1}. In most cases, the percentage of acetonitrile present in reaction solutions was less than 0.5% (v/v).

Surface water used in the experiments was sampled from the upper Yarra River in east-central Victoria, Australia. The initial pH, UV_{254}, UV_{400}, dissolved organic carbon (DOC), conductivity and alkalinity of the river water sample were 7.01, 0.075 Absorbance Units, 0.010 Absorbance Units, 2.9 mg L^{-1}, 75.3 μS cm^{-1} and 0.28 mM (HCO_3^-), respectively. The river water sample was filtered with a 0.45 μm Millipore Millex-HV Hydrophilic PVDF Syringe Filter within 24 h and stored at 4 °C until used. The low concentration of CBZ ($<4.2 \times 10^{-6}$ μM) in surface water did not interfere with the experiments because of the high spiked concentrations for CBZ (20 μM).

2.2. Simulated and natural sunlight irradiation experiments

The removal of CBZ was conducted in borosilicate glass tubes sealed with polytetrafluoroethylene (PTFE) lined lids, using 10 mM phosphate/0.1 M sodium hydroxide buffer solution (pH 6.0–9.5) and Yarra River water sample (pH 7.0). Treatment was undertaken according to the following approaches: (1) exposure to FAC alone ("FAC only"), (2) exposure to simulated or natural sunlight alone ("Light only"), (3) exposure to simulated or natural sunlight in the presence of FAC ("Light/FAC"), and (4) exposure to simulated sunlight in the presence of (a) FAC with 50 mM *t*BuOH ("Light/FAC + *t*BuOH") or (b) FAC without oxygen ("Light/FAC-O_2"). A detailed description of the above experimental set up is given below.

Simulated sunlight experiments: In a series of 25 mL volumetric flasks, CBZ was firstly spiked into the reaction solution to yield 20 μM, then the standardized stock solution of FAC was added to yield a selected concentration (0 μM, 200 μM, 300 μM, 400 μM, 500 μM and 600 μM). The mixed solutions (25 mL) were transferred into borosilicate glass tubes sealed with PTFE lined lids for the following irradiation.

In "FAC only" experiments (Experimental set (1)), glass tubes were covered with aluminum foil to exclude ambient light and placed at room temperature (25 ± 1 °C). For irradiation experiments (Experimental sets (2), (3) and (4)), glass tubes were located in a temperature-controlled ultrapure water bath (15–25 °C) adjusted by a CFT-75 refrigerated recirculator and irradiated with simulated sunlight generated by an Atlas Suntest XLS + solar simulator system (Atlas Material Testing Technology, USA) at an irradiance of 500 W m^{-2} to approximate average annual conditions in temperate zones (Gros et al., 2015). The UV photon fluence rate in the range of 300–400 nm for solar simulator system was determined by means of *p*-nitroanisole/pyridine actinometry according to the method described in Bahnmüller et al. (2014) (Text S1 and Fig. S1, Supplementary Information). Spectral irradiance measurement was obtained using a Black CXR-CR-50 spectroradiometer (StellarNet Inc, USA) equipped with a F400-UV-VIS-SR optical fiber and a CR2-AP cosine corrector.

In order to examine the importance of reactive oxygen species (ROS) such as hydroxyl radical (HO•) and ozone (O_3) in enhancing CBZ removal efficiency, CBZ spiked reaction solutions were amended with 50-mM *t*BuOH in Experimental set (4)-(a) or purged of O_2 by means of N_2-sparging in Experimental set (4)-(b) before adding FAC stock solutions.

At certain time intervals, 1 mL of the reaction solution was sampled for the measurement of residual FAC concentrations using a DPD colorimetry at 510 nm, and 1 mL of the reaction solution was also sampled and quenched with a thiosulfate solution (50 mM, 0.1 mL) to measure residual concentrations of CBZ by HPLC. In Experimental set (4)-(b), eight replicated glass tubes were operated in parallel at the same treatment conditions. At each of four sample times, two of the eight tubes were sacrificed in order to obtain measurements of CBZ and residual FAC without disturbing oxygen levels in the remaining tubes. Temperature within the solar simulator system was assessed during the irradiation experiment using a HOBO Pendant® temperature data logger (Onset, USA). All experiments were performed in duplicate.

Additionally, a higher concentration of CBZ (100 μM) and FAC (1500 μM) were also used for Experimental set (3) to identify the reaction products by liquid chromatography–mass spectrometry analysis and evaluate the changes of toxicity using Microbial Assay for Toxicity Risk Assessment (MARA) bioassay (Wadhia et al., 2007), described in a latter section.

Natural sunlight experiments: Natural sunlight experiments were performed at ground level at the Waite Campus (Urrbrae, South Australia) under clear skies on October 15, 2015 and December 09, 2015. Glass tubes were irradiated at ambient temperature under conditions representative of solar water disinfection (SODIS) applications (McGuigan et al., 2012) without thermostating, consistent with other similar studies on natural sunlight experiments (Forsyth et al., 2013; Zhou et al., 2014). In river water experiments, FAC was redosed to 400 μM for Light/FAC treatment after 50 min of irradiation in order to permit continuation of experiments after