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Radiolysis of carbamazepine aqueous solution using electron beam irradiation combining with hydrogen peroxide: Efficiency and mechanism

Ning Liu [a,1], Zhen-Dong Lei [b,1], Tao Wang [a], Jia-Jun Wang [c], Xiao-Dong Zhang [a], Gang Xu [c], Liang Tang [c,*]

[a] School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai 200093, PR China
[b] Department of Physics, Tsinghua University, Beijing 100084, PR China
[c] School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, PR China

HIGHLIGHTS

- Radiolytic degradation of CBZ with and without H_2O_2 was both studied.
- A removal efficiency of 100% of 75 mg L^{-1} CBZ could be observed within 20 kGy absorbed dose with the absence of H_2O_2.
- A proper H_2O_2 additive could promote the degradation efficiency and mineralization level of CBZ.
- The transformation products were different between the two solution systems.
- Possible transformation pathways of CBZ under irradiation coupling with H_2O_2 were proposed.

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ABSTRACT

Herein, ionizing radiolytic treatment for CBZ in the absence of and in the presence of H_2O_2 was both studied. Although use of electron beam irradiation alone could efficiently decompose CBZ, combination with H_2O_2 could further promote degradation efficiency and mineralization level of CBZ. In the present study, the best degradation efficiency of CBZ was obtained in solution with 10 mM H_2O_2, where the dose constant was 2.63 kGy^{-1}; while the highest mineralization level (41% TOC removal) was achieved in solution with 50 mM H_2O_2. Five carboxylic acids and twelve organic transformation products (TPs) were identified and determined during the irradiation processes. On the basis of the tendency of TPs, possible transformation mechanisms of CBZ with the combinative processes of electron beam and H_2O_2 were proposed. It was found some mutagenic and carcinogenic transformation compounds, such as acridine (ACIN) could be promptly decomposed in the presence of H_2O_2.

1. Introduction

Carbamazepine (CBZ) is a first generation anticonvulsant drug widely used in the clinical treatment for epilepsy, trigeminal neuralgia and some psychiatric diseases [1,2]. CBZ is discharged from private households and from hospitals and eventually reaches municipal wastewater treatment plants [3]. Due to its stable chemical structure, CBZ is resistant to both conventional and advanced wastewater treatment processes, and consequently, it is one of the most persistent pharmaceuticals of concern in water bodies that received wastewater effluents [4]. Thus, many studies have found it is ubiquitous in various environment matrices, such as surface waters [5–7], ground waters [8,9], wastewaters[10,11] and sediments [12]. It is also detectable in drinking water with the concentration level of ng L^{-1} concentrations [13,14].

Apart from being stable in the environment, there are other health risk concerns about CBZ in effluents make this pharmaceutical become a topic of concern. Researches are starting to show a probability of CBZ to be accumulated into plants irrigated with wastewater effluents [15] and bio-accumulated in aquatic organisms. Moreover, CBZ can affect the growth and morphology of human embryonic cells with the mixture of other active pharmaceuticals at environmentally relevant concentrations [16]. Despite proven antiepileptic properties, CBZ has been observed to have teratogenic effects clinically [17] and it is known to aggravate seizures in some patients, particularly children [18]. In addition, CBZ, as a

* Corresponding author. Tel.: +86 21 66137508.
E-mail address: tang1liang@shu.edu.cn (L. Tang).
[1] These authors contributed equally to this work.

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psychoactive drug, has the side effect of antidepressants which can potentially inhibit predator avoidance in fish [19].

Different advanced oxidation processes (AOPs) have been evaluated to remove CBZ from wastewaters [20]. AOPs are introduced as the most adequate treatment technologies that carry mineralization of the target pollutants or in other way the target pollutants are converted into simple biodegradation and harmless products [21,22]. Among the various AOPs, ionizing irradiation technique is quite efficient since oxidizing (·OH) as well as reducing reactive species (e^-_{aq}) are generated simultaneously (Eq. (1)) [23]. The numbers in small bracket are radiation chemical yield (*G*-value) of each species in μmol J^{-1} absorbed energy. Moreover, it can give promising results to accomplish favorable goals in the removal of hazardous wastes [24–26].

$$H_2O \rightarrow (0.28)^{\cdot}OH + (0.27)e^-_{aq} + (0.06)^{\cdot}H + (0.05)H_2 + (0.07)H_2O_2 + (0.27)H^+ \quad (1)$$

Hydrogen peroxide (H_2O_2), is also known as an efficient oxidation agent, has proven to be effective for the degradation of various aqueous pollutants mainly based on the hydroxyl radicals (·OH). The hybrid processes combining electron beam irradiation with H_2O_2 may make some advantages of synergistic effects, as well as some impacts of interfering agents and chemical structures on treating with CBZ. The coupling utilization of H_2O_2 and ionizing irradiation showed obvious synergetic effect that can promote the degradation of refractory pollutant [27], and it was proposed to be an efficient and viable solution to the treatment of CBZ.

This study is novel and of merits, since it explores the mineralization reaction implications of CBZ under a rapidly and active oxidation condition, ionizing irradiation simultaneously activated by H_2O_2. Worth to say, in the previous work of our study [28], the characteristics of CBZ in pure-water with different ions and that in surface water were studied by electron beam irradiation. However, the effect of H_2O_2 and the mineralization of CBZ were not mentioned in the previous study. The determination of the intermediate products and the discussion of mechanism still need further and detailed investigation. Therefore, the aims of this study were to: (1) investigate the electron beam irradiated degradation kinetics of CBZ with H_2O_2; (2) study the synergetic effect of irradiation combining with H_2O_2 and mineralization of CBZ in aqueous solutions; (3) determine the CBZ transformation products (TPs), organic acids and ions generated during the radiolysis processes; (4) propose the main degradation pathway of the removal of CBZ over the actively oxidative schemes.

2. Materials and methods

2.1. Materials

CBZ (>98%, purity) and HPLC grade methanol were obtained from Sigma–Aldrich. Short-chain carboxylic acids including formic acid (HCOOH), acetic acid (CH_3COOH), oxalic acid ($H_2C_2O_4$), malonic acid, fumaric acid, succinic acid, as well as sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$) and 30% hydrogen peroxide (H_2O_2) were purchased from Shanghai Chemical Reagent Co. Ltd. The HPLC-grade water used during the analysis and solutions preparation was obtained from filtering through a Milli-Q-Plus ultra-pure water system (resistance >18.2 MΩ cm) from Milipore (Sartorius 611, Germany). All chemicals and reagents were of analytical grade unless otherwise stated.

2.2. Electron beam irradiation treatment procedure

The samples were irradiated at ambient temperatures by 1.8 MeV and variable current (0–10 mA) electron beam from GJ-2-II electron accelerator (Shanghai Xianfeng electrical plant, China). The samples were pouched in sealed high density polyethylene (HDPE) plastic bags and placed in radiation field about 30 cm away from the radiation source. The thickness of the irradiated sample layer in plastic bags was 2–3 mm. The experiments were carried out at absorbed doses of 0.5, 1, 2, 5, 10, 15 and 20 kGy, and the dose rate was kept 0.045 kGy s^{-1}.

The reliability of HDPE under electron beam irradiation was checked at the beginning of this study: the bags containing pure-water were irradiated with various irradiation doses (from 0.5 to 20 kGy); however, there was no compounds leaked from HDPE into the water with the detection of IC and LC–MS/MS. It was proven that HDPE was suitable for this study. All the concentrations of CBZ aqueous solutions were 75 mg L^{-1}. All the irradiation treatments were done at room temperature and all the samples of radiation of CBZ were carried out in deaerated solution.

2.3. Analytical methods

The analytical methods used are detailed in previous works [28,29]. A high performance liquid chromatography (HPLC, Agilent 1200 series) consisted of C18 column (150 mm × 4.6 mm) and an auto-sampler with 10 μL volume injection. It was used to monitor the change of CBZ concentration at 230 nm by a VWD detector. The mobile phase was a mixture of methanol and water (55:45, v:v) at rate of 1.0 mL min^{-1}.

Small-molecular organic acids formed during the radiolysis processes were detected by ion chromatography (Dionex, ICS1100). A hydrophilic anion exchange column was IonPac AS22 (analytical, 4 mm × 250 mm). The eluent was mixed with 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ at 1.20 mL min^{-1} flow rate and the injection volume was 25 μL. The suppressor was Anion Self-Regenerating Suppressor (ASRS 300 4 mm) under Auto-Suppression Recycle Mode and its applied Current was 31 mA. A hydrophilic cation exchange column was IonPac CS12A (analytical, 4 mm × 250 mm). The eluent was methanesulfonic acid 20 mM, at 1 mL min^{-1} flow and the injection volume was 25 μL. The suppressor was Cation Self-Regenerating Suppressor (CSRS ULTRA II, 4 mm) under Auto-Suppression Recycle Mode and its applied Current was 59 mA.

A high performance LC-MS/MS (6460 Triple Quad LC-MS/MS, Agilent) were employed to identify the by-products generated from decomposition of CBZ, which consists of an Agilent 1260 LC chromatograph coupled to an Agilent 6460 mass spectrometer with an electronspray ionization (ESI) interface and a heated nebulizer. A Porshell 120, 100 × 3 mm EC-C18 end-capped column (2.7 μm particle size) was used, at the flow rate of 0.4 mL min^{-1}. The injection volume was 10 μL. The mobile phase was a mixture of acetonitrile (A) and 0.1% formic acid in water (B); the gradient was operated from 5% to 95% A for 8 min, from 95% to 100% A for 2 min, held at 100% for 2 min, and back to the initial conditions in 3.5 min. Mass spectrometry full scanning analysis was performed in the range of 50–500 *m/z*. The positive electronspray ionization (ESI (+)) operating conditions of the source were as follows: capillary voltage, 4000 V; nebulizer pressure, 40 psi; drying gas flow, 8 mL min^{-1} at a temperature of 300 °C; nozzle voltage, 0 V.

Herein, total organic carbon (TOC) was also determined to explore the mineralization level of CBZ during the radiolysis processes. TOC was systematically monitored using a TOC-VCPN analyzer (Shimadzu, Japan) with the combustion-infrared method. Organic carbon compounds were combusted and converted to CO_2, which was detected and measured by a non-dispersive infrared detector (NDIR). Reproducible TOC values were always obtained using the standard NPOC (Non Purgeable Organic Carbon) method. For each sample, each measurement was triplicated.