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Degradation mechanisms of carbamazepine by δ-MnO_2: Role of protonation of degradation intermediates

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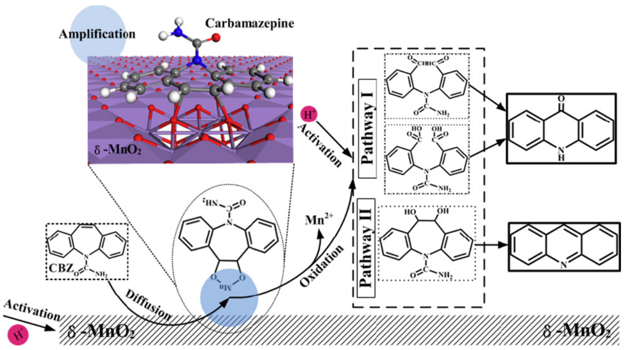
HIGHLIGHTS

- The degradation pathways of CBZ by δ-MnO_2 are clarified.
- The protonation of degradation intermediates is found to play an important role.
- CBZ degradation kinetics is via a diffusion and subsequent rapid reaction model.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbamazepine (CBZ), a widely used antiepileptic drug, is refractory to biological wastewater treatment. Rapid removal of CBZ is possible using synthetic manganese oxide (δ-MnO_2) but the removal mechanisms require further investigation. In this study, CBZ degradation by δ-MnO_2 was carried out at different pH to further explore the degradation mechanisms. Results show that CBZ degradation by δ-MnO_2 was highly pH dependent, and rapid degradation occurred when pH <2.8. Based on the density functional theory calculations, increasing $[H^+]$ not only increased the reactivity of δ-MnO_2, but also enhanced the secondary reactions of the intermediates. During the degradation process, protonation of CBZ degradation intermediates, instead of CBZ, played an important role. The overall kinetics of CBZ degradation was then described by the retarded first-order model. The initial rate (r_{init}) in the model between pH 2.0 and 6.2 was determined to be $r_{init} = (2.41 \pm 0.51) \times 10^{-3}[CBZ]^{1.21}[MnO_2]^{1.07}[H^+]^{1.41}$. This is the first report revealing that protonation of intermediates from CBZ degradation can improve the CBZ oxidation by δ-MnO2. The pathways of CBZ degradation by δ-MnO_2 were also proposed. The results of this study provide a new insight into the processing mechanism.

1. Introduction

The widespread occurrence of pharmaceuticals in municipal wastewater and in the effluents of wastewater treatment plants (WWTPs) has attracted increasing attention. Among the various pharmaceuticals,

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carbamazepine (CBZ) is frequently detected because it is resistant to conventional biological wastewater treatment technologies (Wang et al., 2018). Long-term CBZ exposure is a threat to public health and aquatic ecosystems, and has a high potential to cause eco-toxic effects, since up to 6.3 μg/L and 258 μg/kg CBZ have been reported in WWTP effluents and biosolids, respectively (Tarpani and Azapagic, 2018; Wang et al., 2018).

Advanced oxidation processes (AOPs) can efficiently remove, even mineralize CBZ, including photocatalytic oxidation (Xu et al., 2013), ozonation (Y. Ye et al., 2018), Fenton or Fenton-like oxidation (Sun et al., 2013), solar photolysis of free available chlorine (Yang et al., 2016), and UV/H_2O_2 (Alharbi et al., 2017). However, these technologies usually require high operational cost and high energy input. The synthesis of well-designed photocatalysts or the addition of strong oxidizing agents to treat a large volume of contaminated water with trace amount of CBZ is expensive. Therefore, it is critical to develop cost-effective technologies for CBZ removal.

Delta-manganese dioxide (δ-MnO_2) exists ubiquitously in the natural environment, mainly in the form of birnessite and vernadite. As an important oxidant (standard redox potential of 1.23 V), δ-MnO_2 is able to oxidize a variety of organic pollutants, including CBZ (Remucal and Ginder-Vogel, 2014; Liu et al., 2016). A previous study showed that 5 mg/L CBZ can be rapidly eliminated within 60 min in the presence of 130 mg/L δ-MnO_2, suggesting that δ-MnO_2 might be a promising alternative for CBZ removal (He et al., 2012). However, studies on the oxidation reactions between CBZ and δ-MnO_2 are insufficient and more attentions are required on the CBZ reaction intermediates. It was reported that the teratogenic effects associated with CBZ exposure might be related to its metabolites rather than the parent compound (Li, 2014). Identification of the reaction intermediates and reaction pathway is important to avoid secondary pollution. In addition, the reaction mechanisms at low pH require further investigation. Factors such as improving the adsorption of organic compounds onto the surface of MnO_2, increasing the redox potential of MnO_2, and better electron transfer efficiency (Remucal and Ginder-Vogel, 2014) are the traditional theory attributed to increasing the oxidation rate of organic contaminants at lower pH. However, it fails to explain the role of H^+ in the reaction between MnO_2 and CBZ. Results from previous studies show that the secondary reaction orders with respect to $[H^+]$ depends on the organic contaminates types.

In this study, the reaction mechanisms involved in the degradation of CBZ by δ-MnO_2 are systematically investigated by studying the reaction at different pH. The intermediates and the final product of CBZ oxidation are characterized by a high performance liquid chromatography coupled with a triple quadrupole tandem mass spectrometer (HPLC-MS/MS) analysis. Thereafter, the CBZ degradation pathway is proposed and confirmed by the density functional theory (DFT) calculations. Based on the degradation pathway and removal mechanisms, a new kinetic model is proposed to better describe the CBZ oxidation by δ-MnO_2, especially for the effects of pH.

2. Materials and methods

2.1. Chemicals and δ-MnO_2 preparation

CBZ with a reported purity >99.5% was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Acetonitrile, methanol, and acetic acid (all HPLC-grade) were obtained from Aladdin (Shanghai, China). A CBZ stock solution (200 mg/L) was prepared by 20% methanol solution and stored in a 4 °C fridge in the dark prior to use. Ultrapure water (18.2 MΩ resistivity) was used throughout the experiments unless otherwise noted.

Manganese oxide (δ-MnO_2) was synthesized based on Murray's method (Murray, 1974). The detailed description can be found in Text S1.1. X-ray diffraction (XRD) analysis (Fig. S1) indicated that the as-synthesized δ-MnO_2 was poorly crystallized, similar to vernadite, a mineral in the birnessite family (Gao et al., 2012; Lafferty et al., 2010). The morphology of the as-synthesized δ-MnO_2 was characterized by scanning electron microscopy (SEM). SEM images (Fig. S2) showed that the particles exhibited an amorphous morphology, which was in accordance with the XRD results. In addition, the synthesized δ-MnO_2 aggregates comprised primary small particles (Fig. S2). The specific surface area of the synthesized δ-MnO_2 was determined to be 309.6 ± 0.5 m^2/g by N_2 adsorption using the Brunauer-Emmett-Teller (BET) method on a Micrometrics ASAP 2020 M+C multigas volumetric adsorption analyzer. The point of zero charge (pH_{zpc}) of the δ-MnO_2 was analyzed and it was approximately 2.4 (Fig. S3). Back titration of δ-MnO_2 with sodium oxalate and potassium permanganate (Wang and Cheng, 2015) revealed that the average oxidation state of Mn in the synthesized δ-MnO_2 was +3.75, which agree well with previous studies (Wang and Cheng, 2015).

2.2. CBZ degradation

Experiments were conducted in 250-mL Erlenmeyer flasks wrapped in aluminum foil to prevent photodegradation under ambient O_2 conditions in a shaker (ZHWY-200H), the reaction temperature and rotating speed was set as 30 °C and 240 rpm, respectively. Preliminary experiments indicated that oxygen exposure had no noticeable impact on CBZ transformation by δ-MnO_2 (Fig. S4). The stock δ-MnO_2 suspension was diluted to desired concentrations for the CBZ degradation experiments by adding ultrapure water and then was adjusted to the desired pH using 0.1 M HCl or NaOH solution. The constant ionic strength (10 mM) of the reaction solution was maintained by adding the appropriate amount of NaCl. The diluted δ-MnO_2 suspensions were mixed in a shaker at 480 rpm for approximately 24 h as a pretreatment. Degradation experiments were initiated through adding 1 mL of 200 mg/L CBZ into the pre-equilibrated δ-MnO_2 suspensions with total volumes of 200 mL. Aliquots (~10 mL) were collected at certain time points after adding CBZ, and the reaction in the collected samples was quenched by syringe filtering through 0.22 μm nylon filters and adding 25 μL of 0.1 M ascorbic acid for determining the dissolved CBZ concentration ($[CBZ]_d$) and total CBZ concentration ($[CBZ]_t$, i.e., sum of the adsorbed and dissolved CBZ concentrations). Separate experiments, which have the same procedure with above experiments were conducted to determine the apparent reaction orders of CBZ degradation by δ-MnO_2 with respect to pH, CBZ, and δ-MnO_2. All experiments were performed in triplicate, and the control experiments without either δ-MnO_2 or CBZ were performed in parallel with the CBZ degradation experiments.

2.3. Chemical analysis and degradation products identification

CBZ concentrations were analyzed on an Agilent 1260 HPLC system (Agilent Technologies, USA) coupled with a Zorbax Eclipse XDB-C18 column (2.1 × 100 mm, 3.5 μm, Agilent) and a diode array UV–Vis detector (for more details, see Text S1.2).

To facilitate the identification of the CBZ degradation products, the CBZ degradation experiment was performed with higher initial reactants concentrations (10 mg/L CBZ and 500 mg/L δ-MnO_2 at pH 2.6), and the reaction was quenched after 30, 60, and 120 min by adding ascorbic acid. After quenching, an appropriate number of solution samples were transferred to 2-mL HPLC vials and analyzed on an Agilent 1290/6420MSD HPLC-MS/MS system (for more details, see Text S1.3).

2.4. DFT calculation

The possible structures of CBZ degradation intermediates/products and the proposed degradation pathway were analyzed by DFT calculations using Gaussian09 software (Frisch et al., 2003). The polarizable continuum model (PCM) was used to determine the solvent effects (Thellamurege et al., 2014). All the geometries are fully relaxed by the Becke three-parameter exchange functional and the Lee-Yang-Parr