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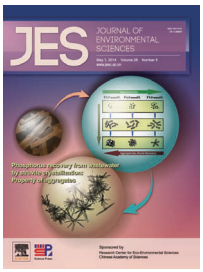

Characterization and reactivity of biogenic manganese oxides for ciprofloxacin oxidation

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ABSTRACT

Biogenic manganese oxides ($BioMnO_x$) were synthesized by the oxidation of Mn(II) with Mn-oxidizing bacteria *Pseudomonas* sp. G7 under different initial pH values and Mn(II) dosages, and were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, and UV-Vis absorption spectroscopy. The crystal structure and Mn oxidation states of $BioMnO_x$ depended on the initial pH and Mn(II) dosages of the medium. The superoxide radical ($O_2^{\bullet-}$) was observed in Mn-containing (III/IV) $BioMnO_x$ suspensions by electron spin resonance measurements. $BioMnO_x$(0.4)-7, with mixed valence of Mn(II/III/IV) and the strongest $O_2^{\bullet-}$ signals, was prepared in the initial pH 7 and Mn(II) dosage of 0.4 mmol/L condition, and exhibited the highest activity for ciprofloxacin degradation and no Mn(II) release. During the degradation of ciprofloxacin, the oxidation of the Mn(II) formed came from biotic and abiotic reactions in $BioMnO_x$ suspensions on the basis of the Mn(II) release and $O_2^{\bullet-}$ formation from different $BioMnO_x$. The degradation process of ciprofloxacin was shown to involve the cleavage of the hexatomic ring having a secondary amine and carbon-carbon double bond connected to a carboxyl group, producing several compounds containing amine groups as well as small organic acids.

Introduction

Pharmaceutical compounds, widely used for various purposes in human and veterinary medicine, have recently been considered as an emerging environmental issue due to their detection in sediments as well as sewage, surface water, groundwater, and drinking water (EI-Shafey et al., 2012; Pereira et al., 2007; Putschew et al., 2001). Ciprofloxacin (CIP; **Fig. 1**), for example, a broad-spectrum fluoroquinolone antibiotic, has been detected at concentrations up to 31 mg/L in wastewater treatment plant (WWTP) effluents originating from the treating of wastewaters of pharmaceutical manufacturers (Larsson et al., 2007). Owing to its resistance to microbiological degradation, conventional WWTPs are not able to eliminate CIP residues efficiently. Thus, physical/chemical technologies are necessary for their degradation prior to discharge into the environment. Advanced oxidation processes, such as ozonation (Huber et al., 2003), sonification (De Bel et al., 2009), and heterogeneous photocatalysis (EI-Kemary et al., 2010), have appeared during the last decade as a viable strategy to remove residual pharmaceuticals in water and wastewaters. Yet, the search for low-cost effective treatment is still needed. Moreover, an increase in mutagenicity and other toxic effects can be expected after ozonation (Forrez et al., 2010).

Manganese oxides (MnO_2), ubiquitously found in soils and sediments, have been broadly studied as the most important naturally occurring oxidants in promoting the transformation of a wide array of complex organic pollutants, including substituted phenols (Stone, 1987), atrazine (Shin and Cheney, 2004), 17α-ethynylestradiol (de Rudder et al., 2004), bisphenol A (Lin et al., 2009), and

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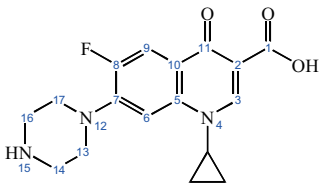

Fig. 1 Structure of ciprofloxacin.

various kinds of antibacterial agents (Zhang and Huang, 2005). Recently, biogenic manganese oxides ($BioMnO_x$) have exhibited higher catalytic reactivity than chemically produced MnO_2 due to their specific characteristics (Forrez et al., 2010). A number of studies have been pursued to clarify the structure of $BioMnO_x$ in recent years. For instance, studies combining X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) have shown that the structures of $BioMnO_x$ formed by diverse bacterial strains, such as the spore-forming marine *Bacillus* sp. strain SG-1 and *Pseudomonas putida* strain MnB1 bacteria, were analogous mixed-valent layered $Mn(III/IV)O_x$ compounds (Bargar et al., 2005; Hocking et al., 2011; Villalobos et al., 2003). In addition, Jürgensen et al. (2004) reported that the structure of $BioMnO_x$ produced by the freshwater bacterium *Leptothrix discophora* SP-6 (SP6-MnO_x) possessed single octahedral-layer microcrystals similarly to Na-birnessite, whereas SP6-MnO_x studied by Kim and Stair (2004) via UV Raman spectroscopy closely resembled the 3 × 3-tunnel todorokite structure. In addition, it has been found that the Mn oxide structure and oxidation state sensitively depended on pH, hydration state, and solution composition, which determined the physicochemical properties and reactivity of $BioMnO_x$ materials (Bargar et al., 2005). Therefore, to obtain higher reactivity $BioMnO_x$ materials, probing the Mn oxide structure and oxidation state is essential. Moreover, the relationship between the structure and performance of $BioMnO_x$ in the elimination of pollutants has not yet been investigated.

The objective of this study was to investigate the reactivity and stability of $BioMnO_x$ materials with different structures in the elimination of pollutants. A series of different $BioMnO_x$ materials were synthesized by the oxidation of Mn(II) with Mn-oxidizing bacteria *Pseudomonas* sp. G7 under different initial pH and Mn(II) dosages. The structures of $BioMnO_x$ were systematically characterized by XRD, X-ray photoelectron spectroscopy (XPS), UV-Vis absorption spectroscopy, and electron spin resonance (ESR). The relationships between the Mn(II) release and reactivity of $BioMnO_x$ were discussed. A degradation mechanism of CIP by $BioMnO_x$ was proposed.

1 Materials and methods

1.1 Reagents

The spin-trapping reagent 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), superoxide radical scavenger superoxide dismutase (SOD), and ciprofloxacin (CIP) were purchased from the Sigma Chemical Co. $MnCl_2{\cdot}4H_2O$ was obtained from Beijing Chemical Co. All other chemicals were analytical reagent grade. Deionized water was used throughout this study.

1.2 Bacterial strain and culture condition

The Mn-oxidizing bacteria *Pseudomonas* sp. G7 was isolated and purified by repeated streaking on solid agar plates, from soil obtained near the Qingdao Sanhe Electronic Component Co. Ltd. in China. The bacteria were identified by molecular biology methods, including DNA extraction, polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE), and sequence analysis. Subsequently, FASTA and BLAST DNA homology searches were performed with the NCBI DNA database software of the US National Institutes of Health, accessed on the internet at http://www.ncbi.nlm.nih.gov (Schwartz et al., 2003). The analysis results indicated that the strain was *Pseudomonas* sp. G7. The *Pseudomonas* sp. G7 was kept on an agar slant at 4°C, and the purity of the laboratory culture was checked at regular time intervals by repeated streaking on solid agar plates.

The *Pseudomonas* sp. G7 was grown aerobically in an axenic culture medium as described previously (Boogerd and De-Vrind, 1987). A loopful of inoculum was introduced into the *Pseudomonas* sp. G7 growth medium, followed by incubation on a platform shaker at 150 r/min and 28°C. The 24 hr grown culture having OD_{600} of 1.0 was used as the mother culture medium.

1.3 Synthesis of biogenic manganese oxides

In the preparation process, 100 mL of *Pseudomonas* sp. G7 growth medium was inoculated with 1 mL of mother culture medium to keep the same cell suspension. The initial pH values of the medium were kept at 5.5, 7 or 8.5, respectively. After 24 hr, the bacterial culture was supplemented with $MnCl_2$ dosed at 0.8 mmol/L from a filtered and sterilized 80 mmol/L stock solution. After 14 days of growth, the $BioMnO_x$ suspension was harvested and washed with deionized water by centrifugation (10 min at 10,000 r/min) until the supernatant had no Mn(II). The washed $BioMnO_x$ suspension was maintained at 4°C prior to use. Batches of $BioMnO_x$ were also prepared by following the same route as described above, but the initial pH value of the medium remained unchanged (at 7), and the $MnCl_2$ supplement was 0.4, 1.6 or 4.8 mmol/L. The nomenclature used to represent the materials is as follows: $BioMnO_x(X)$-Y, where X and Y denote the initial Mn(II) dosage and pH value of the medium, respectively.

The concentrations of Mn in all $BioMnO_x$ suspensions were different and determined by the following method: 50 mg of ascorbic acid was added to 5 mL of the $BioMnO_x$

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