

Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates



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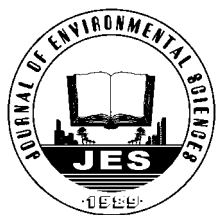
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Characterization and reactivity of biogenic manganese oxides for ciprofloxacin oxidation

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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 (O₂^{•-}) 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 O₂^{•-} 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 O₂^{•-} 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 (MnO₂), 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), 17 α -ethynylestradiol (de Rudder et al., 2004), bisphenol A (Lin et al., 2009), and

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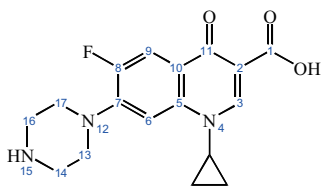


Fig. 1 Structure of ciprofloxacin.

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. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 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: $\text{BioMnO}_x(X)\text{-}Y$, 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

suspension, solubilizing MnO_x into Mn(II) , and then the suspension was filtered through a Millipore filter (pore size $0.22 \mu\text{m}$). The filtrates were analyzed by an inductively coupled plasma optical emission spectrometer (ICP-OES) (OPTIMA 2000DV, PerkinElmer Co., USA). Correspondingly, the biomass concentrations of the suspension were determined as volatile suspended solids (VSS) (Forrez et al., 2010; Greenberg et al., 1992).

1.4 Characterization

X-ray diffraction (XRD; Panalytical X'Pert PRO MPD diffractometer with $\text{CuK}\alpha$ irradiation) was used to identify the crystal structures of the BioMnO_x samples. X-ray photoelectron spectroscopy (XPS) measurements were taken on an AXIS-Ultra instrument from Kratos with an $\text{Al K}\alpha$ monochromatic X-ray source. UV-Vis absorption spectra were recorded on a Hitachi U-3900 spectrophotometer. Electron spin resonance (ESR) signals were obtained on a Bruker electron paramagnetic resonance A300-10/12 spectrometer.

1.5 Procedures and analysis

Aqueous CIP (10 mg/L) was reacted with suspended BioMnO_x in a 250 mL beaker wrapped with aluminum foil at room temperature (ca. 20°C) with continuous magnetic stirring under air-equilibrated conditions. The BioMnO_x in the reaction suspension contained Mn 50 mg/L. Under otherwise identical conditions, a control experiment was conducted consisting of the reaction of CIP in the *Pseudomonas* sp. G7 suspension with Mn-free medium, which was used to evaluate the sorption of CIP by the bacteria. Additionally, to distinguish between removal by sorption and reaction by $\text{BioMnO}_x(0.4)-7$, 4 mg/mL oxalic acid or 10 mg/mL ascorbic acid were added to the withdrawn samples to solubilize BioMnO_x , and dissolution of the BioMnO_x released adsorbed CIP and reaction products. The initial biomass of reaction was maintained at about 4

g/L VSS in BioMnO_x or control experiments.

For all experiments, 3 mL samples were withdrawn at preset time points, and filtered through a $0.22 \mu\text{m}$ pore size membrane to remove any suspended particles before analysis. The concentration of CIP in the filtrates was measured by HPLC (Agilent Technologies, 1200 Series) with an Eclipse XDB-C18 column ($250 \text{mm} \times 4.6 \text{mm}$ i.d., $5 \mu\text{m}$ film thickness). The released Mn(II) concentration in the supernatant was tested by ICP-OES. The main intermediate products were detected qualitatively by gas chromatography/mass spectrometry (GC/MS) using an Agilent 6890GC/5973MSD with a DB-5MS capillary column, while the carboxylic acids produced in the reaction were analyzed with a Dionex model ICS-2000 ion chromatograph (IC) equipped with a dual-piston pump and a Dionex IonPac AS11-HC analytical column ($4 \text{mm} \times 250 \text{mm}$).

2 Results and discussion

2.1 Characterization of BioMnO_x

Figure 2A shows the XRD patterns of $\text{BioMnO}_x(0.8)$ generated at different initial pH of the medium. No additional peak other than a peak at $2\theta = 19.3^\circ$ (centered at d of 4.60 \AA) was observed in the diffraction pattern of *Pseudomonas* sp. G7 and $\text{BioMnO}_x(0.8)-8.5$, while another two peaks at 36.5° and 65.6° (centered at d values of 2.46 and 1.42 \AA) appeared in $\text{BioMnO}_x(0.8)-5.5$ and $\text{BioMnO}_x(0.8)-7$. The peak at $2\theta = 19.3^\circ$ was ascribed to the biological and organic media, whereas the latter two peaks of $\text{BioMnO}_x(0.8)-5.5$ and $\text{BioMnO}_x(0.8)-7$ should be attributed to the (100) and (110) crystal planes of $\delta\text{-MnO}_2$ or birnessite consisting of discrete layers or poorly ordered stacking of adjacent layers, respectively (Brock et al., 1999; Kim et al., 2003). The results indicated that

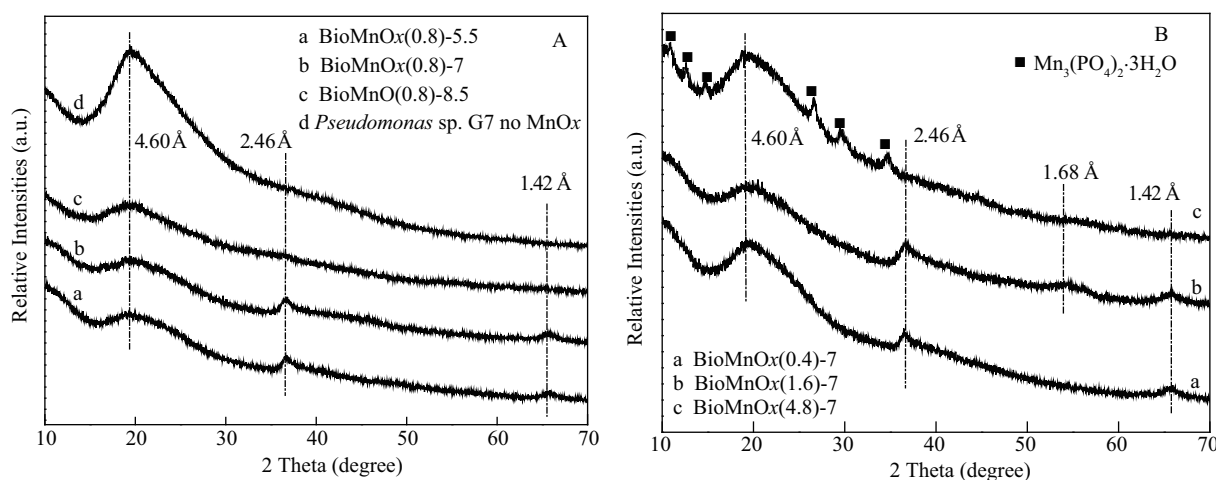


Fig. 2 XRD patterns of different samples under the specified conditions. (A) prepared in different initial pH of medium and (B) prepared in different initial Mn(II) dosages of medium.

alkaline conditions were not favorable for the production of BioMnO_x , in general agreement with previous reports (Boogerd and De-Vrind, 1987; Okazaki, 1997). Furthermore, at pH 7, the initial dosage of Mn(II) also affected the formation of BioMnO_x . As shown in Fig. 2b, the pattern of $\text{BioMnO}_x(0.4)$ -7 was similar for the Mn(II) dosages of 0.4 and 1.6 mmol/L, except for an additional peak at 54.4° (centered at d of 1.68 Å) assigned to the (106) crystal plane at Mn(II) dosage of 1.6 mmol/L. However, these peaks disappeared completely, and peaks corresponding to $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ (JCPDS 03-0426) were observed in the sample with the Mn(II) dosage of 4.8 mmol/L. Excess Mn(II) is toxic to the microbial system, inhibiting the healthy growth of *Pseudomonas* sp. G7 and decreasing the formation of BioMnO_x .

Figure 3 shows the Mn $2p_{3/2}$ and Mn 3s XPS spectra of $\text{BioMnO}_x(0.8)$ at different initial medium pH. Allen et al. (1989) and Zou et al. (2010) reported binding energies (BE) of Mn $2p_{3/2}$ for the manganese cations in MnO, Mn_2O_3 , and MnO_2 at 640.9, 641.8, and 642.4 eV, respectively. Peaks for both Mn(III) and Mn(IV) were clearly visible for $\text{BioMnO}_x(0.8)$ -5.5 and $\text{BioMnO}_x(0.8)$ -7, while the peaks for Mn(II) and Mn(IV) were observed in $\text{BioMnO}_x(0.8)$ -8.5 (Fig. 3A). In addition, the corresponding Mn 3s XPS spectra are shown in Fig. 3B. The obtained Mn 3s multiplet splitting values (ΔE) were 4.6, 4.5, and 6.0 for $\text{BioMnO}_x(0.8)$ -5.5, $\text{BioMnO}_x(0.8)$ -7, and $\text{BioMnO}_x(0.8)$ -8.5, respectively. The average oxidation state (AOS) of Mn in these samples was 3.8, 3.9, and 2.2 through the relationship $\text{AOS} = 8.956 - 1.126 (\Delta E)$ (Galakhov et al., 2002), as shown in Table 1.

For $\text{BioMnO}_x(0.4)$ -7, three peaks at the BE of 640.9, 641.8, and 642.4 eV were observed, indicating the presence of Mn(II), Mn(III), and Mn(IV) oxidation states

in the sample (Fig. 4A). The $\text{BioMnO}_x(1.6)$ -7 contained Mn(III) and Mn(IV), while the $\text{BioMnO}_x(4.8)$ -7 contained Mn(II) and Mn(IV). Meanwhile, it was found that the ΔE values were 5.4, 4.6, and 5.8 for $\text{BioMnO}_x(0.4)$ -7, $\text{BioMnO}_x(1.6)$ -7, and $\text{BioMnO}_x(4.8)$ -7, respectively (Fig. 4B). Correspondingly, their Mn AOS were 2.9, 3.8, and 2.4, as given in Table 1. Furthermore, pyrophosphate (PP) was employed as a complexing ligand for the analysis of Mn(III) on the surface of solid-phase BioMnO_x (Webb et al., 2005). From the UV-Vis absorption spectra shown in Fig. S1, the tested samples exhibited absorption bands at 258 nm, except for $\text{BioMnO}_x(0.8)$ -8.5 and $\text{BioMnO}_x(4.8)$ -7, indicating the absence of Mn(III) in these two samples, consistent with the analysis of Mn $2p_{3/2}$ XPS. The results verified that Mn(II) was oxidized to Mn(IV) without an intermediate under the preparation conditions for both $\text{BioMnO}_x(0.8)$ -8.5 and $\text{BioMnO}_x(4.8)$ -7, while the presence of Mn(III) in the other samples indicated that two sequential one-step electron transfer processes occurred for the oxidation of Mn(II) to Mn(III) and Mn(III) to Mn(IV), which was also observed in a previous report (Webb et al., 2005).

Table 1 XPS results of Mn 3s multiplet splitting, Mn 3s splitting (ΔE), and average oxidation state (AOS) of Mn

Sample	Mn ^5S (eV)	Mn ^7S (eV)	ΔE (eV)	AOS
$\text{BioMnO}_x(0.8)$ -5.5	88.8	84.2	4.6	3.8
$\text{BioMnO}_x(0.8)$ -7	88.9	84.4	4.5	3.9
$\text{BioMnO}_x(0.8)$ -8.5	89.4	83.4	6.0	2.2
$\text{BioMnO}_x(0.4)$ -7	86.8	81.4	5.4	2.9
$\text{BioMnO}_x(1.6)$ -7	89.1	84.5	4.6	3.8
$\text{BioMnO}_x(4.8)$ -7	89.4	83.6	5.8	2.4

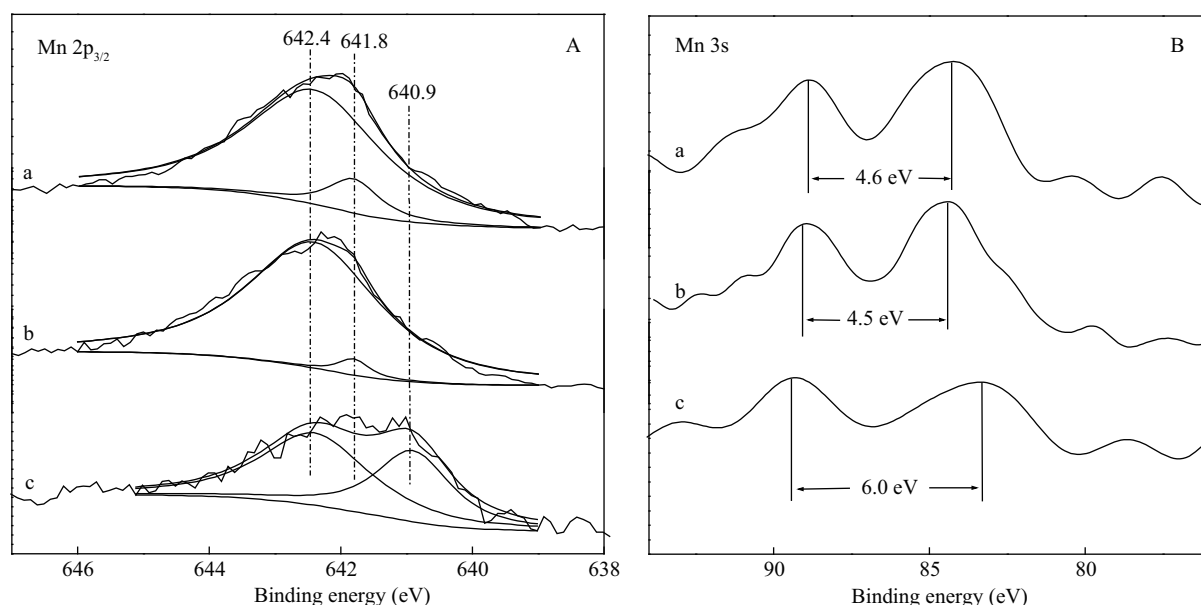


Fig. 3 XPS spectra in the Mn $2p_{3/2}$ (A) and Mn 3s (B) core levels of $\text{BioMnO}_x(0.8)$ -5.5 (line a), $\text{BioMnO}_x(0.8)$ -7 (line b), and $\text{BioMnO}_x(0.8)$ -8.5 (line c).

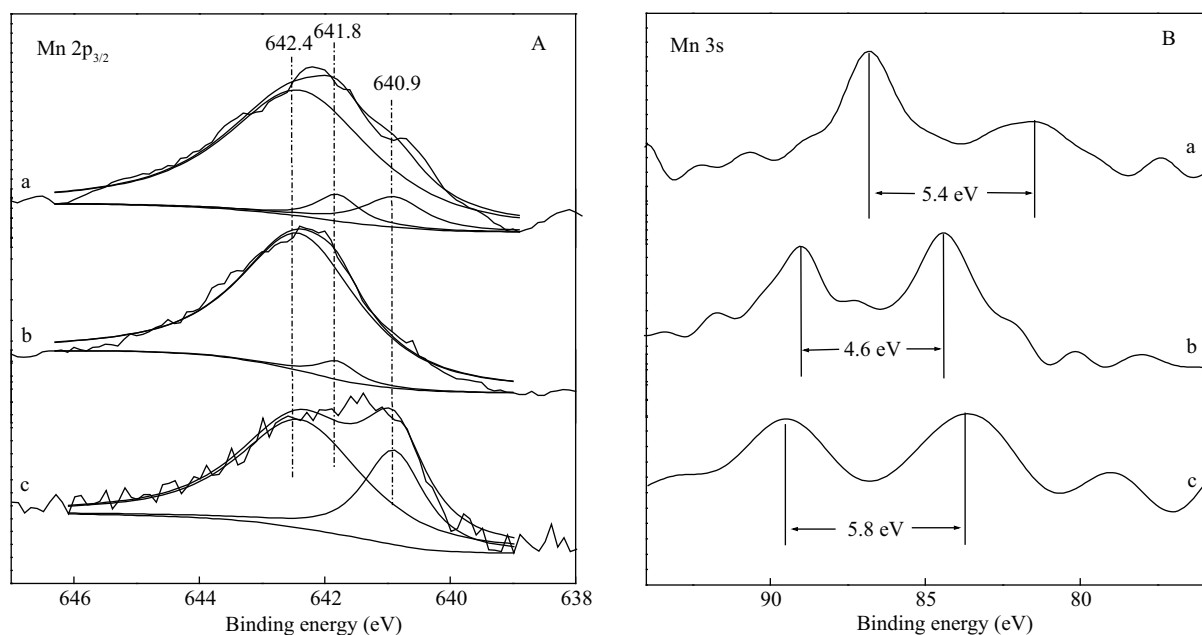


Fig. 4 XPS spectra in the Mn $2p_{3/2}$ (A) and Mn 3s (B) core levels of $\text{BioMnO}_x(0.4)\text{-}7$ (line a), $\text{BioMnO}_x(1.6)\text{-}7$ (line b), and $\text{BioMnO}_x(4.8)\text{-}7$ (line c).

2.2 Reactive oxygen species formation in different BioMnO_x suspensions

The ESR spin-trap technique (with DMPO) was used to detect the nature of the reactive oxygen species generated in different BioMnO_x suspensions. As shown in **Fig. 5**, a signal typical of DMPO-trapped adducts was observed in the ESR spectra of different BioMnO_x suspensions in air. This signal disappeared with the addition of SOD, indicating that the ESR signals were caused by O_2^- . However, no such ESR signals were observed in $\text{BioMnO}_x(0.8)\text{-}8.5$ and $\text{BioMnO}_x(4.8)\text{-}7$ suspensions. The results indicated that the active sites of BioMnO_x may be derived from Mn(III)/Mn(IV) in BioMnO_x . The formation of dioxygen-manganese complexes may be considered to produce activated oxygen (Son et al., 2001). Besides, no O_2^- ESR signals were observed in the $\text{BioMnO}_x(0.4)\text{-}7$ suspension in a N_2 -purged environment, indicating that the production of O_2^- involves molecular oxygen in air. In the $\text{BioMnO}_x(0.4)\text{-}7$ suspension, the signal intensity of O_2^- was higher than those of the other samples. The reactivity was attributed to the capacity of manganese to adopt various oxidation states and oxygen mobility in the oxide lattice. Therefore, the electron transfer in $\text{BioMnO}_x(0.4)\text{-}7$ was much easier than that in another samples due to the presence of three oxidation states of Mn, suggesting that $\text{BioMnO}_x(0.4)\text{-}7$ possibly had higher reactivity.

2.3 Degradation of CIP in different BioMnO_x suspensions

The catalytic activity of different BioMnO_x was evaluated by the degradation of CIP in aqueous dispersions in an

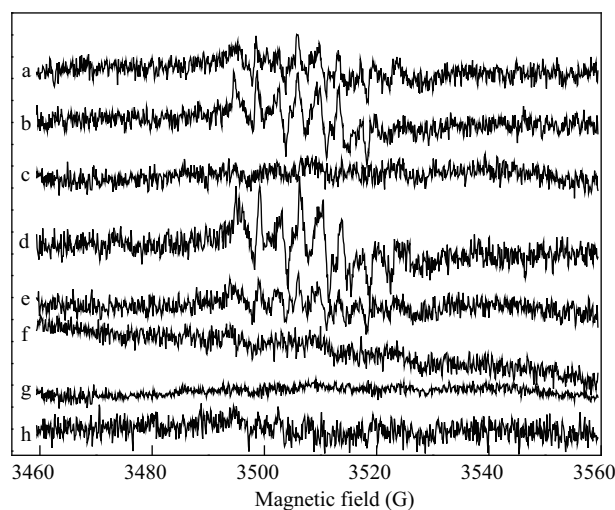


Fig. 5 DMPO spin-trapping ESR spectra recorded in different suspensions with air. (line a) $\text{BioMnO}_x(0.8)\text{-}5.5$; (line b) $\text{BioMnO}_x(0.8)\text{-}7$; (line c) $\text{BioMnO}_x(0.8)\text{-}8.5$; (line d) $\text{BioMnO}_x(0.4)\text{-}7$; (line e) $\text{BioMnO}_x(1.6)\text{-}7$; (line f) $\text{BioMnO}_x(4.8)\text{-}7$; (line g) SOD with $\text{BioMnO}_x(0.4)\text{-}7$; and (line h) $\text{BioMnO}_x(0.4)\text{-}7$ at N_2 atmosphere.

air-equilibrated environment. As shown in **Fig. 6A**, about 38% CIP removal, without the formation of any intermediates, was observed after 96 hr in the *Pseudomonas* sp. G7 suspension. This result implied that sorption onto *Pseudomonas* sp. G7 was responsible for the CIP decrease. Moreover, only approximately 68%, 43%, 61%, and 40% of CIP was removed in $\text{BioMnO}_x(0.8)\text{-}5.5$, $\text{BioMnO}_x(0.8)\text{-}8.5$, $\text{BioMnO}_x(1.6)\text{-}7$, and $\text{BioMnO}_x(4.8)\text{-}7$ suspensions within 60 hr, respectively, while CIP was completely degraded in $\text{BioMnO}_x(0.8)\text{-}7$ suspension in the same time. However, the complete removal of CIP was

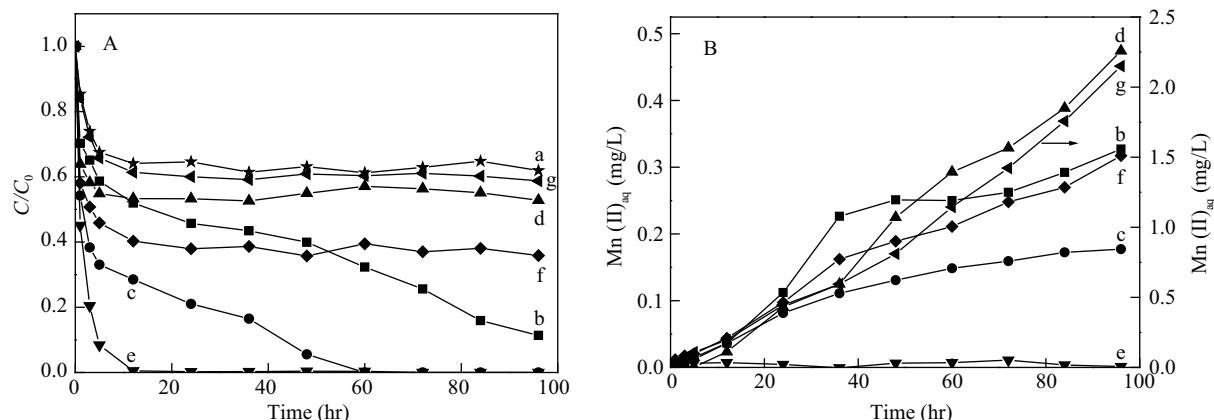


Fig. 6 CIP (10 mg/L) degradation (A) and the corresponding concentration of released Mn(II) (B) with different suspensions. (line a) *Pseudomonas* sp. G7; (line b) $\text{BioMnO}_x(0.8)\text{-}5.5$; (line c) $\text{BioMnO}_x(0.8)\text{-}7$; (line d) $\text{BioMnO}_x(0.8)\text{-}8.5$; (line e) $\text{BioMnO}_x(0.4)\text{-}7$; (line f) $\text{BioMnO}_x(1.6)\text{-}7$; (line g) $\text{BioMnO}_x(4.8)\text{-}7$. Conditions: 50 mg Mn/L in the tested suspensions, biomass content of all BioMnO_x or control experiment were 4 g/L VSS.

observed in the $\text{BioMnO}_x(0.4)\text{-}7$ suspension within 12 hr. In addition, in order to assess whether decreases in CIP concentrations were due to sorption vs. transformation by $\text{BioMnO}_x(0.4)\text{-}7$, oxalic acid or ascorbic acid were added to the withdrawn samples to solubilize manganese oxides and the adsorbed amounts of CIP. After 12 hr reaction, no significant adsorption of CIP was observed on the $\text{BioMnO}_x(0.4)\text{-}7$ surface (**Fig. S2**). The previous studies verified the ability of Mn-oxidation bacteria to oxidize the Mn(II) formed in the degradation of pollutants, inhibiting the release of Mn(II) (Forrez et al., 2010). However, the Mn(II) release increased with reaction time in different BioMnO_x suspensions except for $\text{BioMnO}_x(0.4)\text{-}7$, where no significant Mn(II) release was observed. The initial biomass of the reaction was maintained at about 4 g/L VSS in all experiments. The results indicated that the re-oxidation of the Mn(II) formed should include biological and chemical oxidation. **Figure 6B** shows that the release of Mn(II) decreased with increasing activity of BioMnO_x , and $\text{BioMnO}_x(0.4)\text{-}7$ exhibited the highest activity and hardly released Mn(II). Additionally, from ESR analysis, the O_2^- signals intensities were in line with the CIP removal efficiency and Mn(II) release amount. Therefore, the re-oxidation of Mn(II) depended on the structure and Mn oxidation states of BioMnO_x . $\text{BioMnO}_x(0.4)\text{-}7$ had three oxidation states of Mn with smaller particles and high structural disorder, enhancing the transfer of electrons at the aqueous-solid interface to result in lower Mn(II) release. Therefore, on the surface of $\text{BioMnO}_x(0.4)\text{-}7$, the reduced Mn, including Mn(II) and Mn(III), could undergo complexation with oxygen to produce activated oxygen, causing the inhibition of Mn(II) release and higher activity (Son et al., 2001).

In addition, 1 mg/L of CIP disappeared completely after 2 hr in $\text{BioMnO}_x(0.4)\text{-}7$ suspension. From **Fig. S3**, the rate constant k was 1.50 hr^{-1} , which was 8-fold higher than that of the 10 mg/L CIP degradation in the $\text{BioMnO}_x(0.4)\text{-}7$ suspension. This finding implied that $\text{BioMnO}_x(0.4)\text{-}7$

was highly effective in removing low concentrations of pollutants. Moreover, $\text{BioMnO}_x(0.4)\text{-}7$ did not show any noticeable loss of activity when it was further reused for 6 cycles (**Fig. 7**), indicating that the $\text{BioMnO}_x(0.4)\text{-}7$ had excellent long-term stability.

2.4 Formation of intermediates and reaction pathway

To identify the degradation pathway of CIP, reaction intermediates were monitored at different reaction times by GC/MS and IC in the $\text{BioMnO}_x(0.4)\text{-}7$ suspension. As shown in **Table 2**, the intermediate *N*-methylallylamine appeared at 12 hr and was not observed at 48 hr and 96 hr. However, another three compounds containing amine groups (propionamide, 2-(methylamino)ethanol, and 3-butenamide) were found at every time point. Meanwhile, some carboxylic acids (including formic, acetic, and oxalic acids) were generated quickly at the initial stage of the reaction, and then gradually reached constant concentrations as the reaction time increased, as shown in **Fig. 8**. The concentration of formic, acetic, and oxalic acids could

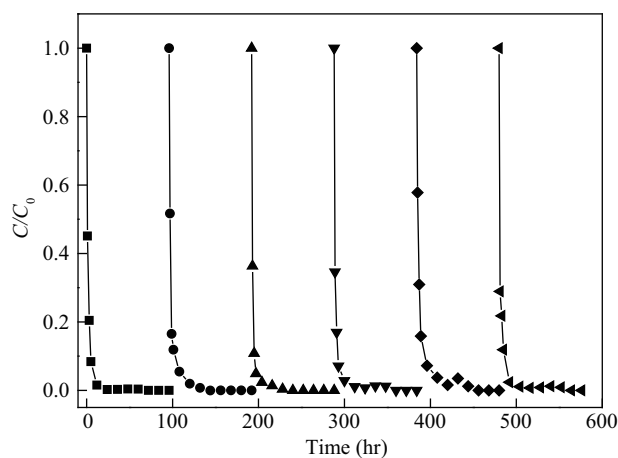


Fig. 7 Cycling runs in degradation of CIP (10 mg/L) in $\text{BioMnO}_x(0.4)\text{-}7$ suspension containing 50 mg Mn/L.

Table 2 Intermediates of CIP (10 mg/L) degradation identified by GC/MS in BioMnO_x(0.4)-7 suspension containing 50 mg Mn/L

Retention time (min)	Compounds	Sample time (hr)		
		12	48	96
17.054	<i>N</i> -Methylallylamine	✓		
35.186	2-(Methylamino)ethanol	✓	✓	✓
39.569	3-Butenamide	✓	✓	✓
43.077	Propionamide	✓	✓	✓

increase up to 0.96, 0.21, and 2.45 mg/L after 96 hr reaction, respectively.

According to the analysis of intermediates by GC/MS and IC, a tentative CIP degradation process in the BioMnO_x(0.4)-7 suspension was proposed. The structure of CIP is seen in Fig. 1. *N*-methylallylamine and 2-(methylamino)ethanol could be ascribed to the cleavage of the C(13)-C(14) or C(16)-C(17) bonds, whereas propionamide and 3-butenamide could be attributed to the scission of the C(14)-N(15) or C(16)-N(15) bond in CIP. The results were in agreement with many earlier works (Dewitte et al., 2008; Liu et al., 2012; Paul et al., 2010; Sturini et al., 2012; Vasconcelos et al., 2009). On the other hand, the bond C(2)-C(3) was cleaved and then rearranged. Thereafter, the small organic acids detected by IC were generated. This observation was in accord with the experimental results obtained during ozonation of an aqueous CIP solution or secondary wastewater effluent containing the antibiotic CIP (Dewitte et al., 2008; Liu et al., 2012). In addition, it could be seen that the C(8)-F bond remained intact, namely, defluorination did not occur in this scenario, because F⁻ could not be detected throughout the CIP degradation reaction. This observation seemed to be different from CIP degradation in photolysis under UV light or natural sunlight irradiation (Paul et al., 2010; Sturini et al., 2012; Vasconcelos et al., 2009).

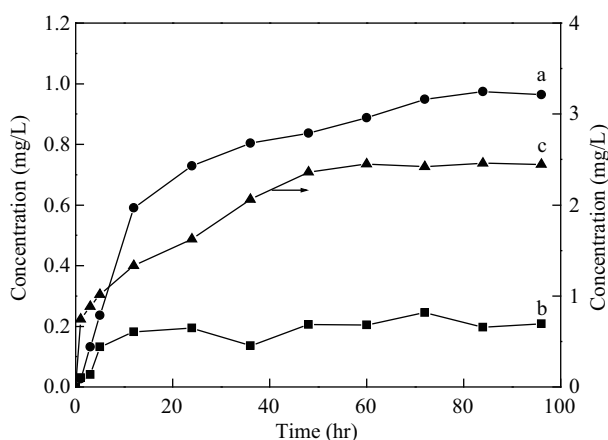


Fig. 8 The formation of organic acids in BioMnO_x(0.4)-7 suspension containing 50 mg Mn/L. (line a) formate; (line b) acetate; (line c) oxalate.

3 Conclusions

Different Mn oxidation states in BioMnO_x were obtained by the oxidation of Mn(II) by *Pseudomonas* sp. G7 under different initial pH and Mn(II) dosages. The Mn(II) release and reactivity depended on the structure and Mn oxidation states present in BioMnO_x. BioMnO_x(0.4)-7, with Mn(II), Mn(III) and Mn(IV), had the highest reactivity for the degradation of CIP and barely any Mn(II) release. The intermediates of CIP degradation in BioMnO_x(0.4)-7 suspension were *N*-methylallylamine, propionamide, 2-(methylamino)ethanol, and 3-butenamide with amine groups and several small organic acids (e.g., formic, acetic, and oxalic acids). The innocuous natural nanomaterial described here could be helpful in new efforts for eliminating unbiodegradable pharmaceutical chemicals in water systems.

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Supporting materials

Supplementary data associated with this article can be found in the online version.

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Supporting materials

Characterization and reactivity of biogenic manganese oxides for ciprofloxacin oxidation

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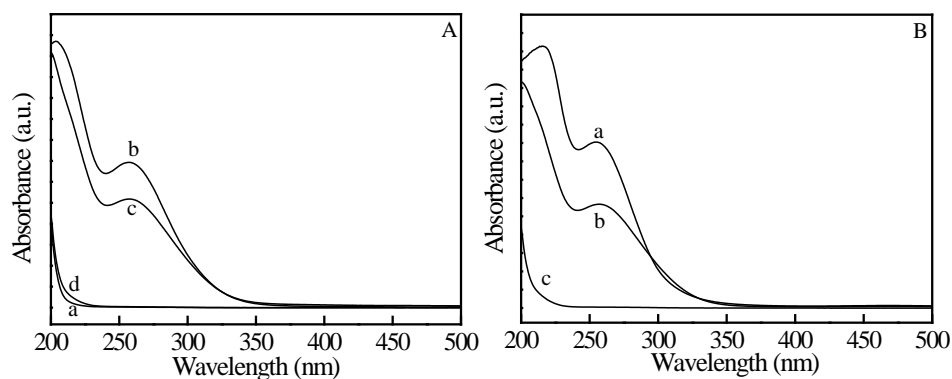


Fig. S1 UV-vis absorption spectra of the supernatant from the reaction of 20 mmol/L pyrophosphate solution (a) with different BioMnO_x (A): (b) BioMnO_x(0.8)-5.5, (c) BioMnO_x(0.8)-7, and (d) BioMnO_x(0.8)-8.5; (B): (a) BioMnO_x(0.4)-7, (b) BioMnO_x(1.6)-7, and (c) BioMnO_x(4.8)-7.

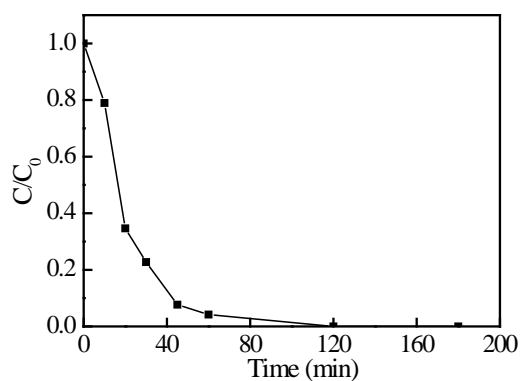


Fig. S2 1 mg/L of CIP degradation curve in BioMnO_x(0.4)-7 suspension containing 50 mg Mn/L.



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