

Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates



CONTENTS

Aquatic environment

A review of environmental characteristics and effects of low-molecular weight organic acids in the surface ecosystem Min Xiao, Fengchang Wu	935
Review on water leakage control in distribution networks and the associated environmental benefits Qiang Xu, Ruiping Liu, Qiuwen Chen, Ruonan Li	955
Synthesis of carbon-coated magnetic nanocomposite (Fe ₃ O ₄ @C) and its application for sulfonamide antibiotics removal from water Xiaolei Bao, Zhimin Qiang, Jih-Hsing Chang, Weiwei Ben, Jiuhui Qu	962
Removal of phosphate from wastewater using alkaline residue Yubo Yan, Xiuyun Sun, Fangbian Ma, Jiansheng Li, Jinyou Shen, Weiqing Han, Xiaodong Liu, Lianjun Wang	970
Immunotoxic effects of an industrial waste incineration site on groundwater in rainbow trout (<i>Oncorhynchus mykiss</i>) Nadjet Benchalga, François Gagné, Michel Fournier	981
Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates (Cover story) Zhilong Ye, Yin Shen, Xin Ye, Zhaoji Zhang, Shaohua Chen, Jianwen Shi	991
Adaptation of microbial communities to multiple stressors associated with litter decomposition of <i>Pterocarya stenoptera</i> Gaozhong Pu, Jingjing Tong, Aimeng Su1, Xu Ma, Jingjing Du, Yanna Lv, Xingjun Tian	1001
Effect of alkalinity on nitrite accumulation in treatment of coal chemical industry wastewater using moving bed biofilm reactor Baolin Hou, Hongjun Han, Shengyong Jia, Haifeng Zhuang, Qian Zhao, Peng Xu	1014
Distribution and seasonal variation of estrogenic endocrine disrupting compounds, N-nitrosodimethylamine, and N-nitrosodimethylamine formation potential in the Huangpu River, China Ai Zhang, Yongmei Li, Ling Chen	1023
Effects of ferrous and manganese ions on anammox process in sequencing batch biofilm reactors Xiaoli Huang, Dawen Gao, Sha Peng, Yu Tao	1034

Atmospheric environment

Characteristics of secondary inorganic aerosol and sulfate species in size-fractionated aerosol particles in Shanghai Shilei Long, Jianrong Zeng, Yan Li, Liangman Bao, Lingling Cao, Ke Liu, Liang Xu, Jun Lin, Wei Liu, Guanghua Wang, Jian Yao, Chenyan Ma, Yidong Zhao	1040
In-vehicle VOCs composition of unconditioned, newly produced cars Krzysztof Brodzik, Joanna Faber, Damian Łomankiewicz, Anna Gołda-Kopek	1052
Sulfur evolution in chemical looping combustion of coal with MnFe ₂ O ₄ oxygen carrier Baowen Wang, Chuchang Gao, Weishu Wang, Haibo Zhao, Chuguang Zheng	1062

Terrestrial environment

Enhancing plant-microbe associated bioremediation of phenanthrene and pyrene contaminated soil by SDBS-Tween 80 mixed surfactants Hewei Ni, Wenjun Zhou, Lizhong Zhu	1071
Growth and metal uptake of energy sugarcane (<i>Saccharum</i> spp.) in different metal mine tailings with soil amendments Xin Zhang, Yongguan Zhu, Yuebin Zhang, Yunxia Liu, Shaochun Liu, Jiawen Guo, Rudan Li, Songlin Wu, Baodong Chen	1080
A restoration-promoting integrated floating bed and its experimental performance in eutrophication remediation Yiming Guo, Yunguo Liu, Guangming Zeng, Xinjiang Hu, Xin Li, Dawei Huang, Yunqin Liu, Yicheng Yin	1090

Environmental biology

Microbial community functional structure in response to micro-aerobic conditions in sulfate-reducing sulfur-producing bioreactor Hao Yu, Chuan Chen, Jincai Ma, Xijun Xu, Ronggui Fan, Aijie Wang	1099
Degradation of dichloromethane by an isolated strain <i>Pandoraea pnomenusa</i> and its performance in a biotrickling filter Jianming Yu, Wenji Cai, Zhuowei Cheng, Jianmeng Chen	1108
Humic acid-enhanced electron transfer of <i>in vivo</i> cytochrome c as revealed by electrochemical and spectroscopic approaches Jiahuan Tang, Yi Liu, Yong Yuan, Shungui Zhou	1118
Evaluation of <i>Bacillus</i> sp. MZS10 for decolorizing Azure B dye and its decolorization mechanism Huixing Li, Ruijing Zhang, Lei Tang, Jianhua Zhang, Zhonggui Mao	1125
Biodegradation of pyrene by <i>Phanerochaete chrysosporium</i> and enzyme activities in soils: Effect of SOM, sterilization and aging Cuiping Wang, Hongwen Sun, Haibin Liu, Baolin Wang	1135

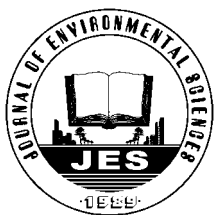
Environmental health and toxicology

Primary neuronal-astrocytic co-culture platform for neurotoxicity assessment of di-(2-ethylhexyl) phthalate Yang Wu, Ke Li, Haoxiao Zuo, Ye Yuan, Yi Sun, Xu Yang.....	1145
---	------

Environmental catalysis and materials

Characterization and reactivity of biogenic manganese oxides for ciprofloxacin oxidation Jinjun Tu, Zhendong Yang, Chun Hu, Jiuhui Qu	1154
Effects of particle composition and environmental parameters on catalytic hydrodechlorination of trichloroethylene by nanoscale bimetallic Ni-Fe Jianjun Wei, Yajing Qian, Wenjuan Liu, Lutao Wang, Yijie Ge, Jianghao Zhang, Jiang Yu, Xingmao Ma	1162
Heterogeneous Fenton-like degradation of 4-chlorophenol using iron/ordered mesoporous carbon catalyst Feng Duan, Yuezhu Yang, Yuping Li, Hongbin Cao, Yi Wang, Yi Zhang	1171
Photocatalytic removal of NO and NO ₂ using titania nanotubes synthesized by hydrothermal method Nhat Huy Nguyen, Hsunling Bai	1180
Efficient dechlorination of chlorinated solvent pollutants under UV irradiation by using the synthesized TiO ₂ nano-sheets in aqueous phase Landry Biyoghe Bi Ndong, Murielle Primaelle Ibondou, Zhouwei Miao, Xiaogang Gu, Shuguang Lu, Zhaofu Qiu, Qian Sui, Serge Maurice Mbadinga.....	1188
Biogenic C-doped titania templated by cyanobacteria for visible-light photocatalytic degradation of Rhodamine B Jiao He, Guoli Zi, Zhiying Yan, Yongli Li, Jiao Xie, Deliang Duan, Yongjuan Chen, Jiaqiang Wang	1195
Dyes adsorption using a synthetic carboxymethyl cellulose-acrylic acid adsorbent Genlin Zhang, Lijuan Yi, Hui Deng, Ping Sun	1203

Serial parameter: CN 11-2629/X*1989*m*277*en*P*29*2014-5

Available online at www.sciencedirect.com

Journal of Environmental Sciences

www.jesc.ac.cn

Characterization and reactivity of biogenic manganese oxides for ciprofloxacin oxidation

Jinjun Tu, Zhendong Yang, Chun Hu*, Jiuhui Qu

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

ARTICLE INFO

Article history:

Received 24 June 2013

revised 21 August 2013

accepted 03 September 2013

Keywords:

Mn oxidation state

Mn-oxidizing bacteria

superoxide radicals

ciprofloxacin degradation

DOI: 10.1016/S1001-0742(13)60505-7

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 (El-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 (El-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

* Corresponding author. E-mail: huchun@rcees.ac.cn

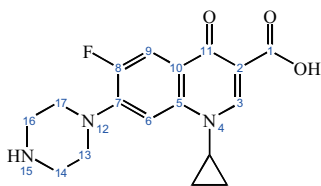


Fig. 1 Structure of ciprofloxacin.

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: $\text{BioMnO}_x(\text{X})\text{-Y}$, 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 $\text{BioMnO}_x(0.4)\text{--}7$, 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 $4.60\ \text{\AA}$) was observed in the diffraction pattern of *Pseudomonas* sp. G7 and $\text{BioMnO}_x(0.8)\text{--}8.5$, while another two peaks at 36.5° and 65.6° (centered at d values of 2.46 and $1.42\ \text{\AA}$) appeared in $\text{BioMnO}_x(0.8)\text{--}5.5$ and $\text{BioMnO}_x(0.8)\text{--}7$. The peak at $2\theta = 19.3^\circ$ was ascribed to the biological and organic media, whereas the latter two peaks of $\text{BioMnO}_x(0.8)\text{--}5.5$ and $\text{BioMnO}_x(0.8)\text{--}7$ 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

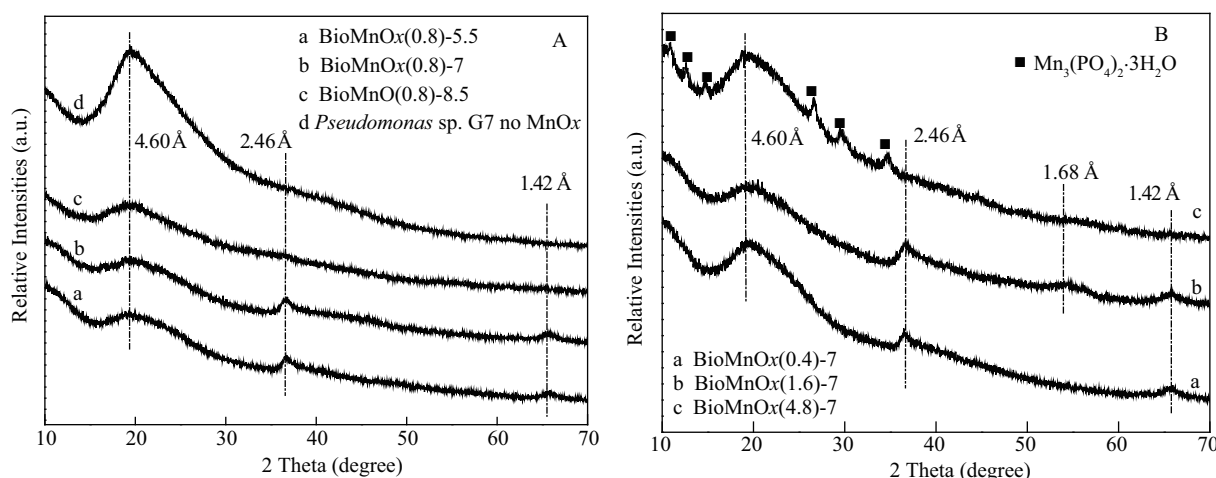


Fig. 2 XRD patterns of different samples under the specified conditions. (A) prepared in different initial pH of medium and (B) prepared in different initial Mn(II) dosages of medium.

alkaline conditions were not favorable for the production of BioMnO_x , in general agreement with previous reports (Booger 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 $2s$ (eV)	Mn $2s$ (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

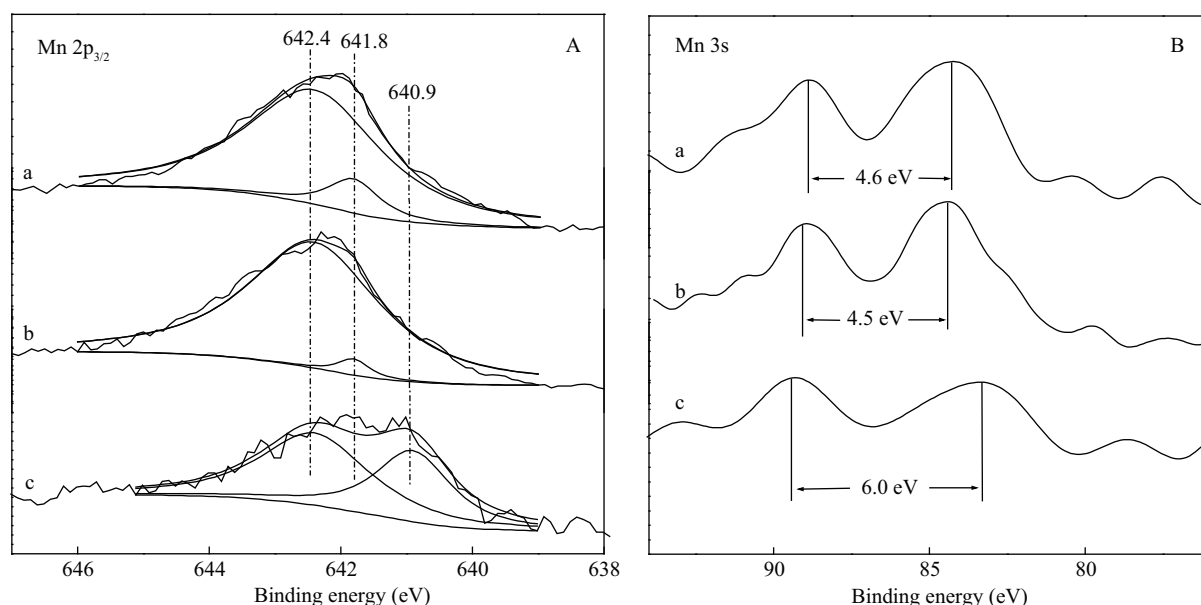


Fig. 3 XPS spectra in the Mn $2p_{3/2}$ (A) and Mn 3s (B) core levels of $\text{BioMnO}_x(0.8)$ -5.5 (line a), $\text{BioMnO}_x(0.8)$ -7 (line b), and $\text{BioMnO}_x(0.8)$ -8.5 (line c).

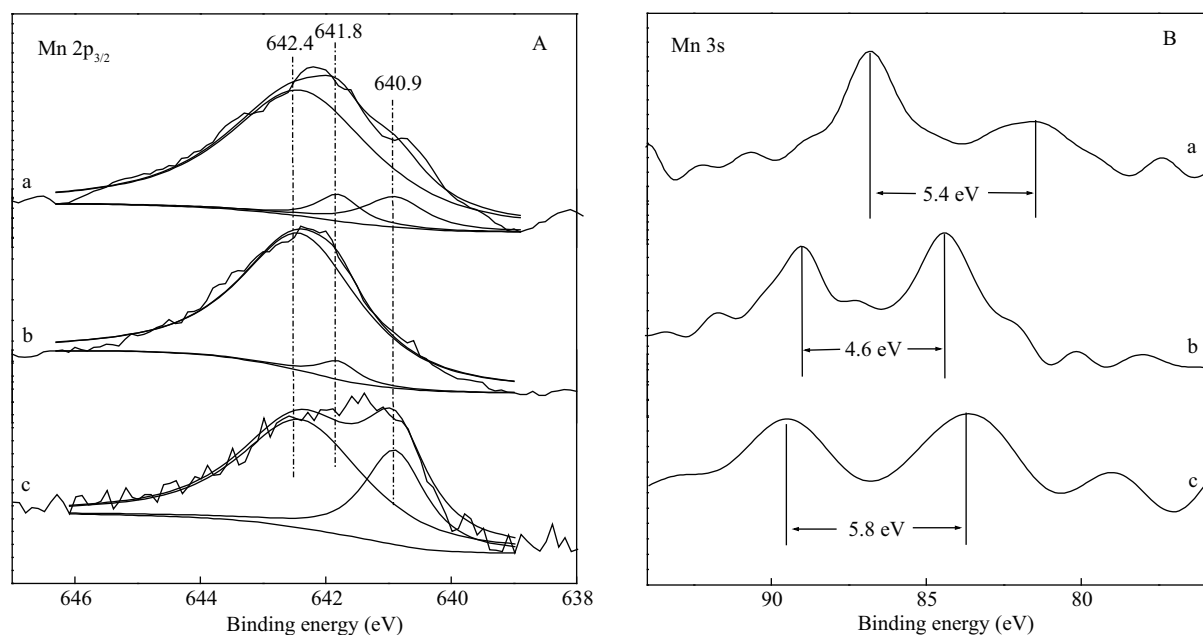


Fig. 4 XPS spectra in the Mn 2p_{3/2} (A) and Mn 3s (B) core levels of BioMnO_x(0.4)-7 (line a), BioMnO_x(1.6)-7 (line b), and BioMnO_x(4.8)-7 (line c).

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 O₂^{•−}. However, no such ESR signals were observed in BioMnO_x(0.8)-8.5 and BioMnO_x(4.8)-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 O₂^{•−} ESR signals were observed in the BioMnO_x(0.4)-7 suspension in a N₂-purged environment, indicating that the production of O₂^{•−} involves molecular oxygen in air. In the BioMnO_x(0.4)-7 suspension, the signal intensity of O₂^{•−} 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 BioMnO_x(0.4)-7 was much easier than that in another samples due to the presence of three oxidation states of Mn, suggesting that BioMnO_x(0.4)-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

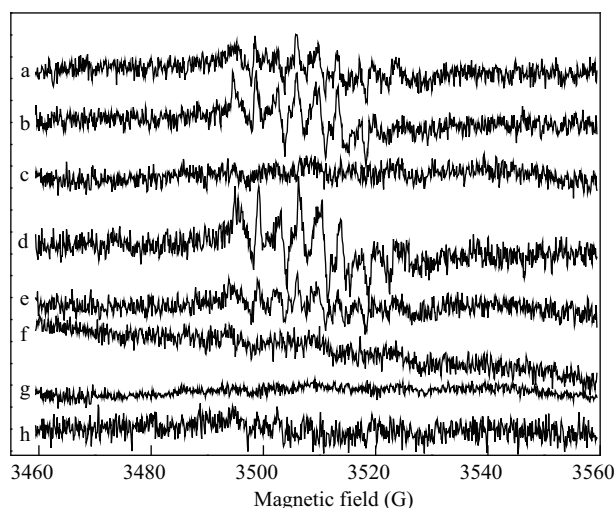


Fig. 5 DMPO spin-trapping ESR spectra recorded in different suspensions with air. (line a) BioMnO_x(0.8)-5.5; (line b) BioMnO_x(0.8)-7; (line c) BioMnO_x(0.8)-8.5; (line d) BioMnO_x(0.4)-7; (line e) BioMnO_x(1.6)-7; (line f) BioMnO_x(4.8)-7; (line g) SOD with BioMnO_x(0.4)-7; and (line h) BioMnO_x(0.4)-7 at N₂ 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 BioMnO_x(0.8)-5.5, BioMnO_x(0.8)-8.5, BioMnO_x(1.6)-7, and BioMnO_x(4.8)-7 suspensions within 60 hr, respectively, while CIP was completely degraded in BioMnO_x(0.8)-7 suspension in the same time. However, the complete removal of CIP was

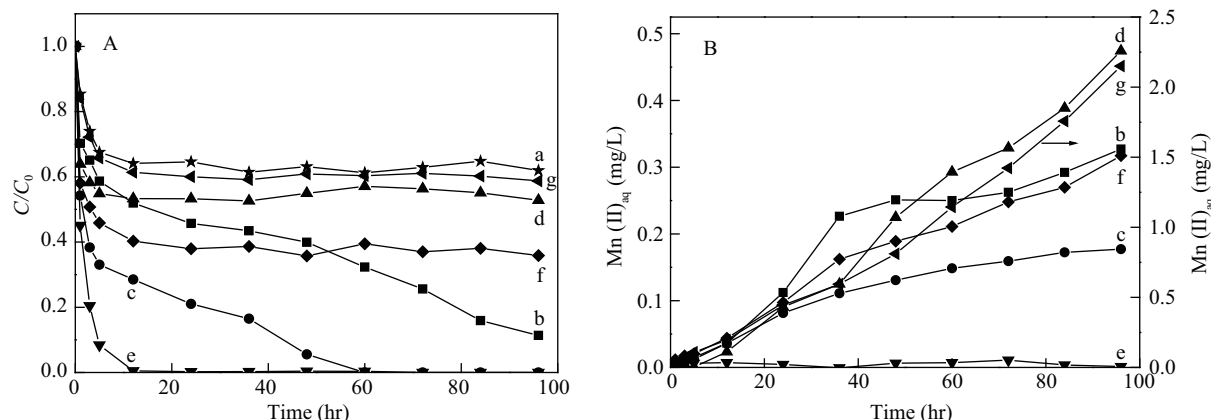


Fig. 6 CIP (10 mg/L) degradation (A) and the corresponding concentration of released Mn(II) (B) with different suspensions. (line a) *Pseudomonas* sp. G7; (line b) BioMnO_x(0.8)-5.5; (line c) BioMnO_x(0.8)-7; (line d) BioMnO_x(0.8)-8.5; (line e) BioMnO_x(0.4)-7; (line f) BioMnO_x(1.6)-7; (line g) BioMnO_x(4.8)-7. 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 BioMnO_x(0.4)-7 suspension within 12 hr. In addition, in order to assess whether decreases in CIP concentrations were due to sorption vs. transformation by BioMnO_x(0.4)-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 BioMnO_x(0.4)-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 BioMnO_x(0.4)-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-oxidization 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 BioMnO_x(0.4)-7 exhibited the highest activity and hardly released Mn(II). Additionally, from ESR analysis, the O₂^{•−} signals intensities were in line with the CIP removal efficiency and Mn(II) release amount. Therefore, the re-oxidization of Mn(II) depended on the structure and Mn oxidation states of BioMnO_x. BioMnO_x(0.4)-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 BioMnO_x(0.4)-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 BioMnO_x(0.4)-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 BioMnO_x(0.4)-7 suspension. This finding implied that BioMnO_x(0.4)-7

was highly effective in removing low concentrations of pollutants. Moreover, BioMnO_x(0.4)-7 did not show any noticeable loss of activity when it was further reused for 6 cycles (**Fig. 7**), indicating that the BioMnO_x(0.4)-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 BioMnO_x(0.4)-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

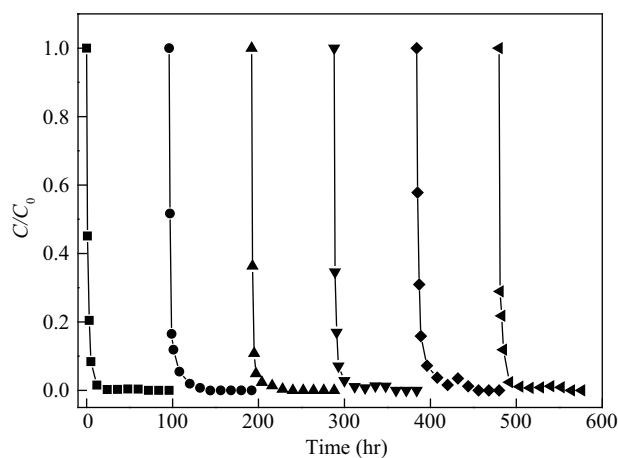


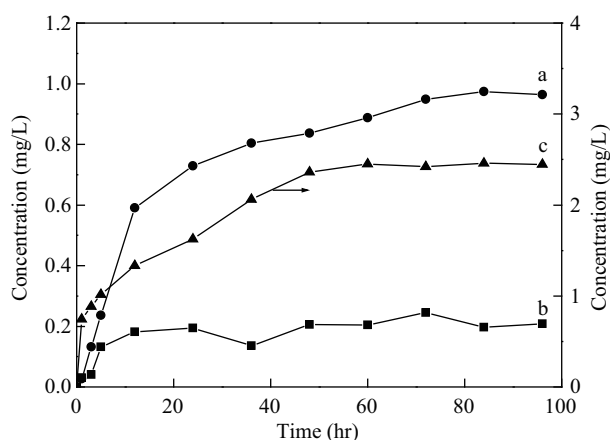
Fig. 7 Cycling runs in degradation of CIP (10 mg/L) in BioMnO_x(0.4)-7 suspension containing 50 mg Mn/L.

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.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51138009, 21125731, 51221892), the National High Technology Research and Development Program of China (No. 2012AA062606), and the project of the Chinese Academy of Sciences (No. KZCX2-EW-410).

Supporting materials

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

REFERENCES

- Allen, G.C., Harris, S.J., Jutson, J.A., Dyke, J.M., 1989. A study of a number of mixed transition-metal oxide spinels using X-ray photoelectron spectroscopy. *Appl. Surf. Sci.* 37(1), 111–134.
- Bargar, J.R., Tebo, B.M., Bergmann, U., Webb, S.M., Glatzel, P., Chiu, V.Q. et al., 2005. Biotic and abiotic products of Mn (II) oxidation by spores of the marine *Bacillus* sp. Strain SG-1. *Amer. Mineral.* 90(1), 143–154.
- Boogerd, F.C., De-Vrind, J.P.M., 1987. Manganese oxidation by *Leptothrix discophora*. *J. Bacteriol.* 169(2), 489–494.
- Brock, S.L., Sanabria, M., Suib, S.L., Urban, V., Thiyagarajan, P., Potter, D.I., 1999. Particle size control and self-assembly processes in novel colloids of nanocrystalline manganese oxide. *J. Phys. Chem. B* 103(35), 7416–7428.
- De Bel, E., Dewulf, J., De Witte, B., Van Langenhove, H., Janssen, C., 2009. Influence of pH on the sonolysis of ciprofloxacin: Biodegradability, ecotoxicity and antibiotic activity of its degradation products. *Chemosphere* 77(2), 291–295.
- de Rudder, J., Van de Wiele, T., Dhooze, W., Comhaire, F., Verstraete, W., 2004. Advanced water treatment with manganese oxide for the removal of 17 α -ethynylestradiol (EE2). *Water Res.* 38(1), 184–192.
- Dewitte, B., Dewulf, J., Demeestere, K., De Vyvere, V.V., De Wispelaere, P., Van Langenhove, H., 2008. Ozonation of ciprofloxacin in water:

- HRMS identification of reaction products and pathways. *Environ. Sci. Technol.* 42(13), 4889–4895.
- El-Kemary, M., El-Shamy, H., El-Mehasseb, I., 2010. Photocatalytic degradation of ciprofloxacin drug in water using ZnO nanoparticles. *J. Lumin.* 130(12), 2327–2331.
- El-Shafey, E.S.I., Al-Lawati, H., Al-Sumri, A.S., 2012. Ciprofloxacin adsorption from aqueous solution onto chemically prepared carbon from date palm leaflets. *J. Environ. Sci.* 24(9), 1579–1586.
- Forrez, I., Carballa, M., Verbeken, K., Vanhaecke, L., Schlusener, M., Ternes, T. et al., 2010. Diclofenac oxidation by biogenic manganese oxides. *Environ. Sci. Technol.* 44(9), 3449–3454.
- Galakhov, V.R., Demeter, M., Bartkowski, S., Neumann, M., Ovechkin, N.A., Kurmaev, E.Z. et al., 2002. Mn 3s exchange splitting in mixed-valence manganites. *Phys. Rev. B* 65(11), 1131021–1131024.
- Greenberg, A.E., Clesceri, L.S., Eaton, A.D., 1992. *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association: Washington, D. C.
- Hocking, R.K., Brimblecombe, R., Chang, L.Y., Singh, A., Cheah, M.H., Glover, C. et al., 2011. Water-oxidation catalysis by manganese in a geochemical-like cycle. *Nature Chem.* 3(6), 461–466.
- Huber, M.M., Canonica, S., Park, G.Y., Von Gunten, U., 2003. Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ. Sci. Technol.* 37(5), 1016–1024.
- Jürgensen, A., Widmeyer, J.R., Gordon, R.A., Bendell-Young, L.I., Moore, M.M., Crozier, E.D., 2004. The structure of the manganese oxide on the sheath of the bacterium *Leptothrix discophora*: An XAFS study. *Amer. Mineral.* 89(7), 1110–1118.
- Kim, H.S., Pastén, P.A., Gaillard, J.F., Stair, P.C., 2003. Nanocrystalline todorokite-like manganese oxide produced by bacterial catalysis. *J. Amer. Chem. Soc.* 125(47), 14284–14285.
- Kim, H.S., Stair, P.C., 2004. Bacterially produced manganese oxide and todorokite: UV Roman spectroscopic comparison. *J. Phys. Chem. B* 108(44), 17019–17026.
- Larsson, D.G.J., de Pedro, C., Paxeus, N., 2007. Effluent from drug manufactures contains extremely high levels of pharmaceuticals. *J. Hazard. Mater.* 148(3), 751–755.
- Lin, K.D., Liu, W.P., Gan, J., 2009. Oxidative removal of bisphenol A by manganese dioxide: Efficacy, products, and pathways. *Environ. Sci. Technol.* 43(10), 3860–3864.
- Liu, C., Nanaboina, V., Korshin, G.V., Jiang, W.J., 2012. Spectroscopic study of degradation products of ciprofloxacin, norfloxacin and lomefloxacin formed in ozonated water. *Water Res.* 46(16), 5235–5246.
- Okazaki, M., Sugita, T., Shimizu, M., Ohode, Y., Iwamoto, K., de Vrindt Jong, E.W. et al., 1997. Partial purification and characterization of manganese-oxidizing factors of *Pseudomonas fluorescens* GB-1. *Appl. Environ. Microbiol.* 63(12), 4793–4799.
- Paul, T., Dodd, M.C., Strathmann, T.J., 2010. Photolytic and photocatalytic decomposition of aqueous ciprofloxacin: Transformation products and residual antibacterial. *Water Res.* 44(10), 3121–3132.
- Pereira, V.J., Weinberg, H.S., Linden, K.G., Singer, P.C., 2007. UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. *Environ. Sci. Technol.* 41(5), 1682–1688.
- Putschew, A., Schittko, S., Jekel, M., 2001. Quantification of triiodinated benzene derivatives and X-ray contrast media in water samples by liquid chromatography-electrospray tandem mass spectrometry. *J. Chromatogr. A* 930(1–2), 127–134.
- Schwartz, T., Kohnen, W., Jansen, B., Obst, U., 2003. Detection of antibiotic-resistant bacterial and their resistance genes in wastewater, surface water, and drinking water biofilms. *FEMS Microbiol. Ecol.* 43(3), 325–335.
- Shin, J.Y., Cheney, M.A., 2004. Abiotic transformation of atrazine in aqueous suspension of four synthetic manganese oxides. *Coll. Surf. A* 242(1–3), 85–92.
- Son, Y.C., Makwana, V.D., Howell, A.R., Suib, S.L., 2001. Efficient, catalytic, aerobic oxidation of alcohols with octahedral molecular sieves. *Angew. Chem. Inter. Ed.* 40(22), 4280–4283.
- Stone, A.T., 1987. Reductive dissolution of manganese (III/IV) oxides by substituted phenols. *Environ. Sci. Technol.* 21(10), 979–988.
- Sturini, M., Speltini, A., Maraschi, F., Profumo, A., Pretali, L., Irastorza, E.A., Fasani, E., Albin, A., 2012. Photolytic and photocatalytic degradation of fluoroquinolones in untreated river water under natural sunlight. *Applied Catalysis B: Environmental* 119–120, 32–39.
- Vasconcelos, T.G., Henriques, D.M., König, A., Martins, A.F., Kummer, K., 2009. Photo-degradation of the antimicrobial ciprofloxacin at high pH: Identification and biodegradability assessment of the primary by-products. *Chemosphere* 76(4), 487–493.
- Villalobos, M., Toner, B., Bargar, J., Sposito, G., 2003. Characterization of the manganese oxide produced by *Pseudomonas putida* strain MnB1. *Geochimica et Cosmochimica Acta* 67(14), 2649–2662.
- Webb, S.M., Dick, G.J., Bargar, J.R., Tebo, B.M., 2005. Evidence for the presence of Mn (III) intermediates in the bacterial oxidation of Mn (II). *Proc. Natl. Acad. Sci. USA* 102(15), 5558–5563.
- Zhang, H.C., Huang, C.H., 2005. Oxidative transformation of fluoroquinolone antibacterial agents and structurally related amines by manganese oxide. *Environ. Sci. Technol.* 39(12), 4474–4483.
- Zou, Z.Q., Meng, M., Zha, Y.Q., 2010. Surfactant-assisted synthesis, characterizations, and catalytic oxidation mechanisms of the mesoporous MnOx-CeO₂ and Pd/MnOx-CeO₂ catalysts used for CO and C₃H₈ oxidation. *J. Phys. Chem. C* 114(1), 468–477.

Supporting materials

Characterization and reactivity of biogenic manganese oxides for ciprofloxacin oxidation

Jinjun Tu, Zhendong Yang, Chun Hu*, Jiuhui Qu

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Received 24 June 2013; revised 21 August 2013; accepted 03 September 2013

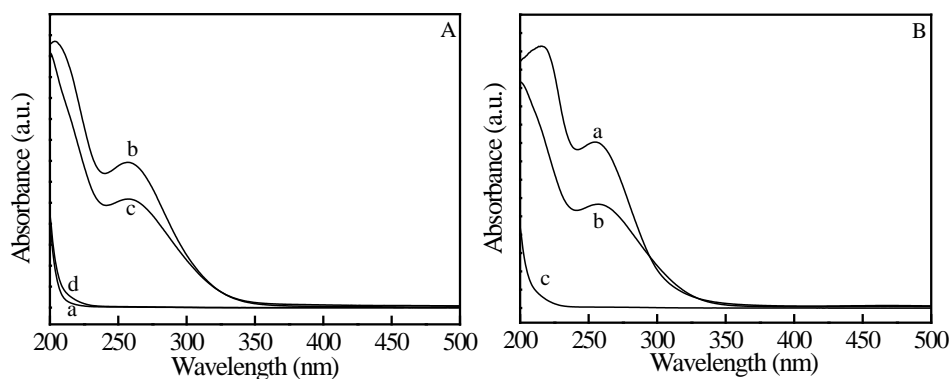


Fig. S1 UV-vis absorption spectra of the supernatant from the reaction of 20 mmol/L pyrophosphate solution (a) with different BioMnO_x (A): (b) BioMnO_x(0.8)-5.5, (c) BioMnO_x(0.8)-7, and (d) BioMnO_x(0.8)-8.5; (B): (a) BioMnO_x(0.4)-7, (b) BioMnO_x(1.6)-7, and (c) BioMnO_x(4.8)-7.

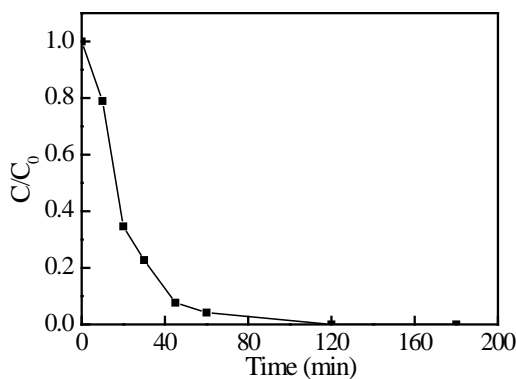


Fig. S2 1 mg/L of CIP degradation curve in BioMnO_x(0.4)-7 suspension containing 50 mg Mn/L.



Editorial Board of Journal of Environmental Sciences

Editor-in-Chief

Hongxiao Tang Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

Associate Editors-in-Chief

Jiuhui Qu Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China
Shu Tao Peking University, China
Nigel Bell Imperial College London, United Kingdom
Po-Keung Wong The Chinese University of Hong Kong, Hong Kong, China

Editorial Board

Aquatic environment

Baoyu Gao
Shandong University, China
Maohong Fan
University of Wyoming, USA
Chihpin Huang
National Chiao Tung University
Taiwan, China
Ng Wun Jern
Nanyang Environment &
Water Research Institute, Singapore
Clark C. K. Liu
University of Hawaii at Manoa, USA
Hokyoung Shon
University of Technology, Sydney, Australia
Zijian Wang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Zhiwu Wang
The Ohio State University, USA
Yuxiang Wang
Queen's University, Canada
Min Yang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Zhifeng Yang
Beijing Normal University, China
Han-Qing Yu
University of Science & Technology of China

Terrestrial environment

Christopher Anderson
Massey University, New Zealand
Zucong Cai
Nanjing Normal University, China
Xinbin Feng
Institute of Geochemistry,
Chinese Academy of Sciences, China
Hongqing Hu
Huazhong Agricultural University, China
Kin-Che Lam
The Chinese University of Hong Kong
Hong Kong, China
Erwin Klumpp
Research Centre Juelich, Agrosphere Institute
Germany
Peijun Li
Institute of Applied Ecology,
Chinese Academy of Sciences, China

Michael Schlöter

German Research Center for Environmental Health
Germany
Xuejun Wang
Peking University, China
Lizhong Zhu
Zhejiang University, China

Atmospheric environment

Jianmin Chen
Fudan University, China
Abdelwahid Mellouki
Centre National de la Recherche Scientifique
France
Yujing Mu
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Min Shao
Peking University, China
James Jay Schauer
University of Wisconsin-Madison, USA
Yuesi Wang
Institute of Atmospheric Physics,
Chinese Academy of Sciences, China
Xin Yang
University of Cambridge, UK

Environmental biology

Yong Cai
Florida International University, USA
Henner Hollert
RWTH Aachen University, Germany
Jae-Seong Lee
Sungkyunkwan University, South Korea
Christopher Rensing
University of Copenhagen, Denmark
Bojan Sedmak
National Institute of Biology, Ljubljana
Lirong Song
Institute of Hydrobiology,
the Chinese Academy of Sciences, China
Chunxia Wang
National Natural Science Foundation of China
Gehong Wei
Northwest A & F University, China
Daqiang Yin
Tongji University, China
Zhongtang Yu
The Ohio State University, USA

Environmental toxicology and health

Jingwen Chen
Dalian University of Technology, China
Jianying Hu
Peking University, China
Guibin Jiang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Sijin Liu
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Tsuyoshi Nakanishi
Gifu Pharmaceutical University, Japan
Willie Peijnenburg
University of Leiden, The Netherlands
Bingsheng Zhou
Institute of Hydrobiology,
Chinese Academy of Sciences, China

Environmental catalysis and materials

Hong He
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China
Junhua Li
Tsinghua University, China
Wenfeng Shangguan
Shanghai Jiao Tong University, China
Yasutake Teraoka
Kyushu University, Japan
Ralph T. Yang
University of Michigan, USA

Environmental analysis and method

Zongwei Cai
Hong Kong Baptist University,
Hong Kong, China
Jiping Chen
Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, China
Minghui Zheng
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Municipal solid waste and green chemistry

Pinjing He
Tongji University, China
Environmental ecology
Rusong Wang
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, China

Editorial office staff

Managing editor Qingcai Feng
Editors Zixuan Wang Suqin Liu Zhengang Mao
English editor Catherine Rice (USA)

JOURNAL OF ENVIRONMENTAL SCIENCES

环境科学学报(英文版)
(<http://www.jesc.ac.cn>)

Aims and scope

Journal of Environmental Sciences is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via <http://www.elsevier.com/locate/jes>.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at <http://www.jesc.ac.cn>. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@263.net, jesc@rcees.ac.cn. Instruction to authors is available at <http://www.jesc.ac.cn>.

Journal of Environmental Sciences (Established in 1989)

Vol. 26 No. 5 2014

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences	Distributed by	Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Domestic	Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
Editor-in-chief	Hongxiao Tang	Foreign	Elsevier Limited http://www.elsevier.com/locate/jes
CN 11-2629/X	Domestic postcode: 2-580	Printed by	Beijing Beilin Printing House, 100083, China
		Domestic price per issue	RMB ¥ 110.00

ISSN 1001-0742



9 771001 074147