



Degradation kinetics and transformation products of chlorophene by aqueous permanganate

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ABSTRACT

This paper evaluates the oxidation of an antibacterial agent, chlorophene (4-chloro-2-(phenylmethyl)phenol, CP), by permanganate (Mn(VII)) in water. Second-order rate constant (k) for the reaction between Mn(VII) and CP was measured as $(2.05 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7.0 for an initial CP concentration of 20.0 μM and Mn(VII) concentration of 60.0 μM . The value of k decreased with increasing pH in the pH range of 5.0–7.0, and then increased with an increase in solution pH from 7.0 to 10.0. The presence of MnO_2 and Fe^{3+} in water generally enhanced the removal of CP, while the effect of humic acid was not obvious. Fourteen oxidation products of CP were identified by an electrospray time-of-flight mass spectrometer, and direct oxidation, ring-opening, and decarboxylation were mainly observed in the reaction process. The initial reaction sites of CP by Mn(VII) oxidation were rationalized by density functional theory calculations. Toxicity changes of the reaction solutions were assessed by the luminescent bacteria *P. phosphoreum*, and the intermediate products posed a relatively low ecological risk during the degradation process. The efficient removal of CP in secondary clarifier effluent and river water demonstrated the potential application of this Mn(VII) oxidation method in water treatment.

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1. Introduction

Chlorophene (4-chloro-2-(phenylmethyl)phenol, CP) is a broad-spectrum antimicrobial agent widely used for general cleaning and disinfecting in hospitals, households, industrial and farming activities (Benitez et al., 2013b; Holzem et al., 2014; Rayaroth et al., 2015; Sirés et al., 2007). Due to the widespread use, CP has been considered as an emerging environmental contaminant. The concentration of CP has been measured at up to mg L^{-1} level in activated sludge sewage systems and $\mu\text{g L}^{-1}$ level in rivers and sewage plant treatment effluents (Sirés et al., 2007). Once released to the environment, CP tends to accumulate in sediments and organisms because of its strong hydrophobicity ($\log K_{ow} = 3.99$) (Zhang and Huang, 2003). Evidence has shown that CP was carcinogenic and mutagenic in *in vitro* mammalian tests (Yamarik, 2003). Moreover,

CP is poorly biodegradable, and thus remains for long periods in the environment (He et al., 2011). Considering the environmental persistence and potential risks of CP, it is imperative to develop an efficient treatment method to remove this pollutant from waters.

To date, many methods have been applied to degrade CP, including sonolysis (Rayaroth et al., 2015), oxidation by manganese oxides (MnO_2 and MnOOH) (Zhang and Huang, 2003), advanced oxidation processes such as electro-Fenton (Sirés et al., 2007), ozonation (Benitez et al., 2013a), photochemical degradation by UV/ H_2O_2 (Benitez et al., 2013b) and UV/ O_3 (He et al., 2011), persulfate oxidation (Bolobajev et al., 2015), as well as laccase-catalyzed reaction (Shi et al., 2016). The present paper demonstrates for the first time the oxidation of CP by permanganate (Mn(VII)) in water.

Mn(VII) is a strong oxidizing agent with a high standard redox potential (0.558 V–1.692 V versus NHE) and a wide operating pH range (Jiang et al., 2009; Yan and Schwartz, 1999). Mn(VII) has been shown to be effective in degrading various organic compounds, for example, triclosan (Chen et al., 2016; Jiang et al., 2009), bromophenols (Jiang et al., 2014), bisphenol A (Zhang et al., 2013),

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tetrabromobisphenol A (Pang et al., 2014), decabromodiphenyl ether (Shi et al., 2015), and drugs such as diclofenac (Cheng et al., 2015), indomethacin (Rodríguez-Álvarez et al., 2013) and salbutamol (Rodríguez-Álvarez et al., 2015). Examples of *in situ* remediation of contaminated soil and waters are also known (Jiang et al., 2009, 2012; Waldemer and Tratnyek, 2006). During the reaction, Mn(VII) can selectively attack the electron-rich moieties by several different mechanisms such as hydrogen abstraction, electron transfer and direct oxygen transfer (Jiang et al., 2012; Waldemer and Tratnyek, 2006). Additionally, manganese (III/IV) solids, the reduction products of Mn(VII), can act as adsorbents/oxidants to enhance the aqueous removal of contaminants (Stone, 1987; Zhang and Huang, 2003).

The objectives of the present paper are: (i) to measure the kinetics of CP oxidation by Mn(VII) in a pH range of 5.0–10.0, (ii) to investigate the effect of MnO₂, Fe³⁺ and humic acid on CP removal, (iii) to identify the transformation products of CP using liquid chromatography-high resolution mass spectrometry (LC-HRMS) technique, (iv) to elucidate the initial reaction of CP by performing density function theory (DFT) calculations, (v) to assess the aquatic toxicity of reaction solutions using luminescent bacteria *P. phosphoreum* as the test organism and (vi) to seek the feasibility of this Mn(VII) oxidation method for CP degradation in natural waters.

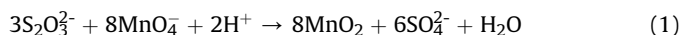
2. Materials and methods

2.1. Chemicals

Potassium permanganate (KMnO₄, purity > 99.9%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). CP (purity > 97.0%) was provided by TCI Development Co., Ltd. (Shanghai, China). The HPLC grade methanol and formic acid were obtained from Merck (Darmstadt, Germany). The HPLC grade ammonium hydroxide solution (~ 25%) was supplied by Roe Scientific Inc. (Newark, USA). All other chemicals were of analytical grade or higher.

The KMnO₄ stock solution (40.0 mM) was prepared in ultrapure water (18.2 MΩ cm) generated from a Millipore Super-Q water system (Millipore, USA). Since CP is slightly soluble in water, the stock solution (5.0 mM) was prepared by dissolving 0.11 g CP in 100 mL of 2 mM NaOH solution. These solutions were stored in amber glass bottles at 4 °C.

A stable colloidal stock solution of MnO₂ (1 mM) was prepared from the reaction of KMnO₄ with Na₂S₂O₃ (Eq. (1)), according to the method of Perez-Benito et al. (1996). More detailed descriptions are given in Text SM-1.



2.2. Origin of different water matrices

Three types of waters, i.e., secondary clarifier effluent (SCE), river water (RW) and synthetic wastewater (SWW), were used for tests. SCE and RW were collected from Wulongkou sewage treatment plant (Zhengzhou, China) and Jiuxiang River (Nanjing, China), respectively, and filtered through 0.45 μm glass fiber membranes (GF/F, Waterman, Maidstone, UK) before use. The SWW was prepared from tap water to contain NaCl (1000 mg L⁻¹), citric acid (50 mg L⁻¹), ascorbic acid (30 mg L⁻¹), saccharose (100 mg L⁻¹) and Na₂HPO₄ (230 mg L⁻¹). The chemical composition of SWW is similar to wastewaters from the pharmaceutical industry (Babić

et al., 2013). All waters were stored at 4 °C and used within 14 days. The main physicochemical parameters of the three water samples were listed in Table SM-1.

2.3. Oxidation procedure

The experiments were conducted in conical flasks at room temperature (25.0 °C). In the 20 mL reaction solutions, the initial concentration of Mn(VII) and CP was 60.0 μM and 20.0 μM, respectively. The reactions were initiated by adding an aliquot of KMnO₄ stock to the CP solutions under mixing on a magnetic stirrer. No buffer was used, and solution pH was adjusted to the desired value of 5.0–10.0 by 0.1 M HCl and 0.1 M NaOH solution. At prescribed time intervals, 1.0 mL of solution was sampled into a 2 mL plastic centrifuge tube containing 50.0 μL of 0.01 M Na₂S₂O₃ to quench the reaction. Then, 500 μL of methanol was added into the tubes to eliminate any possible adsorption effect. These samples were centrifuged for 5 min at 12000 rpm using a Super MiniMax 12k centrifuge (BioMaker, China) to remove MnO₂ particles for subsequent analysis.

In additional experiments, a desired volume of CP stock was spiked into the real water samples to obtain a CP concentration of 20.0 μM for reaction. The pH of the solutions were all adjusted to pH 7.0 using HCl and NaOH to examine the CP removal efficiency.

2.4. Quantification of CP and KMnO₄

The concentration of CP was analyzed by HPLC (Agilent Technologies 1260 infinity II, USA), equipped with a quaternary pump and a variable wavelength detector. Chromatographic separation was achieved on an Agilent ZORBAX SB-C₁₈ column (5 μm, 4.6 × 150 mm) (Agilent Technologies, USA), and the column temperature was 30.0 °C. The mobile phase consisting of methanol (85%) and 0.3% formic acid in water (15%) was eluted at a flow rate of 0.9 mL min⁻¹. The injection volume was 20 μL, and the detection wavelength was 219 nm.

The residual concentration of KMnO₄ was quantified by measuring the absorbance at 525 nm using a TU-1810 UV–Vis spectrophotometer (Purkinje, China) (Jiang et al., 2012).

2.5. Identification of oxidation products (OPs)

The OPs were identified by the solid phase extraction (SPE)-LC-MS method. In this series of experiments, 20 mL of the sample solutions containing 20.0 μM CP and 60.0 μM Mn(VII) were allowed to react for different time (0, 1, 5, 10, 15, 30, 60 and 120 min), and the reaction was terminated by 100 μL of 0.1 M Na₂S₂O₃. These reaction solutions were loaded into CNWBOND LC-C₁₈ SPE cartridges (2.CA0955.0001, 1 g, 6 mL) (CNW, ANPEL Laboratory Technologies, Shanghai, China) in a SPE workstation, washed with 5 mL ultrapure water, dried under vacuum, and then eluted with 4 mL methanol for LC-MS analysis. Samples from different oxidation time were all analyzed to identify as many products as possible.

Separation of OPs was performed on an Agilent 1260 HPLC system. Samples were injected into a Thermo BDS Hypersil C₁₈ column (2.4 μm, 2.1 × 100 mm) (Thermo Fisher Scientific, Waltham, MA) maintained at 30 °C. The mobile phase was 0.1% ammonium hydroxide solution in water (A) and methanol (B) at a flow rate of 0.2 mL min⁻¹. The gradient elution started from 10%B for 4 min, changed to 100%B in 11.5 min and maintained for 9.5 min, then returned to 10%B in 0.5 min and equilibrated for 14.5 min.

Mass detection was conducted using a high resolution hybrid quadrupole time-of-flight mass spectrometer (Triple TOF 5600, AB Sciex, Foster City, CA), equipped with an electrospray ion (ESI)

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