



## Short Communication

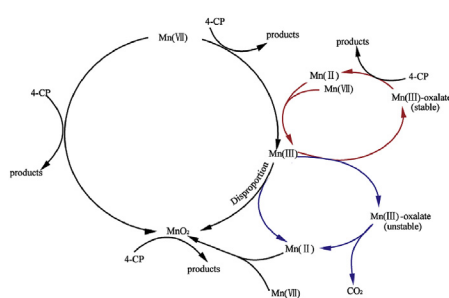
## Role of oxalate in permanganate oxidation of 4-chlorophenol

Zhenyu Shi <sup>a, b</sup>, Jing Zhang <sup>c, \*</sup>, Liang Zhu <sup>a</sup><sup>a</sup> Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes of Ministry of Education, College of Environment, Hohai University, Nanjing, 210098, PR China<sup>b</sup> State Environmental Protection Key Laboratory of Monitoring and Analysis for Organic Pollutants in Surface Water, Environment Monitoring Center of Jiangsu Province, Nanjing, 210036, PR China<sup>c</sup> Key Laboratory of the Three Gorges Reservoir Region's Eco-Environment, Ministry of Education, School of Urban Construction and Environmental Engineering, Chongqing University, Chongqing, 400045, PR China

## HIGHLIGHTS

- The presence of oxalate greatly improved Mn(VII) oxidation of 4-CP at pH 4.0–6.0.
- UV–vis revealed that MnO<sub>2</sub> and Mn(III)-oxalate complexes were formed in situ.
- Oxalate is a strong chelate and reductant in Mn(VII)/oxalate process.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 12 December 2017

Received in revised form

15 March 2018

Accepted 17 March 2018

Available online 20 March 2018

Handling Editor: W Mitch

## Keywords:

Mn(III)

Manganese dioxide

Permanganate

Kinetics

Chlorophenol

## ABSTRACT

The role of oxalate in 4-chlorophenol (4-CP) oxidation by permanganate (Mn(VII)) was explored in this study. The performance of oxalate was heavily depended on pH and oxalate concentration. 4-CP degradation by Mn(VII) was significantly enhanced at pH 4.0–6.0 in the presence of oxalate, while negligible influence was observed at pH 7.0–9.0. The oxalate plays a dual role in Mn(VII) oxidation over the pH range of 4.0–6.0: one is the chelate, which coordinates with Mn(III) to form Mn(III)-oxalate complexes, and the other is the reductant, which reacts with Mn(III) to form Mn(II). The stable Mn(III)-oxalate complexes can work as an efficient oxidant for 4-CP. While their unstable counterparts, due to the lower concentration of oxalate or the higher pH, would auto-decomposed to MnO<sub>2</sub> and Mn(II), and then the MnO<sub>2</sub> works as both a catalyst and an oxidant for the decomposition of 4-CP.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Permanganate (Mn(VII); KMnO<sub>4</sub>) has been widely used as a green oxidant for the in-situ decontamination of soil as well as for

the purification of water and wastewater (Xu et al., 2005; Rodriguez et al., 2007; Liu et al., 2010). It is effective for eliminating taste and odor, controlling the dissolved iron and manganese, and reducing the formation of trihalomethane and other disinfection byproducts. Therefore, more and more researchers are paying attention to Mn(VII) for its high stability, relatively low cost, ease of handling and effectiveness over the wide pH range. In addition, the in situ

\* Corresponding author.

E-mail address: [zhang\\_jing@hhu.edu.cn](mailto:zhang_jing@hhu.edu.cn) (J. Zhang).

formed manganese dioxide is environmentally benign, which serves as a coagulant or adsorbent for the colloids and particles in aqueous (Shaabani et al., 2004). Mn(VII) also has a good selectivity to a wide range of emerging micropollutants, such as chlorophenol, ciprofloxacin, lincomycin, triclosan, estradiol, bisphenol A, sulfamethoxazole, and cefazolin (He et al., 2009; Hu et al., 2010; Jiang et al., 2009, 2012; Zhang et al., 2013, 2015; Li et al., 2016).

Oxalic acid or oxalate, mainly from plant residue decomposition, plant root exudation, and microbial activities, is ubiquitous in the environment (Tu et al., 2007) with its concentration ranging from  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  mol/L in the soil solutions (Xiao and Wu, 2014). It was reported that Mn(III)-oxalate complexes facilitate many redox reactions (Juana and Thomas, 1992; Christelle et al., 1998; Hames et al., 1998; Kurek and Gaudard, 2000), and we also discovered that oxalate increased the performance of Mn(VII) in oxidation. To the best of our knowledge, little information is available on the exact mechanism of oxalate in Mn(VII) oxidation. 4-chlorophenol (4-CP), as a priority pollutant listed by the U.S. EPA, was selected as a model pollutant in this study. The objective of this study was to clarify the exact role of oxalate in Mn(VII) oxidation of 4-CP under various conditions.

## 2. Materials and methods

See Text S1 in Supporting Information.

## 3. Results and discussion

### 3.1. Effect of oxalate dosage on 4-CP removal by Mn(VII) at different pH

As shown in Fig. 1, the addition of oxalate significantly increased the kinetics of 4-CP oxidation by Mn(VII) by 1.7–14.8 folds at pH 4.0. The second-order reaction rate constant ( $k$ ,  $M^{-1} s^{-1}$ ) climbed from 6.89 to  $101.86 M^{-1} s^{-1}$  with the oxalate dosage increasing from 0 to  $60 \mu M$ . But further increasing the oxalate concentration from 60 to  $600 \mu M$  led to a sharp drop of the  $k$  from 101.86 to  $11.94 M^{-1} s^{-1}$ . The same phenomenon was also observed at pH 5.0. But at pH 6.0, the highest removal of 4-CP did not reach until the oxalate concentration increased to  $360 \mu M$ . In the pH range of 7.0–9.0, no enhancement was observed (Fig. S1). Thus, the oxidation of 4-CP by Mn(VII)/oxalate process exhibited a strong pH-dependence. In addition, it should be noted that when the

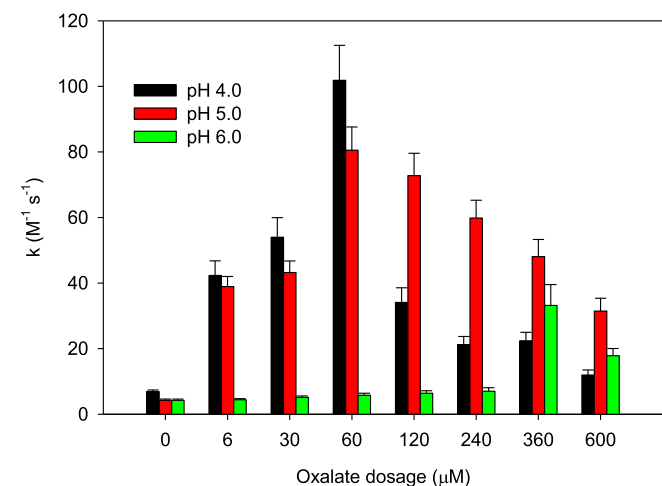


Fig. 1. Effect of oxalate concentration on Mn(VII) oxidation of 4-CP at pH 4.0–6.0. Reaction conditions:  $[4-CP]_0 = 6 \mu M$ ,  $[Mn(VII)]_0 = 60 \mu M$ , and  $T = 25^\circ C$ .

concentration of oxalate was higher than  $60 \mu M$ , the 4-CP presented a stepwise decay at pH 4.0 and 5.0, an initial lag phase and then a rapid phase (Fig. S2). At the end of the reaction, the color of the solution changed from purple to brown with initial oxalate concentration of  $60 \mu M$ , but to colorless with  $600 \mu M$  oxalate (Fig. 2). At pH 6.0, the end solution was dark purple and dark brown in the presence of  $60 \mu M$  and  $600 \mu M$  oxalate, respectively. This indicated that the oxidative mechanism for Mn(VII)/oxalate process at various pH may be different.

### 3.2. Reactive species in Mn(VII)/oxalate process

A variety of reactive intermediates might be formed in the Mn(VII)/oxalate process, one or more of which undoubtedly were responsible for the rapid oxidation of 4-CP. Plausible reactive species included some radicals, i.e. carbon dioxide radicals ( $CO_2^\cdot$ ), superoxide radical ( $O_2^\cdot$ ), and Mn(III), i.e., Mn(IV and III). Carbon dioxide radicals ( $CO_2^\cdot$ ,  $E^0 = -1.9 V$  (NHE)) can be produced through the reaction of oxalate with Mn(III) by abstraction of one electron (Eq. (1)) (Hofrichter et al., 1998; Aken and Agathos, 2002). Moreover, in the presence of oxygen,  $CO_2^\cdot$  might undergo autoxidation (i.e., reaction with  $O_2$ ) with the production of  $CO_2$  and superoxide free radical ( $O_2^\cdot$ ) (Eq. (2)) (Aken and Agathos, 2002), which could enhance 4-CP removal. Thus, experiments were performed under both oxic (dissolved oxygen concentration was  $\sim 8 mg O_2/L$ , i.e.  $250 \mu M$ ) and anoxic conditions at pH 5.0. Fig. S3 shows that the oxygen had no effect on the degradation of 4-CP, which excluded the contribution from radicals in Mn(VII)/oxalate process.

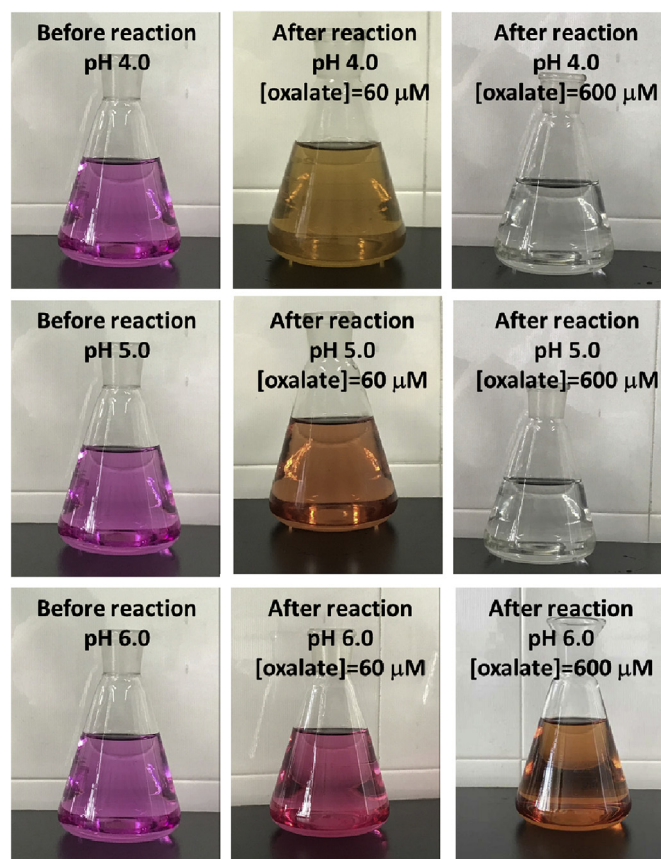
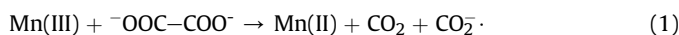


Fig. 2. Photos of reaction solution with different oxalate dosage. Reaction conditions:  $[4-CP]_0 = 6 \mu M$ ,  $[Mn(VII)]_0 = 60 \mu M$ , and  $T = 25^\circ C$ .

Download English Version:

<https://daneshyari.com/en/article/8851311>

Download Persian Version:

<https://daneshyari.com/article/8851311>

[Daneshyari.com](https://daneshyari.com)