



Metal inhibition on the reactivity of manganese dioxide toward organic contaminant oxidation in relation to metal adsorption and ionic potential



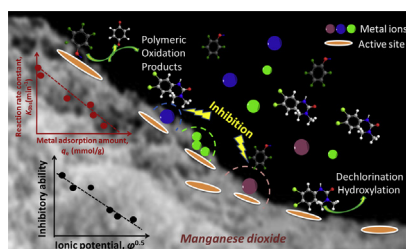
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HIGHLIGHTS

- Dechlorination and hydroxylation are proposed in diuron oxidation by birnessite.
- Metal inhibition efficiencies are determined by metal adsorption on birnessite.
- Intrinsic metal inhibitory ability is correlated with ionic potentials of metals.

GRAPHICAL ABSTRACT



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ABSTRACT

Coexisting metal ions may significantly inhibit the oxidative reactivity of manganese oxides toward organic contaminants in metal-organic multi-pollutant waters. While the metal inhibition on the oxidation of organic contaminants by manganese oxides has previously been reported, the extent of the inhibition in relation to metal properties has not been established. Six alkali, alkaline, and transition metals, as well as two testing metals were evaluated for their abilities to inhibit the reactivity of birnessite. Regardless of the pathways of phenol and diuron oxidation (polymerization vs. breakdown), the extent of metal inhibition depended mainly on the metal itself and its concentration. The observed metal inhibition efficiency followed the order of $Mn^{2+} > Co^{2+} > Cu^{2+} > Al^{3+} > Mg^{2+} > K^+$, consistent with metal adsorption on birnessite. The first-order organic oxidation rate constant (k_{obs}) was linearly negatively correlated with metal adsorption (q_e) on birnessite. These observations demonstrated that the metal inhibition efficiency was determined by metal adsorption on birnessite. The slopes of the k_{obs} - q_e varied among metals and followed the order of $K^+ > Ca^{2+} > Mg^{2+} > Mn^{2+} > Cd^{2+} > Co^{2+} > Cu^{2+} > Al^{3+}$. These slopes defined intrinsic inhibitory abilities of metals. As metals were adsorbed hydrated on birnessite, the intrinsic inhibitory ability was significantly linearly correlated with ionic potentials of metals, leading to a single straight line. Metals with multiple d electrons in the outermost orbit with polarizing energy that promotes hydrolysis sat slightly below the line, and *vice versa*.

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1. Introduction

Via adsorption, catalysis, and redox reaction, manganese oxides

play a critical role in the transport and transformation of organic pollutants (Stone, 1987; Wang et al., 1999; Zhang et al., 2008; Lafferty et al., 2010; Ding et al., 2015). Their excellent oxidative reactivity stems from such characteristics as high standard reduction potential, low zero charge point, and high surface area. They not only transform phenols and aromatic amines into quinones and

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dimer products (Stone and Morgan, 1984; Klausen et al., 1997; Li et al., 2003), but also effectively oxidize low-level pollutants such as pesticides and pharmaceuticals to breakdown products (Gao et al., 2012a; Huguet et al., 2013; Wang et al., 2015; Liao et al., 2016). Steroid estrogens and antibacterial agents with reactive functional groups such as phenol structure can also be oxidized by manganese oxides (Sheng et al., 2009; Xu et al., 2008; Zhang and Huang, 2003, 2005; Mahamallik et al., 2015). Manganese oxides can play roles in the oxidation processes initiated by other oxidizing agents. As an intermediate, for example, MnO₂ was crucial for the humic acid-induced enhancement of phenol oxidation by permanganate (Sun et al., 2013).

Although manganese oxides exhibit high oxidative reactivity toward various organic contaminants, many limitations exist when manganese oxides are applied in water treatment. Usually, manganese oxides are used in the form of fine powder of micron-scale or even nano-scale. This is to retain their desirable high reactivity, but unfavorable for operation in water treatment systems and difficult to separate and recover manganese oxides after reaction. Many strategies have been proposed to overcome these shortcomings with manganese oxides for actual water treatment. Gao et al. (2012b) impregnated hydrous manganese dioxide (HMO) onto a porous polystyrene anion exchange resin to overcome weak HMO mechanical strength to fit the actual removal of sulfadiazine from water. Pan et al. (2014) immobilized nano-HMO with a polystyrene anion exchanger to enhance HMO-mediated phosphate removal. Wu et al. (2005) joined MnO₂ with Fe₂O₃ to form a magnetic oxidizing material and easily recovered adsorbent-catalyst material for the removal of azo-dye from water. Han et al. (2015) synthesized carboxymethyl cellulose (CMC) stabilized MnO₂ nanoparticles to overcome the aggregation of the nanoparticles; the CMC-MnO₂ was more effective than bare MnO₂ for degrading estradiol.

While great progresses have been achieved in evaluating the oxidative reactivity of manganese oxides and overcoming their limitations in actual water treatment, little has been addressed with regard to the performance of manganese dioxides as influenced by the complexity of contaminants in real wastewater with metals and organic contaminants often coexisting. Coexistence of metallic and organic contaminants in wastewater is often encountered, for example, when several effluents of different sources are handled improperly or intentionally combined for treatment in wastewater plants (Hernández-Montoya et al., 2013; Körbahti et al., 2011). Manganese oxides are effective adsorbents for heavy metals; the adsorption competitions occur when two or more metal ions coexist (Qin et al., 2011; Su et al., 2010). The adsorption of a metal is thus expected to influence the oxidative removal of an organic contaminant, when the two contaminants coexist, by manganese oxides. It is imperative to consider the influence of metal ions on the performance of manganese oxides when used in actual contamination removal.

In fact, the inhibition of metal ions on organic oxidation by manganese oxides has been reported and attributed to the occupation of active sites by the metal ions on manganese oxide surface (Stone, 1987; Laha and Luthy, 1999; Barrett and McBride, 2005). Zhang and Huang (2003) compared the inhibition efficiencies of Mn²⁺, Zn²⁺ and Ca²⁺ on triclosan oxidation and found that Mn²⁺ was the strongest inhibitor. When Mn²⁺ was present at 10% of the initial MnO₂ concentration, the initial rate constant, k_{init} , of triclosan oxidation decreased from 1.74 to 0.50 h⁻¹. Xu et al. (2008) evaluated the effects of metal speciation of coexisting Zn²⁺, Cu²⁺, Fe³⁺, and Mn²⁺ on 17 β -estradiol oxidation and found that the metal ions in their uncomplexed species exhibited higher degrees of inhibition than other species. Lin et al. (2009) contributed the high inhibition efficiency of Mn²⁺ to its strong affinity to MnO₂, as well

as a reduction in redox potential of MnO₂/Mn²⁺ when Mn²⁺ concentration increased.

Most of the previous studies have merely determined the inhibition efficiencies of metals at their different initial concentrations. Without a systematic evaluation involving a series of metal ions, the relationship between metal adsorption and organic oxidation by manganese oxides has not been established and the underlying mechanism remains to be unveiled. In this study, the oxidative reactivity of synthetic birnessite as influenced by metal ions was systematically evaluated. Two organic contaminants, phenol and diuron, were chosen as the target contaminants. The two compounds, listed as priority pollutants by the U.S. Environmental Protection Agency and European Commission, respectively, undergo oxidation by MnO₂ via respective polymerization and breakdown pathways. Metal ions (i.e., K⁺, Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Cu²⁺, Cd²⁺ and Al³⁺) were chosen to assess their effects on phenol and diuron oxidation by birnessite. The specific objectives were (a) to assess the influence of different metal ions on oxidation efficiency of MnO₂ toward given organic contaminant, (b) to determine the inhibition efficiency of given metal on the reactivity of MnO₂ toward different organic contaminants, and (c) to correlate the inhibitory abilities of metals to their physicochemical properties. The results of this study are expected to provide an improved understanding of the manganese oxide performance in coexisting metal-organic multi-contaminant water treatment.

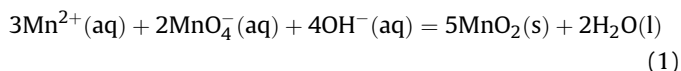
2. Materials and methods

2.1. Reagents and chemicals

Sodium permanganate (NaMnO₄·H₂O, $\geq 97\%$), phenol (C₆H₆O, $\geq 99\%$), and diuron (C₉H₁₀Cl₂N₂O, $\geq 98\%$) were purchased from Sigma-Aldrich and used without further purification. Stock solutions of KCl, MgCl₂, CoCl₂, CuCl₂, MnCl₂, AlCl₃, CaCl₂, and CdCl₂ were prepared from their respective analytical-grade chemicals purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All aqueous solutions were prepared using Milli-Q water.

2.2. Preparation of birnessite

Birnessite was prepared according to the method reported by Murray (1974), which used MnCl₂ and NaMnO₄ in alkaline solution. The ionic reaction equation is as follows:



Briefly, 160 mL of 0.1 M NaMnO₄ and 320 mL of 0.1 M NaOH were added to 3280 mL of N₂-purged Milli-Q water, followed by the dropwise addition of 240 mL of 0.1 M MnCl₂. The reaction took place while constantly stirring and sparging the mixture with nitrogen. The formed birnessite particles were allowed to settle for a period of time and the supernatant was decanted. The remaining suspension was washed with Milli-Q water and centrifuged repeatedly until the electric conductivity of supernatant was below 2.0 $\mu\text{S cm}^{-1}$. Then, birnessite particles were collected by centrifugation and dried by freeze-drying for later use.

X-ray diffraction (XRD) and nitrogen adsorption at low temperature were used to detect the crystal structure and surface area of the synthesized birnessite. Powder X-ray diffraction pattern was recorded using a Bruker D8 powder diffractometer (Germany) equipped with LynxEye array detector using Ni-filtered CuK α radiation. The instrument was operated at a tube voltage of 40 kV and a tube current of 40 mA. Intensities were measured at $2\theta = 5^{\circ}$ – 80° using a scanning rate of $5^{\circ} \text{ min}^{-1}$ at step interval of 0.02° . The

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