Water Research 111 (2017) 234–243

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Role of dissolved Mn(III) in transformation of organic contaminants: Non-oxidative versus oxidative mechanisms

Erdan Hu [a], Ya Zhang [a], Shuyan Wu [a], Jun Wu [a], Liyuan Liang [b], Feng He [a, *]

[a] College of Environment, Zhejiang University of Technology, Hangzhou 310014, China
[b] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, USA

ARTICLE INFO

Article history:
Received 23 October 2016
Received in revised form
14 December 2016
Accepted 5 January 2017
Available online 7 January 2017

Keywords:
Trivalent manganese
Organic contaminants
Non-oxidation
Oxidation

ABSTRACT

Mn(III) is a strong oxidant for one electron transfer, which may be important in the transformation of organic contaminants during water/wastewater treatment and biogeochemical redox processes. This study explored the reaction mechanisms of dissolved Mn(III) with organics. The role of dissolved Mn(III) either as a catalyst or an oxidant in reactions with organics was recognized. Aquo and/or hydroxo (or free) Mn(III), generated from the bisulfite activated permanganate process, facilitated efficient N-dealkylation of atrazine via a β-elimination mechanism, resulting no net redox reaction. In contrast, free Mn(III) degraded 4-chlorophenol via intramolecular redox processes, the same as hydroxyl radical (•OH), resulting in dechlorination,•OH substitution, ring-opening and mineralization. Mn(III)-pyrophosphate compounds did not react with atrazine because complexation by pyrophosphate rendered Mn(III) unable to bond with atrazine, thus the electron and proton transfers between the reactants couldn't occur. However, it degraded 4-chlorophenol at a slower rate compared to free Mn(III), due to its reduced oxidation potential. These results showed two distinct mechanisms on the degradation of organic contaminants and the insights may be applied in natural manganese-rich environments and water treatment processes with manganese compounds.

1. Introduction

Manganese is an important element in environmental processes and in catalytic materials due to its rich redox chemistry and ability to form species of high catalytic activity (Duan et al., 2015; Hocking et al., 2011; Johnson et al., 2016; Palucki et al., 1998; Sun et al., 2015a; b). The most stable and prevalent forms of manganese are Mn(IV) and Mn(II), which have received great attention in Mn biogeochemical studies (Herszage and dos Santos Afonso, 2003; Huynh et al., 2015; Johnson et al., 2016; Luther, 2005; Marafatto et al., 2015). Since the electron acceptance and donation are spatially distinct in the dz^2 and $dx^2{-}y^2$ orbitals of Mn(IV) and Mn(II), one-electron transfer can occur in the reduction of Mn(IV) or oxidation of Mn(II), with intermediates as Mn(III) (Johnson et al., 2016; Luther, 2005; Morgan, 2005; Zhang et al., 2008).

Natural sources of soluble Mn(III) include phytoplankton decomposition in the photosynthetic processes (Webb et al., 2005), biotic or abiotic oxidation of Mn(II) to Mn(IV) (Duckworth et al., 2005; Morgan, 2005; Parker et al., 2004; Webb et al., 2005), microbial (Lin et al., 2012; Myers and Nealson, 1988), photochemical (Marafatto et al., 2015) and chemical reduction of Mn oxides with sulfide (Johnson et al., 2016), Cr^{3+} (Nico and Zasoski, 2000) and organics such as ethylenediaminetetraacetate (Klewicki and Morgan, 1999), triclosan (Zhang and Huang, 2003) and oxalate (Xyla et al., 1992), and nondeductive ligand-promoted dissolution of Mn(III) containing minerals (Duckworth and Sposito, 2005; Klewicki and Morgan, 1999). Recently, aqueous Mn(III) species have been directly detected in suboxic regions of oceanic environments (up to 5 μM and at 100% of the total dissolved Mn) and estuary sediment pore waters (up to 90% of the dissolved Mn) (Dellwig et al., 2012; Madison et al., 2013; Oldham et al., 2015; Trouwborst et al., 2006; Wang and Giammar, 2015; Yakushev et al., 2009). These findings demonstrate that Mn(III) is a major component of dissolved Mn at oxic/anoxic interfaces in the environments. Mn(III) also exists at (sub)nanomolar concentration in oxic waters of lakes and oceans, as has been found for Fe(III) (Trouwborst et al., 2006). Given its ubiquitous and abundant

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* Corresponding author.
E-mail addresses: huerdan@zjut.edu.cn (E. Hu), yazhangsyf@163.com (Y. Zhang), wsy801006@163.com (S. Wu), wujun@zjut.edu.cn (J. Wu), liyuan.liang@pnnl.gov (L. Liang), fenghe@zjut.edu.cn (F. He).

http://dx.doi.org/10.1016/j.watres.2017.01.013

presence in natural waters in comparison to 10^{-16}–10^{-15} M of •OH (He et al., 2014; Schwarzenbach et al., 2003), one of the most common oxidative species in surface waters), the role of Mn(III) in organic cycling may have been overlooked.

Aqueous Mn(III) ion, $Mn^{3+}(aq)$, is a strong Bronsted acid. Two hydrolysis products of monomeric Mn^{3+} have been reported at very low pH solutions with ionic strength of 3 M (Biedermann and Palombari, 1978):

$$Mn^{3+} + H_2O = Mn(OH)^{2+} + H^+ \qquad \log{}^*\beta_1 = 0.4 \pm 0.1 \tag{1}$$

$$Mn^{3+} + 2H_2O = Mn(OH)_2^+ + H^+ \qquad \log{}^*\beta_2 = 0.1 \pm 0.1 \tag{2}$$

Due to its tetragonally distorted electron configuration, free Mn(III) is labile and susceptible to disproportionation to Mn(II) and Mn(IV) according to the following reaction (Davies, 1968):

$$2Mn^{3+}(aq) + 2H_2O = MnO_2(s) + Mn^{2+}(aq) + 4H^+ \ \log K \sim 7–9 \tag{3}$$

Disproportionation of Mn^{3+} is spontaneous and rapid, so Mn^{3+} and its hydrolysis products have short life (seconds) in aqueous solution (Davies, 1968). However, free Mn(III) can be stabilized through complexation with high affinity ligands, such as pyrophosphate (PP), oxalate, citrate, and siderophores, which are widely present in natural aquatic and soil systems (Duckworth and Sposito, 2005; Klewicki and Morgan, 1998; Parker et al., 2004; Wang and Stone, 2008). With a smaller atomic radius and higher electrostatic charge, Mn(III) complexes are even more stable than Mn(II) complexes (Duckworth et al., 2009).

Mn(III) is a strong and important oxidant for one electron transfer reactions (equations (4) and (5)) (Kostka et al., 1995), it could play important roles in water treatment and biogeochemical redox processes.

$$Mn^{3+} + e^- \rightarrow Mn^{2+} \qquad E^0 = +1.51\ V \tag{4}$$

$$MnOOH + 3H^+ + e^- \rightarrow Mn^{2+} + 2H_2O \qquad E^0 = +1.50\ V \tag{5}$$

Mn(III) oxides or complexes are able to rapidly oxidize a variety of organics including ethylenediaminetetraacetic acid (EDTA) (McArdell et al., 1998), nitrilotrismethylenephosphonic acid (NTMP) (Nowack and Stone, 2002), phenol (Nico and Zasoski, 2001), and citrate (Klewicki and Morgan, 1999). Mn(III) centers on the surface of Mn oxides are also involved in the redox processes of Mn minerals (Li et al., 2015; Nico and Zasoski, 2001; Simanova and Peña, 2015). A recent study demonstrated that addition of oxalate could dramatically accelerate the oxidative degradation of carbadox ($C_{11}H_{10}N_4O_4$) by MnO_2, as the reaction of MnO_2 and oxalate can produce dissolved Mn(III) (Chen et al., 2013). Additionally, during Mn(VII) oxidation of triclosan (TCS) and bisphenol A (BPA), dissolved Mn(III) was also identified as an intermediate and considered to enhance the reaction rate (Jiang et al., 2010, 2012).

As soluble, free Mn(III) are unstable under typical environmental conditions, up to now, most of the studies on transformation or interaction of organic contaminants with Mn(III) have been performed with long-lived Mn(III) species, including Mn(III)-rich MnO_2 (Li et al., 2015; Nico and Zasoski, 2000; Zhang and Huang, 2003), naturally occurring Mn(III/IV) oxides (Jun and Martin, 2003; McArdell et al., 1998; Stone, 1987), and soluble Mn(III) complexes (Kostka et al., 1995; Wang et al., 2014). Although dissolved Mn(III) species have been anticipated as a potential environmental oxidant, their reactivity and kinetic characteristics are not fully appreciated or understood. Recently, Sun et al. (2015a; b) reported that soluble free Mn(III) (including aquo and hydroxo Mn^{3+}, i.e., only complexed with H_2O and OH^-) could be generated in permanganate reduction by bisulfite, serving as a strong oxidant for extremely rapid (40–80 ms) degradation of organic contaminants at micromolar concentration. However, the interaction mechanism of organic contaminants with free Mn(III) has not been studied. It remains unknown if the extraordinarily fast reaction of Mn(III) with organics is caused by its strong oxidative capability. Even for reactions of Mn(III) complexes with organics, only simple oxidation mechanism was assumed. In addition, although numerous studies have shown that dissolved Mn(III) intermediates can significantly accelerate the degradation of organic compounds by Mn oxides, the role of Mn(III) remains unclear.

This study was conducted to explore the reaction mechanism of dissolved Mn(III) with organics, with an aim to explain the differences in reaction rates and pathways between organics and various manganese species. Specifically, two typical organics, atrazine and 4-chlorophenol, which are common pollutants in soil, surface water, and groundwater, were selected as the model reactants to probe effects of molecular structure of the organics in the interaction with dissolved Mn(III). Free Mn(III) was generated by permanganate/bisulfite (PM/BS) process (Sun et al., 2015a; b). Degradation of atrazine and 4-chlorophenol by free Mn(III) and Mn(III)-pyrophosphate (Mn(III)-PP) compound was investigated, and compared with the most common oxidant hydroxyl radical (•OH). The use of free Mn(III) and Mn(III)-PP allows us to study Mn(III) as a catalyst or oxidant or both. The results make a new breakthrough on the reaction mechanism of Mn(III) with organics and can provide a better understanding on the degradation of organic contaminants in natural manganese-rich environments and in water treatment processes using manganese compounds.

2. Materials and methods

2.1. Chemicals

Potassium permanganate (99.5%) and sodium thiosulfate pentahydrate (greater than 99.0% purity) were purchased from the Xiaoshan Chemical Reagent Co., Ltd. (Zhejiang, China); sodium bisulfite (AR grade) was obtained from Shisihewei Chemical Reagent Co., Ltd. (Shanghai, China); ferrous sulfate ($FeSO_4 \cdot 7H_2O$, AR grade) and hydrogen peroxide (30.0%, AR grade) were supplied by the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); atrazine (greater than 99.0% purity) was purchased from Yiji Chemical Reagent Co., Ltd. (Shanghai, China); sodium pyrophosphate (PP, AR grade) and 4-chlorophenol (AR grade) were obtained from Aladdin Reagent (Shanghai, China); 1,4-benzoquinone (99.0%), hydroquinone (99.5%), 1,2,4-trihydroxybenzene (99.0%), maleic acid (99.0%), salicylic acid (99.0%), 2,3-dihydroxybenzoic acid (99.0%), 2,5-dihydroxybenzoic acid (99.0%), and catechol (99.0%) were obtained from J&K Scientific Ltd. (Beijing, China); ammeline (98.0%) was obtained from Dr. Ehrenstorfer (Augsburg, Germany); deethydeisopropylatrazine (98.0%) was obtained from AccuStandard (New Haven, U.S.). HPLC grade methanol was supplied by CNW Technologies (Dusseldorf, Germany). All chemicals were used as received. The standard mixtures for instrument calibration were prepared from the single-compound solutions in methanol. Laboratory distilled, deionized water (resistivity of 18.2 MΩ cm) was used in preparation of all aqueous solutions. All samples were stored at 4 °C in the dark, and analyzed within 2 weeks (aqueous-based samples were analyzed within 2 days). The stock solution of $NaHSO_3$ (50.0 mM), $Na_2S_2O_3$ (50.0 mM), and $FeSO_4$ (50.0 mM) were freshly prepared for each set of experiments to avoid oxidation by oxygen. The solutions were adjusted to the target pH levels by adding H_2SO_4 or NaOH.