Oxidation of nonylphenol and octylphenol by manganese dioxide: Kinetics and pathways

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ABSTRACT

Due to their potent estrogenicity and ubiquitous occurrence, non-ionic surfactant metabolites nonylphenol (NP) and octylphenol (OP) are of significant concern. Abiotic chemical oxidation by naturally abundant metal oxides may be an important route of their environmental attenuation, but is poorly understood. We investigated the reaction kinetics and pathways of NP and OP with MnO_2. At pH 5.5 and 100 mg/L δ-MnO_2, 92, 84 and 76% of 4-*n*-NP, 4-*tert*-OP and technical nonylphenol (tNP) was transformed in 90 min, respectively. A further experiment using a Mn-containing soil and Mn-removed soil confirmed that soil MnO_2 caused NP removal. Multiple reaction products, including hydroquinone, hydroxylated products, dimers and trimers were identified through fragmentation analysis by GC–MS/MS and UPLC–MS/MS, allowing the construction of tentative pathways. This study suggested that abiotic oxidation by MnO_2 may contribute to the dissipation of tNP, 4-*n*-NP, 4-*tert*-OP and their analogues in the natural environment.

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1. Introduction

Nonylphenol (NP) and octylphenol (OP) are raw materials and also hydrolytic metabolites of NP ethoxylates (NPEOs) and OP ethoxylates (OPEOs) which are non-ionic surfactants widely used in agricultural, industrial and domestic products (Soares et al., 2008; Ying et al., 2002). Nonylphenol is one of the high production volume chemicals and the production of the technical nonylphenol (tNP, mixture of ring and chain isomers) in the United States was 45–227 thousand tons in 2006 (USEPA, 2006) and the estimated annual release to soil by sewage sludge disposal and application was about 1.03–3.31 thousand tons (Venkatesan and Halden, 2013). Due to the widespread use of NPEOs and OPEOs, NP and OP are frequently found in soil, water and sediment (Mao et al., 2012). For example, Writer et al. (2012) investigated the fate of NP in Redwood River of Minnesota and found that the mean concentrations of NP in water and sediment downstream from a wastewater treatment plant were 620 ng/L and 140 μg/kg, respectively. Nonylphenol and OP are known as environmental estrogens and many studies have shown that NP and OP may have developmental toxicity and other effects on aquatic and terrestrial species or potentially human health (Domene et al., 2009; Soares et al., 2008). In different *in vivo* and *in vitro* studies, the potency of NP relative to 17β-estradiol ranges from 7.2×10^{-7} to 0.05, with

an arithmetic mean potency of 0.003 from *in vitro* studies and 0.023 from *in vivo* studies (Soares et al., 2008).

To assess the potential health and ecological risks of NP and OP, a thorough understanding of their fate and transport processes is essential. Photolysis, biodegradation, and chemical oxidation may all contribute to the attenuation of NP and OP in water, soil and sediment. So far, however, the importance of abiotic oxidation has been largely ignored in the elucidation of environmental fate of NP and OP. Manganese oxides/hydroxides are important components of most soils, sediments and water ecosystems. Their characteristic properties, such as low point of zero charge, dynamic redox behavior and large surface areas make them chemically active in oxidizing organic and inorganic compounds (Negra et al., 2005). Previous studies showed that manganese oxides/hydroxides were effective at oxidizing sulfamethazine, lincosamide, acid azo dyes, bisphenol A, tetrachlorophenols and trichlorophenols (Chen et al., 2010; Clarke et al., 2010; Gao et al., 2012; Lin et al., 2009a; Xu et al., 2008; Zhang et al., 2008; Zhao et al., 2009). It may thus be hypothesized that MnO_2 facilitated oxidation is potentially important for NP and OP in the environment. However, the substituted phenols commonly studied in the literature so far are either chlorinated or short alky substituted. Nonylphenol and octylphenol have numerous isomers and much longer alky substitutions (9 and 8 carbons respectively). The long alky substitutions are expected to affect sorption onto MnO_2 surfaces, and reactivity with radicals, potentially leading to differences in reaction kinetics and pathways. The objective of this study was to investigate the kinetics, influencing factors and pathways of the oxidation of tNP, 4-*n*-NP and

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4-*tert*-OP by MnO_2. The oxidation kinetics were measured under different conditions, including different initial MnO_2 concentrations or pH, and presence of cosolutes such as Mn^{2+}, Ca^{2+} and humic acids. The role of MnO_2 dioxide-catalyzed oxidation in the natural attenuation of NP was further validated in soil.

2. Materials and methods

2.1. Chemicals and soil

Technical NP (tNP), a mixture of NP isomers with branched side chains (CAS: 84852-15-3) was purchased from TCI America (Portland, OR); 4-*n*-NP (>98%, CAS: 104-40-5) was from Alfa Aesar (Ward Hill, MA); and 4-*tert*-OP (>97%, CAS: 140-66-9) and hydroxylamine hydrochloride (99+%) were from Sigma–Aldrich (St. Louis, MO). Information on other chemicals is given in Supplementary Information (SI).

Manganese dioxide (δ-MnO_2) was synthesized according to Murray's method (Murray, 1974). Briefly, 6.56 L of reagent water was constantly sparged with nitrogen and then mixed with 320 mL of 0.1 M $NaMnO_4$ and 640 mL of 0.1 M NaOH. The constantly stirred solution was added drop-wise with 80 mL of 0.1 M $MnCl_2$. The newly formed MnO_2 particles were allowed to settle, and the supernatant was decanted and replaced with fresh reagent water several times until the conductivity of the supernatant was below 2 μS/cm. The MnO_2 suspensions were stored at 4 °C and were diluted to appropriate concentrations prior to use. The surface area of MnO_2 was measured to be 269.1 m^2/g (Micromeritics 2100, Micromeritics, Norcross, GA). Powder X-ray diffraction (XRD) analysis (Bruker D8 Advance Diffractometer, Bruker AXS, WI) with Cu Kα radiation showed that the synthetic MnO_2 was poorly crystallized (Fig. S1). The XRD pattern showed that the synthesized MnO_2 was turbostratic birnessite (Na^+ and H_2O) having hexagonal layer symmetry, which is commonly found in soils (Drits et al., 2007). A well characterized fine, sequic, mesic Typic Kandihumult soil with high Mn content was taken at the 700 m elevation in the Klamath Mountains, CA. The soil was sieved through a 2 mm mesh and air dried. The Mn and Fe contents were 4.2 and 438 g/kg as determined by the standard citrate-bicarbonate-dithionite method and other selected properties of the soil are given in Table S1. The soil was further ground to pass a 60 mesh (0.25 mm) sieve, and a subsample was selectively removed the indigenous Mn oxides with hydroxylamine hydrochloride to produce Mn-removed soil (Neaman et al., 2004).

2.2. Reaction setup

Batch experiments were conducted in 125-mL wide mouth amber borosilicate glass bottles with Teflon-faced caps at room temperature. The reaction solution temperature was 25.2 ± 0.5 °C (mean ± standard deviation). Reaction solutions (methanol: water, 40:60, v/v) were maintained at the desired pH using 0.01 mol/L of the following pH buffers: pH 4.5 and pH 5.5, acetic acid/sodium acetate; pH 6.5 and pH 7.5, 4-morpholinepropanesulfonic acid (MOPS) and its sodium salt; pH 8.6 and pH 9.6, 2-(cyclohexylamino) ethanesulfonic acid (CHES) and its sodium salt. Sodium perchlorate was added to maintain the ionic strength at 0.01 mol/L. The addition of methanol was necessary to increase the solubility of NP and OP. The effects of methanol on the recoveries and reaction rates of NP and OP are given in SI. The MnO_2 solution (50 mL) was first stirred at 480 rpm for 1 h and the reaction was initiated by adding 50 μL of 1000 mg/L tNP, 4-*n*-NP or 4-*tert*-OP stock solution. At different time intervals from the onset of reaction, 1.0 mL of the reaction solution was withdrawn with a pipette and transferred to 2-mL HPLC vials containing 10 μL L-ascorbic acid solution (50 mg/mL) and immediately vortexed for 10 s for quenching. All samples were stored at 4 °C and analyzed by HPLC within 24 h. Preliminary experiments showed that there was no change in the concentration during the short storage.

The effect of pH was evaluated in solutions maintained at different pH values under the fixed conditions of 100 mg/L MnO_2, 1 mg/L NP or OP, and 0.01 mol/L ionic strength. The cosolute effects of cations were investigated by fortifying 0.01 mol/L of $CaCl_2$ or $MgCl_2$, or 1×10^{-5} mol/L $MnCl_2$ at pH 5.5. The effect of humic acid was determined at pH 5.5 by amending the reaction solution with Sigma–Aldrich humic acid (CAS: 68131-04-4. Sigma–Aldrich, St. Louis, MO) at 0.1 or 10 mg/L under the fixed conditions of 100 mg/L MnO_2, 1 mg/L NP or OP, and 0.01 mol/L ionic strength.

To validate the role of MnO_2-catalyzed oxidation in soil, tNP (50 μg/L) was reacted with 100 mg/L synthetic MnO_2, or suspension of 0.6 g Mn-containing soil in 40 mL water, or 0.6 g Mn-removed soil in 40-mL water. No pH buffers were used in this experiment and the measured pH values were both 6.30. Before the reaction, the soils were autoclaved at 121 °C for 45 min over three consecutive days and sodium azide was added at 200 mg/L to the soil suspension to suppress microbial transformation. At selected time intervals (0, 2, 4, 6, 10, 20, 30 min for synthetic MnO_2; 0, 4, 12, 24, 36 and 48 h for Mn-containing soil; and 0, 12, 24, 48, 96 and 168 h for Mn-removed soil), 0.5 mL of 50 mg/mL L-ascorbic acid solution was added to quench the reaction.

2.3. Chemical analysis

Analysis of tNP, 4-*n*-NP and 4-*tert*-OP was carried out on an Agilent 1100 HPLC (Agilent Technologies, Wilmington, DE) coupled with a fluorescence detector. Samples containing low concentrations of tNP were extracted by 15 mL hexane twice and analyzed on an Agilent 6890 GC with 5973 MSD. Both GC–MS/MS (with or without silylation) and UPLC–MS/MS were used in this study for the identification of reaction products. For silylation derivatization, 150 μL of *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride (TMCS) was added, and the mixture kept at room temperature for 2 h. More detailed information is given in SI. All data analysis was done using SPSS 16.0 (IBM, Armonk, NY).

3. Results and discussion

3.1. Kinetics and influencing factors

3.1.1. Removal efficacy

In general, oxidation of tNP, 4-*n*-NP and 4-*tert*-OP by MnO_2 was fast and efficient, with the rate of oxidation following the order of 4-*n*-NP > 4-*tert*-OP > tNP (Fig. 1A). For example, with 1.0 mg/L tNP, 4-*n*-NP or 4-*tert*-OP and 100 mg/L MnO_2 at pH 5.5, after 90 min, 76.3 ± 0.2, 92 ± 2 and 83.7 ± 0.5% of the initial chemical disappeared from the solution, respectively, and the corresponding half-lives were about 45, 23 and 35 min (Fig. 1A). In contrast, the levels of these chemicals remained unchanged in the MnO_2-free controls (Table S2). The details on the derivation of kinetic expressions are given in Text S3 of SI.

3.1.2. Effect of initial MnO_2 loadings

With increasing initial MnO_2 concentrations, the removal of tNP, 4-*n*-NP or 4-*tert*-OP increased. For example, at pH 5.5, the removal after 90 min for 1.0 mg/L tNP with initially 100, 50, 25 and 12.5 mg/L MnO_2 were 76.3 ± 0.2, 48.8 ± 0.9, 34.1 ± 0.6 and 21 ± 2%, respectively (Fig. 1B). The removal of 4-*n*-NP and 4-*tert*-OP also showed a similar trend (Figs. S2 and S3). According to Equation S6, when plotting $\log_{10} k_{oberv}$ against $\log_{10}$ [MnO_2], the slope of the regression line was the order with respect to MnO_2 (Fig. 1C). When reacting with tNP, 4-*n*-NP and 4-*tert*-OP, the orders of MnO_2 were determined to be 0.94 ± 0.05, 0.6 ± 0.1 and 1.01 ± 0.09, respectively. In previous studies, the orders of MnO_2 were 0.8 and 1.25, respectively, when reacting with tetrabromobisphenol A (TBBPA) and bisphenol F (Lin et al., 2009b; Lu et al., 2011). Zhao et al. (2009) showed that the order of MnO_2 ranged from 0.45 to 1.64 when reacting with three tetrachlorophenols and three trichlorophenols. Therefore, the order of MnO_2 was highly dependent on the substrates. In this study, the orders of MnO_2 were similar between tNP and 4-*tert*-OP, but were smaller for 4-*n*-NP. This may be attributed to the structural differences among these three substrates. It is known that tNP is a mixture of branched nonyl-substituted phenols, mostly with a quaternary α carbon, e.g., 4-[1,1,2-trimethylhexyl]phenol (Thiele et al., 2004); while the nonyl substitution in 4-*n*-NP is linear. 4-*tert*-Octylphenol also has the quaternary α carbon with two methyl substitutions. Thus, structurally, tNP is more similar to 4-*tert*-OP than to 4-*n*-NP. This phenomenon indicates that the side chain properties such as the length and bulkiness may significantly affect the chemical reactivity of NP isomers.

3.1.3. Effect of solution pH

The oxidation of tNP, 4-*n*-NP and 4-*tert*-OP by MnO_2 was significantly influenced by pH, with the reaction rate consistently decreasing with increasing pH (Figs. 1D, E and S4 and S5). For example, after 90 min, the removal for 1.0 mg/L tNP with 100 mg/L MnO_2 at pH 4.5, 5.5, 6.5, 7.5 and 8.6 were 94.3 ± 0.4, 76.3 ± 0.2, 24 ± 2, 21 ± 2, and 13 ± 2%, respectively; while at pH 9.6 there was no appreciable dissipation of tNP (data not shown). According to Equation S7, plotting $\log_{10} k_{oberv}$ against pH would yield a slope representing the reaction order with respect to H^+ (Fig. 1E). When reacting with tNP, 4-*n*-NP and 4-*tert*-OP, the orders of H^+ were 0.35 ± 0.06, 0.36 ± 0.08 and 0.37 ± 0.03, respectively (Fig. 1E). Thus, the effect of pH was generally similar among tNP, 4-*n*-NP and 4-*tert*-OP and the order of H^+ between pH 4.5 to 8.6 was about 0.36.