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Oxidation of bisphenol F (BPF) by manganese dioxide

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ABSTRACT

Bisphenol F (BPF), an environmental estrogen, is used as a monomer in plastic industry and its environmental fate and decontamination are emerging concern. This study focused on the kinetics, influencing factors and pathways of its oxidation by MnO_2. At pH 5.5, about 90% of BPF was oxidized in 20 min in a solution containing 100 μM MnO_2 and 4.4 μM BPF. The reaction was pH-dependent, following an order of pH 4.5 > pH 5.5 > pH 8.6 > pH 7.5 > pH 6.5 > pH 9.6. Humic acids inhibited the reaction at low (≤pH 5.5) and high pH (≥pH 8.6) at high concentrations. In addition, metal ions and anions also suppressed the reaction, following the order $Mn^{2+} > Ca^{2+} > Mg^{2+} > Na^{+}$ and $HPO_4^{2-} > Cl^{-} > NO_3^{-} \approx SO_4^{2-}$, respectively. A total of 5 products were identified, from which a tentative pathway was proposed.

1. Introduction

Bisphenol F (4,4′-dihydroxydiphenyl-methane, BPF) is a member of bisphenols, which are a group of compounds with two hydroxyphenyl functionalities. Bisphenol F is structurally similar to bisphenol A (4,4′-dihydroxydiphenyl-propane, BPA) – the most widely used bisphenol (Fig. 1). Like BPA, BPF is used as the starting monomer for polycarbonate plastics and epoxy resins that are commonly found in household items, such as plastic bottles and cups, bicycle and motorcycle helmets, dental materials, protective coatings on food, soft drink cans and water pipes (Cabaton et al., 2009; Danzl et al., 2009). Bisphenol F epoxy resin has lower viscosity and better resistance against solvents than BPA epoxy resin, and hence the production of BPF has increased over the years (Danzl et al., 2009).

Like BPA, BPF is increasingly detected in environmental media due to its widespread use. For instance, Fromme et al. (2002) found BPF in 77% of the surface water samples (0.0001–0.180 μg/L, $n = 25$), 72% of the sewage water samples (0.022–0.123 μg/L, $n = 25$), and 58% of the sediment samples (1.2–7.3 μg/kg, $n = 7$) in Germany. Stachel et al. (2003) also detected BPF in surface water and freshly deposited sediments in River Elbe and its tributaries in Germany. Bisphenol F is a xenoestrogen as shown *in vivo* in the uterotrophic assay of BPF-exposed rats (Yamasaki et al., 2002). *In vitro*, BPF showed higher estrogenicity than BPA in a yeast two-hybrid system, human MCF-7 cells and human HepG2 cells (Cabaton et al., 2009; Stroheker et al., 2004). For example, in the human MCF-7 cell proliferation assay (E-Screen assay), estrogenicity of BPF was about 5 times higher than BPA (Stroheker et al., 2004).

Elucidation of transformations of BPF is important for understanding its natural attenuation in the environment as well as for exploring possibilities for decontamination. Inoue et al. (2008) reported that BPF was completely degraded in 9 h by *Sphingobium yanoikuyae* isolated from river water. Suzuki et al. (2010) and Yamada et al. (2010) found that peroxidase and tyrosinase effectively oxidized BPA, BPF and other bisphenol derivatives, especially in the presence of H_2O_2. Xiao et al. (2007) further observed that β-cyclodextrin (β-CD) was able to enhance photodegradation of BPF by TiO_2.

Manganese oxides/hydroxides are important components in most soils, waters and sediments. The average hydroquinone-extractable Mn content in 50 field-moist soils was 5.5 mmol/kg (0.03% by weight) (Tebo et al., 2004). One study shows the level of manganese oxides in sediment as high as 205 mmol/kg (Tessier et al., 1996). Owing to their high negative surface charge, low point of zero charge, large surface area, low crystallinity and dynamic redox behavior, they are geochemically more active than that indicated by their abundance (Negra et al., 2005). Many studies show that manganese oxides/hydroxides are efficient in degrading different organic pollutants, including phenolic compounds (Lin et al., 2009), amines (Chen et al., 2010), azo compounds (Clarke et al., 2010), and steroid hormones (Xu et al., 2008).

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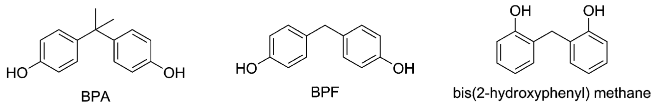

Fig. 1. Chemical structures of bisphenol A (BPA), bisphenol F (BPF) and bis (2-hydroxyphenyl) methane.

In this study, we examined degradation of BPF by synthesized manganese dioxide (δ-MnO_2) that was similar to the naturally abundant birnessite. The kinetics of the reaction and the reaction pathways were explored, and the influences of pH and common cosolutes, including humic acid, common cations and anions, on the reaction were considered.

2. Materials and methods

2.1. Chemicals

Hydroquinone (99%), and bisphenol F (98%), bisphenol A (98%), bis (2-hydroxyphenyl) methane (98%) and 2,2′-diphenol (97%) and analytical grade chemicals of manganese chloride (>98%), sodium permanganate (>97%), humic acid (sodium saturated), 4-morpholinepropanesulfonic acid (MOPS), 2-(cyclohexylamino) ethanesulfonic acid (CHES), and L-ascorbic acid were purchased from Sigma–Aldrich (St. Louis, MO). Silylation reagent *N*, *O*-bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane (BSTFA + TMCS, 99:1) was purchased from Supelco (Bellefonte, PA). 4-Hydroxybenzaldehyde (98%) was purchased from VWR (West Chester, PA). 4-Hydroxybenzyl alcohol (97%) and other chemicals and solvents were all purchased from Fisher Scientific (Fair Lawn, NJ). Reagent water (18.3 M-cm resistivity) was prepared using a Barnstead Nanopure water system (Barnstead/Thermolyne, Dubuque, IA). Stock solution of 4.40 mM BPF was prepared in methanol and stored at 4 °C prior to use.

Manganese dioxide (δ-MnO_2) was synthesized according to Murray's method (Murray, 1974). Briefly, 320 mL of 0.1 M $NaMnO_4$ and 640 mL of 0.1 M NaOH were added to 6.56 L of nitrogen-purged reagent water, followed by a dropwise addition of 480 mL of 0.1 M $MnCl_2$ while keeping the solution constantly sparged with nitrogen. The 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 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 was measured to be 269.1 m^2/g on a Micromeritics 2100 system (Micromeritics, Norcross, GA). Powder X-ray diffraction analysis carried out on a Bruker D8 Advance Diffractometer (Bruker AXS, WI) with Cu Kα radiation showed that the synthetic MnO_2 was amorphous, as shown in the X-ray diffractogram in the Supplementary data. The synthesized MnO_2 was structurally similar to the naturally occurring mineral birnesite.

2.2. Reaction setup

Batch experiments were conducted in 125-mL wide-mouth amber borosilicate glass bottles with Teflon-faced caps at room temperature with the reaction solution temperature measured to be 25 ± 2 °C. Reaction mixtures were constantly stirred with Teflon-coated magnetic stir bars at 480 rpm on a Variomag® Poly 15 plate (Fisher Scientific, Fair Lawn, NJ). Reaction solutions were maintained at a constant ionic strength of 0.01 M (by adding suitable amount of sodium chloride) and different pH with 10 mM of these following buffers: pH 4.5 and pH 5.5, acetic acid/sodium acetate; pH 6.5 and pH 7.5, MOPS and its sodium salt; pH 8.6 and pH 9.6, CHES and its sodium salt.

Prior to the initiation of reactions, MnO_2 suspensions in buffer solutions (40 mL) with or without cosolutes (e.g., $CaCl_2$, $MnCl_2$, $MgCl_2$, humic acid) were constantly stirred at 480 rpm for about 16 h. Reactions were initiated by adding 40 μL of 4.4 mM BPF in methanol to the continuously stirred MnO_2 suspensions. Aliquots of 1.0 mL of reaction mixture were periodically withdrawn with a pipette, transferred to 2-mL HPLC vials containing 5 μL L-ascorbic acid solutions (50 mg/mL) and immediately vortexed for 10 s. Dissolution of the MnO_2 by L-ascorbic acid released the adsorbed BPF and reaction products and quickly quenched the reaction. All samples were stored at 4 °C and analyzed within 24 h. Preliminary experiments showed that there was no change in concentration during the storage.

The effect of initial MnO_2 loadings on BPF removal was studied by considering different MnO_2 concentrations (0, 12.5, 25, 50, 100 and 200 μM) under the fixed conditions of pH 5.5, 4.4 μM BPF, and 0.01 M ionic strength. The effect of pH was evaluated in solutions with different pH values (4.5, 5.5, 6.5, 8.6, and 9.6), under the fixed conditions of 100 μM MnO_2, 4.4 μM BPF, and 0.01 M ionic strength. The cosolute effects of cations and anions were investigated by fortifying two different concentrations (e.g., 0.01 and 0.05 M) of the cosolutes including $CaCl_2$, $MgCl_2$, $MnCl_2$, Na_2SO_4, Na_2HPO_4 and $NaNO_3$ under the fixed conditions of 100 μM MnO_2, 4.4 μM BPF, and pH 5.5. The effect of humic acid was determined at pH 5.5 and 8.6 by amending the reaction solution with humic acid (Sigma–Aldrich St. Louis, MO) at 0.1 or 10 mg/L under the fixed conditions of 100 μM MnO_2, 4.4 μM BPF, and 0.01 M ionic strength. As analogs to BPF, BPA and bis(2-hydroxyphenyl) methane were also reacted with 100 μM MnO_2 at pH 5.5 and 0.01 M ionic strength for the purpose of structure–activity relationship evaluation.

2.3. Chemical analysis

Analysis of BPF, BPA and bis(2-hydroxyphenyl) methane was carried out on an Agilent 1100 HPLC (Agilent Technologies, Wilmington, DE) coupled with a multi-wavelength UV detector and a Dionex Acclaim® 120 C18 column (4.6 × 250 mm, 5 μm). For BPF, the isocratic mobile phase was acetonitrile (50%)–water (50%) at 1.0 mL/min and the UV wavelength was 200 nm. The injection volume was 25 μL. Under these conditions, the typical retention time for BPF was 5.4 min. For BPA and bis(2-hydroxyphenyl) methane, all the HPLC conditions were the same except the mobile phase was acetonitrile (75%)–water (25%).

Identification of reaction products followed a similar procedure described in Lin et al. (2009). Briefly, 100 mL of reaction solution containing 44 μM BPF and 800 μM MnO_2 were reacted in 10 mM sodium acetate solutions (pH 5.5), and the reaction was quenched after 4 h by adding an excess amount of L-ascorbic acid. The products in the reaction solution were extracted twice with 50 mL methylene chloride and the extract was then condensed to near dryness and dissolved in 350 μL benzene. The sample was derivatized by addition of 150 μL of BSTFA + TMCS and analyzed on an Agilent 6890 GC coupled with 5975 mass spectrometer (MS) (Agilent Technologies, Wilmington, DE). Tentative identification of reaction products was based on comparison with authentic standards for their retention times and mass spectra. Detailed information may be found in the Supplementary Data.

2.4. Molecular modeling

Molecular modeling was performed using a Hyperchem 8.0 program (Hypercube, Gainesville, FL). Semiempirical quantum mechanical Austin model 1 (AM1) molecular orbital method was used for geometry optimization with Polak–Ribiere algorithm until RMS gradient (total energy gradient calculated as a root mean square) less than 0.01 kcal/mol. The highest occupied molecular orbitals (HOMO) for gas and aqueous phases were calculated.

3. Results and discussion

3.1. Removal efficiency and orders of reaction

In the presence of MnO_2, BPF rapidly dissipated from the reaction mixture at pH 5.5 (Fig. 2). For example, about 90% of the initial BPF was reacted in 20 min in the solution containing 100 μM MnO_2,

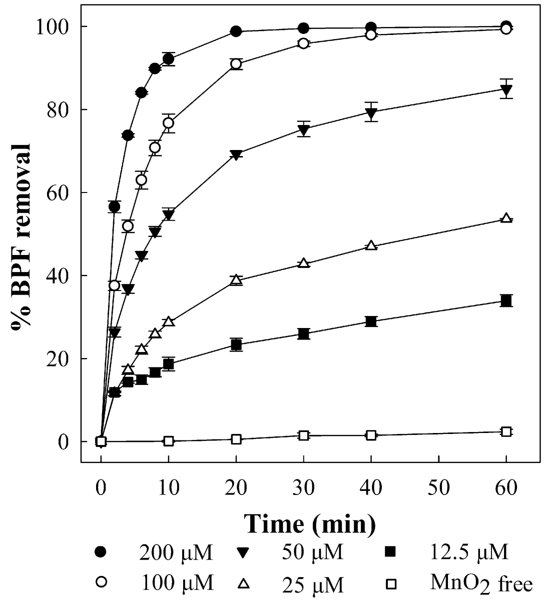

Fig. 2. Removal efficiency of bisphenol F (BPF) at different initial MnO_2 concentrations. Data points are given as mean ± standard deviation ($n = 3$). The other initial conditions are pH 5.5, ionic strength 10 mM, and BPF concentration 4.4 μM.