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Oxidation of bisphenol A by nonradical activation of peroxymonosulfate in the presence of amorphous manganese dioxide

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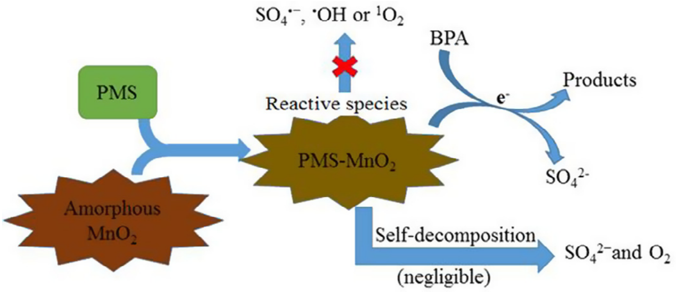
HIGHLIGHTS

- Amorphous MnO_2 was successfully prepared for heterogeneous PMS activation.
- Reactive complexes of PMS-MnO_2 were responsible for selective degradation of organic compounds.
- The effects of water matrices on BPA degradation were investigated in detail.
- Degradation pathways of BPA were illustrated.
- Linear free energy relationships were well-established.

GRAPHICAL ABSTRACT



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ABSTRACT

This work demonstrated that bisphenol A (BPA) was rapidly degraded by peroxymonosulfate (PMS) in the presence of amorphous manganese dioxide (MnO_2). Chemical quenching experiments and electron paramagnetic resonance spectroscopy (EPR) suggested that hydroxyl radical ($^{\cdot}OH$), sulfate radical ($SO_4^{\cdot -}$), and singlet oxygen ($^1O_2$) were unlikely responsible for BPA oxidation. As such, a nonradical mechanism involving the formation of reactive complexes between amorphous MnO_2 and PMS was tentatively proposed based on the PMS decomposition and Raman spectra. The presence of phosphate ions ($H_2PO_4^-$) remarkably suppressed the degradation of BPA, while the addition of divalent metal ions (Ca^{2+}, Mg^{2+}, and Zn^{2+}) appreciably enhanced BPA degradation. The discrepancy was likely resulted from their contrasting influences on the formation of reactive PMS-MnO_2 complexes. Based on identified oxidation products (i.e., dimers, 4-hydroxycumyl alcohol, mono-hydroxylated BPA and its quinone derivative) by liquid chromatography tandem mass spectrometry, the transformation pathways of BPA in amorphous MnO_2/PMS system involving one-electron oxidation, radical coupling, bond cleavage, and hydroxylation were proposed. In addition to BPA, thirteen other selected phenolic compounds were also efficiently degraded by amorphous MnO_2/PMS system, and good correlations between apparent pseudo-first-order reaction rate constants (k_{obs}) and descriptor variables (i.e., Hammett constants σ^+ and half-wave potentials $E_{1/2}$) were obtained.

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1. Introduction

Advanced oxidation processes (AOPs) based on peroxymonosulfate (PMS) have attracted great interests for water decontamination in recent years [1,2]. PMS, in the form of Oxone, is a stable white solid for convenient storage and transportation, and it has a great solubility in water (> 250 g/L at 20 °C) [3]. Various methods have been reported for activating PMS in literatures, including energy (i.e., UV [4], heat [5], ultrasound [6]), transition metals ions or oxides [7–9], carbon materials [10,11], and organics [12,13].

Recently, manganese dioxide (MnO_2) with different crystallographic phases have been deemed to be promising heterogeneous catalysts of PMS for the degradation of phenols [14] and antibiotics [15] due to their less toxicity and high catalytic efficiency, as well as large natural abundance of manganese element. The crystal structure [16], chemical state [17], and nanoarchitecture [18] all exert profound influences on the catalytic efficiency of crystalline MnO_2. It is generally accepted that crystalline MnO_2 can induce the decomposition of PMS producing sulfate radicals ($SO_4^{\cdot -}$) and hydroxyl radicals ($^{\cdot}OH$) through Eqs. (1)–(3) [16,19]:

$$HSO_5^- + 2MnO_2 \rightarrow SO_5^{\cdot -} + OH^- + Mn_2O_3 \tag{1}$$

$$HSO_5^- + Mn_2O_3 \rightarrow SO_4^{\cdot -} + H^+ + 2MnO_2 \tag{2}$$

$$SO_4^{\cdot -} + H_2O \rightarrow HO^{\cdot} + H^+ + SO_4^{2-} \tag{3}$$

Although crystalline MnO_2 shows good catalytic ability for PMS, the preparation processes are complex and need great energy input, which may limit its practical application. In this regard, amorphous MnO_2 may be an attractive alternative, because it can be easily obtained through simple oxidation-reduction reactions involving MnO_4^- or Mn^{2+} under ambient conditions [20–22]. Many literatures have reported the oxidative capacity of amorphous MnO_2 for phenols [23], anilines [24,25], and antibiotics [25–27], but only few studies focused on its catalytic ability for PMS activation. For example, Mao et al. [28,29] reported that amorphous MnO_2 prepared by stoichiometrically mixing $KMnO_4$ and $Na_2S_2O_3$ could activate PMS for the degradation of acid orange 7 and phenol. However, to the best of our knowledge, the mechanism of amorphous MnO_2 for PMS activation remains ambiguous, which was reported to be likely determined by catalysts nature [30]. Additionally, a systematic study concerning the influences of water matrices on contaminants degradation in amorphous MnO_2/PMS system also has not been conducted yet.

In this work, the feasibility of amorphous MnO_2 to activate PMS for degrading bisphenol A (BPA), a ubiquitous endocrine disruptor in the aquatic environment [31], was systematically investigated. The primary oxidizing species in amorphous MnO_2/PMS system was identified and underlying mechanism was explored from chemical quenching experiments, electron paramagnetic resonance spectroscopy (EPR), and Raman spectroscopy. Moreover, the influences of MnO_2 and PMS dosages, solution pH, as well as common inorganic anions and metal ions on BPA degradation were evaluated. Oxidative effectiveness of amorphous MnO_2/PMS system for BPA treatment in real waters was examined. The oxidation products of BPA in amorphous MnO_2/PMS system were subsequently explored by high pressure liquid chromatography with electrospray ionization-triple quadrupole mass spectrometry (HPLC/ESI-QqQMS), and transformation pathways were tentatively proposed. Finally, the degradation of thirteen other selected phenolic compounds was comparatively studied and linear free energy relationships (LFERs) were established to evaluate the effect of substituents on the reaction kinetics of various phenolic compounds.

2. Materials and methods

2.1. Chemicals

PMS (Oxone, $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$), 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO), 2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonic acid diammonium (ABTS), furfuryl alcohol (FFA) and selected organic compounds including BPA, phenol (PN), 3 methylphenols (MPs), 4 chlorophenols (CPs), 3 methoxyphenols (MeOPs), 4-phenoxyphenol (4-POP), triclosan (TCS), carbamazepine (CBZ), nitrobenzene (NB), benzoic acid (BA) were all purchased from Sigma-Aldrich Co. Ltd. The chemical structures of these compounds were shown in Table S1. 2,2,6,6-Tetramethyl-4-piperidinol (TEMP) was supplied by J&K Scientific Co. Ltd. Other reagents were obtained from Sinopharm Chemical Reagent Co. Ltd., China. All solutions were prepared using deionized (DI) water (18.2 MΩ/cm) from a Milli-Q purification system (Millipore, Billerica, MA), except for some organic compounds (BPA, 4-POP, and TCS) with acetonitrile as cosolvent. Stock solutions of PMS were prepared daily and standardized by an ABTS method [32].

2.2. Synthesis and characterization of amorphous MnO_2

Amorphous MnO_2 (similar to naturally occurring birnessite) was synthesized by mixing the appropriate amounts of $MnSO_4$ and $KMnO_4$ in alkaline solution according to the modified Murray's method [33]. The average particle size of synthesized MnO_2 was evaluated to be about 240.6 nm and the pH of zero point charge was reported to be about 2.4 [33]. The average surface area of the freeze-dried MnO_2 particles was measured to be 308.72 m^2/g. The average oxidation state of MnO_2 was calculated to be 3.97 from the iodometric techniques [20] and inductively coupled plasma-mass spectrometry (ICP-MS) for total Mn measurement, which was corroborated by X-ray photoelectron spectroscopy (XPS) data (Fig. S1). The X-ray diffraction (XRD) analysis (Fig. S2) indicated that the synthesized MnO_2 was amorphous. Detailed information on the synthesis procedures and characterization methods was presented in Text S1.

2.3. Experimental procedures

Batch experiments were conducted in 100 mL glass conical bottles in water bath at 25 ± 1 °C under magnetic stirring. Reactions were initiated by simultaneously adding predetermined volumes of PMS and MnO_2 stock solutions into pH buffered solutions containing target organic compound and a constituent of interest (quenching reagent, inorganic anion, or metal ion) at desirable concentrations. Samples were periodically withdrawn and quenched with ascorbic acid solution before analyzed by HPLC/UV for parent organics or by HPLC/ESI-QqQMS for oxidation products. Parallel samples were also obtained by filtering through 0.22 μm syringe filters for determination of PMS residues by an ABTS colorimetric method [32] and dissolved Mn^{2+} by ICP-MS. Solution pH was controlled by 10 mM acetate (pH 5) or borate (pH 7 and 9) buffer, and adjusted by H_2SO_4 and/or NaOH if necessary, and the change of solution pH was within ± 0.3 during the reactions.

The oxidation dynamics of BPA in real waters were carried out in ground water and surface water. The main quality parameters of two water samples were supplied in Table S2. The water samples were filtered through the glass fiber filters, stored at 4 °C, and buffered to pH 7 by 10 mM borate before use. The experimental steps followed the similar procedures used in synthetic buffer solutions.

All experiments were performed in duplicate, and the average values as well as their standard deviations were presented.

2.4. Analytical methods

A Waters 2695 high performance liquid chromatograph (HPLC) equipped with a Waters symmetry C18 column (4.6 × 150 mm, 5 μm