Journal of Hazardous Materials 352 (2018) 157–164

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Critical role of oxygen for rapid degradation of organic contaminants in permanganate/bisulfite process

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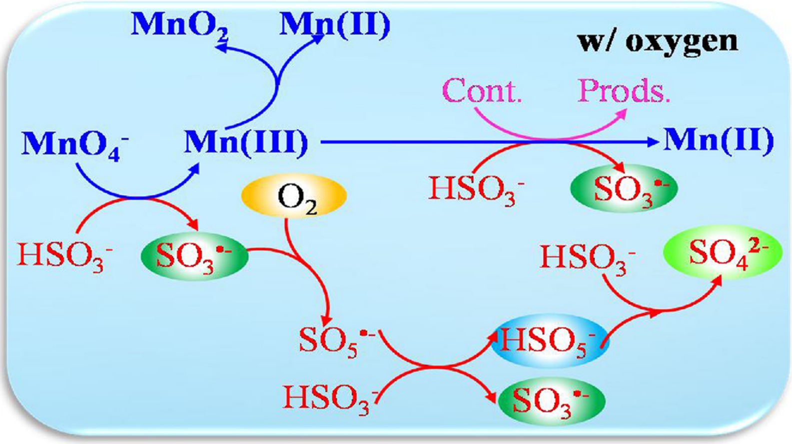
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Advanced oxidation
Permanganate
Bisulfite
Oxygen
Organic contaminant

ABSTRACT

Organic contaminants can be oxidized rapidly in permanganate/bisulfite (PM/BS) process due to generation of $Mn(III)_{aq}$. However, the influence of O_2 and its role in contaminants degradation in PM/BS process are poorly understood. Thus, the influence of O_2 concentration on phenol removal was quantified and isotopic oxygen tracers (^{18}O-labeled water and $^{18}O_2$) were employed to further unravel the mechanisms of PM/BS process. The introduction of O_2 to PM/BS process appreciably improved phenol oxidation. Under oxic conditions the oxidation products of bisulfite included SO_4^{2-} and HSO_5^- while SO_4^{2-} was the single stable oxidation product under anaerobic conditions. The oxygen isotope labeling experiments confirmed that HSO_5^- originated from the oxidation of $SO_3^{\cdot -}$ by O_2 to $SO_5^{\cdot -}$ and the following reduction of $SO_5^{\cdot -}$ by HSO_3^-. Incorporation of oxygen isotope from $H_2{}^{18}O$ to MnO_2 due to the disproportionation of $Mn(III)_{aq}$ was observed, which verified the generation of $Mn(III)_{aq}$ in PM/BS process. The critical influence of O_2 on PM/BS process was mainly associated with rapid oxidation of $SO_3^{\cdot -}$ by O_2 to $SO_5^{\cdot -}$, which otherwise competed with target contaminants for $Mn(III)_{aq}$. Oxygen from H_2O and/or O_2 can also be incorporated in the degradation products of organics in PM/BS process.

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https://doi.org/10.1016/j.jhazmat.2018.03.024
Received 11 October 2017; Received in revised form 6 March 2018; Accepted 13 March 2018

1. Introduction

Considering the presence of various organic contaminants in natural water and their potential negative effects on human health, chemical oxidation processes are widely used to ensure the safety of drinking water [1–4]. During the degradation of organic contaminants by oxidants, the participation of molecular oxygen (O_2), ubiquitous in surface water and wastewater, in oxidative transformation of substrates has frequently been observed. The ^{18}O-kinetic isotope effects for the reactions of aqueous O_2 and the impact of radical scavengers on NDMA formation implied that N-peroxyl radicals from the reaction of aminyl radicals with aqueous O_2 was part of the NDMA formation mechanism [5]. Oxygen had also been reported to participate in the oxidation of 4-chlorophenol by Fenton system [6]. Quite a few studies also reported the involvement of O_2 during organics oxidation initiated by manganese containing compounds. Nowack demonstrated the interception of methylene radical by O_2, which led to different products during homogeneous nitrilotrismethylenephosphonic acid oxidation in Mn^{II}-O_2 containing solution [7]. Aken et al. elaborated the requirement of O_2 for the autoxidation of formyl free radicals, COO^{-}, during the transformation of nitroaromatic compounds by manganese peroxidase [8]. Furthermore, O_2 might also be involved during the transformation of oxidative intermediates by Mn(III). Sugimoto et al. reported the effect of oxygen pressure on the methanol yield in the process of syringyl alcohol oxidation initiated by manganese(III)-acetate, which was attributed to the generation of some active species from the reaction of Mn(II) with O_2 and to the simple oxygen-alkali oxidation [9].

We recently demonstrated very rapid oxidation of several organic contaminants in permanganate/bisulfite (PM/BS) process, due to generation of $Mn(III)_{aq}$ (noncomplexed with ligands other than H_2O and OH^{-}) with high reactivity in this process [10,11]. With the advantages of high oxidation rate over a wide pH range, the PM/BS process has the potential to become a new class of advanced oxidation processes. Therefore, this novel process has attracted great attention among researchers. The performance of this process for activated sludge conditioning and the degradation pathway of organic contaminants in this process had been investigated [12,13]. The possible role of bisulfite as $Mn(III)_{aq}$ stabilizing agent in activating permanganate had been explored [14]. In our previous study, we proposed the general reaction mechanisms, as shown by Eqs. (1)–(5).

$$2HSO_3^- + MnO_4^- \rightarrow Mn(III) + 2OH^- + 2SO_4^{2-} \tag{1}$$

$$2Mn(III) + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+ \tag{2}$$

$$HSO_3^- + Mn(III) + H_2O \rightarrow 2Mn^{2+} + SO_4^{2-} + 3H^+ \tag{3}$$

$$Mn(III) + \text{contaminant} \rightarrow Mn^{2+} + \text{products} \tag{4}$$

$$2HSO_3^- + O_2 \rightarrow 2H^+ + 2SO_4^{2-} \tag{5}$$

The optimal BS/PM molar ratio had been determined to be 5:1, which was much larger than the stoichiometric ratio shown in Eq. (1) [10,11,14]. The over-stoichiometric bisulfite consumption had been ascribed to the consumption of bisulfite by O_2 dissolved in water (DO), as described in Eq. (5), in our previous study [10,11]. However, a close inspection of the literature revealed that the oxidation rate of bisulfite by oxygen, even in the presence of Mn(II), was much slower than that of bisulfite by permanganate [15,16]. Thus, the direct oxidation of bisulfite by O_2 (Eq. (5)) may not count as much as we expected and the proposed mechanism should be further modified. In our previous study, sulfite radicals ($SO_3^{\cdot -}$) was generated in PM/BS process [10], and it is well known that $SO_3^{\cdot -}$ can be rapidly oxidized by oxygen with the rate constant as high as $2.5 \times 10^9\,M^{-1}\,s^{-1}$ [17]. Thus, the participation of oxygen in PM/BS process may arise from the oxidation of $SO_3^{\cdot -}$ by oxygen, which needs further verification.

Therefore, the objectives of this study were to assess the critical role of O_2 in PM/BS process and further delineate the reaction mechanisms of PM/BS process involving oxygen. To this end, we investigated the oxidation of phenol and consumption of oxygen in PM/BS process at various initial O_2 concentrations and BS/PM molar ratios. Secondly, the source of oxygen in the generated sulfur and manganese species was studied by isotopic labeling method using stable isotope of oxygen (^{18}O) contained in $H_2{}^{18}O$ and $^{18}O_2$. Thirdly, the incorporation of oxygen was traced in phenol, one of the major oxidation products of benzene in PM/BS process, and degradation products of ciprofloxacin (CIP) to illustrate the oxidation mechanisms of organics in PM/BS process.

2. Materials and methods

2.1. Materials

A complete listing of reagents is provided in Supplementary Material Text S1.

2.2. Experimental procedures

To accurately control the concentration of DO, a sealed reactor with a sampling pipe, as shown in Fig. S1, was employed. The details of this reactor are shown in the title of Fig. S1. The working solution was adjusted to the target pH level by adding HCl or NaOH and no buffer was used. The initial DO concentration of the working solution, ranging from 0 to 20 mg/L, was controlled by bubbling N_2, O_2, or the mixture of N_2 and O_2 gas. Reaction was initiated by quickly spiking permanganate into the working solution containing bisulfite and the constituent(s) of interest while being mixed with a magnetic stirrer. The reactor was sealed immediately without headspace after spiking permanganate to avoid the influence of air on DO. DO was continuously monitored during the reaction. At a predetermined interval, 10.0 mL of sample was rapidly transferred into a 25 mL beaker and immediately quenched with 100 μL sodium thiosulfate stock solution. Then, the quenched samples were quickly filtrated with a membrane filter (pore size: 0.22 μm) before subject to analysis with ultraperformance liquid chromatography (UPLC) or UPLC-electrosprayionization quadrupole time-of-flight mass spectrometer (UPLC-QTOFMS). To avoid the influence of quencher (thiosulfate) on generated sulfur intermediates and manganese dioxide, quenching reaction was omitted in the experiments of product analysis of sulfur and manganese.

2.3. Oxygen isotope labeling experiments

Prior to reaction, solutions were bubbled with pure N_2 (99.999%) gas for 30 min to prepare O_2-free water. Then, bisulfite and other constituents were spiked into the O_2-free water and pH was adjusted to the desired level. 40 mL solution was transferred to a plastic syringe and commercial $^{18}O_2$ gas was injected to the sealed syringe with 20 mL headspace formed. After shaking for 3 min, permanganate was dosed into the solution by the sealed connecting tube. To determine the involvement of H_2O in PM/BS process, 2% (v/v) of ^{18}O-labeled water (99%) was spiked into the prepared working solution. Then, the reaction was initiated by quickly spiking permanganate into the working solution. The following procedure of the experiments was identical to those described in last section.

2.4. Analytical methods

^{18}O-labeled phenol was measured with gas chromatography-mass spectrometry (Agilent Technologies 7890 A GC System, Agilent Technologies 5975 C inert XL MSD with Triple-Axis Detector). The sulfur species after reaction were analyzed by ion chromatograph (Thermo Scientific Dionex ICS-5000) connected with mass spectrometer (Thermo Scientific TSQ Quantum Access). Oxygen isotopic composition of MnO_2 was measured with an isotope-ratio mass spectrometer

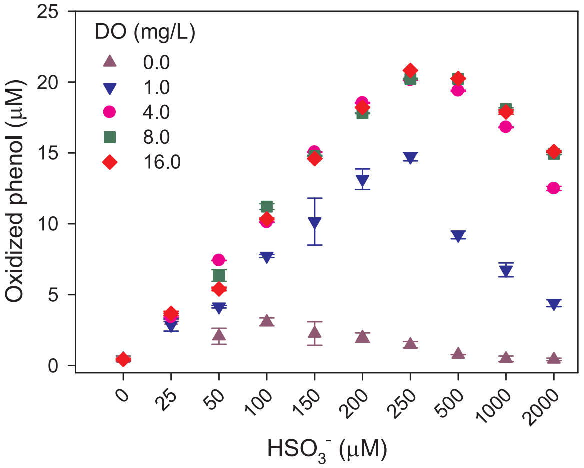


Fig. 1. Influence of oxygen and bisulfite concentration on phenol oxidation in PM/BS process. Experimental conditions: $[KMnO_4]_0 = 50\ \mu M$, $[phenol]_0 = 25\ \mu M$, $pH_{ini} = 5.0$, reaction time: 5 s.

(Thermo Scientific MAT 253). The oxygen isotope ratios in MnO_2 are expressed in the deltanotation as $\delta^{18}O$ in permil (Eq. (6)) relative to international KNO_3 reference material (IAEA-N3) [18].

$$\delta^{18}O=\left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}}-1\right]\times 1000 \tag{6}$$

Where $(^{18}O/^{16}O)_{standard}$ is the isotope ratio of KNO_3.

The details of these three methods are present in Text S2. A detailed description of other analytical methods is provided in Text S2–S4.

3. Results and discussion

3.1. Influence of oxygen on phenol oxidation in PM/BS process

The removal of phenol in PM/BS process at fixed permanganate concentration (50 μM) was strongly influenced by the initial concentrations of DO and bisulfite, as demonstrated in Fig. 1. It should be specified that the degradation of phenol by permanganate alone was negligible in 5 seconds [19], the reaction time for collecting the data in Fig. 1, and thus the removed phenol shown in Fig. 1 was ascribed to the oxidation by $Mn(III)_{aq}$ generated in PM/BS process. There are several obvious features for the data shown in Fig. 1. Firstly, under anaerobic conditions, the amount of removed phenol dropped progressively from 3.2 to 0.50 μM as the initial concentration of sulfite increased from 25 to 2000 μM. Secondly, the introduction of oxygen to PM/BS process appreciably improved phenol oxidation. When the initial concentration of DO was 1.0 mg/L, the degraded phenol increased gradually from 2.6 to 14.9 μM with increasing bisulfite concentration from 25 to 250 μM but a further increase in bisulfite dosage resulted in a drop in phenol removal. Thirdly, the maximum removal of phenol was always achieved at BS/PM molar ratio of 5:1 under aerobic conditions, independent on the initial DO concentration. Elevating the initial DO concentration from 1.0 to 4.0 mg/L generally improved phenol oxidation in PM/BS process and the improvement was greater at larger BS/PM molar ratio. However, a further increase in DO concentration had little influence on phenol removal in PM/BS process. It should be noted that the optimum removal of phenol was achieved at the initial DO concentrations of 4.0 and 8.0 mg/L rather than 16.0 mg/L, respectively, when bisulfite was dosed at low concentration, i.e., at 50 and 100 μM. This may be due to the shortage of bisulfite resulting from the extra consumption of bisulfite by DO of high concentration.

Our previous study stated that the competition between bisulfite and phenol for $Mn(III)_{aq}$ could depress phenol removal in PM/BS process [10], which can well explain the trend observed under anaerobic conditions and that obtained at BS/PM molar ratio of ≥ 5.0 under aerobic conditions shown in Fig. 1. It was found that phenol degradation was significantly enhanced when low concentration of oxygen (1.0 mg/L) was introduced into the reaction solution in the presence of 1000–2000 μM bisulfite (as shown in Fig. 1). Theoretically, 1.0 mg/L oxygen could only consume 62.5 μM and should not influence phenol oxidation remarkably according to our speculation in published paper [10]. Therefore, the influence of oxygen deviated from our previous conjecture. Recently, Gao et al. reported that bisulfite worked as a complexing agent to stabilize Mn(III) and Mn(III)-sulfito complex was responsible for the oxidation of bisphenol S in PM/BS process [14]. According to the mechanisms proposed by these authors, oxygen would not influence organics contaminant in PM/BS process since oxygen did not affect the complexation of bisulfite with Mn(III), which was obviously contradictory to the phenomena shown in Fig. 1. Therefore, there must be other reactions responsible for the influence of oxygen on PM/BS process.

We did observe the generation of $SO_3^{\cdot -}$ in PM/BS process with electron spin resonance (ESR) spectrometer in our previous study [10]. However, we only excluded its role as active oxidant in PM/BS process but did not consider its role as a reductant at that time. Since $SO_3^{\cdot -}$ can be rapidly oxidized by oxygen with the rate constant as high as $2.5 \times 10^9\ M^{-1}\ s^{-1}$ [17], we collected the ESR spectra of PM/BS process at different initial DO concentrations in this study. As illustrated in Fig. S2, the ESR spectra had hyperfine coupling constants $\alpha_N = 14.53$ and $\alpha_{\beta\text{-}H} = 16.12$, consistent with the previously published ESR spectrum for the DMPO/$SO_3^{\cdot -}$ adduct [20]. Moreover, the intensity of the detected ESR signals for DMPO/$SO_3^{\cdot -}$ adduct was stronger at lower DO concentration, verifying the fast reaction of $SO_3^{\cdot -}$ with O_2. Since phenol oxidation was favored while the accumulation of $SO_3^{\cdot -}$ was inhibited in PM/BS process under aerobic conditions, it was expected that $SO_3^{\cdot -}$ was an important reductant competing with phenol for $Mn(III)_{aq}$. Therefore, the oxidation of phenol was minor under anaerobic conditions.

To verify the involvement of oxygen in PM/BS process, DO consumption in 30 s was quantified, as shown in Fig. 2A. The concentration of DO dropped very rapidly after initiating the reaction, which should be primarily due to the consumption by $SO_3^{\cdot -}$ and secondly due to the consumption by bisulfite in PM/BS process. When the initial concentrations of DO and bisulfite were ≤ 4 mg/L and ≥ 250 μM, respectively, DO was exhausted due to the generation of sufficient $SO_3^{\cdot -}$. Surprisingly, the amount of consumed oxygen dropped by increasing the bisulfite concentration from 500 to 1000 μM when the initial DO concentration was fixed at 8 or 20 mg/L, which might be ascribed to the transformation of $SO_3^{\cdot -}$ by excessive bisulfite or generated species (such as $SO_5^{\cdot -}$) and thus suppressed the combination of $SO_3^{\cdot -}$ with oxygen.

The data of phenol removal and the corresponding oxygen consumption under various conditions are summarized in Fig. 2B. It was interesting to find that the data fell in two regions and for the data in each region there was a linear correlation between phenol removal and oxygen consumption. The data around the left line represented the cases with insufficient bisulfite while the data around the right line represented the cases with insufficient oxygen. Phenol removal in PM/BS process in the presence of insufficient bisulfite increased with increasing dosage of bisulfite, following the left line, but decreased sharply when bisulfite was in excess and started to follow the right line. The slope of the left line is dependent on the concentration of permanganate. With increasing the dosage of permanganate, the slope of the left line will increase which result in more phenol removal. As long as permanganate concentration was fixed, phenol removal should be in the region under the two red lines in Fig. 2B no matter how to change the dosage of bisulfite and oxygen. Therefore, proper ratio of permanganate, bisulfite, and oxygen is critical for economical and effective removal of phenol in PM/BS process.

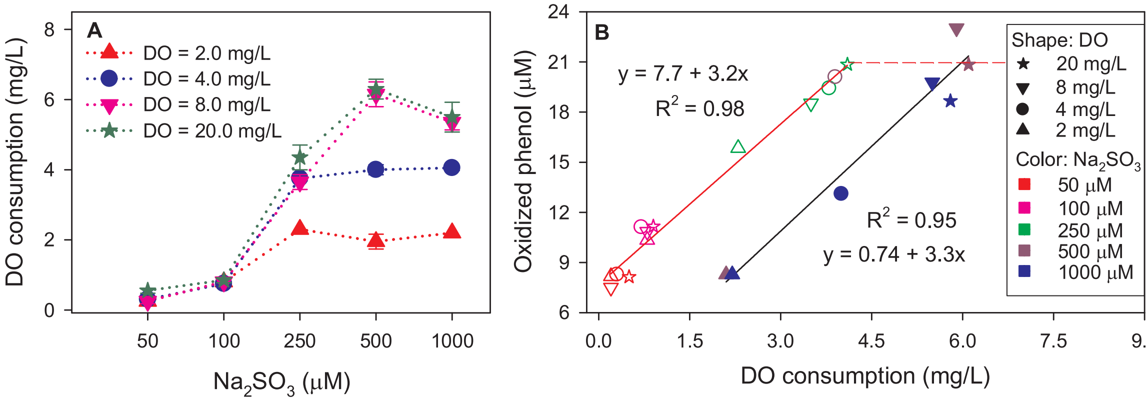


Fig. 2. Consumption of oxygen (A) and the correlation of oxidized phenol and consumed oxygen (B). Experimental conditions: $[KMnO_4]_0 = 50\,\mu M$, $[phenol]_0 = 100\,\mu M$, $pH_{ini} = 5.0$, reaction time was set to 30 s in order to get stable DO value.

3.2. Oxygen source in sulfate, peroxymonosulfate, and MnO_2 generated in PM/BS process

Permanganate was transformed to Mn(II) and MnO_2 after the reaction. IC-MS was employed to survey the possible products of bisulfite after reaction. IC-MS analysis revealed that sulfate was the only product of bisulfite oxidation in PM/BS process, regardless of the presence of O_2, as shown in Fig. S3. To exclude the influence of mobile phase, which is very alkaline, on detection of other possible products of bisulfite oxidation, the reaction solution after PM/BS process was directly injected into the mass spectrometer and the results are shown in Fig. S4. It was interesting to find that peroxymonosulfate besides sulfate was found to be generated in PM/BS process in the presence of oxygen but not in the absence of oxygen.

To further clarify the specific roles of dissolved O_2 and H_2O in PM/BS process, the reaction was carried out in an atmosphere of pure $^{18}O_2$ in normal water and in ^{18}O-enriched water ($H_2{}^{18}O$) using $^{16}O_2$ in the air. The contents of ^{18}O labeled peroxymonosulfate, sulfate, and MnO_2 obtained under different conditions are summarized in Fig. 3. As shown in Fig. 3A, the ^{18}O content in commercial $HSO_5{}^{-}$ and that generated in PM/BS process with normal air as oxygen source was negligible. However, when $KMnO_4$ was reduced by $NaHSO_3$ in normal water but under $^{18}O_2$ atmosphere, $\eta_{HSO_5^-}$, the molar ratio of generated $HS^{18}O_2{}^{16}O_3{}^{-}$ to $HS^{16}O_5{}^{-}$, was as large as 18.03 ± 7.61 when the initial concentration of dissolved $^{18}O_2$ was 10.0 mg/L. This verified the rapid reaction of $SO_3{}^{\cdot -}$ with oxygen, which generated $SO_5{}^{\cdot -}$ (Eq. (7)). The generated $SO_5{}^{\cdot -}$ was further transformed to $HSO_5{}^{-}$ by reacting with HSO_3- (Eq. (8)) [15]. Fig. S5 shows the concentration of generated $HSO_5{}^{-}$ as functions of initial bisulfite and DO concentrations. The maximum production of $HSO_5{}^{-}$ was achieved at 250 μM bisulfite and O_2 was favorable for HSO_5- formation. The generated HSO_5- could be reduced to sulfate by excess bisulfite (Eq. (9)), which may account for the failure of detecting HSO_5- in the presence of excess bisulfite. According to Eqs. (7)–(9), the content of ^{18}O in sulfate would increase greatly due to the presence of $^{18}O_2$. Fig. 3B does illustrate that $\eta_{SO_4^{2-}}$, the molar ratio of $S^{18}O^{16}O_3{}^{2-}$ to $S^{16}O_4{}^{2-}$, was enhanced appreciably from ~0.05 to ~0.45 when $^{16}O_2$ was replaced with $^{18}O_2$. It should be specified that the value of $\eta_{SO_4^{2-}}$ for sulfate generated from the reduction of $HSO_5{}^{-}$ by $HSO_3{}^{-}$ was not affected by the O_2 atmosphere, as demonstrated in Fig. 3C, confirming the non-involvement of oxygen in the reaction of HSO_5- with HSO_3- (Eq. (9)). Compared to the content of ^{18}O-labeled $HSO_5{}^{-}$ (about 95%) in normal water but under $^{18}O_2$ atmosphere, the low ratio of ^{18}O-labeled sulfate indicated that considerable $SO_3{}^{\cdot -}$ was transformed to $SO_4{}^{2-}$ by other paths, including Mn(III) oxidation [17,21].

$$SO_3^{\cdot -} + O_2 \rightarrow SO_5^{\cdot -} \quad k = 2.5 \times 10^9 M^{-1}s^{-1} \tag{7}$$

$$SO_5^{\cdot -} + HSO_3^{-} \rightarrow HSO_5^{-} + SO_3^{\cdot -} \quad k = 8.3 \times 10^3 M^{-1}s^{-1} \tag{8}$$

$$HSO_5^{-} + HSO_3^{-} \rightarrow 2SO_4^{2-} + 2H^{+} \quad k = 5.6 \times 10^6 [H^{+}] M^{-1}s^{-1} \tag{9}$$

Fig. 3B also demonstrates the increase of $\eta_{SO_4^{2-}}$ when $H_2{}^{18}O$ was added into the reaction solution under normal air atmosphere, which suggested the participation of $H_2{}^{18}O$ during the conversion of bisulfite to sulfate in PM/BS process. Müller et al. reported that the oxygen isotope exchange between sulfite species and water (Eq. (10)) with equilibrium constants $K_4 = 10^{-1.37}$ M was rapid at circum-neutral pH conditions [22].

$$SO_2 + H_2O(\leftrightarrow(H_2SO_3)(\overset{K_4}{\leftrightarrow}))2HSO_3^{-}+2H^{+} \tag{10}$$

Therefore, ^{18}O incorporated in sulfate from $H_2{}^{18}O$ may arise from the oxygen isotope exchange between bisulfite species and water. To verify this point, we determined the abundance of labeled sulfate ($S^{16}O_4{}^{2-}/S^{18}O^{16}O_3{}^{2-}$) and peroxymonosulfate ($HS^{16}O_5{}^{-}/HS^{18}O^{16}O_4{}^{-}$) generated in PM/BS process in ^{18}O-enriched water, as summarized in Table S1. The incorporation of one ^{18}O atom in both $HSO_5{}^{-}$ and $SO_4{}^{2-}$ was observed under this condition. Moreover, the molar ratio of $HS^{16}O_5{}^{-}$ to $HS^{18}O^{16}O_4{}^{-}$ and that of $S^{16}O_4{}^{2-}$ to $S^{18}O^{16}O_3{}^{2-}$ was almost identical, suggesting that the ^{18}O atom in both $HS^{18}O^{16}O_4{}^{-}$ and $S^{18}O^{16}O_3{}^{2-}$ was attributed to the oxygen exchange between bisulfite and water.

Fig. 3D summarizes the O isotope ratios in MnO_2 from different sources. As can be seen, $\delta^{18}O$ of the generated MnO_2 in PM/BS process under $^{18}O_2$ atmosphere was close to that of natural MnO_2, which suggested that O_2 did not participate in the transformation of manganese species. Surprisingly, $\delta^{18}O$ of MnO_2 increased significantly when the reaction was carried out in ^{18}O-enriched water. The incorporation of oxygen isotope from $H_2{}^{18}O$ to MnO_2 should be ascribed to the disproportionation of Mn(III) (Eq. (2)), which further verified the generation of $Mn(III)_{aq}$ in PM/BS process.

3.3. Reaction mechanisms of PM/BS process

Based on the results of oxygen labeling experiments, the roles of oxygen and $SO_3{}^{\cdot -}$ in PM/BS process were uncovered and various reactions involved in PM/BS process are summarized in Fig. 4. Conversion of one bisulfite species to another is rapid and often involves the incorporation of oxygen from water, resulting in rapid oxygen isotope exchange between bisulfite species and water [22]. When $MnO_4{}^{-}$ was mixed with bisulfite solution, violent reactions occurred with generating various manganese intermediates and $SO_3{}^{\cdot -}$. The reduction of permanganate to Mn(III) requires transfer of four electrons per mole of Mn. Because only one or two electrons can be transferred in one step [23], intermediate Mn species with oxidation states between +3 and +7 may be formed in the process of Mn(VII) transformation to Mn(III).

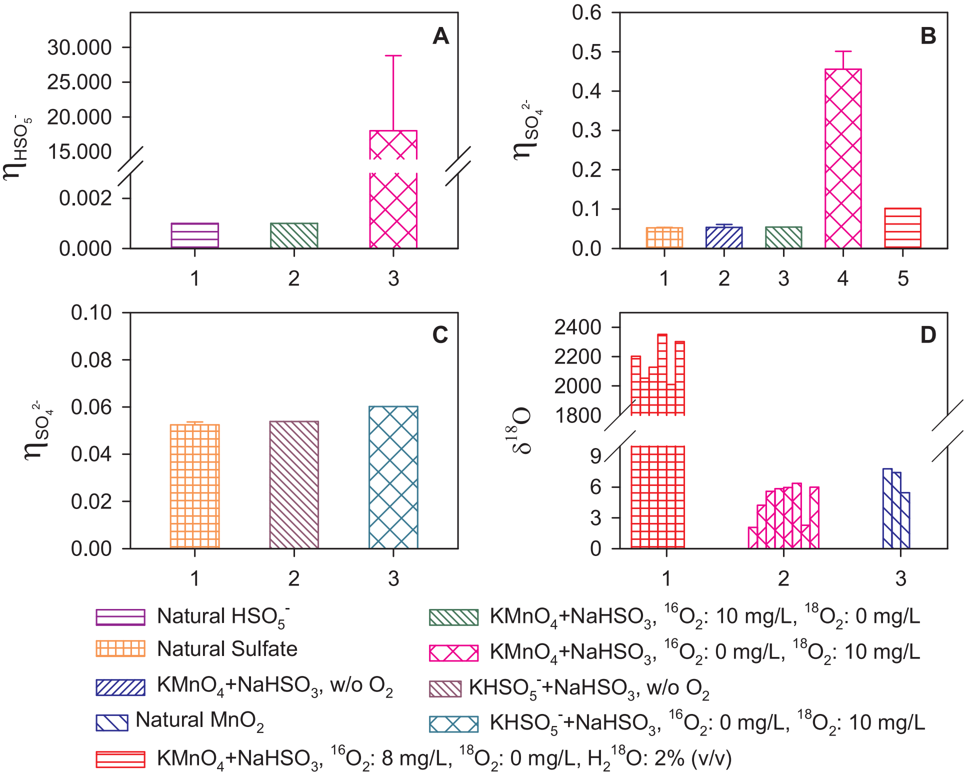


Fig. 3. Contents of ^{18}O labeled peroxymonosulfate (A), sulfate (B), sulfate (C) and MnO_2 (D) obtained under different conditions. Experimental conditions for (A), (B) and (D): $[KMnO_4]_0 = 300\,\mu M$, $[NaHSO_3]_0 = 1000\,\mu M$, $pH_{ini} = 5.0$. Experimental conditions for (C): $[HSO_5^-]_0 = 100\,\mu M$, $[HSO_3^-]_0 = 250\,\mu M$, $pH_{ini} = 5.0$.

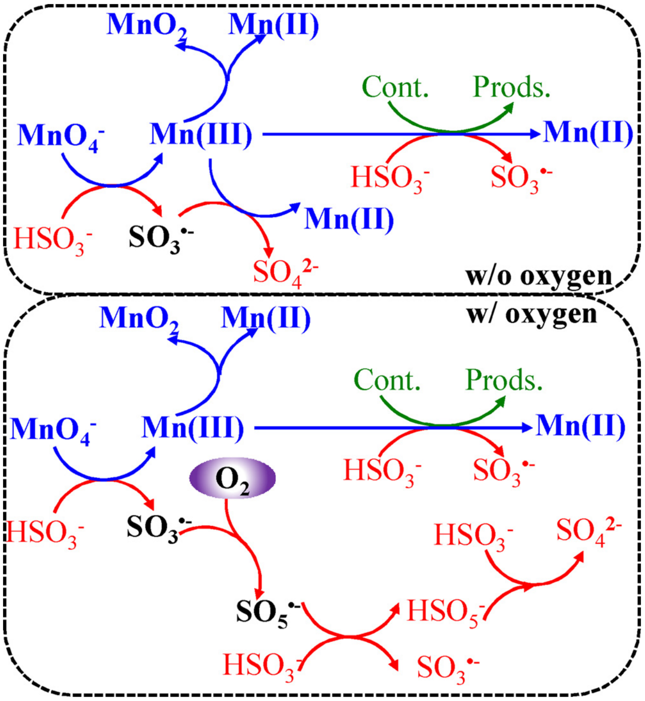
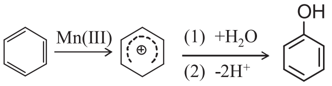


Fig. 4. Proposed reaction mechanisms of PM/BS process (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

However, attempts failed to detect Mn(VI), Mn(V), and Mn(IV) in PM/BS process made it difficult to delineate the detailed reaction pathway of Mn(III) generation. Their instability or the high reaction rate of these manganese intermediates with bisulfite and/or $SO_3^{\bullet-}$ might result in the failure of detecting them in PM/BS process.

Less HSO_5^- was generated during the reaction of 50 μM MnO_4^- with 250 μM HSO_3^- in the presence of 2.0 mg/L DO compared to the case in the presence of higher concentration of DO (Fig. S5). On one hand, oxygen at low concentration may limit the generation of $SO_5^{\bullet-}$ and thus the generation of HSO_5^- (Eqs. (7) and (8)). On the other hand, the generated HSO_5^- was reduced to SO_4^{2-} by excess HSO_3^- (Eq. (9)) under oxygen-limited conditions. Without DO, $SO_3^{\bullet-}$ was generated in PM/BS process but it could not be oxidized to $SO_5^{\bullet-}$ by oxygen and thus no production of HSO_5^- was observed. The generated $Mn(III)_{aq}$ under anaerobic conditions was reduced by $SO_3^{\bullet-}$ and excess HSO_3^-, resulting in very low utilization rate of $Mn(III)_{aq}$ for oxidizing organic contaminants, especially at high HSO_3^- concentration. This was consistent with the influence of bisulfite concentration on the degradation of phenol in PM/BS process under anaerobic conditions, as demonstrated in Fig. 1. Therefore, the fast reaction of $SO_3^{\bullet-}$ with oxygen was the crucial step for the effective utilization of $Mn(III)_{aq}$ for oxidizing organic contaminants in PM/BS process.

The generated $Mn(III)_{aq}$ was unstable and tends to disproportionate to Mn(II) and MnO_2 with equilibrium constant as high as 1×10^9 (Eq. (2)) [24]. According to Eq. (2), the disproportionation of $Mn(III)_{aq}$ was favored at high pH. Both Mn(II) and MnO_2 could accelerate the oxidation of bisulfite by oxygen via radical chain mechanism [16]. Although the reaction of MnO_2 with HSO_3^- could also generate $Mn(III)_{aq}$ and degrade organic contaminants, this reaction was very slow compared to that of $KMnO_4$ with HSO_3^- [10] and was neglected in this study. Besides taking part in the disproportionation reaction, $Mn(III)_{aq}$ could oxidize excess HSO_3^- and organic contaminants in PM/BS process open to the atmosphere. Therefore, the utilization rate of $Mn(III)_{aq}$ was strongly dependent on pH, oxygen concentration, and HSO_3^-/MnO_4^- molar ratio, as demonstrated by the data in Fig. 2B and Fig. 2 in our published paper [11].



Scheme 1. Incorporation of oxygen from H_2O during benzene oxidation to phenol in PM/BS process.

3.4. Oxygen incorporation from O_2 and H_2O in the process of organic contaminants oxidation

Our previous study demonstrated the generation of phenol during benzene oxidation in PM/BS process [11]. Since the oxygen-exchange rate between phenol and water and that between phenol and O_2 have been confirmed to be slow [25], the ^{18}O atom observed in phenol should arise from the participation of $^{18}O_2$ and $H_2{}^{18}O$ in the transformation of benzene to phenol. No ^{18}O-labeled phenol ($m/z = 96$) was detected under the $^{18}O_2$ atmosphere without $H_2{}^{18}O$ (Fig. S6), excluding the possible source of oxygen atom from molecular O_2. The reaction in ^{18}O-enriched water resulted in the generation of considerable ^{18}O-labeled phenol, as shown in Fig. S7. Generally, the formation of benzene cation radical was considered to be the first step of benzene oxidation [25]. Thus, the involvement of H_2O in generating phenol should be associated with the hydration of benzene cation radical [26], which was formed by one-electron transfer from benzene to $Mn(III)_{aq}$, as shown in Scheme 1.

The oxygen atom from O_2 does not take part in the transformation of benzene to phenol in PM/BS process, which does not exclude its incorporation in the oxidation of other contaminants in PM/BS process. Therefore, CIP was selected as another model compound to identify the involvement of O_2 during CIP oxidation in PM/BS process. Six intermediates were detected during CIP decomposition in PM/BS process. The QTOFMS scan data and the proposed chemical structures of the degradation products under $^{18}O_2$ or $^{16}O_2$ atmosphere are given in Fig. S8–S13. Based on the variation of molecular weight of the detected products when the reaction was carried out under $^{18}O_2$ atmosphere instead of $^{16}O_2$, the degradation mechanism of CRP by PM/BS process was proposed with a focus on clarifying the incorporation of O_2 into the degradation products, as shown in Fig. 5.

Similar to the oxidation of amine by permanganate [27] or iridium-catalyzed dehydrogenation of tertiary amines [28], dehydrogenation reaction of amine moiety in CIP was initiated by $Mn(III)_{aq}$ and enamine (*Int. A*) was formed. After hydration and subsequent hydrolysis, enamine was further transformed to aldehyde (*Product A*) [29]. As shown in Fig. S8, the replacement of $^{16}O_2$ with $^{18}O_2$ has no influence on the molecular weight of *Product A*, implying that the oxygen atoms in this product are all from H_2O. These results supported our speculation on enamine transformation to aldehydes.

According to the Hofmann hypobromite reaction in the conversion of amides to amines, isocyanate (*Int. B*) was proposed to generate as the intermediate of *Product A*, resulting from the direct rearrangement of amides [30]. Isocyanate could be easily hydrolyzed in aqueous medium through the attack of water on carbonyl (*Int. C*), and then decarboxylated to from *Int. D*.

Product B was originated from *Int. D* by losing an aldehyde group. No oxygen atom was incorporated into *Product B* compared with its mother compound CIP, thus the molecular weight of product B did not change when the reaction was carried out under $^{18}O_2$ atmosphere instead of $^{16}O_2$ (Fig. S9). Considering that the change in the structure as CIP was converted to product A was similar to that as *Product B* was transformed to *Product C*, *Product B* was transformed to *Product C*, through dehydrogenation, addition with H_2O and subsequent hydrolysis. Fig. S10 shows that the replacement of $^{16}O_2$ with $^{18}O_2$ did not change the content ^{18}O in *Product C*, which was consistent with our speculation that water was used as the oxygen source in the conversion from *Product B* to *Product C*.

An alternative conversion path of *Int. D* to *Product C* was proposed with the generation of *Product D*. Fig. S11 reveals that the molecular weight of *Product D* was increased from 349.0809 to 351.0912 when the reaction was carried out under $^{18}O_2$ atmosphere instead of $^{16}O_2$, implying that one oxygen atom from O_2 was incorporated into *Product D*. Hereby, the auto-oxidation of aldehyde to carboxylic acid was proposed with the incorporation of oxygen into carboxyl group [31]. Firstly, formation of dialdehyde (*Int. E*) through the conversion of amine to aldehyde by using water as the oxygen source was anticipated. According to the reported reaction mechanisms of aldehyde auto-oxidation, the aerobic oxidation of aldehyde (*Int. E*) can be initiated by a free radical chain reaction [32] to form the corresponding peracid (*Int. G*) [33]. The generation of carbonyl free radical (*Int. F*) could be ascribed to the transfer of one electron from carbonyl to Mn(III). The following nucleophilic addition of the peracid (*Int. G*) to another molecule of aldehyde generated a tetrahedral adduct *Int. H* [33]. Generally, the rearrangement of the tetrahedral adduct *Int. H* proceeded

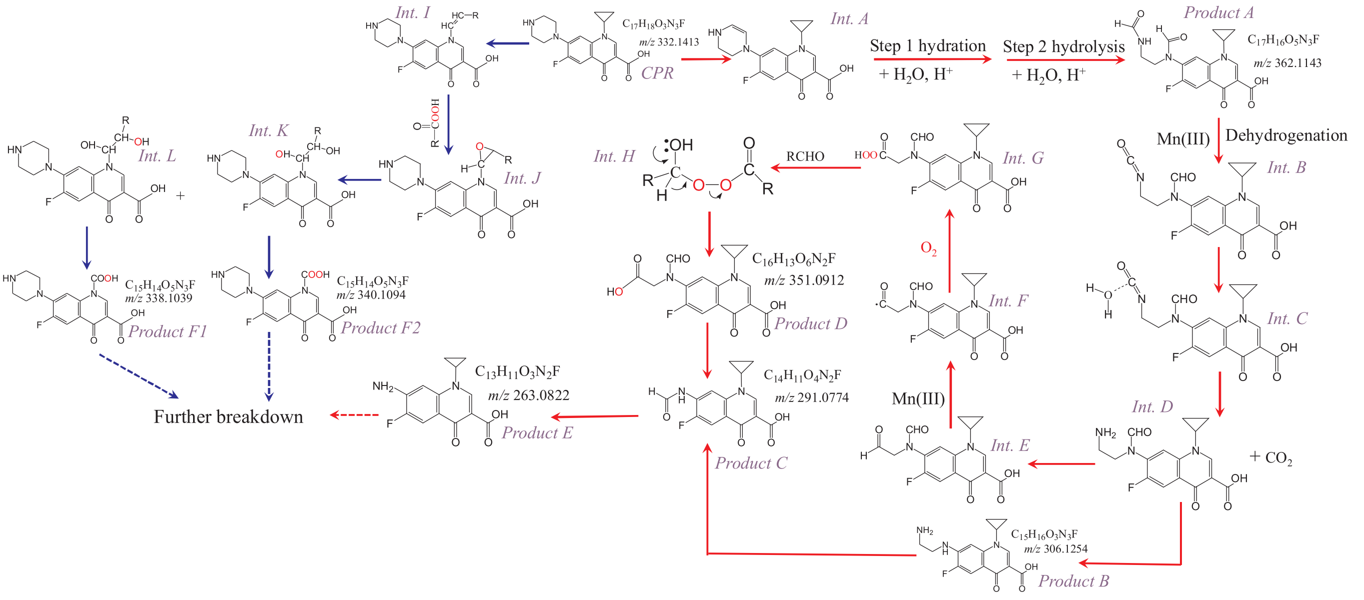


Fig. 5. Incorporation of molecular oxygen during CPR degradation in PM/BS process. Experimental conditions: $[MnO_4{}^-]_0 = 100\,\mu M$, $[HSO_3{}^-]_0 = 500\,\mu M$, $[CPR]_0 = 25\,\mu M$, $^{18}O_2$: 10 mg/L, $^{16}O_2$: 0 mg/L, $pH_{ini} = 5.0$. All ^{18}O atoms in the degradation products are present in red characters.

predominantly via migration of hydrogen to form two molecules of carboxylic acid (*Product D*). This conversion path from aldehyde to carboxylic acid could well explain the incorporation of oxygen atom in *Product D*. Similar to the transformation process from *Int. D* to *Product B*, *Product E* (Fig. S12) was generated from *Product C* by losing an aldehyde group.

When $^{16}O_2$ was replaced by $^{18}O_2$, the *m/z* of *Product F* increased from 336.0994 to *m/z* 338.1039 or 340.1094, as shown in Fig. S13, indicating that either one or two oxygen atoms of *Product F* were from O_2 and thus *Product F* could be generated via two alternative reaction pathways. Based on above analysis and related ring-opening reaction [34,35], the transformation pathway of cyclopropyl in CIP was proposed. Firstly, one electron was transferred to $Mn(III)_{aq}$ from the nitrogen atom which formed conjugated structure with the cyclopropyl group [34,35]. Then, cyclopropane ring-opened product (*Int. I*) was obtained. Epoxidation of olefin by peracid was a common reaction in organic synthesis [36,37]. Therefore, the conversion of *Int. I* by *in situ* formed peracid (including *Int. G*) through epoxidation was proposed, which resulted in the generation of *Int. J*. It was generally accepted that epoxides underwent initial protonation in a fast reversible step followed by opening of the conjugate acid [38]. Then carbocation was attacked by H_2O with the generation of vicinal diols. Because of the alternative cleavage of C—O, the position of oxygen atom transferred from the peracid might be different (*Int. L* and *Int. K*), resulting in the different content of oxygen isotope in *Products F1* and *F2*. Considering the high activity of $Mn(III)_{aq}$ towards organics, further oxidation of *Products E*, *F1*, *and F2* was expected if sufficient oxidants were supplied.

4. Conclusions

This study demonstrated the critical role of oxygen for the effective utilization of $Mn(III)_{aq}$ for organic contaminants degradation in PM/BS process. With the oxygen isotope labeling method, the transformation of sulfur in PM/BS process has been unraveled and the oxygen source in MnO_2 generated in this process has been identified. Bisulfite is initially oxidized by permanganate to $SO_3^{\cdot -}$ and oxygen is necessary for transforming $SO_3^{\cdot -}$ to $SO_5^{\cdot -}$, which otherwise competes with target contaminants for $Mn(III)_{aq}$. Besides improving the utilization of $Mn(III)_{aq}$ in PM/BS process by transforming $SO_3^{\cdot -}$ to $SO_5^{\cdot -}$, O_2 can also directly participate the process of contaminant degradation. Thus, reasonable BS/PM molar ratio and proper oxygen concentration are crucial for effective removal of organic contaminants in PM/BS process, especially for removing the organic contaminants of high concentration.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21522704), and the State Key Laboratory of Pollution Control and Resource Reuse Foundation (No. PCRRK16001). Bo Sun thanks Hong Kong Branch of Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution (The Hong Kong University of Science and Technology, Hong Kong, China) and the Shanghai Tongji Gao Tingyao Environmental Science & Technology Development Foundation (STGEF).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2018.03.024.

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