



# Why does dissolved oxygen govern Mn(III) formation and micro-pollutant abatement in the permanganate/bisulfite process?

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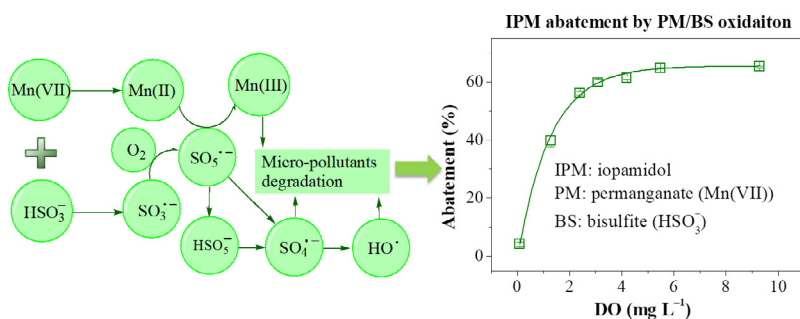
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## HIGHLIGHTS

- DO governed removal of micro-pollutants in PM/BS process.
- Formed Mn(III),  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^\cdot$  contributed to the accelerated degradation.
- Mn(III) is the oxidation product of Mn(II) by  $\text{SO}_5^{\cdot-}$ .
- Actual DO consumption in the presence of micro-pollutants is proposed  $> 1.5[\text{PM}]_0$ .

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Permanganate/bisulfite (PM/BS) process is a novel advanced oxidation process for degradation of micro-pollutants in water/wastewater treatment. The abatements of iopamidol (IPM), metribuzin (MET) and phenol by the PM/BS process after 15 s were 65%, > 99% and > 99%, respectively, while no obvious abatements were observed with PM or BS alone. These accelerated degradations by the PM/BS process were attributed to the formations of Mn(III), sulfur radical ( $\text{SO}_4^{\cdot-}$ ) and hydroxyl radical ( $\text{HO}^\cdot$ ). Interestingly, it was found that dissolved oxygen (DO) governed the abatement of micro-pollutants in PM/BS process. When DO was around  $0.1 \text{ mg L}^{-1}$ , the abatements of all tested micro-pollutants were  $< 5\%$ , significantly lower than those under  $9.1 \text{ mg L}^{-1}$  DO (65%–99%). Moreover, the formation of Mn(III) in the PM/BS process exhibited a positive dependence on DO consumption. Via electron paramagnetic resonance and quenching experiments, it was further found that the reduction of PM by BS generated  $\text{SO}_3^{\cdot-}$ , which could be oxidized by DO to  $\text{SO}_5^{\cdot-}$ . The Mn(III) formation stoichiometry of  $[\text{PM}]:[\text{BS}]:[\text{DO}]$  in the PM/BS process was determined to be 1:5:1.5 ratio.  $\text{SO}_5^{\cdot-}$  promoted the formations of not only Mn(III), but also  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^\cdot$ , among which Mn(III) and  $\text{SO}_4^{\cdot-}$  mainly contributed to the degradation of micro-pollutants. Especially, this study illustrates that the formation pathway of Mn(III) in PM/BS process is not the direct reduction of Mn(VII), but the oxidation of Mn(II) by  $\text{SO}_5^{\cdot-}$ . Meanwhile, maintaining enough DO is indispensable for the degradation of micro-pollutants by the PM/BS process.

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## 1. Introduction

Aquatic micro-pollutants include low-molecular-weight pharmaceuticals, personal care products, industrial compounds, pesticides, hormones, and surfactants used in energy extraction [1,2]. Due to their potential to cause undesirable ecological and human health effects such as endocrine disruption [3], behavioral alteration [4], and antibiotic resistance [5], the widespread occurrence of micro-pollutants has become an emerging issue of environmental concern. Because of the biological recalcitrance of some micro-pollutants, continued physico-chemical efforts have been devoted to the effective degradation of micro-pollutants during wastewater and drinking water treatment [6]. Various oxidation processes, including Fenton [7], UV/H<sub>2</sub>O<sub>2</sub> [8], electrochemical oxidation [9], and O<sub>3</sub>/peroxymonosulfate [10], have been exploited for the abatement of micro-pollutants via generating strong radical oxidants (e.g., hydroxyl radical (HO<sup>•</sup>), oxysulfur radicals (e.g., SO<sub>5</sub><sup>•-</sup> and SO<sub>4</sub><sup>•-</sup>)).

Permanganate/bisulfite (PM/BS) process is a novel oxidation process [11]. It was reported that PM could be activated by BS and micro-pollutants could be oxidized with the observed rates several orders of magnitude higher than those by common oxidation processes [12]. As the oxidation rates of micro-pollutants by PM alone are highly variable, and moderate to slow for some pollutants [13,14], the PM/BS process could enhance the oxidation kinetics of pollutants significantly [15]. It was reported that the degradation rates (*k*<sub>obs</sub>) of phenol, ciprofloxacin, and methylene blue approximate to 60–150 s<sup>-1</sup>, which were 5–6 orders of magnitude higher than those for PM alone, and similar to 5–7 orders of magnitude higher than conventional oxidation processes [11]. The formation of Mn(III) was observed in the PM/BS process [11], which usually has short life in aqueous solution due to its spontaneous and rapid disproportionation. Mn(III) could be stabilized by strong ligands (e.g., pyrophosphate (PP), oxalate, citrate and siderophores) [16,17]. As the complexation of Mn(III) by PP in the PM/BS process usually inhibited the degradation of micro-pollutants, aquo and hydroxo Mn(III) complexes were considered as the main contributor to accelerated degradation of micro-pollutants in the PM/BS process and in situ formation pathways of aquo and hydroxo Mn(III) in the PM/BS process

were proposed as eqs. 1–3 in Table 1 [11,12].

Although the PM/BS process provides a new option to promote the abatement of micro-pollutants, the reaction mechanism and key intermediates governing the accelerated degradation in the PM/BS process were unclear and inconsistent with the observed stoichiometry. For example, the optimum stoichiometry of [PS]<sub>0</sub>: [BS]<sub>0</sub> should be 1:2 if Mn(III) was directly produced from Mn(VII) by HSO<sub>3</sub><sup>-</sup> or SO<sub>3</sub><sup>2-</sup> according to eqs. 1 and 2, which is inconsistent with the previously observed 1:5 ratio [11,12]. Gao et al. proposed that Mn(III)-sulfito complexes and unknown reactive species acted as the oxidant contributing to the oxidation of micro-pollutants rather than aquo and hydroxo Mn(III) [11,12,18,19]. Thus, these discrepancies warrant a further investigation for identifying key intermediates and reaction mechanism in the PM/BS process.

Dissolved oxygen (DO) is one of the most important components of water quality, which could take part in oxidation reaction and impact the final abatement efficiency of micro-pollutants. Sun et al. observed that under oxic conditions the oxidation products of BS included SO<sub>4</sub><sup>2-</sup> and HSO<sub>5</sub><sup>-</sup> while under anaerobic condition SO<sub>4</sub><sup>2-</sup> was the final oxidation product, indicating that DO may participate in the oxidation reactions in the PM/BS process [20]. It was reported that elevating DO concentration led to the formation of more O<sub>2</sub><sup>•-</sup> and subsequent formation of SO<sub>4</sub><sup>•-</sup> during persulfate activation, which favored the degradation of pollutants [21]. In Fe<sup>0</sup>/sulfite process, increasing DO concentration promoted the formation of SO<sub>4</sub><sup>•-</sup> via the oxidation of SO<sub>3</sub><sup>•-</sup> to SO<sub>5</sub><sup>•-</sup> and the subsequent transformation of SO<sub>5</sub><sup>•-</sup> to SO<sub>4</sub><sup>•-</sup> [22]. Transition metals (e.g., copper, iron, manganese) could catalyze the autoxidation of BS via the formation (eq. 4) and further transformation of SO<sub>3</sub><sup>•-</sup> [23–25]. As shown in eq. 5, SO<sub>3</sub><sup>•-</sup> could be quickly oxidized by DO into SO<sub>5</sub><sup>•-</sup> (*k*<sub>SO<sub>3</sub><sup>•-</sup>-O<sub>2</sub></sub> = 1.6 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>) [26]. Even if the SO<sub>5</sub><sup>•-</sup> has a relatively low redox potential (only 1.1 V) [26], it can be rapidly converted to a higher oxidized HSO<sub>5</sub><sup>-</sup> (redox potential of 1.82 V) under the catalysis of Mn(II) [23,27], which could also promote the formations of SO<sub>4</sub><sup>•-</sup> (E(SO<sub>4</sub><sup>•-</sup>/SO<sub>4</sub><sup>2-</sup>) = 2.5–3.1 V), HO<sup>•</sup> (E(HO<sup>•</sup>) = 1.9–2.7 V) and SO<sub>3</sub><sup>•-</sup> (E(SO<sub>3</sub><sup>•-</sup>/SO<sub>3</sub><sup>2-</sup>) = 0.72 V<sub>NHE</sub>) via multiple radical chain reactions in eqs. 6–11 [26,28–31]. Meanwhile, DO played an important role in the abatement of pollutant in Cr(VI)/

**Table 1**  
Possible reactions in the PM/BS process.

No.	Reactions	Rate constants (M <sup>-1</sup> s <sup>-1</sup> )	References
1	MnO <sub>4</sub> <sup>-</sup> + 2HSO <sub>3</sub> <sup>-</sup> → Mn(III) + 2OH <sup>-</sup> + 2SO <sub>3</sub> <sup>2-</sup>	–	[11]
2	MnO <sub>4</sub> <sup>-</sup> + 2SO <sub>3</sub> <sup>2-</sup> + 2H <sub>2</sub> O → Mn(III) + 4OH <sup>-</sup> + 2SO <sub>4</sub> <sup>2-</sup>	–	[11]
3	Mn(III) + micro-pollutants → Mn(II) + products	–	[11]
4	M <sup>n+</sup> + SO <sub>3</sub> <sup>2-</sup> → M <sup>(n-1)+</sup> + SO <sub>3</sub> <sup>•-</sup>	–	[23]
5	SO <sub>3</sub> <sup>•-</sup> + O <sub>2</sub> → SO <sub>5</sub> <sup>•-</sup>	<i>k</i> <sub>5</sub> = 1.5 × 10 <sup>9</sup>	[26]
6	SO <sub>5</sub> <sup>•-</sup> + HSO <sub>3</sub> <sup>-</sup> → HSO <sub>4</sub> <sup>-</sup> + SO <sub>4</sub> <sup>•-</sup>	–	[30]
7	SO <sub>5</sub> <sup>•-</sup> + HSO <sub>3</sub> <sup>-</sup> → HSO <sub>5</sub> <sup>-</sup> + SO <sub>3</sub> <sup>•-</sup>	–	[30]
8	HSO <sub>5</sub> <sup>-</sup> $\xrightarrow{M^{(n-1)+}}$ SO <sub>4</sub> <sup>•-</sup> + OH <sup>-</sup>	–	[30]
9	SO <sub>4</sub> <sup>•-</sup> + HSO <sub>3</sub> <sup>-</sup> → HSO <sub>4</sub> <sup>-</sup> + SO <sub>5</sub> <sup>•-</sup>	<i>k</i> <sub>9</sub> = 1.0 × 10 <sup>6</sup>	[30]
10	SO <sub>4</sub> <sup>•-</sup> + SO <sub>3</sub> <sup>2-</sup> → SO <sub>3</sub> <sup>•-</sup> + SO <sub>5</sub> <sup>•-</sup>	<i>k</i> <sub>10</sub> = 1.0 × 10 <sup>8</sup>	[30]
11	SO <sub>4</sub> <sup>•-</sup> + OH <sup>-</sup> → SO <sub>4</sub> <sup>2-</sup> + HO <sup>•</sup>	<i>k</i> <sub>11</sub> = 6.5 × 10 <sup>7</sup>	[31]
12	SO <sub>5</sub> <sup>•-</sup> + Mn(II) + H <sup>+</sup> → Mn(III) + HSO <sub>5</sub> <sup>-</sup>	<i>k</i> <sub>12</sub> ≈ 1.0 × 10 <sup>8</sup>	[37]
13	SO <sub>3</sub> <sup>•-</sup> - e <sup>-</sup> → SO <sub>3</sub> <sup>-</sup>	–	[38]
14	MnO <sub>4</sub> <sup>-</sup> + 5HSO <sub>3</sub> <sup>-</sup> + 3H <sup>+</sup> → Mn(II) + 5SO <sub>3</sub> <sup>2-</sup> + 4H <sub>2</sub> O	–	This study
15	MnO <sub>4</sub> <sup>-</sup> + 5HSO <sub>3</sub> <sup>-</sup> + 1.5O <sub>2</sub> → Mn(III) + 5SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup> + 2H <sub>2</sub> O	–	This study
16	5HSO <sub>5</sub> <sup>-</sup> + 4Mn(II) + 6H <sub>2</sub> O → 4MnO <sub>4</sub> <sup>-</sup> + 5HSO <sub>3</sub> <sup>-</sup> + 12H <sup>+</sup>	–	[66]
17	HSO <sub>5</sub> <sup>-</sup> + Mn(II) → Mn(III) + OH <sup>-</sup> + SO <sub>4</sub> <sup>•-</sup>	–	[63]
18	2SO <sub>4</sub> <sup>•-</sup> → S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	<i>k</i> <sub>18</sub> = 7.0 × 10 <sup>8</sup>	[30]
19	2SO <sub>5</sub> <sup>•-</sup> → 2SO <sub>4</sub> <sup>•-</sup> + O <sub>2</sub>	<i>k</i> <sub>19</sub> = 2.1 × 10 <sup>8</sup>	[30]
20	2SO <sub>5</sub> <sup>•-</sup> → S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> + O <sub>2</sub>	<i>k</i> <sub>20</sub> = 2.2 × 10 <sup>8</sup>	[30]
21	SO <sub>4</sub> <sup>•-</sup> + Mn(II) → Mn(III) + SO <sub>4</sub> <sup>2-</sup>	<i>k</i> <sub>21</sub> ≈ (1.6–8.3) × 10 <sup>7</sup> (pH 3.0)	[63]
22	2MnO <sub>4</sub> <sup>-</sup> + 3Mn <sup>2+</sup> + 4OH <sup>-</sup> → 5MnO <sub>2</sub> (s) + 2H <sub>2</sub> O	–	[64]
23	2Mn(III) + H <sub>2</sub> O → MnO <sub>2</sub> + Mn <sup>2+</sup> + 4H <sup>+</sup>	log <i>K</i> ≈ 7–9	[65]

sulfite, Fe(VI)/sulfite and PM/BS processes [25,32]. Given that the formation of  $\text{SO}_3^{\cdot-}$  in the PM/BS process was verified [11], the presence of DO may also impact the abatement of micro-pollutants via the reaction with  $\text{SO}_3^{\cdot-}$  (eq. 5).

In this study, three micro-pollutants including iopamidol (IPM), metribuzin (MET) and phenol were selected as target pollutants to investigate their abatements by the PM/BS process (Fig. S1). IPM is a typical iodinated X-ray contrast media compound, which was detected a few orders of magnitude higher than those of many other pharmaceuticals in aquatic environment [33]. MET is one of the nitrogen-containing herbicides in the family of triazine herbicides [34]. Phenol and its chemical derivatives are essential functional groups for the synthesis and production of micro-pollutants (e.g., benzene and ciprofloxacin) [20], and the electron-rich nature of hydroxyl group and its benzene ring structure makes it more facile targets for selective oxidation than MET (with nitrogen heterocyclic group). Not to mention IPM has an extremely stable symmetrical aromatic structure. It is expected to investigate and verify the mechanism and applicability of the PM/BS process treating different micro-pollutants with various functional groups and structures. The aims of this study were (1) to investigate the role of DO on the abatements of micro-pollutants including IPM, MET and phenol by the PM/BS process; (2) to reveal key intermediates and mechanisms during the accelerated degradation of micro-pollutants; (3) to ascertain the reaction pathway and stoichiometry of Mn(III) formation in the PM/BS process.

## 2. Materials and methods

### 2.1. Materials

All chemicals were commercially available and used as received: IPM, 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO) from Sigma-Aldrich; potassium permanganate (PM,  $\text{KMnO}_4$ ), sodium bisulfite (BS,  $\text{NaHSO}_3$ ), sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), Oxone (PMS,  $2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$ ), (EtOH), sodium pyrophosphate (PP,  $\text{Na}_4\text{P}_2\text{O}_7$ ), 1-hexanol and *tert*-butanol (TBA) from Sinopharm Chemical Reagent Co. Ltd. China. All stock solutions were prepared in ultra-pure water ( $18.2\text{ M}\Omega\cdot\text{cm}$ ) produced by an Advantage A10 Milli-Q system (Millipore). PM stock solution was standardized by spectrophotometry at 525 nm ( $\epsilon = 2500\text{ M}^{-1}\text{ s}^{-1}$ ) [35]. The aqueous stock solution of spin-trapping agents for radicals was frozen and stored at  $-20\text{ }^\circ\text{C}$  before used.

### 2.2. Experimental procedures

Degradation experiments were carried in 100 mL glass conical flask, which was mechanically stirred under constant rate ( $250\text{ r min}^{-1}$ ) at  $25 \pm 2\text{ }^\circ\text{C}$ . Reactions were initiated by quickly spiking PM into the solutions containing micro-pollutants and BS with a magnetic stirrer in glass bottles. To investigate the effect of DO concentration ( $0.1\text{--}9.3\text{ mg L}^{-1}$ ) on the abatement of micro-pollutants by the PM/BS process, different flows of high-purity nitrogen were purged for 30 min in advance into the working solution under magnetic stirring. The DO concentration of working solution was real-time monitored by a DO meter to make sure that the DO kept around the desired concentration before the startup of the reaction. The phosphate buffer solution was used in most experiments for maintaining stable pH values during the PM/BS oxidation. NaOH (0.1 M) and  $\text{H}_2\text{SO}_4$  (0.1 M) solutions were used to adjust pH. At predetermined intervals, 1.0 mL of sample was immediately transferred into a 5-mL beaker and immediately quenched by adding 20- $\mu\text{L}$  of  $\text{Na}_2\text{S}_2\text{O}_3$  solution (10 mM). The quenched samples were then filtrated with 0.2- $\mu\text{m}$  polyethersulfone filters (ion chromatography acrodisc, PALL) and analyzed using a high performance liquid chromatograph with diode array detector (HPLC-DAD). PP, TBA, EtOH, and 1-hexanol were used to stabilize Mn(III) and scavenge  $\text{HO}^\cdot$ ,  $\text{SO}_4^{\cdot-}$  and oxysulfur radicals (e.g.,  $\text{SO}_4^{\cdot-}$ ,  $\text{SO}_5^{\cdot-}$  and  $\text{HSO}_5^{\cdot-}$ ) for checking the abatement mechanism of micro-pollutants in the PM/BS process. DMPO

was adopted as the spin-trapping agent in the electron paramagnetic resonance (EPR) experiments. The detailed description of EPR experiment is provided in in Text S1. The EPR spectrum was deconvoluted and simulated by WinSim software [36].

### 2.3. Analytical methods

UV-vis absorbance in the range 200–800 nm was determined by a HACH DR 6000 UV-vis spectrophotometer. All the concentration variations of IPM, MET and phenol were determined with an Agilent 1200 Series HPLC system equipped with an Atlantis C18 column ( $4.6 \times 250\text{ mm}$ ,  $5.0\text{ }\mu\text{m}$ ) at wavelengths of 242, 230 and 254 nm, respectively. A mixture of methanol/water (60/40, v/v) was used as the mobile phase at a flow rate of  $1.0\text{ mL min}^{-1}$ . The column temperature was maintained at  $25\text{ }^\circ\text{C}$  and the injection volume was 100  $\mu\text{L}$ . The limit of detection (LOD), limit of quantitation (LOQ) and concentration range of IPM, MET and phenol by HPLC analysis are listed in Table S1. The DO concentration and pH were measured using a Cellox 325 DO electrode (WTW) and a pH meter (Mettler), respectively, calibrated by pH 4.0, 7.0 and 9.0 standards.

## 3. Results and discussion

### 3.1. Possible reaction stoichiometry in the PM/BS process

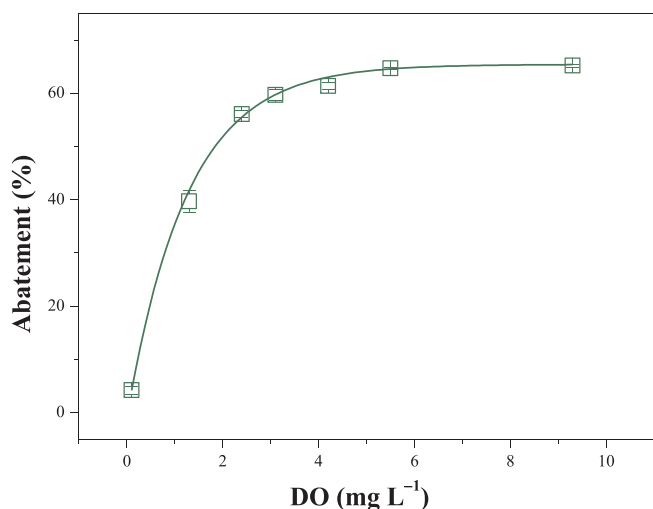
As reported in the majority literatures, the reaction of PM:BS ratio has been well recognized in experiments for oxidative degradation of contaminants. [11,12,19,37]. However, the reaction mechanism of PM/BS process is still unclear, and it is worthwhile to pay attention to comprehensively studying this issue from different angles. In this study, the EPR spectra of different  $[\text{PM}]_0:[\text{BS}]_0$  were examined by using DMPO as a spin trap (Fig. S3). An analysis of the spectrum yielded the hyperfine splittings of  $\alpha_N = 14.5\text{ G}$  and  $\alpha_H = 16.1\text{ G}$ , where  $\alpha_N$  and  $\alpha_H$  denote hyperfine splittings of nitroxyl nitrogen and  $\alpha$ -hydrogen, respectively. The  $\alpha_N$  and the  $\alpha_H$  were in good agreement with those reported in the literature for DMPO- $\text{SO}_3^{\cdot-}$  adduct [24,38,39]. The highest intensity of DMPO- $\text{SO}_3^{\cdot-}$  adduct in EPR spectra was obtained at  $[\text{PM}]_0:[\text{BS}]_0 = 1:5$ . It is revealed that the optimal  $[\text{PM}]_0:[\text{BS}]_0$  ratio in ESR experiments is consistent with previously observed results [11,12,19,37]. As  $\text{SO}_3^{\cdot-}$  is usually considered as a weak oxidant [40], the contribution of  $\text{SO}_3^{\cdot-}$  to the abatement of micro-pollutants by the PM/BS process may be limited. Because  $\text{SO}_3^{\cdot-}$  could be quickly oxidized by DO into  $\text{SO}_5^{\cdot-}$ , the multiple radical chain reactions (eqs. 5–12) involving the formations of  $\text{SO}_4^{\cdot-}$ ,  $\text{SO}_5^{\cdot-}$  and Mn(III) may be the key reactions for the accelerated degradation of micro-pollutants in the PM/BS process.

### 3.2. Mechanism of the PM/BS process

#### 3.2.1. Key intermediates in the PM/BS process

During the abatement of micro-pollutants by the PM/BS process, the oxidation of formed  $\text{SO}_3^{\cdot-}$  by DO to  $\text{SO}_5^{\cdot-}$  and a subsequent transformation of  $\text{SO}_5^{\cdot-}$  would generate  $\text{SO}_4^{\cdot-}$ ,  $\text{SO}_5^{\cdot-}/\text{HSO}_5^{\cdot-}$  and  $\text{HO}^\cdot$  (eqs. 5–12) [41]. Thus, apart from Mn(III), a variety of reactive intermediate species could be formed in the PM/BS process. To identify the key intermediate contributed to the accelerated degradation, PP, TBA, EtOH and 1-hexanol were used as scavengers in the PM/BS process at pH 6.5, which were dosed separately with varying concentrations (0–20 mM) for a verification of key intermediates.

In previous studies, the enhanced abatement of micro-pollutants by the PM/BS process was typically ascribed to Mn(III) [11,15]. As PP could stabilize Mn(III) formed in situ and prevent its spontaneous disproportionation and oxidation of micro-pollutants, PP is widely adopted to evaluate the role of Mn(III) [15]. As shown in Fig. S4, the abatement of IPM exhibited a decreased trend with the increase of  $[\text{PP}]_0$ , which decreased from 66% (control group) to 26% in the



**Fig. 1.** Effect of DO concentration on the abatement of IPM by the PM/BS process. Experiment conditions:  $[IPM]_0 = 5 \mu\text{M}$ ,  $[PM]_0 = 50 \mu\text{M}$ ,  $[BS]_0 = 250 \mu\text{M}$ ,  $\text{pH} = 6.5$  with 10 mM phosphate buffer,  $[DO] = 0.1\text{--}9.1 \text{ mg L}^{-1}$ ,  $T = 25 \text{ }^\circ\text{C}$ . Error bars represent standard deviation ( $n = 3$ ).

presence of 20-mM PP. Note that 20-mM PP has greatly inhibited the abatement of IPM, indicating that the formed Mn(III) played an important role in the PM/BS process. Elevating the concentration of PP, more aquo and hydroxo Mn(III) was complexed, which promoted the movement of the reaction to the formation of hydrolyzed Mn(III), the other radical species were relatively inhibited, resulted the degradation efficiency of IPM was reduced. Conversely, previous studies have reported that the degradation of the substrates (e.g. arsanilic acid, NB, BPA and carbendazim) were not inhibited whether increasing the PP concentration to 1 mM or 20 mM [42,43]. The analysis was as follows: 1) the oxidizing ability of hydrolyzed Mn(III) and Mn(III)-PP complex was related to the molecular structure and electronic properties of the contaminants in the PM/BS process, which was relatively lower than the former; 2) owing to the powerful oxidizing ability of hydrolyzed Mn(III) and other radical species were sufficient, the reduction of easily degradable pollutants (compared to IPM) were not affected. In addition, it has been found that that manganese intermediates (possibly Mn(V)) other than Mn(III) are likely involved in the PM/BS systems responsible for the efficient degradation of organics [18,37]. Moreover, the mechanism of “catalytic role exchange” for the degradation of organic compounds by the PM/BS process has also been proposed [44]. However, the mechanism of PM/BS system for degrading pollutants is very complicated, and there is still controversy. The specific role of Mn(III) is still unclear and needs further research in the future.

As shown in eqs. 24 and 25, TBA is a specific scavenger for  $\text{HO}^\bullet$  in advanced oxidation process ( $k_{\text{TBA},\text{HO}^\bullet} = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{TBA},\text{SO}_4^{\bullet-}} = 4.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) [26,42,45]. The addition of TBA (1–20 mM) to the PM/BS process inhibited the degradation of IPM with limited extent (Fig. S5), indicating a limited contribution of  $\text{HO}^\bullet$  to the IPM abatement. Based on a competition kinetic calculation (i.e.,  $(k_{\text{HO}^\bullet\text{-IPM}} \times [IPM]) / (k_{\text{HO}^\bullet\text{-TBA}} \times [\text{TBA}]) = (3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \times 5 \times 10^{-6} \text{ M}) / (6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \times 1 \times 10^{-3} \text{ M}) = 0.028$ ) (eq. 26) [46], the oxidation contribution of  $\text{HO}^\bullet$  should be inhibited completely in the presence of 1-mM TBA. However, the abatement of IPM in the presence of 1-mM TBA just decreased 5% (from 66% to 61%).

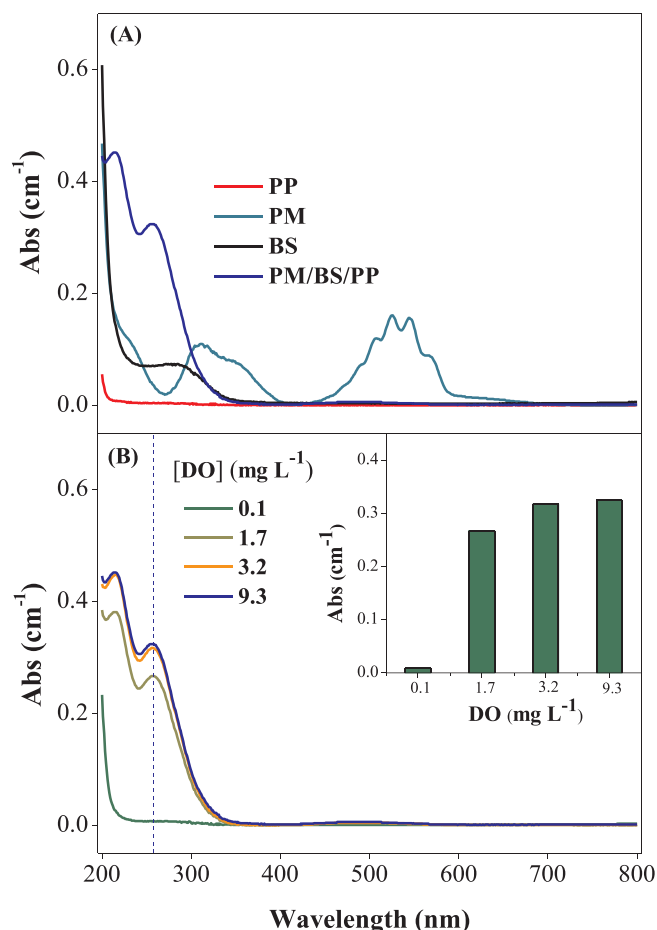
The reaction rate constant of EtOH with  $\text{HO}^\bullet$  is approximately  $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which is about 50 folds that with  $\text{SO}_4^{\bullet-}$  (i.e.,  $3.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) (eqs. 27 and 28) [26,31,47]. And it is well reported that alcohols are inert toward  $\text{SO}_5^{\bullet-}$  and  $\text{SO}_3^{\bullet-}$  radicals ( $k \leq 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) [25]. Thus, the role of radicals could also be evaluated by comparing the difference between the abatements of IPM after adding an excessive TBA or EtOH. As shown in Fig. S6, the abatement of IPM in

the presence of 20-mM EtOH decreased to  $< 6.0\%$ , 60% lower than control group (i.e., in the absence of EtOH). Compared to excess TBA, inhibition is more pronounced in the presence of excess EtOH, which may be an important role for  $\text{SO}_4^{\bullet-}$  radical. In addition, 1-hexanol is a stronger inhibitor to oxysulfur radicals than EtOH and TBA [48,49]. The reaction rate constant of 1-hexanol with  $\text{SO}_4^{\bullet-}$  is approximately  $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (eq. 29) [50], which is about 4.6 folds that of EtOH with  $\text{SO}_4^{\bullet-}$  (i.e.,  $3.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) [51]. The quenching effect of oxysulfur radicals by 1-hexanol was conducted and it was found that the addition of 1-hexanol significantly inhibited the degradation of IPM ( $< 6\%$ ) even at the 1-mM dosage (Fig. S7). Zhang et al. also observed that the abatement of atrazine by the PM/BS process in the presence of 1-hexanol was  $< 4\%$  [52]. According to a series of studies by Simándi and co-workers, EtOH was used as a acceptor in the Mn(VII)-reduction systems, which could be ascribed to: 1) the oxidation of Mn(III) was ruled out; 2) Mn(V) showed a low reactivity toward to EtOH ( $\text{IF} = 0.16$  at  $\text{pH} = 3.8$ ) [53]. Besides, the second-order rate constants for reaction of alcohols oxidation with Mn(VI) were  $\sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$  [54]. Thus, apart from the reactivity of Mn(III) Mn(VI), and Mn(V) toward TBA, EtOH and 1-hexanol, the formed  $\text{SO}_5^{\bullet-}$  radical also contributed to the generation of the  $\text{SO}_4^{\bullet-}$  radical to accelerate degradation of IPM by the PM/BS process. Although the transformation of  $\text{SO}_4^{\bullet-}$  could induce the formation of  $\text{HO}^\bullet$  (eq. 11), the reaction of  $\text{SO}_4^{\bullet-}$  with  $\text{OH}^-$  is a slow reaction among radical reactions [31]. Therefore, the formed concentration of  $\text{HO}^\bullet$  and its contribution to the degradation of IPM by the PM/BS process was postulated to be limited. As mentioned above, the following conclusions can be drawn: 1)  $\text{SO}_5^{\bullet-}$  as an important intermediate related to the oxidation of  $\text{SO}_3^{\bullet-}$  by oxygen; 2) the Mn(III) and  $\text{SO}_4^{\bullet-}$  induced by  $\text{SO}_5^{\bullet-}$  could be the main causes of the abatement of micro-pollutants by the PM/BS process.

### 3.2.2. Role of DO

As DO could oxidize  $\text{SO}_3^{\bullet-}$  to  $\text{SO}_5^{\bullet-}$  (eq. 5), the effect of DO on the abatement of IPM by the PM/BS process was then investigated by sparging different fluxes of nitrogen into the working solution, with DO ranging from 0.1 to 9.3  $\text{mg L}^{-1}$ . As shown in Fig. 1, a possible response curve between DO concentration and pollutant degradation was obtained. Elevating DO concentration from 0.1 to 2.4  $\text{mg L}^{-1}$  significantly enhanced the abatement of IPM from 4% to 56%. When DO concentration was further elevated, the abatement of IPM remained around 60%. In addition, it can be seen from Fig. 1 that the half DO concentration corresponding to the target pollutant removal rate limit may become the highest utilization point of DO, which is worthy of attention in practice. Consistent with the abatement of IPM, DO also played vital roles in both the degradations of MET and phenol (Fig. S8). Besides, some research groups have observed a good positive linear relationship between DO consumption and pollutant degradation within a certain range through the PM/BS process [20]. However, controlling DO concentrations at a fixed optimal ratio may be practical for production compared to exploring the relationship between DO concentration consumption and contaminant reduction, which is more instructive and facilitates the promotion and application of the technology. Moreover, they further found that the oxidation products of  $\text{HSO}_3^-$  in the PM/BS process under oxic conditions were  $\text{SO}_4^{2-}$  and  $\text{HSO}_5^-$ , while  $\text{SO}_4^{2-}$  was the single oxidation product under anaerobic condition. Via oxygen isotope labeling experiments, they further confirmed that  $\text{HSO}_5^-$  originated from the oxidation of  $\text{SO}_3^{\bullet-}$  by  $\text{O}_2$  to  $\text{SO}_5^{\bullet-}$  (eq. 5). Based on these results, it is speculated that the DO promoted the formation of  $\text{SO}_5^{\bullet-}$  via the oxidation of  $\text{SO}_3^{\bullet-}$ , which is a key intermediate for the accelerated degradation of micro-pollutants in the PM/BS process.

As Mn(II) could be rapidly oxidized to Mn(III) by  $\text{SO}_5^{\bullet-}$  ( $k_{\text{SO}_5^{\bullet-}\text{-Mn(II)}} \approx 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), DO may indirectly impact the formation of Mn(III) in the PM/BS process [25,55]. To investigate the role of DO on the formation of Mn(III) in the PM/BS process, the UV-vis spectra of PM/BS/PP under different DO concentrations were compared. As shown in Fig. 2A, in the presences of 10-mM PP and 9.3- $\text{mg L}^{-1}$  DO, an



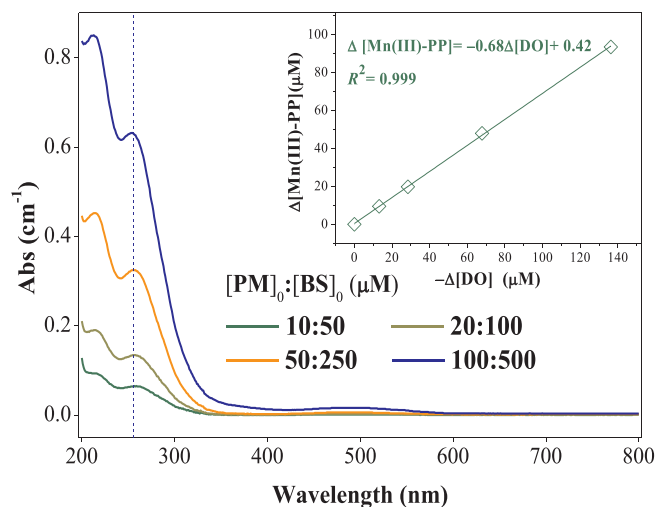
**Fig. 2.** UV-vis spectra of PM, BS, PP and PM/BS/PP systems (A) and effect of [DO] on the UV-vis spectra of PM/BS/PP system (B). Experiment conditions:  $[IPM]_0 = 5 \mu\text{M}$ ,  $[PM]_0 = 50 \mu\text{M}$ ,  $[BS]_0 = 250 \mu\text{M}$ ,  $\text{pH} = 5.0$  with 10 mM PP buffer,  $[\text{DO}] = 9.3 \pm 0.2 \text{ mg L}^{-1}$  for (A),  $[\text{DO}] = 0.1\text{--}9.3 \text{ mg L}^{-1}$  for (B),  $T = 25 \text{ }^\circ\text{C}$ . Error bars represent standard deviation ( $n = 3$ ).

absorbance peak at 258 nm is evident, which is the characteristic peak of Mn(III)-PP complex [56]. In the PM/BS/PP system, the absorbance at 525 nm of residual PM was negligible, and the peak absorbance value at 258 nm was  $0.32 \text{ cm}^{-1}$ , consistent with  $[\text{Mn(III)-PP}] = 48 \mu\text{M}$  (assuming a molar absorption coefficient at 258 nm =  $6750 \text{ M}^{-1} \text{ cm}^{-1}$ ) [56]. Interestingly, the 258-nm absorbance peak value decreased to  $< 0.01 \text{ cm}^{-1}$  ( $[\text{Mn(III)-PP}] < 1.5 \mu\text{M}$ ) when  $[\text{DO}]$  was  $0.1 \text{ mg L}^{-1}$ . When  $[\text{DO}]$  was increased from  $3.2 \text{ mg L}^{-1}$  to  $9.3 \text{ mg L}^{-1}$ , there was no further increase of formed Mn(III)-PP. Thus, DO indeed impacted the formation of Mn(III) in the PM/BS process especially when  $[\text{DO}]$  was  $< 3.2 \text{ mg L}^{-1}$ . Proposed that  $\text{SO}_5^{\cdot-}$  radical is not the only pathway for the oxidation of Mn(II) to Mn(III) in the PM/BS process, Mn(II) can be oxidized by several oxidizing species in the system such as Mn(VII), other high-valent Mn species and  $\text{SO}_4^{\cdot-}$  radical. Under the mechanism of high-valent Mn species ( $> \text{Mn}^{2+}$ ), the production of Mn(III) in anoxic conditions (i.e.  $[\text{DO}] = 0.1 \text{ mg L}^{-1}$ ) should be similar to that in the case of sufficient DO, evidence for rejecting this hypothesis in Fig. 2B. Although the previous study has investigated the absence of spectral signals for Mn(VI) and Mn(V) during stopped flow or batch experiments in the PM/BS system [11], it is worth noting that Jiang et al. recently applied PMSO (appropriate model compound) to study PM/BS system. They proposed that Mn(V) may be an important intermediate species by comparing the degradation of PMSO by Mn(VI) and Mn(V) (no degradation of PMSO by Mn(VI) was observed at 10 s at pH 1, while the fast degradation of PMSO by Mn(V) species) [37]. Besides, their finding suggested that DO had no influence on the reactivity of Mn

(V) species toward PMSO [37], which may be a good evidence that the oxidizability of Mn(V) is relatively limited in this experiment, and it is necessary to explore selectivity of Mn(V) species in different experiment conditions. Therefore, one possible explanation for the inhibitory effect of  $\text{O}_2$  on the oxidation of Mn(II) and micro-pollutants by PM/BS system may be that  $\text{SO}_3^{\cdot-}$  as a reductant preferentially consumes these strongly oxidizing species. Due to  $\text{SO}_4^{\cdot-}$  radical is a secondary radical of  $\text{SO}_5^{\cdot-}$  radical, it is hypothesized that the formation pathway of Mn(III) should not be the direct oxidation of  $\text{SO}_4^{\cdot-}$  in the PM/BS process, but the oxidation of Mn(II) by  $\text{SO}_5^{\cdot-}$  under the catalyzed role of Mn(II). Additionally, electrons might prone to migration in the presence of Mn(III)/Mn(II) pairs and the reaction rate of  $\text{SO}_5^{\cdot-}$  with Mn(II) was much faster than the generation of  $\text{SO}_4^{\cdot-}$ .

The critical role of DO governing the formation of Mn(III) sheds light on the formation pathway of Mn(III) in the PM/BS process. As discussed above, DO participated in the oxidation of  $\text{SO}_3^{\cdot-}$  to  $\text{SO}_5^{\cdot-}$  in the PM/BS process. In the absence of DO, both the formations of  $\text{SO}_5^{\cdot-}$  and Mn(III) were limited. Therefore, the oxidation of Mn(II) by  $\text{SO}_5^{\cdot-}$  into Mn(III) may be the potential formation pathway of Mn(III) in the PM/BS process, which was different with the direct reduction pathway of Mn(VII) to Mn(III) [12]. The reduction of Mn(VII) to Mn(II) requires five-electron equivalents ( $5e^-$ ) and during the oxidation of  $\text{HSO}_3^-$  to  $\text{SO}_3^{\cdot-}$   $1e^-$  is abstract (eq. 13 and 14). The proposed mechanism of PM/BS process indicated that Mn(VII) was reduced to Mn(II) in the absence of DO, which is an interesting work that can be determined by measuring the concentration of Mn(II) in the future. Thus, one mole of Mn(VII) could oxidize five moles of  $\text{HSO}_3^-$  according to the electron equivalent relationship, which was also consistent with the observed optimal molar ratio of  $[\text{PM}]_0:[\text{BS}]_0$  in Fig. S3, Figs. S9 and S10. However, the excess consumption of  $\text{HSO}_3^-$  by manganese intermediates (e.g. Mn(III),  $\text{MnO}_2$ , Mn(V)) and radicals (e.g.  $\text{SO}_3^{\cdot-}$ ,  $\text{SO}_4^{\cdot-}$  and  $\text{SO}_5^{\cdot-}$ ), optimal molar ratio of  $[\text{PM}]_0:[\text{BS}]_0$  should be higher than 5, where it maximized at the ratio of 1:10–1:5 [18]. Then the further oxidation of  $\text{SO}_3^{\cdot-}$  needed the participation of DO. Based on mass equivalent and electron equivalent relationship, the theoretical reaction stoichiometry for the formation of Mn(III) in the PM/BS process could be proposed as eq. 15.

To confirm the proposed formation stoichiometry of Mn(III) in eq. 15, the stoichiometric molar ratio between the DO consumption ( $-\Delta[\text{DO}]$ ) and Mn(III) formation in the presence of PP buffer ( $\Delta[\text{Mn(III)-PP}]$ ) is investigated and illustrated in Fig. 3. After the additions of



**Fig. 3.** Effect of molar  $[\text{PM}]_0:[\text{BS}]_0$  ratios on the formation of Mn(III)-PP complex in the presence of PP buffer. Inset demonstrates a positive linear correlation between  $-\Delta[\text{DO}]$  and  $\Delta[\text{Mn(III)-PP}]$  in PM/BS process. Experimental conditions:  $[\text{PM}]_0 = 10\text{--}100 \mu\text{M}$ ,  $[\text{BS}]_0 = 50\text{--}500 \mu\text{M}$ ,  $\text{pH} = 5.0$  with 10 mM PP buffer,  $[\text{DO}]_0 = 9.1 \pm 0.3 \text{ mg L}^{-1}$ ,  $T = 25 \text{ }^\circ\text{C}$ .

PM and BS to the working solution, instant decreases of DO were always observed. Then the relationship between  $-\Delta[\text{DO}]$  and  $\Delta[\text{Mn(III)-PP}]$  was analyzed. As expected, a positive linear relationship ( $\Delta[\text{Mn(III)-PP}] = -0.68\Delta[\text{DO}] + 0.42$ ;  $R^2 = 0.999$ ) was observed. The observed molar transformation ratio of DO to Mn(III) was 0.68, and the DO concentration in the solution would increase to a certain extent (observation might not be obvious) in a relatively short period of time even if the flow rate of nitrogen was stability controlled, consistent with the reaction stoichiometry proposed in eq. 15 (i.e., 1.5 mol of oxygen is consumed per mol of Mn(III) formed). In the presence of micro-pollutants, the formed  $\text{SO}_5^{\cdot-}$  and its transformation products (e.g.,  $\text{SO}_4^{\cdot-}$ ,  $\text{HO}^{\cdot}$  and  $\text{HSO}_5^-$ ) might oxidize micro-pollutants and Mn(II) or directly self-assemble (eq. 16-18). Thus, the theoretical maximized DO consumption of the PM/BS process in the presence of micro-pollutants should be the complete oxidation of formed  $\text{SO}_3^{\cdot-}$  by DO (i.e.,  $[\text{DO}]_0 : [\text{BS}]_0 = 1:1$ ). However, in the absence of micro-pollutants, the transformation of  $\text{SO}_5^{\cdot-}$  to  $\text{SO}_4^{\cdot-}$  also simultaneously yields oxygen, which subsequently lowers the oxygen demand for the oxidation of  $\text{SO}_3^{\cdot-}$  (eq. 19 and 20). Note that the observed instant decreases of DO in the presence of micro-pollutants were always higher than those in the absence of micro-pollutants (Table S2). The presence of micro-pollutant in the PM/BS system may react with  $\text{SO}_5^{\cdot-}$ , lowering the formation of oxygen in eq. 19. Moreover, DO could be consumed in side reactions of short-lived intermediates of the micro-pollutants. The formation of hydrogen peroxide by disproportionation of superoxide (from reaction of oxygen with carbon centered radicals) may also be a potential sink for oxygen, which increase the DO consumption subsequently [57]. Therefore, the actual DO consumption for the degradation of micro-pollutants by the PM/BS process is proposed  $> 1.5[\text{PM}]_0$ .

EPR spectroscopic analysis was conducted to examine the formation of radical species under different DO concentrations (Fig. 4). The characteristic signal of DMPO- $\text{SO}_3^{\cdot-}$  adduct could be observed after 1 min of reaction time when DO was 0.1 and 9.3 mg L<sup>-1</sup> [58]. However, the plausible characteristic signal of DMPOX adduct was only observed when DO was 9.3 mg L<sup>-1</sup>, indicating that DO promoted the formation of DMPOX [59]. Similar DMPO-adduct was also observed in the metal-related reactions and chlorine species-induced oxidations [60,61]. 1-hexanol was added as a quencher of oxysulfur radicals (especially  $\text{SO}_4^{\cdot-}$  and  $\text{SO}_5^{\cdot-}$ ) to investigate its impact on  $\text{SO}_3^{\cdot-}$

transformation ( $[\text{DO}] = 9.3 \text{ mg L}^{-1}$ ). The presence of 1-hexanol lowered the peak intensity of DMPO- $\text{SO}_3^{\cdot-}$  adduct obviously. As 1-hexanol could quench oxysulfur radicals, the addition of 1-hexanol accelerated the transformation of  $\text{SO}_3^{\cdot-}$  indirectly. Therefore, the oxysulfur radicals and high initial concentrations of DO and manganese species are very important routes that can produce the relatively stable DMPOX. Compared with DMPO- $\text{SO}_3^{\cdot-}$  adduct, the signal intensity of DMPOX adduct was much lower, suggesting that the possibility of DMPO was trapped by primary radical is much higher than it was oxidized. Although  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$  were expected to exist due to a series of transformations of  $\text{SO}_3^{\cdot-}$ , the peak of DMPO- $\text{SO}_4^{\cdot-}$  and DMPO-OH adduct were too weak to be identified at the high concentration of DMPO [62]. Besides, there is a difference in the rate between the formation and decay of captured radicals and the oxidation of DMPO [59], which could also be well explained the above mentioned. As expected, the contribution of  $\text{HO}^{\cdot}$  to the degradation of IPM by the PM/BS process may be limited, consistent with the quenching results in Fig. S5, and it was found by probe experiments of nitrobenzene and coumarin [11,42].

To better understand the reaction mechanism of the PM/BS process, the  $\text{Co}^{2+}$ /PMS process was chosen as a suitable model for the generation of  $\text{SO}_4^{\cdot-}$  radical reactions, rather than complex chain reactions of Mn(III) (eq. 16, 21-23) [63-66]. As shown in Fig. S11, these pollutants were selectively degraded in the  $\text{Co}^{2+}$ /PMS and PM/BS processes, and the oxidation selectivity sequence was phenol < MET < IPM in the sulfate radical-dominated  $\text{Co}^{2+}$ /PMS process. Both PMS ( $\text{HSO}_5^-$ ) and BS ( $\text{SO}_3^{2-}$ ) can be activated to produce more oxidized sulfate radicals ( $\text{SO}_4^{\cdot-}$ ). Under the same concentration of both, the rate of oxidative degradation of micro-pollutants by  $\text{Co}^{2+}$ -activated PMS slower than the PM/BS process, which may be because PM can rapidly activate BS to sulfite radicals ( $\text{SO}_3^{\cdot-}$ ), resulting in higher  $\text{SO}_4^{\cdot-}$  steady-state concentrations. Additionally, as illustrated in Fig. S12, at 0 o'clock, the peak intensity of the DMPO- $\text{SO}_3^{\cdot-}$  adduct produced in the PM/BS process was much higher than that in the  $\text{Co}^{2+}$ /PMS process. In addition, their peak strength decreased as the reaction progresses, which was consistent with its pollutant degradation kinetics. Therefore, we can consider that the high steady-state concentration of  $\text{SO}_4^{\cdot-}$  may be the cause of rapid degradation of pollutants. Analogous to Mn(VII) and Fe(VI), Cr(VI) also has a higher standard oxidation potential ( $E^0(\text{HCrO}_4^-/\text{Cr}^{3+}) = 1.35 \text{ V}_{\text{NHE}}$ ), which may be an alternative activator for transforming sulfite to active radical species (i.e.,  $\text{SO}_4^{\cdot-}$ ) [25,67]. Additionally, it was also observed the signal intensity of DMPO- $\text{SO}_3^{\cdot-}$  adduct in the PM/BS process was significantly higher ( $\sim 4 \times 10^6 \text{ a.u.}$ ) than that of the Cr(VI)/S(IV) process (Fig. S13).

Though the dominant role of  $\text{SO}_4^{\cdot-}$  in PM/BS process has been proposed [42,43], the role of  $\text{SO}_5^{\cdot-}$  as an important intermediate should be emphasized, and the important contribution of Mn(III) to the degradation of IPM during PM/BS process cannot be ignored. However, the contribution rates of  $\text{SO}_4^{\cdot-}$ , Mn(III) and other radical species (i.e., Mn(V)) remain unclear in the PM/BS process, still needs a further investigation.

Based on the discussion above, a simplified reaction pathway for the abatement of micro-pollutant by the PM/BS process is proposed in Scheme 1. The first step involved the direct reduction of Mn(VII) by BS. Mn(VII) accepted  $5e^-$  from BS yielding Mn(II) and BS was rapidly oxidized to  $\text{SO}_3^{\cdot-}$  (eq. 13), which was in accordance with the optimal molar ratio of  $[\text{PM}]_0 : [\text{BS}]_0$  (i.e., 1:5) in Figs. S9 and S10. Then the formed  $\text{SO}_3^{\cdot-}$  is readily oxidized by DO into  $\text{SO}_5^{\cdot-}$ , which is the key reaction step to ensure subsequent reactions in the PM/BS process. In the absence of DO, both the formations of  $\text{SO}_5^{\cdot-}$  and Mn(III) were restricted, indicating that the formation of Mn(III) in the PM/BS process was not reduced from Mn(VII) directly, but from the oxidation of Mn(II) by  $\text{SO}_5^{\cdot-}$  under the catalysis of yield Mn(II). Due to the powerful oxidation ability of Mn(III) and the transformation products of  $\text{SO}_5^{\cdot-}$  ( $\text{SO}_4^{\cdot-}$ ,  $\text{HO}^{\cdot}$  and  $\text{HSO}_5^-$ ), all could contribute to the degradation of micro-pollutants in the PM/BS process.

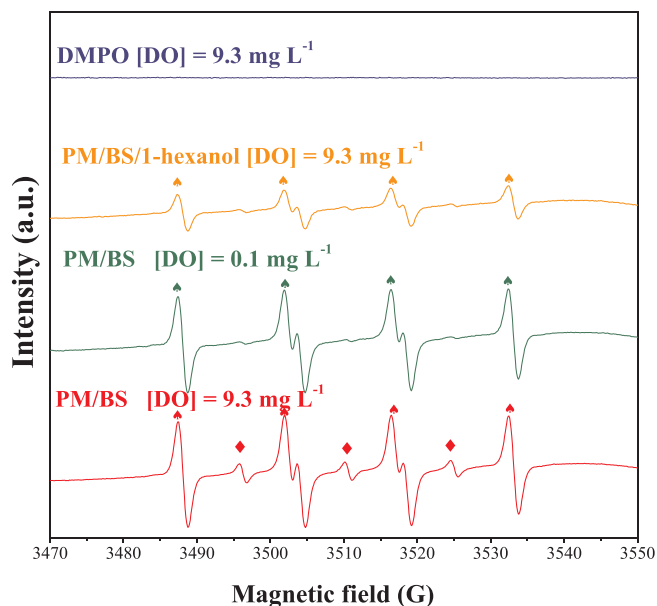
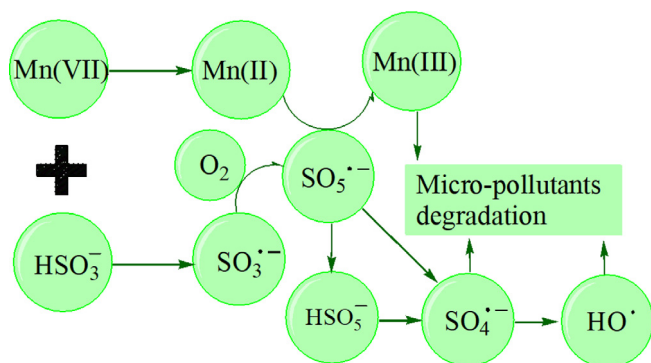


Fig. 4. Effects of DO and 1-hexanol on the EPR spectra of PM/BS process. Experimental conditions:  $[\text{IPM}]_0 = 5 \mu\text{M}$ ,  $[\text{PM}]_0 = 50 \mu\text{M}$ ,  $[\text{BS}]_0 = 250 \mu\text{M}$ ,  $[\text{DMPO}]_0 = 25 \text{ mM}$ ,  $\text{pH} = 6.5$  with 10 mM phosphate buffer,  $[\text{1-hexanol}]_0 = 10 \text{ mM}$ ,  $T = 25 \text{ }^\circ\text{C}$ . Symbols:  $\blacktriangle$  DMPO- $\text{SO}_3^{\cdot-}$ ,  $\blacklozenge$  DMPOX.



**Scheme 1.** Proposed degradation mechanism of micro-pollutants by PM/BS process.

#### 4. Conclusions

This study investigated the accelerated degradation of micro-pollutants by the PM/BS process from mechanistic aspects. Based on the results obtained, the following conclusions can be drawn:

- 1) The role of DO showed importantly on the degradation of micro-pollutants in the PM/BS process, and the stoichiometry of  $[\Delta\text{Mn(III)-PP}]:[-\Delta\text{DO}] = 1.5$  was obtained in this work.
- 2)  $\text{SO}_5^{\bullet-}$  was a key intermediate for the formations of Mn(III),  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^{\bullet}$  radicals in the PM/BS process, which may be beneficial to accelerate the reaction between PM and BS.
- 3) The contributors to the accelerated abatement of micro-pollutants by the PM/BS process mainly contributed to the high yields of Mn(III) and  $\text{SO}_4^{\bullet-}$ .

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2019.123556>.

#### References

- [1] S.D. Richardson, S.Y. Kimura, Water analysis: emerging contaminants and current issues, *Anal. Chem.* 88 (2016) 546–582.
- [2] R.L.L. Eggen, J. Hollender, A. Joss, M. Scharer, C. Stamm, Reducing the discharge of micropollutants in the aquatic environment: the benefits of upgrading wastewater treatment plants, *Environ. Sci. Technol.* 48 (2014) 7683–7689.
- [3] J.O. Tijani, O.O. Fatoba, O.O. Babajide, L.F. Petrik, Pharmaceuticals, endocrine disruptors, personal care products, nanomaterials and perfluorinated pollutants: a review, *Environ. Chem. Lett.* 14 (2016) 27–49.
- [4] T. Negishi, K. Kawasaki, S. Suzaki, H. Maeda, Y. Ishii, S. Kyuwa, Y. Kuroda, Y. Yoshikawa, Behavioral alterations in response to fear-provoking stimuli and tranlycpromine induced by perinatal exposure to bisphenol a and nonylphenol in male rats, *Environ. Health Persp.* 112 (2004) 1159–1164.
- [5] A. Novo, S. Andre, P. Viana, O.C. Nunes, C.M. Manaia, Antibiotic resistance, antimicrobial residues and bacterial community composition in urban wastewater, *Water Res.* 47 (2013) 1875–1887.
- [6] Y. Lee, U. von Gunten, Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine,

- chlorine dioxide, ferrate(VI), and ozone) and non-selective oxidants (hydroxyl radical), *Water Res.* 44 (2010) 555–566.
- [7] N. Klamerth, S. Malato, A. Aguera, A. Fernandez-Alba, G. Mailhot, Treatment of Municipal Wastewater Treatment Plant Effluents with Modified Photo-Fenton As a Tertiary Treatment for the Degradation of Micro Pollutants and Disinfection, *Environ. Sci. Technol.* 46 (2012) 2885–2892.
- [8] R. Zhang, Y. Yang, C.-H. Huang, L. Zhao, P. Sun, Kinetics and modeling of sulfonamide antibiotic degradation in wastewater and human urine by UV/H<sub>2</sub>O<sub>2</sub> and UV/PDS, *Water Res.* 103 (2016) 283–292.
- [9] B. Thokchom, P.P. Qiu, M.C. Cui, B. Park, A.B. Pandit, J. Khim, Magnetic Pd@Fe<sub>3</sub>O<sub>4</sub> composite nanostructure as recoverable catalyst for sono-electrohybrid degradation of Ibuprofen, *Ultrason. Sonochem.* 34 (2017) 262–272.
- [10] Y. Yang, J. Jiang, X. Lu, J. Ma, Y. Liu, Production of Sulfate Radical and Hydroxyl Radical by Reaction of Ozone with Peroxymonosulfate: A Novel Advanced Oxidation Process, *Environ. Sci. Technol.* 49 (2015) 7330–7339.
- [11] B. Sun, X. Guan, J. Fang, P.G. Tratnyek, Activation of manganese oxidants with bisulfite for enhanced oxidation of organic contaminants: the involvement of Mn(III), *Environ. Sci. Technol.* 49 (2015) 12414–12421.
- [12] B. Sun, H. Dong, D. He, D. Rao, X. Guan, Modeling the kinetics of contaminants oxidation and the generation of manganese(III) in the permanganate/bisulfite process, *Environ. Sci. Technol.* 50 (2016) 1473–1482.
- [13] J. Jiang, S.Y. Pang, J. Ma, H.L. Liu, Oxidation of phenolic endocrine disrupting chemicals by potassium permanganate in synthetic and real waters, *Environ. Sci. Technol.* 46 (2012) 1774–1781.
- [14] Y. Song, J. Jiang, J. Ma, S.-Y. Pang, Y.-Z. Liu, Y. Yang, C.-W. Luo, J.-Q. Zhang, J. Gu, W. Qin, ABTS as an electron shuttle to enhance the oxidation kinetics of substituted phenols by aqueous permanganate, *Environ. Sci. Technol.* 49 (2015) 11764–11771.
- [15] E. Hu, Y. Zhang, S. Wu, J. Wu, L. Liang, F. He, Role of dissolved Mn(III) in transformation of organic contaminants: Non-oxidative versus oxidative mechanisms, *Water Res.* 111 (2017) 234–243.
- [16] D.L. Parker, G. Sposito, B.M. Tebo, Manganese(III) binding to a pyoverdine siderophore produced by a manganese(II)-oxidizing bacterium, *Geochim. Cosmochim. Acta* 68 (2004) 4809–4820.
- [17] Y. Wang, A.T. Stone, Phosphonate- and carboxylate-based chelating agents that solubilize (hydr)oxide-bound Mn(III), *Environ. Sci. Technol.* 42 (2008) 4397–4403.
- [18] Y. Gao, J. Jiang, Y. Zhou, S.Y. Pang, C.C. Jiang, Q. Guo, J.B. Duan, Does soluble Mn(III) oxidant formed in situ account for enhanced transformation of triclosan by Mn(VII) in the presence of ligands? *Environ. Sci. Technol.* 52 (2018) 4785–4793.
- [19] Y. Gao, J. Jiang, Y. Zhou, S.-Y. Pang, J. Ma, C. Jiang, Z. Wang, P.-X. Wang, L.-H. Wang, J. Li, Unrecognized role of bisulfite as Mn(III) stabilizing agent in activating permanganate (Mn(VII)) for enhanced degradation of organic contaminants, *Chem. Eng. J.* 327 (2017) 418–422.
- [20] B. Sun, Q.Q. Bao, X.H. Guan, Critical role of oxygen for rapid degradation of organic contaminants in permanganate/bisulfite process, *J. Hazard. Mater.* 352 (2018) 157–164.
- [21] G.D. Fang, J. Gao, D.D. Dionysiou, C. Liu, D.M. Zhou, Activation of persulfate by quinones: free radical reactions and implication for the degradation of PCBs, *Environ. Sci. Technol.* 47 (2013) 4605–4611.
- [22] P.C. Xie, Y.Z. Guo, Y.Q. Chen, Z.P. Wang, R. Shang, S.L. Wang, J.Q. Ding, Y. Wan, W. Jiang, J. Ma, Application of a novel advanced oxidation process using sulfite and zero-valent iron in treatment of organic pollutants, *Chem. Eng. J.* 314 (2017) 240–248.
- [23] D. Zhou, L. Chen, J. Li, F. Wu, Transition metal catalyzed sulfite auto-oxidation systems for oxidative decontamination in waters: A state-of-the-art minireview, *Chem. Eng. J.* 346 (2018) 726–738.
- [24] M.V. Alipazaga, R.G.M. Moreno, N. Coicchev, Synergistic effect of Ni(II) and Co(II) ions on the sulfite induced autoxidation of Cu(II)/tetraglycine complex, *Dalton T.* 13 (2004) 2036–2040.
- [25] B. Jiang, Y.K. Liu, J.T. Zheng, M.H. Tan, Z.H. Wang, M.B. Wu, Synergetic transformations of multiple pollutants driven by Cr(VI)-sulfite reactions, *Environ. Sci. Technol.* 49 (2015) 12363–12371.
- [26] P. Neta, R.E. Huie, A.B. Ross, Rate constants for reactions of inorganic radicals in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 1027–1284.
- [27] E.A. Betterton, M.R. Hoffmann, Kinetics and Mechanism of the Oxidation of Aqueous Hydrogen Sulfide by Peroxymonosulfate, *Environ. Sci. Technol.* 24 (1990) 1819–1824.
- [28] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $\cdot\text{OH}/\text{O}^{\bullet-}$ ) in Aqueous Solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [29] T.N. Das, R.E. Huie, P. Neta, Reduction potentials of  $\text{SO}_3^{\bullet-}$ ,  $\text{SO}_5^{\bullet-}$ , and  $\text{S}_4\text{O}_6^{\bullet-}$  radicals in aqueous solution, *J. Phys. Chem. A.* 103 (1999) 3581–3588.
- [30] Tomi Nath Das, Reactivity and Role of  $\text{SO}_5^{\bullet-}$  Radical in Aqueous Medium Chain Oxidation of Sulfite to Sulfate and Atmospheric Sulfuric Acid Generation, *J. Phys. Chem. A* 105 (2001) 9142–9155.
- [31] E. Hayon, A. Treinin, J. Wilf, Electronic spectra, photochemistry, and autoxidation mechanism of the sulfite-bisulfite-pyrosulfite systems, The  $\text{SO}_2^{\bullet-}$ ,  $\text{SO}_3^{\bullet-}$ ,  $\text{SO}_4^{\bullet-}$ , and  $\text{SO}_5^{\bullet-}$  radicals, *J. Am. Chem. Soc.* 94 (1972) 47–57.
- [32] S.F. Sun, S.Y. Pang, J. Jiang, J. Ma, Z.S. Huang, J.M. Zhang, Y.L. Liu, C.B. Xu, Q.L. Liu, Y.X. Yuan, The combination of ferrate(VI) and sulfite as a novel advanced oxidation process for enhanced degradation of organic contaminants, *Chem. Eng. J.* 333 (2018) 11–19.
- [33] D. Simazaki, R. Kubota, T. Suzuki, M. Akiba, T. Nishimura, S. Kunikane, Occurrence of selected pharmaceuticals at drinking water purification plants in Japan and implications for human health, *Water Res.* 76 (2015) 187–200.
- [34] C.Y. Hu, A.P. Li, Y.L. Lin, X. Ling, M. Cheng, Degradation kinetics and DBP formation during chlorination of metribuzin, *J. Taiwan Inst. Chem. E.* 80 (2017)

- 255–261.
- [35] X. Zhao, E. Salhi, H. Liu, J. Ma, U. von Gunten, Kinetic and mechanistic aspects of the reactions of iodide and hypiodous acid with permanganate: oxidation and disproportionation, *Environ. Sci. Technol.* 50 (2016) 4358–4365.
- [36] D.R. Duling, Simulation of multiple isotropic spin-trap EPR spectra, *J. Magn. Res. Ser. B* 104 (1994) 105–110.
- [37] Y. Gao, Y. Zhou, S.-Y. Pang, J. Jiang, Z. Yang, Y. Shen, Z. Wang, P.-X. Wang, L.-H. Wang, New Insights into the Combination of Permanganate and Bisulfite as a Novel Advanced Oxidation Process: Importance of High Valent Manganese-Oxo Species and Sulfate Radical, *Environ. Sci. Technol.* 53 (2019) 3689–3696.
- [38] X.L. Shi, N. Dalal, K.S. Kasprzak, Enhanced generation of hydroxyl radical and sulfur trioxide anion radical from oxidation of sodium sulfite, nickel(II) sulfite, and nickel subsulfide in the presence of nickel(II) complexes, *Environ. Health. Persp.* 102 (1994) 91–96.
- [39] K. Rangelova, S. Chatterjee, M. Ehrenshaft, D.C. Ramirez, F.A. Summers, M.B. Kadiiska, R.P. Mason, Protein radical formation resulting from eosinophil peroxidase-catalyzed oxidation of sulfite, *J. Biol. Chem.* 285 (2010) 24195–24205.
- [40] R.E. Huie, P. Neta, Chemical behavior of  $\text{SO}_3^{\cdot-}$  and  $\text{SO}_5^{\cdot-}$  radicals in aqueous solution, *J. Phys. Chem.* 88 (1984) 5665–5669.
- [41] D.T.F. Kuo, D.W. Kirk, C.Q. Jia, The chemistry of aqueous S(IV)-Fe-O<sub>2</sub> system: state of the art, *J. Sulfur Chem.* 27 (2006) 461–530.
- [42] Z.Y. Shi, C. Jin, J. Zhang, L. Zhu, Insight into mechanism of arsenic acid degradation in permanganate-sulfite system: Role of reactive species, *Chem. Eng. J.* 359 (2019) 1463–1471.
- [43] L. Xu, H. Dong, K. Xu, J. Li, Z. Qiang, Accelerated degradation of pesticide by permanganate oxidation: A comparison of organic and inorganic activations, *Chem. Eng. J.* 369 (2019) 1119–1128.
- [44] S. Zhong, H. Zhang, New insight into the reactivity of Mn(III) in bisulfite/permanganate for organic compounds oxidation: The catalytic role of bisulfite and oxygen, *Water Res.* 148 (2019) 198–207.
- [45] Y.-H. Guan, J. Ma, X.-C. Li, J.-Y. Fang, L.-W. Chen, Influence of pH on the Formation of Sulfate and Hydroxyl Radicals in the UV/Peroxymonosulfate System, *Environ. Sci. Technol.* 45 (2011) 9308–9314.
- [46] J. Jeong, J. Jung, W.J. Cooper, W.H. Song, Degradation mechanisms and kinetic studies for the treatment of X-ray contrast media compounds by advanced oxidation/reduction processes, *Water Res.* 44 (2010) 4391–4398.
- [47] J.G. Muller, R.P. Hickerson, R.J. Perez, C.J. Burrows, DNA damage from sulfite autoxidation catalyzed by a nickel(II) peptide, *J. Am. Chem. Soc.* 119 (1997) 1501–1506.
- [48] Y. Dhayal, C.P.S. Chandel, K.S. Gupta, The influence of hydroxyl volatile organic compounds on the oxidation of aqueous sulfur dioxide by oxygen, *Environ. Sci. Pollut. Res.* 21 (2014) 7805–7817.
- [49] V.K. Meena, Y. Dhayal, D.S. Rathore, C.P.S. Chandel, K.S. Gupta, Inhibition of aqueous sulfur dioxide autoxidation by aliphatic, acyclic, aromatic, and heterocyclic volatile organic compounds, *Int. J. Chem. Kinet.* 49 (2017) 221–233.
- [50] G. Scholes, R.L. Willson,  $\gamma$ -Radiolysis of aqueous thymine solutions. Determination of relative reaction rates of OH radicals, *Trans. Faraday Soc.* 63 (1967) 2983–2993.
- [51] R.E. Huie, C.L. Clifton, N. Alstein, A pulse radiolysis and flash photolysis study of the radicals  $\text{SO}_2^{\cdot-}$ ,  $\text{SO}_3^{\cdot-}$ ,  $\text{SO}_4^{\cdot-}$  and  $\text{SO}_5^{\cdot-}$ , *Inter. J. Radiat. Appl. Instrum. Part C, Radiat. Phys. Chem.* 33 (1989) 361–370.
- [52] J.M. Zhang, J. Ma, H.R. Song, S.F. Sun, Z.X. Zhang, T. Yang, Organic contaminants degradation from the S(IV) autoxidation process catalyzed by ferrous-manganous ions: A noticeable Mn(III) oxidation process, *Water Res.* 133 (2018) 227–235.
- [53] É. Záhonyi-Budó, L.I. Simándi, Selective oxidations with short-lived manganese(V), *Studies in Surface Science and Catalysis*, Elsevier (1994) 623–628.
- [54] É. Záhonyi-Budó, L. Simándi, Oxidations with unstable manganese(VI) in acidic solution, *Inorg. Chim. Acta* 237 (1995) 173–175.
- [55] J. Berglund, S. Fronaeus, L.I. Elding, Kinetics and mechanism for manganese catalyzed oxidation of sulfur(IV) by oxygen in aqueous-solution, *Inorg. Chem.* 32 (1993) 4527–4538.
- [56] S.M. Webb, G.J. Dick, J.R. Bargar, B.M. Tebo, Evidence for the presence of Mn(III) intermediates in the bacterial oxidation of Mn(II), *P. Natl. Acad. Sci. USA* 102 (2005) 5558–5563.
- [57] Sonntag, C. V., H.P., S. Peroxyl radicals in aqueous solutions-Peroxyl radicals, Wiley: New York 1997.
- [58] C. Mottley, R.P. Mason, Sulfate anion free radical formation by the peroxidation of (bi)sulfite and its reaction with hydroxyl radical scavengers, *Arch. Biochem. Biophys.* 267 (1988) 681–689.
- [59] R.A. Floyd, L.M. Soong, Spin trapping in biological systems. Oxidation of the spin trap 5,5-dimethyl-1-pyrroline-1-oxide by a hydroperoxide-hematin system, *Biochem. Biophys. Res. Co.* 74 (1977) 79–84.
- [60] J. Fontmorin, R.B. Castillo, W. Tang, M. Sillanpää, Stability of 5,5-dimethyl-1-pyrroline-N-oxide as a spin-trap for quantification of hydroxyl radicals in processes based on Fenton reaction, *Water. Res.* 99 (2016) 24–32.
- [61] S.D. Stan, M.A. Daeschel, 5,5-Dimethyl-2-pyrrolidone-N-oxyl formation in electron spin resonance studies of electrolyzed NaCl solution using 5, 5-dimethyl-1-pyrroline-N-oxide as a spin trapping agent, *J. Agr. Food Chem.* 53 (2005) 4906–4910.
- [62] K. Rangelova, R.P. Mason, The fidelity of spin trapping with DMPO in biological systems, *Magn. Reson. Chem.* 49 (2011) 152–158.
- [63] C. Brandt, R. Van Eldik, transition metal-catalyzed oxidation of sulfur(IV) oxides. Atmospheric-relevant processes and mechanisms, *Chem. Rev.* 95 (1995) 119–190.
- [64] J.E. Van Benschoten, W. Lin, W.R. Knocke, Kinetic modeling of manganese (II) oxidation by chlorine dioxide and potassium permanganate, *Environ. Sci. Technol.* 26 (1992) 1327–1333.
- [65] J.K. Klewicki, J.J. Morgan, Kinetic behavior of Mn(III) complexes of pyrophosphate, EDTA, and citrate, *Environ. Sci. Technol.* 32 (1998) 2916–2922.
- [66] M. Ahmadi, F. Ghanbari, A. Alvarez, S.S. Martinez, UV-LEDs assisted peroxy-monosulfate/Fe<sup>2+</sup> for oxidative removal of carmoisine: The effect of chloride ion, *Korean J. Chem. Eng.* 34 (2017) 2154–2161.
- [67] H. Dong, G. Wei, W. Fan, S. Ma, H. Zhao, W. Zhang, X. Guan, T.J. Strathmann, Reinvestigating the role of reactive species in the oxidation of organic co-contaminants during Cr(VI) reactions with sulfite, *Chemosphere* 196 (2018) 593–597.