Fe(III)-Activated Sulfite Revisited: The Overlooked Role of High-Valent Iron(IV)-Oxo Complex (Fe(IV)) in Water Treatment

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Research Article

Keywords: Fe(III)/sulfite system, Methyl phenyl sulfoxide (PMSO), High-valent iron(IV)-oxo complex, Free radicals, Kinetic modeling, Water treatment

Posted Date: July 30th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-724195/v1>

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**Fe(III)-activated sulfite revisited: The overlooked role of high-valent
iron(IV)-oxo complex (Fe(IV)) in water treatment**

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Abstract

Sulfate radical ($\text{SO}_4^{\bullet-}$) and its secondary radical (hydroxyl radical, $\cdot\text{OH}$) are commonly recognized as the primary reactive intermediates formed by Fe(III)/sulfite system. However, it still remains unknown whether Fe(IV) is involved in this system where the well documented Fe(IV)-precursors (i.e., Fe(II) and persulfates) were in-situ generated. Intriguingly, we observed that methyl phenyl sulfone (PMSO_2), indicative of Fe(IV) formation, was formed during methyl phenyl sulfoxide (PMSO) transformation in Fe(III)/sulfite system, which unprecedentedly verified that Fe(IV) played a crucial role in it. In parallel, the involvement of $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ in this system were also identified, but the limited $\cdot\text{OH}$ was proposed to be derived from hydrolysis of both Fe(IV) and $\text{SO}_4^{\bullet-}$, rather than by self-decay of $\text{SO}_4^{\bullet-}$ alone. Moreover, the contribution of Fe(IV) relative to it of free radicals was explored by monitoring the yield of PMSO_2 . It was disclosed that the relative contribution of Fe(IV) was progressively promoted as Fe(III)-sulfite reaction proceeding with an upper limit of 80%-90%, and it was accelerated by promoting Fe(III) and sulfite dosages, while was declined with increasing pH. Furthermore, a kinetic model was developed, which precisely simulated kinetic traces of PMSO transformation and dissolved oxygen evolution in Fe(III)/sulfite system. More importantly, the kinetic model offered the first insight into the evolution of Fe(IV), $\text{SO}_4^{\bullet-}$, and $\cdot\text{OH}$, which provided in-depth mechanistic understanding of the iron-catalyzed sulfite auto-oxidation process. Considering the different chemical properties between Fe(IV) and free radicals, it is urgent to re-evaluate the decontamination process by iron/sulfite system.

Keywords: Fe(III)/sulfite system; Methyl phenyl sulfoxide (PMSO); High-valent iron(IV)-oxo complex; Free radicals; Kinetic modeling; Water treatment

1. Introduction

In recent years, sulfate radical ($\text{SO}_4^{\bullet-}$)-based advanced oxidation processes (AOPs) have attracted a lot of attention for pollutants abatement due to the high standard reduction potential of $\text{SO}_4^{\bullet-}$ (2.5-3.1 V) (Zhou *et al.* 2015a, Oh *et al.* 2016, Lee *et al.* 2020). The sulfite and persulfates (peroxomonosulfate (HSO_5^-) and peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$)) are the most frequently used precursors of $\text{SO}_4^{\bullet-}$. Comparing with persulfates, the low cost, high solubility, and eco-friendly features single out sulfite as an excellent alternative chemical source of $\text{SO}_4^{\bullet-}$ in practical application scenarios (Zhou *et al.* 2018). Among several AOPs of activating sulfite to produce reactive oxidants (Brandt. and Eldik. 1995, Chen *et al.* 2017), the iron-catalyzed sulfite auto-oxidation process has been widely investigated not merely because of the high reactivity, cost-effective, and environmental-friendly characters of iron activator, but because this process plays a vital role in the conversion of atmospheric sulfur species (Brandt. and Eldik. 1995, Chen *et al.* 2017, Zhou *et al.* 2018).

This auto-catalysis process is initiated by Fe(III)-sulfite (FeSO_3^+) complex formation (Eq. 1) and its self-decomposition with forming $\text{SO}_3^{\bullet-}$ radical (Eq. 2). Subsequently, dissolved oxygen (DO) oxidizes $\text{SO}_3^{\bullet-}$ to produce the peroxymonosulfate anion radical ($\text{SO}_5^{\bullet-}$, Eq. 3), which triggers radical chain reactions (simplified to Eqs. 4-11) with forming the key reactive oxidative species (ROS) precursors (HSO_5^- and $\text{S}_2\text{O}_8^{2-}$) and the final reactive species ($\text{SO}_4^{\bullet-}$). In light of this paradigm, numerous researches recognized that $\text{SO}_4^{\bullet-}$ and the

secondary radical (hydroxyl radical, $\cdot\text{OH}$) generated by $\text{SO}_4^{\cdot-}$ hydrolysis are the primary ROS formed in Fe(III)/sulfite system (Chen *et al.* 2012, Guo *et al.* 2013, Zhou *et al.* 2014, Zhou *et al.* 2015b, Yu *et al.* 2016, Xie *et al.* 2017, Du *et al.* 2018, Xie *et al.* 2019, Chen *et al.* 2020).

However, it is noteworthy that the primary ROS formed by Fe(II)/ HSO_5^- and Fe(II)/ $\text{S}_2\text{O}_8^{2-}$ systems has been recognized as the aqueous high-valent iron(IV)-oxo complex ($\text{Fe}^{\text{IV}}=\text{O}^{2+}$, simplified as Fe(IV)), rather than the long recognized $\text{SO}_4^{\cdot-}$, based on methyl

phenyl sulfoxide (PMSO) probe assay (Wang *et al.* 2018, Wang *et al.* 2019b, Wang *et al.* 2019c, Wang *et al.* 2020). In these studies, Wang *et al.* firstly identified that Fe(IV) oxidized PMSO to methyl phenyl sulfone (PMSO₂) through oxygen-atom transfer, markedly different from the SO₄^{•-} and [•]OH involved oxidation products of PMSO (Wang *et al.* 2018). Further, they observed that PMSO was almost completely transformed to PMSO₂, the indicative of Fe(IV) formation, in Fe(II)/HSO₅⁻ (Eq. 12) and Fe(II)/S₂O₈²⁻ (Eq. 13) systems (Wang *et al.* 2018, Wang *et al.* 2019b).

Unfortunately, there are few studies devoted to exploring the role of Fe(IV) in Fe(III)/sulfite system. There is thereby an urgent need but it is still a significant challenge to reveal the exact nature of ROS formed in this system and explore their complex evolution trends.

To this end, the possibility of Fe(IV) involvement in Fe(III)/sulfite system was investigated by using PMSO as the probe, paying special attention to quantifying the relative contribution of Fe(IV) and free radicals by calculating the yield of PMSO₂ ($\eta(\text{PMSO}_2)$, the molar ratio of PMSO₂ production to PMSO loss). Moreover, electron paramagnetic resonance (EPR) technique and alcohol scavenging experiment were employed to identify the role of free radicals. In parallel, effects of reactants dosage and solution pH on PMSO transformation in Fe(III)/sulfite system were monitored. Furthermore, a kinetic model was established to simulate the PMSO transformation kinetic profiles in Fe(III)/sulfite system and provided the mechanistic insights into the evolution of different ROS therein.

2. Experimental

Details regarding the chemicals are supplied in supplementary materials Text S1. The procedure of the batch experiments of transforming PMSO in Fe(III)/sulfite system are given in Text S2. The analytical methods of PMSO and PMSO₂ as well as the operation of ESR analysis are provided in Text S3.

3. Results and discussion

3.1 Probing Fe(IV) and free radicals formation in Fe(III)/sulfite system

3.1.1 Oxidation of PMSO and production of PMSO₂

Transformation of PMSO by Fe(III)/sulfite system was investigated under a typical condition ([PMSO]₀ = 50 μM, [Fe(III)]₀ = 1 mM, [sulfite]₀ = 0.5 mM, and pH 3.0) to probe Fe(IV) formation. As shown in **Figure 1**, PMSO₂ was progressively formed along with PMSO degradation by Fe(III)/sulfite system. No PMSO degradation was obtained in control experiments with Fe(III) or sulfite alone (**Figure 1a**). Moreover, η(PMSO₂) value gradually increased from 30% at 10 s to 90% at 300 s (**Figure 1c**). These results strongly supported that Fe(IV) was generated in Fe(III)/sulfite system, and the relative contribution of Fe(IV) was increased as the reaction progress. Interestingly, this was quite different from the result reported by Dong et al. (2020), who claimed that Fe(IV) was not formed in Fe(III)/sulfite system based on their observation that no PMSO₂ was produced during PMSO transformation by Fe(III)/sulfite system ([PMSO]₀ = 20 μM, [Fe(III)]₀ = 0.1 mM, [sulfite]₀ = 0.5 mM, pH = 3.0). This discrepancy was rationalized by the effect of reactants dosage on Fe(IV) relative contribution in Fe(III)/sulfite system, as discussed later.

Figure 1. PMSO degradation (a) and PMSO₂ production (b), as well as the calculated $\eta(\text{PMSO}_2)$ value (c) by Fe(III) alone, sulfite alone or in Fe(III)/sulfite system. Experimental conditions: $[\text{PMSO}]_0 = 50 \mu\text{M}$, $[\text{Fe(III)}]_0 = 1 \text{ mM}$, $[\text{sulfite}] = 0.5 \text{ mM}$, and $\text{pH} = 3.0$.

3.1.2 EPR spectra analysis

EPR was employed to identify the nature of free radicals produced in Fe(III)/sulfite system with using DMPO as the spin-trapping agent ($[\text{PMSO}]_0 = 50 \mu\text{M}$, $[\text{Fe(III)}]_0 = 1 \text{ mM}$,

[sulfite]₀ = 0.5 mM, and pH 3.0). As illustrated in **Figure 2a**, strong signals of both DMPO[•]-OH and DMPO[•]-OSO₃⁻ adducts were observed in EPR spectrum of Fe(III)/sulfite system. Generally, the occurrence of DMPO[•]-OH signal was explained by the fast transformation from DMPO[•]-OSO₃⁻ to DMPO[•]-OH adduct (**Figure S1**) and the decay of SO₄^{•-} with forming [•]OH as the secondary free radical (Eqs. 14-15) (Davies *et al.* 1992, Wei *et al.* 2017, Du *et al.* 2018, Xie *et al.* 2019, Gao *et al.* 2020).

Figure 2. EPR spectra obtained from Fe(III)/sulfite system in the presence of DMPO (a), and the effect of TBA on PMSO degradation (b), PMSO₂ production (c), as well as calculated η(PMSO₂) values (d) by Fe(III)/sulfite system. Experimental conditions: [PMSO]₀ = 50 μM,

[Fe(III)]₀ = 1 mM, [sulfite]₀ = 0.5 mM, [DMPO]₀ = 100 mM, and pH = 3.0. [●] Represented the DMPO[•]-OSO₃⁻ adduct signal ($\alpha_N = 1.52$ mT, $\alpha_{\beta-H} = 1.00$ mT, $\alpha_{\gamma-H1} = 0.14$ mT, $\alpha_{\gamma-H2} = 0.08$ mT); [◆] Represented the DMPO[•]-OH adduct signal ($\alpha_N = 1.49$ mT, $\alpha_H = 1.51$ mT)].

In addition to this explanation, the transformation of DMPO by Fe(IV) (**Figure S2**) (Xu *et al.* 2017) and the formation of [•]OH from Fe(IV) hydrolysis (Eq. 16) (Jacobsen *et al.* 1998) might also made contribution to DMPO[•]-OH signal occurrence in Fe(III)/sulfite system:

This inference was supported by Wang *et al.* (2018) who found that DMPO[•]-OH adduct signal also occurred in DMPO trapped EPR spectra of Fe(II)/O₃, Fe(II)/PDS, and Fe(II)/PMS systems, which were identified as Fe(IV)-dominated AOPs. Moreover, Zong *et al.* (2021) also reported that [•]OH, formed by Fe(IV) self-decay, was responsible for DMPO[•]-OH adduct signal occurrence in the EPR spectra of Fe(II)/periodate system. Collectively, EPR spectra analysis identified that both SO₄^{•-} and [•]OH were formed in Fe(III)/sulfite system where [•]OH was derived from the hydrolysis of both Fe(IV) and SO₄^{•-}, which was quite different from the literature assertion that [•]OH was the only secondary ROS of SO₄^{•-} decay.

3.1.3 Alcohol scavenging effect

To further clarify the relative contribution of [•]OH, effect of TBA on PMSO transformation in Fe(III)/sulfite system ([PMSO]₀ = 50 μM, [Fe(III)]₀ = 1 mM, [sulfite]₀ = 0.5 mM, and pH 3.0) was explored. The second-order rate constants for TBA and PMSO with the three ROS (Fe(IV), SO₄^{•-}, and [•]OH) implied that TBA has higher reactivity in scavenging [•]OH, while was less reactive in capturing Fe(IV) and SO₄^{•-} (see **Table S1** for the specific rate

constants). As shown in **Figures 2b-2d**, 10 mM TBA ($[TBA]_0:[PMSO]_0 > 100$) slightly inhibited PMSO degradation, and thus marginally promoted $\eta(PMSO_2)$ value, consistent with previous studies where TBA mildly inhibited the degradation of contaminants (e.g., carbamazepine, Orange II, diclofenac, chloramphenicol, aniline, sulfamethoxazole, propranolol, etc.) in iron/sulfite systems (Chen *et al.* 2012, Xie *et al.* 2017, Du *et al.* 2018, Wang *et al.* 2019a, Xie *et al.* 2019, Yuan *et al.* 2019, Chen *et al.* 2020, Dong *et al.* 2020). This result disclosed that $\cdot OH$ was involved in PMSO transformation by Fe(III)/sulfite system, but the relative contribution of $\cdot OH$ was limited and far less than that of Fe(IV) and $SO_4^{\cdot-}$, which might be ascribed to the slow hydrolysis rate of Fe(IV) (Eq. 16) and $SO_4^{\cdot-}$ (Eqs. 14-15). For instance, it had been evidenced that $< 0.1\%$ $SO_4^{\cdot-}$ would react with H_2O to generate $\cdot OH$ under acidic conditions (Eq.14) (Brandt *et al.* 1994, Zhou *et al.* 2015b), and the reaction between $SO_4^{\cdot-}$ and OH^- (Eq. 15) could be ignored at $pH < 7$ (Furman *et al.* 2010, Guan *et al.* 2011).

3.2 Factors affecting the transformation of PMSO in Fe(III)/sulfite system

3.2.1 Effect of Fe(III) concentration

Effect of Fe(III) initial concentration ($[Fe(III)]_0 = 0.1-5$ mM) on PMSO (50 μM) transformation was investigated in Fe(III)/sulfite system ($[sulfite]_0 = 0.5$ mM, pH 3.0). As shown in **Figure S3**, $\Delta[PMSO]$ at 300 s ($\Delta[PMSO]_{300s}$) increased from 4.3 to 12.4 μM with increasing $[Fe(III)]_0$ from 0.1 to 1 mM. This was attributed to the significant promotion of $FeSO_3^+$ complex content as the increase of $[Fe(III)]_0$ (see the simulated $[FeSO_3^+]$ by Visual MINTEQ in **Figure S4**). However, $\Delta[PMSO]_{300s}$ declined to 11.5 μM with further increasing

[Fe(III)]₀ to 5 mM, because excess Fe(II), derived from FeSO₃⁺ complex decomposition (Eq. 2), competitively consumed ROS (Eqs. 7-8 and Eq.17) (Lee and Rochelle 1987, Brandt. and Eldik. 1995, Mártire *et al.* 2002):

Moreover, no PMSO₂ was formed with 0.1 mM [Fe(III)]₀, while Δ[PMSO₂] at 300 s (Δ[PMSO₂]_{300s}) increased from 6 to 10.8 μM with increasing [Fe(III)]₀ from 0.5 to 5 mM (**Figure S3b**). As for the concerned η(PMSO₂) value, it was increased with increasing [Fe(III)]₀ (**Figure S3c**). For instance, η(PMSO₂) value at 300 s was significantly increased from 0 to 94% with increasing [Fe(III)]₀ from 0.1 to 5 mM, implying that the relative contribution of Fe(IV) was strongly promoted with the increase of [Fe(III)]₀. This was rationalized by the fact that the increase of Fe(III) promoted Fe(II) content through accelerating FeSO₃⁺ complex formation and decay (Eqs. 1-2), which further enhanced Fe(II)-HSO₅⁻ (Eq. 12) and Fe(II)-S₂O₈²⁻ (Eq. 13) interaction. The [Fe(III)]₀-dependent variation of PMSO₂ production well explained the aforementioned one-sided statement by Dong et al. (2020), who asserted that no Fe(IV) was formed in Fe(III)/sulfite system according to the absence of PMSO₂ formation in the case with a low [Fe(III)]₀ ([Fe(III)]₀:[sulfite]₀ = 0.2:1).

3.2.2 Effect of sulfite concentration

Figure S5 showed PMSO transformation by Fe(III)/sulfite system with different sulfite initial concentration (0.1-0.75 mM) at a fixed [Fe(III)]₀ (1 mM). Increasing [sulfite]₀ from 0.1 to 0.5 mM gave rise to a larger Δ[PMSO]_{300s} (from 4.0 to 12.4 μM), while Δ[PMSO]_{300s}

decreased to 9.4 μM as $[\text{sulfite}]_0$ further increasing to 0.75 mM. The Visual MINTEQ calculation results showed that the increase of $[\text{sulfite}]_0$ also led to a higher $[\text{FeSO}_3^+]$ (**Figure S6**) (Brandt *et al.* 1994). However, excessive sulfite would quench ROS (Huie and Neta 1987, Brandt. and Eldik. 1995, Buxton *et al.* 1996, Jacobsen *et al.* 1998). Meanwhile, $\Delta[\text{PMSO}_2]_{300\text{s}}$ increased from 3.1 to 10.4 μM with increasing $[\text{sulfite}]_0$ from 0.1 to 0.5 mM, and then further decreased to 8.1 μM with increasing $[\text{sulfite}]_0$ to 0.75 mM (**Figure S5b**). Furthermore, a positive correlation between $\eta(\text{PMSO}_2)$ value and $[\text{sulfite}]_0$ was obtained (**Figure S5c**). This might be attributed to the fact that: (i) the increase of $[\text{sulfite}]_0$ enhanced the reduction of Fe(III) to Fe(II) (Eq. 2), similar to the effect of $[\text{Fe(III)}]_0$; (ii) the reactivity of sulfite towards $\text{SO}_4^{\bullet-}$ ($1.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Brandt. and Eldik. 1995) and $\cdot\text{OH}$ ($4.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Huie and Neta 1987) was much higher than it towards Fe(IV) ($2.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) (Jacobsen *et al.* 1998).

3.2.3 Effect of solution pH

Transformation of PMSO (50 μM) by Fe(III)/sulfite system ($[\text{Fe(III)}]_0 = [\text{sulfite}]_0 = 0.5 \text{ mM}$) was investigated at pH range of 3.0-6.0. As shown in **Figure S7**, $\Delta[\text{PMSO}]_{300\text{s}}$ was significantly declined from 7.5 μM at pH 3.0 to less than 3.5 μM at pH 4.0 and almost no PMSO was degraded at pH 4.5-6.0. At the same time, $\Delta[\text{PMSO}_2]_{300\text{s}}$ decreased from 6.0 μM at pH 3.0 to 2.9 μM at pH 4.0. These results might be ascribed to the precipitation of Fe(III) at high pH. Moreover, $\eta(\text{PMSO}_2)$ value at 300 s was decreased from 83% at pH 3.0 to 53% at pH 4.0, indicating that the relative contribution of Fe(IV) was decreased with increasing pH. This was attributed to the fact that Fe(IV) oxidation ability decreased with the increasing of pH (Louwerse *et al.* 2008, Bataineh *et al.* 2012, Lu *et al.* 2018), while the reactivity of $\text{SO}_4^{\bullet-}$

and $\cdot\text{OH}$ was insensitive to pH (Zhou *et al.* 2015a, Lee *et al.* 2020).

3.3 Kinetic modeling

3.3.1 PMSO transformation kinetics

The complex pathways of Fe(IV) , $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ generation in Fe(III)/sulfite system, as well as the consumption of them by contaminants and side reactions were illustrated in **Figure 3a**. Based on this schematic, a kinetic model was established (see **Table S2**), which provided a powerful tool for taking the further mechanistic insights into ROS evolution in Fe(III)/sulfite system. The program Kintecus (Ianni) was employed to perform the simulation. As shown in **Figures 3b-3d**, the experimental data of PMSO degradation, PMSO_2 formation, and $\eta(\text{PMSO}_2)$ values were well simulated, verifying the accuracy of the proposed kinetic model.

Figure 3. Schematic illustration for the mechanism of possible reaction intermediates in Fe(III)/sulfite system (a), kinetic simulation for PMSO degradation (b) and PMSO₂ production (c) as well as $\eta(\text{PMSO}_2)$ values (d) by Fe(III)/sulfite system. (symbols: experimental data; dashed lines: model simulations). Experimental conditions: $[\text{PMSO}]_0 = 50$ μM; $[\text{Fe(III)}]_0 = 0.5\text{--}10$ mM, $[\text{sulfite}]_0 = 0.5$ mM, and pH = 3.0.

3.3.2 Dissolved oxygen evolution kinetics

As shown in **Figure 3a**, the fast oxidation of $\text{SO}_3^{\bullet-}$ by DO (Eq. 3) triggered the formation of various ROS in Fe(III)/sulfite system. The essential role of DO in ROS formation was evidenced by the fact that PMSO degradation was negligible with removing

O₂ in Fe(III)/sulfite system (**Figure S8**). Similarly, Yuan et al. (2019) reported that aniline elimination in Fe(III)/sulfite system was significantly inhibited with purging nitrogen. Further, the evolution of DO during the activation of sulfite (0.5 mM) by Fe(III) (1 mM) was monitored at pH 3.0. It was observed that DO instantaneously decreased from 8 mg/L to only 0.4 mg/L in the first 30 s, which was a little bit slower than the simulation results (**Figure 4a**). Considering the response delay of the DO measuring instrument, the kinetic model also accurately simulated the time-dependent evolution of DO in Fe(III)/sulfite system.

3.3.3 Fe(IV), SO₄^{•-}, and [•]OH formation and decay kinetics

Evolution of the key precursors of ROS (HSO₅⁻ and S₂O₈²⁻) and the final ROS (Fe(IV), SO₄^{•-}, and [•]OH) formed in Fe(III)/sulfite system were simulated under a typical condition ([PMSO]₀ = 50 μM, [Fe(III)]₀ = 1mM, [sulfite]₀ = 0.5 mM, and pH = 3.0). As depicted in **Figure 4b**, HSO₅⁻ was rapidly accumulated to the maximum at 5 s, and then it was completely depleted within only 40 s. However, S₂O₈²⁻ reached to the maximum (112 μM) until 17 s and dropped slowly in 300 s. The relatively slow decomposition of S₂O₈²⁻, comparing with that of HSO₅⁻, might be ascribed to the fact that the interaction between Fe(II) and S₂O₈²⁻ (26 M⁻¹s⁻¹) (Brandt. and Eldik. 1995) is far slower than that between Fe(II) and HSO₅⁻ (3.0 × 10⁴ M⁻¹s⁻¹) (Wacławek *et al.* 2017).

Figure 4. Evolution of O_2 (a), HSO_5^- and $S_2O_8^{2-}$ (b), $Fe(IV)$, $\cdot OH$, and $SO_4^{\cdot -}$ (c) in $Fe(III)/sulfite$ system predicted by the kinetic model. Experimental conditions: $[PMSO]_0 = 50 \mu M$, $[Fe(III)]_0 = 1 mM$, $[sulfite]_0 = 0.5 mM$, and $pH = 3.0$.

Furthermore, the time-dependent evolution of $Fe(IV)$, $SO_4^{\cdot -}$, and $\cdot OH$ exhibited similar kinetic behaviors that they rapidly increased to the maximum initially, and subsequently they were consumed immediately to a low level (**Figure 4c**). A closer inspection of these kinetic curves (inset of **Figure 4c**) revealed that $[SO_4^{\cdot -}]$ reached to the peak at 6.5 s, which was earlier than $[Fe(IV)]$ (8.2 s). This result implied that the primary ROS gradually converted from $SO_4^{\cdot -}$ to $Fe(IV)$, which well explained the former observation that the relative

contribution of Fe(IV) increased with Fe(III)-sulfite reaction proceeding. Moreover, it was apparent that the steady-state concentration of Fe(IV) was much higher than that of $\text{SO}_4^{\bullet-}$ that the maximum of [Fe(IV)] ($7.8 \times 10^{-2} \mu\text{M}$) was three orders of magnitude higher than the peak of [$\text{SO}_4^{\bullet-}$] ($2.0 \times 10^{-5} \mu\text{M}$) (**Figure 4c**), consistent with the high $\eta(\text{PMSO}_2)$ values (up to about 80%-90%) obtained in Fe(III)/sulfite system. By comparison, the proportion of $\cdot\text{OH}$ was extreme small that the maximum of [$\cdot\text{OH}$] was only $3.2 \times 10^{-7} \mu\text{M}$, in accordance with the former inference that the relative contribution of $\cdot\text{OH}$ is limited.

Additionally, effect of $[\text{Fe(III)}]_0$ on Fe(IV) evolution was examined by kinetic simulation. As shown in **Figure S9**, the increase of $[\text{Fe(III)}]_0$ from 0.5 to 5 mM significantly promoted the maximum of [Fe(IV)] from $3.3 \times 10^{-2} \mu\text{M}$ to $9.3 \times 10^{-2} \mu\text{M}$, and shortened the time of reaching the peak from 15 s to 4 s. This result was in concordance with the experimental data that PMSO_2 production and $\eta(\text{PMSO}_2)$ value was promoted with adding more Fe(III) (**Figure S3**).

4. Conclusions

In this study, both Fe(IV) and free radicals ($\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$) were identified as the reactive intermediates formed in Fe(III)/sulfite system, which was quite different from literature assertion that only free radicals was involved in it. Specifically, formation of PMSO_2 during PMSO transformation in Fe(III)/sulfite system unambiguously evidenced the involvement of Fe(IV). EPR spectra analysis and alcohol scavenging experiment implied that $\text{SO}_4^{\bullet-}$ was the primary free radical, while $\cdot\text{OH}$ contribution was limited. Moreover, it was disclosed that $\cdot\text{OH}$ was formed by the hydrolysis of both Fe(IV) and $\text{SO}_4^{\bullet-}$. The relative

contribution of Fe(IV) was increased as Fe(III)-sulfite reaction proceeded and was enhanced by promoting Fe(III) and sulfite dosages, while it was declined with increasing pH. Further, a kinetic model was developed, which accurately simulated the kinetic curves of PMSO transformation and DO evolution in Fe(III)/sulfite system. More intriguingly, the kinetic simulation provided the first insights into the formation and decay mechanism of Fe(IV), $\text{SO}_4^{\cdot-}$, and $\cdot\text{OH}$ in this complex system. Comparing with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, aqueous Fe(IV) was more selective in eliminating organic pollutants, which would broaden the application scenario of iron/sulfite system.

Declarations

This study was supported by Guangdong Key R&D Program (2019B110205004), Key Special Project for Introduced Talents Team of Southern Marine Science and Engineering Guangdong Laboratory (GML2019ZD0403), Program for Guangdong Introducing Innovative and Entrepreneurial Teams (2019ZT08L213), Guangdong Natural Science Foundation-Outstanding Youth Program (2019B151502023), and National Natural Science Foundation of China (51979044).

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. **Luna Luo**: Conceptualization, Writing - Original Draft, Investigation. **Zhen Wang**: Investigation, Validation, Writing - Review & Editing. **Qin Guo**: Investigation, Data Curation. **Xipeng Wei**: Investigation. **Jianpeng Hu** and **Yu Luo**: Data Curation. **Jin Jiang**: Project administration, Funding acquisition, Writing - Review & Editing, Supervision.

Reference

- Bataineh H, Pestovsky O, Bakac A (2012) pH-induced mechanistic changeover from hydroxyl radicals to iron(IV) in the Fenton reaction. *Chem Sci* **3** (5), 1594. <https://doi.org/10.1039/c2sc20099f>
- Brandt C, Fabian I, van Eldik R (1994) Kinetics and mechanism of the iron(III)-catalyzed autoxidation of sulfur(IV) oxides in aqueous solution. Evidence for the redox cycling of iron in the presence of oxygen and modeling of the overall reaction mechanism. *Inorg Chem* **33** (4), 687-701. <https://doi.org/10.1021/ic00082a012>
- Brandt. C, Eldik. Rv (1995) Transition metal-catalyzed oxidation of sulfur(IV) oxides. atmospheric-relevant processes and mechanisms. *Chem Rev* **95** (1), 119-190. <https://doi.org/10.1021/cr00033a006>
- Buxton GV, McGowan S, Salmon GA, Williams JE, Wood ND (1996) A study of the spectra and reactivity of oxysulphur-radical anions involved in the chain oxidation of S(IV): A pulse and γ -radiolysis study. *Atmos Environ* **30** (14), 2483-2493. [https://doi.org/10.1016/1352-2310\(95\)00473-4](https://doi.org/10.1016/1352-2310(95)00473-4)
- Chen L, Peng X, Liu J, Li J, Wu F (2012) Decolorization of orange II in aqueous solution by an Fe(II)/sulfite system: replacement of persulfate. *Ind Eng Chem Res* **51** (42), 13632-13638. <https://doi.org/10.1021/ie3020389>
- Chen L, Tang M, Chen C, Chen M, Luo K, Xu J, Zhou D, Wu F (2017) Efficient bacterial inactivation by transition metal catalyzed auto-oxidation of sulfite. *Environ Sci Technol* **51** (21), 12663-12671. <https://doi.org/10.1021/acs.est.7b03705>

- Chen X, Miao W, Yang Y, Hao S, Mao S (2020) Aeration-assisted sulfite activation with ferrous for enhanced chloramphenicol degradation. *Chemosphere* **238**, 124599. <https://doi.org/10.1016/j.chemosphere.2019.124599>
- Cheung PCW, Williams DR (2014) Separation of transition metals and chelated complexes in wastewaters. *Environ Prog Sustain Energy* **34** (3), 761-783. <https://doi.org/10.1002/ep.12065>
- Davies MJ, Gilbert BC, Stell JK, Whitwood AC (1992) Nucleophilic substitution reactions of spin adducts. Implications for the correct identification of reaction intermediates by EPR/spin trapping. *J Chem Soc, Perkin Trans 2* (3), 333. <https://doi.org/10.1039/p29920000333>
- Dong H, Chen J, Feng L, Zhang W, Guan X, Strathmann TJ (2019) Degradation of organic contaminants through activating bisulfite by cerium(IV): A sulfate radical-predominant oxidation process. *Chem Eng J* **357**, 328-336. <https://doi.org/10.1016/j.cej.2018.09.024>
- Dong H, Wei G, Yin D, Guan X (2020) Mechanistic insight into the generation of reactive oxygen species in sulfite activation with Fe(III) for contaminants degradation. *J Hazard Mater* **384**, 0304-3894. <https://doi.org/10.1016/j.jhazmat.2019.121497>
- Du J, Guo W, Wang H, Yin R, Zheng H, Feng X, Che D, Ren N (2018) Hydroxyl radical dominated degradation of aquatic sulfamethoxazole by Fe(0)/bisulfite/O₂: Kinetics, mechanisms, and pathways. *Water Res* **138**, 323-332. <https://doi.org/10.1016/j.watres.2017.12.046>
- Furman OS, Teel AL, Watts RJ (2010) Mechanism of base activation of persulfate. *Environ Sci Technol* **44** (16), 6423-6428. <https://doi.org/10.1021/es1013714>
- Gao H-Y, Huang C-H, Mao L, Shao B, Shao J, Yan Z-Y, Tang M, Zhu B-Z (2020) First direct

and unequivocal electron spin resonance spin-trapping evidence for pH-dependent production of hydroxyl radicals from sulfate radicals. *Environ Sci Technol* **54** (21), 14046–14056.

<https://doi.org/10.1021/acs.est.0c04410>

Guan YH, Ma J, Li XC, Fang JY, Chen LW (2011) Influence of pH on the formation of sulfate and hydroxyl radicals in the UV/peroxymonosulfate system. *Environ Sci Technol* **45** (21), 9308-9314. <https://doi.org/10.1021/es2017363>

Guo Y, Lou X, Fang C, Xiao D, Wang Z, Liu J (2013) Novel photo-sulfite system: toward simultaneous transformations of inorganic and organic pollutants. *Environ Sci Technol* **47** (19), 11174-11181. <https://doi.org/10.1021/es403199p>

H. H, A. R, R. Z (1995) Time-resolved UV/VIS diode array absorption spectroscopy of SO_x ($x=3, 4, 5$) radical anions in aqueous solution. *J Mole Stru* **348**, 183–186. [https://doi.org/10.1016/0022-2860\(95\)08619-7](https://doi.org/10.1016/0022-2860(95)08619-7)

Huie RE, Neta PA (1987) Rate constants for some oxidations of S(IV) by radicals in aqueous solutions. *Atmos Environ* **21** (8), 1743-1747. [https://doi.org/10.1016/0004-6981\(87\)90113-2](https://doi.org/10.1016/0004-6981(87)90113-2)

Ianni JCK, Windows Version 6.00; 2017. www.kintecus.com (accessed November 2017).

Jacobsen F, Holcman J, Sehested K (1998) Reactions of the ferryl ion with some compounds found in cloud water. *Int J Chem Kinet* **30** (3), 215-221. [https://doi.org/10.1002/\(SICI\)1097-4601\(1998\)30:33.0.CO;2-V](https://doi.org/10.1002/(SICI)1097-4601(1998)30:33.0.CO;2-V)

Lee J, von Gunten U, Kim JH (2020) Persulfate-based advanced oxidation: critical assessment of opportunities and roadblocks. *Environ Sci Technol* **54** (6), 3064-3081. <https://doi.org/10.1021/acs.est.9b07082>

- Lee YJ, Rochelle GT (1987) Oxidative degradation of organic acid conjugated with sulfite oxidation in flue gas desulfurization: products, kinetics, and mechanism. *Environ Sci Technol* **21** (3), 266-272. <https://doi.org/10.1021/es00157a007>
- Louwerse MJ, Vassilev P, Baerends EJ (2008) Oxidation of methanol by FeO^{2+} in water: DFT calculations in the gas phase and ab initio MD simulations in water solution. *J Phys Chem A* **112** (5), 1000-1012. <https://doi.org/10.1021/jp075914n>
- Lu HF, Chen HF, Kao CL, Chao I, Chen HY (2018) A computational study of the Fenton reaction in different pH ranges. *Phys Chem Chem Phys* **20** (35), 22890-22901. <https://doi.org/10.1039/c8cp04381g>
- Mártire DO, Caregnato P, Furlong J, Allegretti P, Gonzalez MC (2002) Kinetic study of the reactions of oxoiron(IV) with aromatic substrates in aqueous solutions. *Int J Chem Kinet* **34** (8), 488-494. <https://doi.org/10.1002/kin.10076>
- Oh W-D, Dong Z, Lim T-T (2016) Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: Current development, challenges and prospects. *Appl Catal B* **194**, 169-201. <https://doi.org/10.1016/j.apcatb.2016.04.003>
- Wacławek S, Lutze HV, Grübel K, Padil VV, Č erník M, Dionysiou DD (2017) Chemistry of persulfates in water and wastewater treatment: A review. *Chem Eng J* **330**, 44-62. <https://doi.org/10.1016/j.cej.2017.07.132>
- Wang H, Wang S, Liu Y, Fu Y, Wu P, Zhou G (2019a) Degradation of diclofenac by Fe(II)-activated bisulfite: Kinetics, mechanism and transformation products. *Chemosphere* **237**, 124518. <https://doi.org/10.1016/j.chemosphere.2019.124518>

Wang Z, Jiang J, Pang S, Zhou Y, Guan C, Gao Y, Li J, Yang Y, Qiu W, Jiang C (2018) Is sulfate radical really generated from peroxydisulfate activated by iron(II) for environmental decontamination? *Environ Sci Technol* **52** (19), 11276-11284. <https://doi.org/10.1021/acs.est.8b02266>

Wang Z, Qiu W, Pang S-y, Zhou Y, Gao Y, Guan C, Jiang J (2019b) Further understanding the involvement of Fe(IV) in peroxydisulfate and peroxymonosulfate activation by Fe(II) for oxidative water treatment. *Chem Eng J* **371**, 842-847. <https://doi.org/10.1016/j.cej.2019.04.101>

Wang Z, Qiu W, Pang S, Gao Y, Zhou Y, Cao Y, Jiang J (2020) Relative contribution of ferryl ion species (Fe(IV)) and sulfate radical formed in nanoscale zero valent iron activated peroxydisulfate and peroxymonosulfate processes. *Water Res* **172**, 115504. <https://doi.org/10.1016/j.watres.2020.115504>

Wang Z, Qiu W, Pang S, Jiang J (2019c) Effect of chelators on the production and nature of the reactive intermediates formed in Fe(II) activated peroxydisulfate and hydrogen peroxide processes. *Water Res* **164**, 114957. <https://doi.org/10.1016/j.watres.2019.114957>

Wei Z, Villamena FA, Weavers LK (2017) Kinetics and mechanism of ultrasonic activation of persulfate: an in situ EPR spin trapping study. *Environ Sci Technol* **51** (6), 3410-3417. <https://doi.org/10.1021/acs.est.6b05392>

Xie P, Zhang L, Chen J, Ding J, Wan Y, Wang S, Wang Z, Zhou A, Ma J (2019) Enhanced degradation of organic contaminants by zero-valent iron/sulfite process under simulated sunlight irradiation. *Water Res* **149**, 169-178. <https://doi.org/10.1016/j.watres.2018.10.078>

Xie PC, Guo YZ, Chen YQ, Wang ZP, Shang R, Wang SL, Ding JQ, Wan Y, Jiang W, Ma J (2017) Application of a novel advanced oxidation process using sulfite and zero-valent iron in treatment of organic pollutants. *Chem Eng J* **314**, 240-248. <https://doi.org/10.1016/j.cej.2016.12.094>

Xu K, Ben W, Ling W, Zhang Y, Qu J, Qiang Z (2017) Impact of humic acid on the degradation of levofloxacin by aqueous permanganate: Kinetics and mechanism. *Water Res* **123**, 67-74. <https://doi.org/10.1016/j.watres.2017.06.037>

Yu Y, Li S, Peng X, Yang S, Zhu Y, Chen L, Wu F, Mailhot G (2016) Efficient oxidation of bisphenol A with oxysulfur radicals generated by iron-catalyzed autoxidation of sulfite at circumneutral pH under UV irradiation. *Environ Chem Lett* **14** (4), 527-532. <https://doi.org/10.1007/s10311-016-0573-3>

Yuan YN, Luo T, Xu J, Li JJ, Wu F, Brigante M, Mailhot G (2019) Enhanced oxidation of aniline using Fe(III)-S(IV) system: Role of different oxysulfur radicals. *Chem Eng J* **362**, 183-189. <https://doi.org/10.1016/j.cej.2019.01.010>

Zhou D, Chen L, Li J, Wu F (2018) Transition metal catalyzed sulfite auto-oxidation systems for oxidative decontamination in waters: A state-of-the-art minireview. *Chem Eng J* **346**, 726-738. <https://doi.org/10.1016/j.cej.2018.04.016>

Zhou D, Chen L, Zhang C, Yu Y, Zhang L, Wu F (2014) A novel photochemical system of ferrous sulfite complex: kinetics and mechanisms of rapid decolorization of Acid Orange 7 in aqueous solutions. *Water Res* **57**, 87-95. <https://doi.org/10.1016/j.watres.2014.03.016>

Zhou D, Zhang H, Chen L (2015a) Sulfur-replaced Fenton systems: can sulfate radical

substitute hydroxyl radical for advanced oxidation technologies? *J Chem Technol Biotechnol*

90 (5), 775-779. <https://doi.org/10.1002/jctb.4525>

Zhou DN, Yuan YA, Yang SJ, Gao H, Chen L (2015b) Roles of oxysulfur radicals in the oxidation of acid orange 7 in the Fe(III)-sulfite system. *J Sulphur Chem* **36** (4), 373-384. <https://doi.org/10.1080/17415993.2015.1028939>

Zong Y, Shao Y, Zeng Y, Shao B, Xu L, Zhao Z, Liu W, Wu D (2021) Enhanced oxidation of organic contaminants by iron(II)-activated periodate: the significance of high-valent iron-oxo species. *Environ Sci Technol* **55** (11), 7634–7642. <https://doi.org/10.1021/acs.est.1c00375>

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