



## Revisiting the contribution of $\text{Fe}^{\text{IV}}\text{O}^{2+}$ in Fe(II)/peroxydisulfate system

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### ABSTRACT

Recent studies have proposed that the high-valent iron species (such as  $\text{Fe}^{\text{IV}}\text{O}^{2+}$ ) rather than sulfate radical ( $\text{SO}_4^{\cdot-}$ ) and hydroxyl radical ( $\cdot\text{OH}$ ) are the main reactive oxidant species (ROS) in Fe(II)/peroxydisulfate (PDS) system with the methyl phenyl sulfoxide (PMSO) as the  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  probe. However, many operational factors may interfere with the accuracy of this method, so the contribution of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  calculated by this method is controversial. In this study, the possible effect of Fe(II) concentration, pollutant type, reducing agent, or coexisted anions on  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  production and its corresponding contribution to the removal of target pollutants in the Fe(II)/PDS system were investigated in detail, and the intrinsic mechanisms involved were also explored. This study shows that ROS generation is a complex process in the Fe(II)/PDS system, and multiple combinatorial approaches are urgently required to deeply explore the contribution of ROS to the elimination of target contaminants.

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Advanced oxidation processes (AOPs) derived from peroxydisulfate (PDS,  $\text{S}_2\text{O}_8^{2-}$ ) activation have attracted increasing interest in the elimination of recalcitrant organic contaminants due to their excellent oxidant capacity and adaptability [1–4]. Iron-based materials are among the most cost-effective and eco-friendly activators for PDS activation [5–7]. Initially, researchers recognized that Fe(II) could provide one electron to PDS, and the  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  produced are the main reactive oxidant species (ROS) for pollutant removal in Fe(II)/PDS system [8–11].

However, Wang *et al.* [12,13] proposed that the dominant ROS in Fe(II)/PS system was  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  (Eq. 1) rather than  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  using methyl phenyl sulfoxide (PMSO) as the  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  probe. They discovered that the specific oxidation product of PMSO by  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  is methyl phenyl sulfone ( $\text{PMSO}_2$ ) (Eq. 2), and its yield ( $\eta(\text{PMSO}_2)$ ), *i.e.*, molar quantities of  $\text{PMSO}_2$  produced from the oxidation of per mole of PMSO) was approximately 100% [12,14]. Speculating down this mechanism, two electrons were transferred from Fe(II) to PDS while producing  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  and sulfates [14,15]. However, researchers recently found that many factors may inter-

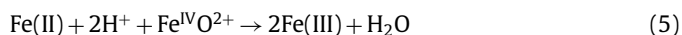
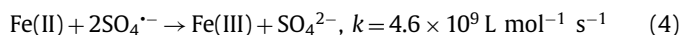
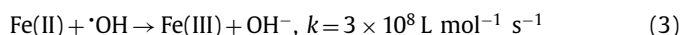
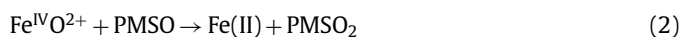
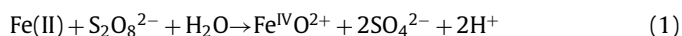
fer with removing target pollutants by  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  in the Fe(II)/PDS system. For instance, Dong *et al.* [15] found that the contribution of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to the removal of organic contaminant depended on the steady concentrations of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  and the second-order rate constant of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  with the organic contaminant. Wang *et al.* [13] confirmed that the reactive intermediates in Fe(II)/PDS system changed from  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to free radicals with the addition of chelating agents such as oxalate acid (OA), citric acid (CA), nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA). Li *et al.* [16] found that the common reducing agent hydroxylamine (HA) could coordinate rapidly with Fe(III) or Fe(II), and interfered with the production of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  from Fe(II)-PDS intermediates. In Fe(II)/PDS system, the steady-state concentration of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  is 4 or 5 orders of magnitudes higher than  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ . Taking into account the rapid scavenging of these ROS by Fe(II) (Eqs. 3–5) [12,17,18], the variation of Fe(II) concentration caused by HA addition might be an essential factor that interfered with the  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  production in Fe(II)/HA/PDS system. Nevertheless, in the study of Li and his coworkers [16], the Fe(II) concentration was only 10  $\mu\text{mol/L}$ , thus the interfering effect of Fe(II) on  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  production in Fe(II)/HA/PDS and Fe(II)/PDS systems should be revisited. In addition, the interference of various contaminants on  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  production in Fe(II)/HA/PDS and Fe(II)/PDS systems also need to be investigated in depth. Apart from these factors, the

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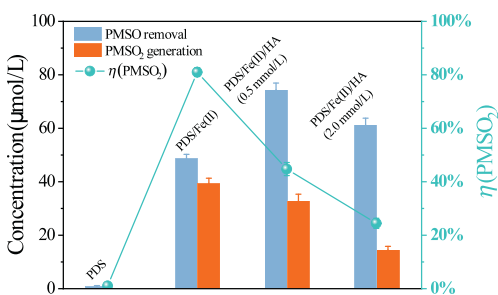
possible effect of common anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  on  $\text{Fe}^{\text{IV}}\text{O}_2^+$  generation in  $\text{Fe}(\text{II})/\text{PDS}$  system are still unidentified.



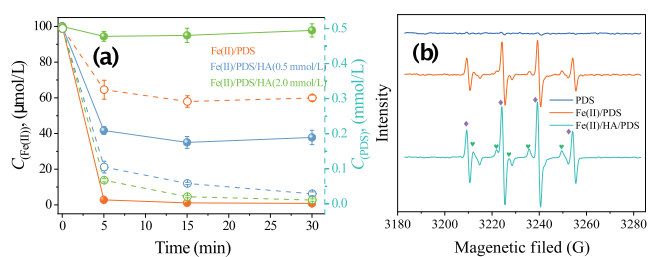
Therefore, the main objectives are as follows: (1) Exploring the role of  $\text{Fe}(\text{II})$  concentration on  $\text{Fe}^{\text{IV}}\text{O}_2^+$  production in  $\text{Fe}(\text{II})/\text{HA}/\text{PDS}$  and  $\text{Fe}(\text{II})/\text{PDS}$  systems, (2) investigating the influence of different target pollutants such as PMSO, Amoxicillin (AML), and sulfamethoxazole (SMX) on  $\text{Fe}^{\text{IV}}\text{O}_2^+$  production in  $\text{Fe}(\text{II})/\text{HA}/\text{PDS}$  and  $\text{Fe}(\text{II})/\text{PDS}$  systems, (3) gaining insights into the possible effect of common anions on  $\text{Fe}^{\text{IV}}\text{O}_2^+$  production in  $\text{Fe}(\text{II})/\text{PDS}$  system. This study aims to understand better the internal catalytic mechanism of  $\text{Fe}(\text{II})$ -activated PDS and reveal the probe method's possible drawbacks for the  $\text{Fe}^{\text{IV}}\text{O}_2^+$  identification.

Chemicals and reagents and analytical methods, are provided in Texts S1 and S2 in Supporting information. Batch experiments were performed in a 300 mL silica glass beaker containing a 200 mL aqueous solution, which was continuously stirred by a magnetic stirrer at approximately 250 rpm. Typically, the experiments were started by dosing 200 mL PMSO solution (0.1 mmol/L) to the beaker at  $25 \pm 1$  °C. The initial solution pH was adjusted to 3.0 using dilute NaOH and  $\text{HClO}_4$  [15]. 1 mL of 10 mmol/L  $\text{Fe}(\text{II})$  and 1 mL of 0.1 mol/L HA stock solution were firstly added, then 1 mL of 0.1 mol/L PDS was added to initiate the reaction. The solution was periodically sampled and filtered through a 0.22  $\mu\text{m}$  microporous membrane filter, and then a 2 mL sample was immediately quenched by 100  $\mu\text{L}$  pure methanol. Finally, all samples were immediately analyzed. All experiments were performed in duplicate, and mean deviations were reported.

Fig. 1 shows that PDS alone could not remove PMSO, which excluded the possibility that PDS directly oxidized PMSO to produce  $\text{PMSO}_2$ . Upon adding  $\text{Fe}(\text{II})$ , rapid removal of PMSO (48.8%) was observed while producing 39.5  $\mu\text{mol/L}$   $\text{PMSO}_2$ . The calculated  $\eta(\text{PMSO}_2)$  was 80.8% in  $\text{Fe}(\text{II})/\text{PDS}$  system. As reported in a previous study [12],  $\text{PMSO}_2$  was the individualized product of PMSO oxidation by  $\text{Fe}^{\text{IV}}\text{O}_2^+$  in  $\text{Fe}(\text{II})/\text{PDS}$  system, indicating that the  $\text{Fe}^{\text{IV}}\text{O}_2^+$  was the main ROS for PMSO elimination in  $\text{Fe}(\text{II})/\text{PDS}$  system. Notably, the removal of PMSO in our study was unsatisfactory (less than 50%). Fig. 2a reveals that only about 0.2 mmol/L PDS



**Fig. 1.** Effect of HA on PMSO removal,  $\text{PMSO}_2$  production and the corresponding  $\eta(\text{PMSO}_2)$  in  $\text{Fe}(\text{II})/\text{PDS}$  system. Experimental condition: Initial pH 3.0,  $[\text{PDS}] = 0.5 \text{ mmol/L}$ ,  $[\text{PMSO}] = 0.1 \text{ mmol/L}$ ,  $[\text{Fe}(\text{II})] = 0.1 \text{ mmol/L}$ .



**Fig. 2.** Effect of HA on the  $\text{Fe}(\text{II})$  concentration (full line) and PDS (dotted line) in  $\text{Fe}(\text{II})/\text{PDS}$  system (a), EPR profiles of PDS,  $\text{Fe}(\text{II})/\text{PDS}$  and  $\text{Fe}(\text{II})/\text{HA}/\text{PDS}$  system (b). Experimental condition: Initial pH 3.0,  $[\text{PDS}] = 0.5 \text{ mmol/L}$ ,  $[\text{PMSO}] = 0.1 \text{ mmol/L}$ ,  $[\text{Fe}(\text{II})] = 0.1 \text{ mmol/L}$ ,  $[\text{HA}] = 2.0 \text{ mmol/L}$ ,  $[\text{DMPO}] = 0.1 \text{ mmol/L}$ , (♦ represents  $\cdot\text{OH}$  adduct and ♥ represents  $\text{SO}_4^{\cdot-}$  adduct).

was consumed after 30 min, while  $\text{Fe}(\text{II})$  was wholly consumed, indicating that the further removal of PMSO was limited due to the lack of  $\text{Fe}(\text{II})$ . Similar results [12–15] were found in previous studies where the PMSO removal was also undesirable and PDS consumption was incomplete (Table S1 in Supporting information). However, according to Eq. 2 [12], PMSO could reduce  $\text{Fe}^{\text{IV}}\text{O}_2^+$  to  $\text{Fe}(\text{II})$ , which should react with PDS and produce  $\text{Fe}^{\text{IV}}\text{O}_2^+$  again (Scheme S1 in Supporting information). This cycle should lead to a more efficient elimination of PMSO in the  $\text{Fe}(\text{II})/\text{PDS}$  system if PDS were sufficient. This result could be assigned to the fact that  $\text{Fe}(\text{II})$  regenerated (Eq. 2) was re-oxidized by  $\text{Fe}^{\text{IV}}\text{O}_2^+$  or free radicals (Eqs. 3–5), resulting in a lack of  $\text{Fe}(\text{II})$  in the  $\text{Fe}(\text{II})/\text{PDS}$  system and thus inhibited the PMSO removal.

To verify this, we used different  $\text{Fe}(\text{II})$  concentrations to investigate the PMSO removal in  $\text{Fe}(\text{II})/\text{PDS}$  system. As shown in Fig. S1a (Supporting information), the PMSO removal significantly increased when the  $\text{Fe}(\text{II})$  concentration increased from 0.1 mmol/L to 0.5 mmol/L. However, PMSO removal was inhibited when the  $\text{Fe}(\text{II})$  concentration increased to 1.0 mmol/L. A similar result was also achieved in previous reports [5,19], which suggested that  $\text{Fe}(\text{II})$  could promote the PDS activation and also scavenge ROS generated in  $\text{Fe}(\text{II})/\text{PDS}$  system when  $\text{Fe}(\text{II})$  was in excess. Interestingly, the trend of  $\text{PMSO}_2$  generation was different from the PMSO removal (Fig. S1b in Supporting information), and the  $\eta(\text{PMSO}_2)$  gradually decreased with the increase in  $\text{Fe}(\text{II})$  concentration (Fig. S2 in Supporting information). The reason might be that in  $\text{Fe}(\text{II})/\text{PDS}$  system, the scavenging effect of  $\text{Fe}(\text{II})$  on  $\text{Fe}^{\text{IV}}\text{O}_2^+$  was slightly higher than that of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ . Thus, the interference of  $\text{Fe}(\text{II})$  on  $\text{Fe}^{\text{IV}}\text{O}_2^+$  production was not apparent when the  $\text{Fe}(\text{II})$  concentration was much lower than that of PDS because most of  $\text{Fe}(\text{II})$  was consumed by PDS rather than ROS. However, in the presence of excess  $\text{Fe}(\text{II})$ , the scavenging effect of  $\text{Fe}(\text{II})$  on ROS became more prominent, which significantly interfered with the  $\text{Fe}^{\text{IV}}\text{O}_2^+$  production in  $\text{Fe}(\text{II})/\text{PDS}$  system.

HA could accelerate the  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$  cycle (Eq. 6) [4,20] to enhance the PDS activation, but it also could scavenge some ROS generated in  $\text{Fe}(\text{II})/\text{PDS}$  system. At pH 3.0, HA was mainly present as  $\text{NH}_3\text{OH}^+$  [10], and the reaction rate constants of HA with  $\text{Fe}^{\text{IV}}\text{O}_2^+$ ,  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  were approximately  $5.0 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $1.5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ , and  $1.15 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ , respectively [10,16]. Furthermore, considering the steady-state concentrations of  $\text{SO}_4^{\cdot-}/\cdot\text{OH}$  ( $\sim 10^{-13} \text{ mol/L}$ ) and  $\text{Fe}^{\text{IV}}\text{O}_2^+$  ( $\sim 10^{-8} \text{ mol/L}$ ) in the  $\text{Fe}(\text{II})/\text{PDS}$  system (Text S3 and Fig. S3 in Supporting information), HA would preferentially scavenge  $\text{Fe}^{\text{IV}}\text{O}_2^+$ . This inhibited the production of  $\text{Fe}^{\text{IV}}\text{O}_2^+$  in the  $\text{Fe}(\text{II})/\text{PDS}$  system. However, the reaction rate constant of HA with  $\text{Fe}(\text{III})$  was about  $2.8 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$  [4], so the presence of  $\text{Fe}(\text{III})$  would interfere with the scavenging effect of HA on these ROS.

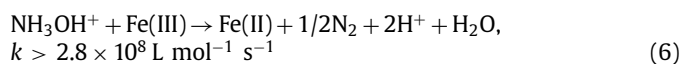


Fig. 2a shows that in Fe(II)/PDS system, almost all Fe(II) was oxidized to Fe(III) within 5 min, which limited the activation of PDS and resulted in a low PMSO removal. In the presence of 0.5 mmol/L HA, the Fe(II) concentration was maintained at about 0.4 mmol/L. Sufficient Fe(II) significantly enhanced the PDS activation and promoted ROS generation, ultimately increasing PMSO removal. However, PMSO<sub>2</sub> generation was suppressed, and  $\eta(\text{PMSO}_2)$  decreased to 44.2% compared to the Fe(II)/PDS system (80.8%). Li *et al.* [16] proposed that Fe(II) could form double coordination intermediates with PDS and HA and the decomposition of this intermediate transformed the major ROS from  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ . However, HA could also rapidly coordinate with Fe(III) and form Fe(III)-HA coordination intermediates to produce Fe(II) [4]. Taking into account the reaction rate of Fe(III) with HA and the Fe(III), Fe(II) concentration in Fe(II)/HA (0.5 mmol/L)/PDS system, HA readily coordinated with Fe(III) rather than Fe(II). Therefore, some other reasons might lead to the decrease of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  production and the increase of free radicals.

Based on the steady-state concentrations and reaction rate constants of HA with Fe(III),  $\text{Fe}^{\text{IV}}\text{O}^{2+}$ ,  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ , it could be inferred that HA reacted mainly with Fe(III) and some  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  in Fe(II)/HA(0.5 mmol/L)/PDS system, while the scavenging effect of HA to  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  might be neglected. Therefore, although the total ROS could be elevated when 0.5 mmol/L HA was added to the Fe(II)/PDS system, the molar ratio of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to free radicals decreased. These results led to increased PMSO removal but a significant decrease in  $\eta(\text{PMSO}_2)$ .

The above point could be further demonstrated by introducing an excess of HA (2.0 mmol/L) in the Fe(II)/PDS system. As shown in Fig. 1, compared to the Fe(II)/HA(0.5 mmol/L)/PDS system, the PMSO removal decreased from 74.4% to 61.3% and  $\eta(\text{PMSO}_2)$  further decreased to 23.7% in Fe(II)/HA(2.0 mmol/L)/PDS system. Simultaneously, Fe(II) concentration was close to the initial concentration throughout the reaction (Fig. 2a), indicating that the generated Fe(III) and  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  were immediately reduced to Fe(II) by the excess HA. Theoretically, the excess HA could completely reduce Fe(III) and  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to Fe(II), but only 23.7% PMSO was oxidized by  $\text{Fe}^{\text{IV}}\text{O}^{2+}$ . The reason was that sufficient Fe(II) enhanced the PDS activation, promoting Fe(III) and ROS generation rates. Hence, although most of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  was scavenged by HA and Fe(II), some  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  was still involved in the oxidation process of PMSO. Moreover, since the Fe(II)/HA(2.0 mmol/L)/PDS system had a much higher Fe(II) concentration, HA would coordinate with Fe(II)-PDS intermediates, which not only enhanced the  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  generation [16] (as also evidenced by the results of electron paramagnetic resonance (EPR) experiments (Fig. 2b), but also inhibited its effect on  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  scavenging. As a result, both PMSO removal and  $\eta(\text{PMSO}_2)$  decreased compared to the Fe(II)/HA(0.5 mmol/L)PDS system.

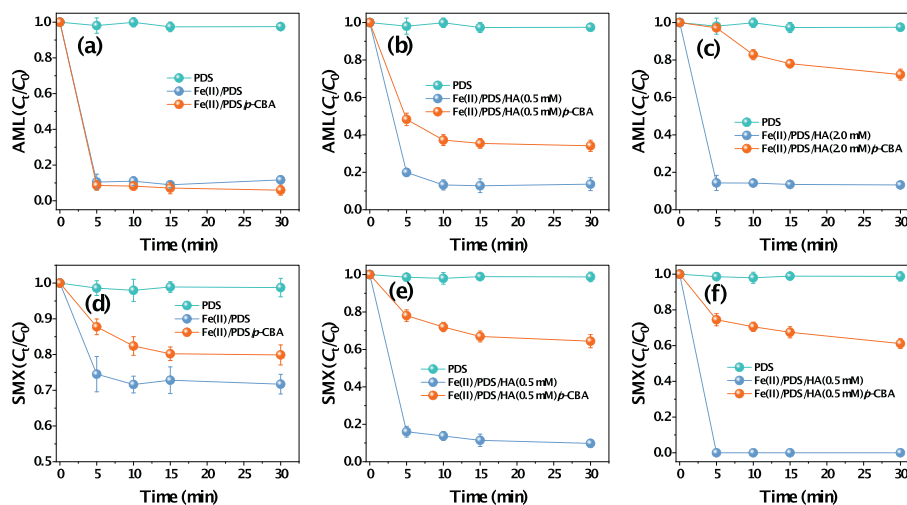
Dong *et al.* [15] found that the contribution of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to the elimination of organic contaminant depended on the steady concentrations of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  and the second-order rate constant of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  with the organic contaminant. To assess whether this phenomenon also existed in Fe(II)/HA/PDS system, we selected some organic contaminants, including amoxicillin (AML) and sulfamethoxazole (SMX) (Fig. 3). As shown in Fig. 3, AML and SMX were hardly degraded by PDS alone, while with the addition of Fe(II), their removal reached 88.3% and 28.3%, respectively. The above result indicates that Fe(II) reacted with PDS and produced ROS, which degraded these contaminants. Notably, the addition of HA slightly inhibited the removal of AML, but significantly enhanced SMX degradation. The oxidative capacity of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  ( $E^0(\text{Fe}^{\text{IV}}\text{O}^{2+}/\text{Fe}(\text{III})) = 2.0 \text{ V/SHE}$ ) was lower than that of  $\text{SO}_4^{\cdot-}$  ( $E^0(\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}) = 2.5\text{--}3.1 \text{ V/SHE}$ ) and  $\cdot\text{OH}$  ( $E^0(\cdot\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$ ) [5,21,22]. For organic contaminants containing electron-rich moieties such as AML [3],  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  was more

likely to be the main ROS in their degradation [15]. This was because the electron-rich group could reduce  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to Fe(II) (such as PMSO), which favored the  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  production in Fe(II)/PDS system (Le Chatelier's principle). In Fe(II)/HA/PDS system, the source of Fe(II) regeneration would change from the  $\text{Fe}^{\text{IV}}\text{O}^{2+}/\text{AML}$  reaction to the  $\text{Fe}^{\text{IV}}\text{O}^{2+}/\text{HA}$  and Fe(III)/HA reactions. Therefore, the  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  production would decrease while the production of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  increased. Besides, although the addition of HA accelerated the Fe(II) regeneration and the PDS activation, the scavenging of ROS by HA and Fe(II) was also enhanced, which further led to a slight decrease in the removal rate of AML.

For SMX, its removal in Fe(II)/PDS system was much lower than that of AML, indicating that the Fe(II) regeneration from the pathway of  $\text{Fe}^{\text{IV}}\text{O}^{2+}/\text{SMX}$  reaction was not obvious. Hence, it could be inferred that the reduced ability of SMX was lower than AML, and the contribution of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  to the removal of SMX was higher than that of AML. In Fe(II)/HA(0.5 mmol/L)/PDS system, the Fe(II) regeneration was accelerated, which favored PDS activation and ROS generation. As discussed above, the  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  production decreased, while the rate of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  production increased. However, SMX removal was not suppressed the Fe(II)/HA(2.0 mmol/L)/PDS system. Similar to the case of PMSO, probably because  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  played a more critical role in SMX removal in Fe(II)/HA/PDS system, while the scavenging of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  by HA was lower than that by  $\text{Fe}^{\text{IV}}\text{O}^{2+}$ .

To further verify the above findings, the contributions of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  and free radicals to the removal of the contaminants in the Fe(II)/PDS process and Fe(II)/HA/PDS systems was evaluated, and the corresponding scavenging experiments were conducted (Fig. 3). Dong *et al.* [15] found that *p*-chlorobenzoic acid (*p*-CBA) was readily oxidized by  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ , whereas the reaction between  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  and *p*-CBA was negligible. Hence, the inhibition of *p*-CBA to the removal of AML and SMX was ascribed to its scavenging effect on  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ , *i.e.*, *p*-CBA could be utilized to identify the contributions of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to the AML and SMX removals by advanced oxidation processes. As shown in Fig. 2, the degradation efficiency of AML in Fe(II)/PDS system was almost unaffected by the excess *p*-CBA, indicating that the contributions of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to AML removal in Fe(II)/PDS system was approximately 100%. However, in the presence of HA, *p*-CBA showed a significant inhibitory effect on AML removal in Fe(II)/PDS system. Specifically, with the addition of *p*-CBA, the AML removal decreased from 86.3% to 65.8% in Fe(II)/PDS/HA (0.5 mmol/L) process, so the contributions of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to AML removal could be calculated to be 65.8%/86.3%, *i.e.*, 76.2%. Based on a similar method, the contributions of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to AML removal in Fe(II)/PDS/HA (2.0 mmol/L) process was 32.0%, and the contributions of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  to SMX removal in Fe(II)/PDS, Fe(II)/PDS/HA (0.5 mmol/L), and Fe(II)/PDS/HA (2.0 mmol/L) processes were 71.7%, 39.4% and 38.9%, respectively (Figs. 3e and f).

Furthermore, inorganic salt ions, such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$ , are often present in natural water and wastewater. Thus, we also investigated their possible interference on  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  production in Fe(II)/PDS systems. As shown in Fig. S4 (Supporting information),  $\text{NO}_3^-$  nearly did not affect the PMSO removal and  $\eta(\text{PMSO}_2)$ , indicating that  $\text{NO}_3^-$  did not interfere with the production of  $\text{Fe}^{\text{IV}}\text{O}^{2+}$  in the Fe(II)/PDS system. When  $\text{SO}_4^{2-}$  concentration was more than 2.0 mmol/L, the PMSO removal in Fe(II)/PDS system was slightly suppressed, but the  $\eta(\text{PMSO}_2)$  was not affected. The reason was that  $\text{SO}_4^{2-}$  could be complex with Fe(II) to form ion pairs ( $\text{FeSO}_4$ ) which might reduce the electron transfer efficiency of Fe(II) in slightly acidic solutions [23,24], eventually inhibiting the PDS activation. When  $\text{HCO}_3^-$  concentration in Fe(II)/PDS system exceeded 2.0 mmol/L, the PMSO removal was significantly inhibited. However, the  $\eta(\text{PMSO}_2)$  did not change much. The reason might be that the scavenging effect of  $\text{HCO}_3^-$  on



**Fig. 3.** Effect of excess *p*-CBA on the removal of AML (a–c) and SMX (d–f) in Fe(II)/PDS and Fe(II)/PDS/HA systems. Experimental condition: Initial pH 3.0, [PDS] = 0.5 mmol/L, [Fe(II)] = 0.1 mmol/L, [AML] = [SMX] = 0.01 mmol/L, [*p*-CBA] = 0.25 mmol/L.

Fe<sup>IV</sup>O<sup>2+</sup> produced in the Fe(II)/PDS system was negligible, and hence, the PMSO<sub>2</sub> production from the oxidation of PMSO by Fe<sup>IV</sup>O<sup>2+</sup> was almost unaffected by the addition of HCO<sub>3</sub><sup>-</sup>; However, HCO<sub>3</sub><sup>-</sup> could rapidly interact with Fe(II) and Fe(III) to form bicarbonate-iron complexes, reducing the soluble metal ions available for PDS activation [25], in addition, HCO<sub>3</sub><sup>-</sup> could significantly increase the solution pH due to its inherent basic and buffering characteristics (Fig. S5 in Supporting information). All those above lead to a decrease in Fe<sup>IV</sup>O<sup>2+</sup> production, which ultimately inhibited the oxidation of PMSO. Surprisingly, in Fe(II)/PDS system, both PMSO removal and  $\eta$ (PMSO<sub>2</sub>) gradually decreased with the increase in Cl<sup>-</sup> concentration (Fig. S4d). Li *et al.* [26] found that Cl<sup>-</sup> could facilitate the shift of ROS from Fe<sup>IV</sup>O<sup>2+</sup> to free radicals (SO<sub>4</sub><sup>•-</sup> or <sup>•</sup>OH) in the Fe(II)/PMS system, meanwhile, Cl<sup>-</sup> could rapidly scavenge SO<sub>4</sub><sup>•-</sup> ( $k = 2.7 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ ) [26] and <sup>•</sup>OH ( $k = 7.8 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ) [27] to produce a less oxidizing Cl<sup>•</sup>. In addition, to evaluate the degradation of pollutants in the actual wastewater, we used the Xiangjiang River water (Hunan Province) as the target water source. The characteristics of Xiangjiang River water are listed in Table S2 (Supporting information). As shown in Fig. S6 (Supporting information), the degradation of pollutants was slightly inhibited in Xiangjiang River water samples, which might be due to the high concentrations of total organic carbon and HCO<sub>3</sub><sup>-</sup> in the actual water body [28].

In summary, in this study, we found that the Fe(II) concentration in Fe(II)/PDS system could slightly interfere with the Fe<sup>IV</sup>O<sup>2+</sup> production and thus affect the contribution of Fe<sup>IV</sup>O<sup>2+</sup> to the target pollutants. In Fe(II)/HA/PDS system, the molar ratio of Fe(II) to Fe(III) dominated the order of HA coordination. HA was more likely to coordinate with Fe(III) than Fe(II). The scavenging effect of Fe(II) and HA was higher than that of SO<sub>4</sub><sup>•-</sup> and <sup>•</sup>OH. Thus, the contribution of Fe<sup>IV</sup>O<sup>2+</sup> to the target pollutant was reduced in Fe(II)/HA/PDS system. In addition, the contributions of Fe<sup>IV</sup>O<sup>2+</sup> to contaminant removal in the Fe(II)/HA/PDS system were closely related to the target contaminant species, and the use of PMSO as a probe to estimate the contribution of ROS to pollutant removal should be handled with caution. The contribution of Fe<sup>IV</sup>O<sup>2+</sup> to the elimination of target pollutants might be overestimated in the case where the reduction potential of organic pollutants was weaker than that of PMSO. Moreover, we found that although NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> hardly affected the contribution of Fe<sup>IV</sup>O<sup>2+</sup> to the removal of the target pollutants in the Fe(II)/PDS system. Cl<sup>-</sup> could facilitate the transfer of ROS from Fe<sup>IV</sup>O<sup>2+</sup> to free radicals (SO<sub>4</sub><sup>•-</sup> or

<sup>•</sup>OH) in Fe(II)/PDS system. Therefore, new probe reagents or methods should be created as soon as possible to more precisely estimate the contribution of Fe<sup>IV</sup>O<sup>2+</sup> to target contaminant removals in the Fe(II)/PS system. Finally, additional quenching experiments, EPR analyses, or other verification methods should be combined to quantify ROS contributions to organic pollutants degradation better.

#### 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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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2022.05.069.

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