1	Both Fe(IV) and radicals are active oxidants in the						
2	Fe(II)/peroxydisulfate process						
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22	Totally 16 pages including 6 Text, 2 Tables, and 8 Figures.						
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### 58 Text S1. Chemicals and Reagents

Sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), ferrous sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O), acetic acid, 59 2,4-dinitrophenylhydrazine (DNPH), caffeine (CAF), carbamazepine (CBZ), 60 diclofenac (DCF), phenol, formaldehyde (HCHO), sodium bromide (NaBr), phosphoric 61 62 acid (H<sub>3</sub>PO<sub>4</sub>), and perchloric acid (HClO<sub>4</sub>, GR grade, 70.0 - 72.0%) were purchased 63 from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Benzoic acid (BA), p-64 hydroxybenzoic acid (p-HBA), p-chlorobenzoic acid (p-CBA), p-nitrobenzoic acid (p-NBA), nitrobenzene (NB), acetaminophen (ACT), penicillinG (PENG), amoxicillin 65 66 (Amoxi), ibuprofen (IBU), dimethyl sulfoxide (DMSO), methyl phenyl sulfoxide (PMSO), methyl phenyl sulfone (PMSO<sub>2</sub>), sodium acetate anhydrous, and sodium 67 hypochlorite solution (active chlorine > 5%) were obtained from Aladdin Biological 68 69 Technology Co., Ltd. (Shanghai, China). Sodium thiosulfate pentahydrate 70 (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, GR grade), sodium hydroxide (NaOH, GR grade), and potassium 71 permanganate (Mn(VII), GR grade) were supplied by the Tianjin Chemical Reagent Co., Ltd. (Tianjin, China). Sulfamethoxazole (SMX, 98% pure) was supplied by 72 73 Shanghai Qiangshun Chemical Reagent Co., Ltd. (Shanghai, China). 5,5-dimethyl-1pyrrolidine-N-oxide (DMPO) (≥99% (GC)) was purchased from Dojindo Laboratory. 74 75 Methanol, acetonitrile, and formic acid of chromatographic grade were supplied by J.T 76 Baker (USA).

<sup>77</sup> Unless otherwise specified, all chemicals were analytical grade. All chemicals <sup>78</sup> were used as received and all solutions were prepared in deionized water (>18.2 <sup>79</sup>  $M\Omega$ ·cm resistivity, Millipore Milli-Q system).

#### 80 Text S2. Analytical methods

The concentrations of organic contaminants were determined with ultra-performance liquid chromatography (ACQUITY UPLC H-Class, Waters Co.) equipped with both UV-visible and fluorescence detectors. The compounds were separated with a BEH C18 column ( $2.1 \times 100$  mm, 1.7 µm; Waters Co.) in an isocratic mode of elution at 35  $\pm 1$  °C. The detailed analytical parameters for the selected contaminants are displayed in **Table S2**. The injection volume was 10 µL.

Solution pH was monitored with a Shanghai Leici pH meter. The concentration of
 generated HCHO was analyzed by UPLC with a UV-visible detector after derivatization

with 2,4-dinitrophenylhydrazine (DNPH) and the brief procedures were described in our previous study.<sup>1</sup> The correlation between the concentration of HCHO and the peak area is shown in **Figure S1**. Note that the background HCHO was deducted when the concentration of HCHO was determined using the standard curve of HCHO after derivatization with 2,4-dinitrophenylhydrazine.

94 Electron paramagnetic resonance (EPR) spectra were collected using a Bruker 300E spectrometer to identify the radicals generated in the Fe(II)/PDS process. DMPO 95 96 was applied as the spin-trapping agent for SO4<sup>--</sup> and HO<sup>-</sup> detection. Aliquots of Fe(II) 97 solution and DMPO were first mixed and then PDS solution was injected into the mixed solution. Subsequently, the reaction solution was transferred to a capillary tube and 98 99 inserted into the cavity of the spectrometer for analysis. In the presence of bromide 100 (Br<sup>-</sup>), aliquots of Fe(II) solution, Br<sup>-</sup>, and DMPO were firstly mixed and the following procedure was identical to that described above. The EPR spectra were obtained under 101 the following conditions: center field, 3480 G; microwave frequency, 9.617 GHz; 102 receiver gain  $2.0 \times 10^3$ ; microwave power, 10 mW; modulation frequency, 100 kHz. 103

### 104 Text S3. The PMSO<sub>2</sub> yield from the oxidation of PMSO by Mn(VII)

In order to verify that the methods of quantifying PMSO and PMSO<sub>2</sub> were reliable, the 105 degradation of PMSO and the generation of PMSO<sub>2</sub> by Mn(VII) were investigated. As 106 107 shown in Figure S4, the concentration of oxidized PMSO was almost equal to that of produced PMSO<sub>2</sub> and the PMSO<sub>2</sub> yield from the oxidation of PMSO by Mn(VII) was 108 always close to 100% regardless of reaction time. Theoretically, Mn(VII) could 109 selectively convert PMSO to PMSO<sub>2</sub> via oxygen transfer.<sup>2</sup> The experimental result in 110 111 Figure S4 was consistent with the theoretical result, suggesting that the methods of quantifying PMSO and PMSO<sub>2</sub> were reliable in this study. 112

## 113 Text S4. The effects of Br<sup>-</sup> on the degradation of different organic contaminants in 114 the Fe(II)/PDS process

Br had different influences on the degradation of different organic contaminants in the
 Fe(II)/PDS process (Figure 2b), which was associated with the rapid reactions of Br

with HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup>. On one hand, the rapid oxidation of Br<sup>-</sup> by HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> reduces 117 the amount HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> available for organic contaminants abatement. On the other 118 hand, bromine radicals such as BrOH<sup>--</sup>, Br<sup>-</sup>, and Br<sup>2<sup>--</sup></sup> (Eqs. R1–R5)<sup>3-5</sup> are generated 119 from the rapid oxidation of Br by HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup>, which are reported to be reactive to 120 organic contaminants with electron-rich moieties.<sup>6</sup> Therefore, the presence of Br had 121 122 different effects on the degradation of different organic contaminants in the Fe(II)/PDS process, as shown in Figure 2b, which further verified the generation of HO<sup>•</sup> and SO4<sup>•-</sup> 123 124 in the Fe(II)/PDS process. Similar results were reported in the literature<sup>6</sup> where organic 125 contaminants were oxidized in UV/Cl<sub>2</sub> process.

126 
$$HO^{\bullet} + Br^{-} \to BrOH^{\bullet-}$$
 1.1×10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> (S1)

127 
$$\text{BrOH}^{\bullet-} + \text{H}^+ \to \text{Br}^{\bullet} + \text{H}_2\text{O}$$
  $4.4 \times 10^{10} \,\text{M}^{-1} \,\text{s}^{-1}$  (S2)

128 
$$BrOH^{\bullet-} + Br^- \to Br_2^{\bullet-} + OH^ 1.9 \times 10^8 M^{-1} s^{-1}$$
 (S3)

129 
$$Br^{\bullet} + Br^{-} \to Br_{2}^{\bullet-}$$
 1.2×10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> (S4)

130 
$$SO_4^{\bullet-} + Br^- \to Br^{\bullet} + SO_4^{2-}$$
 3.5×10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> (S5)

### 131 Text S5. The reaction between Fe(II) with hypochlorous acid

It was reported that Fe(IV) could be generated by the reaction of Fe(II) with 132 hypochlorous acid (HClO) [Fe(II)/HClO process].<sup>3</sup> The yield of PMSO<sub>2</sub> {i.e., mole of 133 PMSO<sub>2</sub> produced per mole of PMSO oxidized [n-(PMSO<sub>2</sub>)]} in the Fe(II)/HClO 134 process was employed to verify the formation of Fe(IV). Figure S5 shows the kinetics 135 of PMSO degradation and PMSO<sub>2</sub> production as well as n-(PMSO<sub>2</sub>) in the Fe(II)/HClO 136 system. The degradation of PMSO and production of PMSO<sub>2</sub> was rapid and achieved 137 the equilibrium within 30 s due to the rapid reaction between Fe(II) and HClO  $(3.2 \times 10^3)$ 138 M<sup>-1</sup> s<sup>-1</sup>).<sup>3</sup> It should be noted that the degradation of PMSO by HClO alone was 139 negligible within 30 s (data not shown). The  $\eta$ -(PMSO<sub>2</sub>) was up to ~85% in the 140 141 Fe(II)/HClO process at pH 1.0 and pH 3.0 (Figure S5), indicating Fe(IV) was formed 142 but not the single reactive species in the Fe(II)/HClO process.

Since the one-electron reduction of HClO was suggested to generate HO<sup>•</sup> and chlorine radical (Cl<sup>•</sup>),<sup>4</sup> HO<sup>•</sup> and Cl<sup>•</sup> may be formed in the Fe(II)/HClO process. However, negligible *p*-NBA was degraded in the Fe(II)/HClO process ([Fe(II)]<sub>0</sub> = 0.10 mM,

 $[HClO]_0 = 0.10 \text{ mM}, [p-NBA]_0 = 5 \mu M, pH 3.0.$ ), which excluded the involvement of 146 HO<sup>•</sup> in the Fe(II)/HClO process under the investigated conditions since HO<sup>•</sup> readily 147 reacted with *p*-NBA at high reaction rate  $(2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ .<sup>5</sup> Since the rate constant of 148 reaction between Fe(IV) and BA was reported to be 80 M<sup>-1</sup> s<sup>-1</sup>,<sup>6</sup> Fe(IV) can contribute 149 to the degradation of BA in the Fe(II)/HClO process with the initial concentration of 150 BA in the micromolar range. As shown in Figure S6a, no p-HBA was formed from the 151 oxidation of BA in the Fe(II)/HClO process under the investigated conditions, which 152153demonstrated that the reaction between Fe(IV) and BA could not result in the formation of p-HBA. Therefore, the formation of p-HBA from the oxidation of BA in the 154Fe(II)/PDS process (Figure S6b) indicated that p-HBA was generated from the 155oxidation of BA by SO4<sup>--</sup> and HO<sup>•</sup> but not by Fe(IV) in the Fe(II)/PDS process. 156

157 As shown in **Figure S7**, excess p-CBA (0.50 mM) had negligible influence on the 158 production of PMSO<sub>2</sub> from the PMSO oxidation in the Fe(II)/HClO process, indicating 159 that the reaction between Fe(IV) and p-CBA was negligible.

# 160 Text S6. The steady state concentrations of SO4<sup>--</sup>, HO<sup>-</sup>, and Fe(IV) in the 161 Fe(II)/PDS process

162 The steady state concentrations of HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> in the Fe(II)/PDS process can be 163 calculated using NB and BA as probe compounds. The degradation of NB and BA in 164 the Fe(II)/PDS process can be expressed as follows:

165 
$$\frac{\mathrm{d}[\mathrm{NB}]}{\mathrm{dt}} = -k_{\mathrm{NB},\mathrm{HO}} \cdot [\mathrm{HO}^{\bullet}]_{\mathrm{ss}}[\mathrm{NB}]$$
(S6)

166 
$$\frac{d[BA]}{dt} = -(k_{BA,HO} \cdot [HO^{\bullet}]_{ss} + k_{BA,SO_4^{\bullet-}}[SO_4^{\bullet-}]_{ss})[BA]$$
(S7)

167 Integrating Eqs. S6-S7 can yield:

168 
$$\ln \frac{[\text{NB}]}{[\text{NB}]_0} = -k_{\text{NB,HO}} \cdot [\text{HO}^{\bullet}]_{\text{ss}} t = -k_{\text{obs,BA}} t$$
(S8)

169 
$$\ln \frac{[BA]}{[BA]_0} = -(k_{BA,HO} \cdot [HO^{\bullet}]_{ss} + k_{BA,SO_4^{\bullet-}} [SO_4^{\bullet-}]_{ss})t = -k_{obs,BA}t$$
(S9)

170 Then, [HO<sup>•</sup>]ss and [SO4<sup>•–</sup>]ss could be obtained:

171 
$$[\mathrm{HO}^{\bullet}]_{\mathrm{ss}} = \frac{k_{\mathrm{obs,NB}}}{k_{\mathrm{NB,HO}^{\bullet}}}$$
(S10)

172 
$$[SO_4^{\bullet-}]_{ss} = \frac{k_{obs,BA} - k_{BA,HO^{\bullet}}[HO^{\bullet}]_{ss}}{k_{BA,SO_4^{\bullet-}}}$$
(S11)

Where [NB] and [BA] are the concentrations of NB and BA at time t, respectively; 173 [NB]<sub>0</sub> and [BA]<sub>0</sub> respresent the initial concentrations of NB and BA, respectively; 174 $k_{\rm NB,HO}$  is the second-order rate constant of NB with HO<sup>•</sup> (4.7×10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>);  $k_{\rm BA,HO}$ . 175and  $k_{BA,SO_4^{-}}$  are the second-order rate constants of HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> with BA, 176respectively  $(k_{BA,HO} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ and } k_{BA,SO_4} = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}); [HO^{\bullet}]_{ss}$  and 177 [SO4<sup>•-</sup>]<sub>ss</sub> refer to the steady-state concentrations of HO<sup>•</sup> and SO4<sup>•-</sup>, respectively. The 178 pseudo-first-order rate constants of NB (kobs,NB) and BA (kobs,BA) can be obtained from 179 the plots of  $-\ln([NB]/[NB]_0)$  and  $-\ln([BA]/[BA]_0)$  versus time, respectively, as shown 180 in Figure S8a. The steady-state concentrations of HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> were calculated to be 181  $2.97 \times 10^{-13}$  M and  $9.33 \times 10^{-13}$  M, respectively, in the Fe(II)/PDS process following this 182 method. 183

The steady state concentration of Fe(IV) in the Fe(II)/PDS process can be determined based on the kinetics of PMSO<sub>2</sub> generation from the oxidation of PMSO. The generation kinetics of PMSO<sub>2</sub> in the Fe(II)/PDS process can be expressed as follows:

188 
$$\frac{d[PMSO_2]}{dt} = -k_{PMSO,Fe(IV)}[Fe(IV)]_{ss}[PMSO]$$
(S12)

189 
$$\eta = \frac{[IMSO_2]}{[PMSO]_0 - [PMSO]}$$
 (S13)

190 Substitution of Eq. S13 into Eq. S12 yields:

191 
$$\frac{\mathrm{d}[\mathrm{PMSO}_2]}{[\mathrm{PMSO}]_0 - \frac{1}{\eta}[\mathrm{PMSO}_2]} = k_{\mathrm{PMSO,Fe(IV)}}[\mathrm{Fe(IV)}]_{\mathrm{ss}}\mathrm{dt}$$
(S14)

192 Integrating Eq. S14 can yield:

193 
$$\eta \ln \frac{[PMSO]_0}{[PMSO]_0 - \frac{1}{\eta} [PMSO_2]} = k_{PMSO,Fe(IV)} [Fe(IV)]_{ss} t = -k_{obs} t$$
(S15)

194 
$$[Fe(IV)]_{ss} = \frac{k_{obs}}{k_{PMSO,Fe(IV)}}$$
(S16)

Where [PMSO] and [PMSO<sub>2</sub>] are the concentrations of PMSO and PMSO<sub>2</sub> at time
 t, respectively; [PMSO]<sub>0</sub> respresents the initial concentration of PMSO, respectively; η
 is the yield of PMSO<sub>2</sub> (i.e., mole of PMSO<sub>2</sub> produced per mole of PMSO oxidized);

198	$k_{\text{PMSO,Fe(IV)}}$ is the second-order rate constant of PMSO with Fe(IV) (1.23×10 <sup>5</sup> M <sup>-1</sup> s <sup>-1</sup>
199	at pH 1.0); [Fe(IV)]ss refer to the steady-state concentration of Fe(IV). The pseudo-first-
200	order rate constants ( $k_{obs}$ ) can be obtained from the plots of $\eta \ln \frac{[PMSO]_0}{[PMSO]_0 - \frac{1}{\eta}[PMSO_2]}$
201	versus time, as shown in Figure S8b. Thus, steady-state concentration of Fe(IV) was
202	calculated to be $9.76 \times 10^{-9}$ M in the Fe(II)/PDS process. Since the reactivity of Fe(IV)
203	decreased with increasing pH, the second-order rate constant of PMSO with Fe(IV) at
204	pH 3.0 would be lower than that at pH 1.0, indicating that the steady-state concentration
205	of Fe(IV) should be larger than $9.76 \times 10^{-9}$ M in the Fe(II)/PDS process at pH 3.0.
206	Consequently, the steady-state concentration of Fe(IV) was at least four orders of
207	magnitude larger than those of HO <sup>•</sup> and SO <sub>4</sub> <sup>•–</sup> in the Fe(II)/PDS process. Thus, Fe(IV)
208	could contribute to the degradation of organic contaminants in the Fe(II)/PDS process
209	although the second-order rate constants between $SO_4$ -/HO and contaminants are
210	several orders of magnitude larger than Fe(IV).
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Contamin	ants	$k (M^{-1} s^{-1})$			
	но•	SO4•-	Fe(IV)*		
phenol	6.6×10 <sup>9</sup> –1.8×10 <sup>10</sup> (pH	8.8×10 <sup>9</sup> (pH 3.0) <sup>7</sup>	(1.5±0.2)×10 <sup>4</sup> (pH 1.0) <sup>8</sup>		
	$6.0-7.7)^5$		4.0×10 <sup>3</sup> (pH 1.0) <sup>6</sup>		
NB	3.2×10 <sup>9</sup> (pH 7.0) <sup>9</sup>	$\leq 10^{6}  (\mathrm{pH} \; 7.0)^{11}$	(1.05±0.3)×10 <sup>3</sup> (pH 1.0) <sup>8</sup>		
	4.7×10 <sup>9</sup> (pH 1.0) <sup>10</sup>				
<i>p</i> -NBA	2.6×10 <sup>9</sup> (pH 6.0–9.4) <sup>9</sup>	$\leq 10^{6}  (\mathrm{pH} \; 7.0)^{11}$	-		
p-CBA	5.0×10 <sup>9</sup> (pH 6.0–9.4) <sup>9</sup>	3.6×10 <sup>8</sup> (pH	-		
		$(7.0)^{11}$			
BA	6.0×10 <sup>9</sup> (pH 6.0–9.4) <sup>9</sup>	1.2×10 <sup>9</sup> (pH	80 (pH 1.0) <sup>6</sup>		
	4.3×10 <sup>9</sup> (pH 3.0) <sup>12</sup>	$(7.0)^{11}$			
DMSO	$7.0 \times 10^9 \ (pH > 2.0)^{13}$	2.7×10 <sup>9</sup> (pH 4.0	1.26×10 <sup>5</sup> (pH 1.0) <sup>15</sup>		
		and pH 6.5) <sup>14</sup>			
PMSO	$9.7 \times 10^9 \ (pH > 2.0)^{13}$	3.17×10 <sup>8</sup> (pH	1.23×10 <sup>5</sup> (pH 1.0) <sup>15</sup>		
	3.61×10 <sup>9</sup> (pH 3.0) <sup>16</sup>	$(3.0)^{16}$			
Br⁻	$1.1\times10^{10}$ (neutral and	3.5×10 <sup>9</sup> (pH	-		
	acid aqueous	$(7.0)^{18}$			
	solutions) <sup>17</sup>				

227 **Table S1**. The second-order rate constants of selected organic contaminants and Br<sup>-</sup>

228 with HO<sup>•</sup>, SO<sub>4</sub><sup>--</sup>, and Fe(IV).

229 -No available second-order rate constants.

	mobile phase					
organic contaminants	water (0.1% formic acid)	acetonitrile	water	methanol	detection wavelength (nm)	flow rate (mL/min)
NMBS	72	28			220	0.20
IBU			33	67	224	0.25
CAF	65			35	273	0.18
CBZ	50	50			286	0.22
SMX	60	40			265	0.22
DCF	40	60			274	0.26
ACT	85	15			254	0.25
phenol	63			37	273	0.20
Amoxi	90	10			230	0.23
PENG	60	40			220	0.20
BA	50	50			227	0.20
PMSO	72	28			230	0.25
PMSO <sub>2</sub>	72	28			264	0.25
<i>p</i> -HBA	75	25			251	0.25
<i>p</i> -NBA		30		70	272	0.20

Table S2. Operation parameters for organic contaminant analysis with UPLC.

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233

Figure S1. Standard curve of HCHO after derivatization with 2,4dinitrophenylhydrazine.



237

Figure S2. Generation of HCHO from oxidation of DMSO in the Fe(II)/PDS process.



pH 3.0, reaction time of 15 min.



Figure S3. Effect of the PDS/Fe(II) molar ratio on PMSO degradation and PMSO<sub>2</sub>

- 243 production in the presence and absence of excess BA in the Fe(II)/PDS process.
- 244 Reaction conditions:  $[Fe(II)]_0 = 0.10 \text{ mM}$ ,  $[PDS]_0 = 0.10-10 \text{ mM}$ ,  $[PMSO]_0 = 100 \mu M$ ,
- 245 [BA]<sub>0</sub> = 1.0 mM, pH 3.0, reaction time of 15 min.



Figure S4. PMSO degradation, PMSO<sub>2</sub> production, and the molar yield of PMSO<sub>2</sub> in the Mn(VII) system. Reaction conditions:  $[Mn(VII)]_0 = 50 \ \mu M$ ,  $[PMSO]_0 = 50 \ \mu M$ , pH 3.0.



Figure S5. Kinetics of PMSO degradation, PMSO<sub>2</sub> production, and the molar yield of PMSO<sub>2</sub> during PMSO abatement in the Fe(II)/HClO process conducted at pH 1.0 and 3.0. Reaction conditions: [Fe(II)]<sub>0</sub> = 0.10 mM, [HClO]<sub>0</sub> = 0.10 mM, [PMSO]<sub>0</sub> = 20  $\mu$ M.



Figure S6. The formation of *p*-HBA during the oxidation of BA (a) in the Fe(II)/HClO process and (b) in the Fe(II)/PDS process. Reaction conditions:  $[Fe(II)]_0 = 0.10 \text{ mM}$ , [HClO]\_0 = 0.10 mM,  $[PDS]_0 = 0.50 \text{ mM}$ ,  $[BA]_0 = 1.0 \text{ mM}$ , pH 3.0.

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Figure S7. Effect of *p*-CBA on PMSO<sub>2</sub> production during PMSO oxidation in the Fe(II)/HClO process. Reaction conditions:  $[Fe(II)]_0 = 0.10 \text{ mM}$ ,  $[HClO]_0 = 0.10 \text{ mM}$ ,

263 [PMSO] $_0 = 50 \ \mu$ M, pH 3.0, reaction time of 30 s.



Figure S8. (a) Degradation kinetic of NB and BA in the Fe(II)/PDS process; and (b) The plots of  $\eta \ln \frac{[PMSO]_0}{[PMSO]_0 - \frac{1}{\eta}[PMSO_2]}$ ) versus time in the Fe(II)/PDS process ( $\eta \ln \frac{[PMSO]_0}{[PMSO]_0 - \frac{1}{\eta}[PMSO_2]}$  denoted as A). Reaction conditions: [Fe(II)]\_0 = 0.10 mM, [PDS]\_0 = 0.50 mM, [NB]\_0 = [BA]\_0 = 2.5 \mu M, [PMSO]\_0 = 20 \mu M pH 3.0.

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