

Supporting Information

Is Sulfate Radical Really Generated from Peroxydisulfate Activated by Iron(II) for Environmental decontamination?

Zhen Wang[†], Jin Jiang^{*,†}, Suyan Pang[‡], Yang Zhou[†], Chaoting Guan[†], Yuan Gao[†], Juan Li[†],
Yi Yang[†], Wei Qiu[†], Chengchun Jiang[§]

[†]State Key Laboratory of Urban Water Resource and Environment, School of Environment,
Harbin Institute of Technology, Harbin 150090, China

[‡]School of Municipal and Environmental Engineering, Jilin Jianzhu University, Changchun
130118, China

[§]School of Civil and Environmental Engineering, Shenzhen Polytechnic, Shenzhen 518055,
China

*E-mail: jiangjinhit@126.com or jiangjin@hit.edu.cn

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Text S1. The experimental instrument for UV irradiation

The collimated beam system was equipped with four low-pressure mercury lamps (254 nm, GPH212T5L/4, 10 W, Heraeus). UV light passed through a vertical tube down onto 100 mL pH-adjusted solutions stirred within an open-top cylindrical glass dish with an initial sample depth of 4 cm. The distance between the solution surface and the UV lamps was 30 cm. The photon fluence rate of the sample surface (8.69×10^{-7} Einsteins L⁻¹s⁻¹) was determined by iodide-iodate actinometry¹.

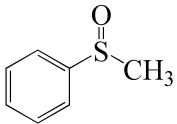
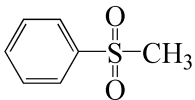
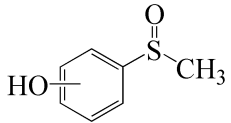
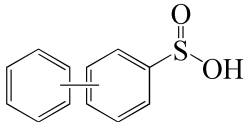
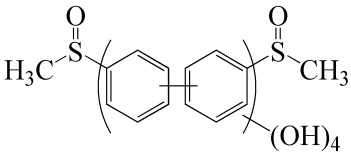
Text S2. Operating parameters for HPLC/ESI-QqQMS analysis

The chromatographic separation was carried out on a Poroshell 120 EC-C18 column (3.0 × 50 mm, 2.7 μm particle size) using acetonitrile and ultrapure water as the mobile phase at a flow rate of 0.1 mL/min. The gradient mobile phase ratio of acetonitrile/water was set as follows: the ratio maintained at 10/90 for 5 min at the beginning, and then changed linearly from 10/90 to 90/10 in the next 30 min and held for 20 min, following by a sharp decline to 10/90 in 0.1 min, and kept for 10 min for re-equilibration. Sample injection volume was 10 μL. A switch valve between the outlet of HPLC column and the inlet of the mass detector was used to divert the HPLC effluent to the waste in the first 5 min and last 10 min to avoid the possible contamination of mass spectrometer.

The HPLC/ESI-QqQMS analysis was operated in full scan mode with both positive and negative ESI, as well as in selective ion monitoring (SIM) and enhanced product ion (EPI) modes with negative ESI. The MS parameters were set as follows: ionspray voltage, 4500 V or -4500 V; source temperature, 500°C; gas I, 50 arbitrary units; gas II, 50 arbitrary units; curtain

gas, 30 arbitrary units; collision energy (CE), 35 V or -35 V; declustering potential (DP), 100 V or -100 V; entrance potential (EP), 10 V or -10 V; collision cell exit potential (CXP), 13 V or -13 V; collision energy spread (CES), 15.0 V. The data acquisition and its analysis were accomplished by Analyst 1.5.2 software (AB Sciex).

Table S1. Oxidation products detected by LC-MS/MS during the treatment of PMSO by UV/H₂O₂ and UV/PDS.

Product ID	ESI (+/-)	Experimental Mass (m/z)	Molecular formula	Proposed chemical structure	Retention time (min)	UV/H ₂ O ₂	UV/PDS
PMSO	+	140.9	C ₇ H ₈ SO		24.66		
PMSO ₂	-	155.0	C ₇ H ₈ SO ₂		28.10		
P-156	-	155.0	C ₇ H ₈ SO ₂		15.88	√	
					17.52	√	
					21.76	√	
P-218	-	216.9	C ₁₂ H ₁₀ SO ₂		30.12		√
					31.37		√
P-342	-	341.0	C ₁₄ H ₁₄ S ₂ O ₆		30.85		√

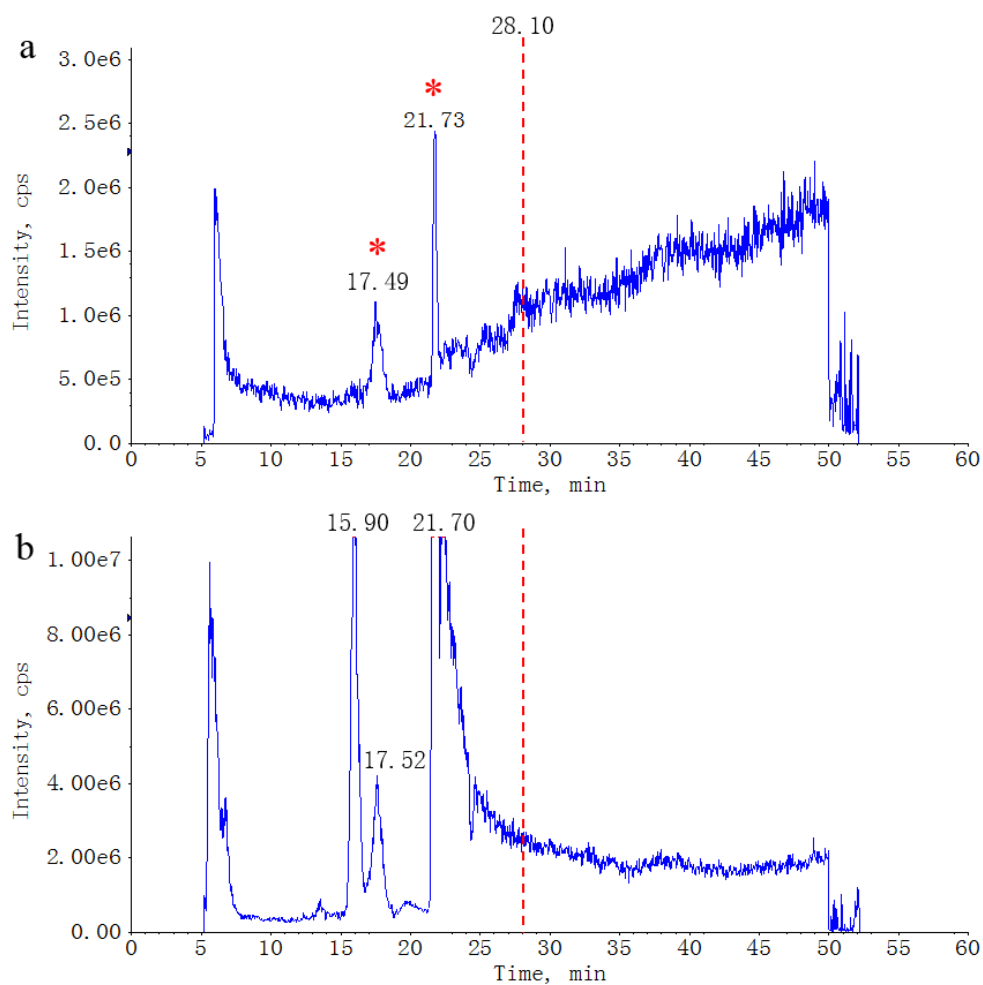


Figure S1. HPLC/ESI-QqQMS SIM (m/z 155.0) chromatograms in negative ESI of PMSO treated by UV/H₂O₂ (a) and UV/PDS (b) at pH 7. Experimental conditions: [PMSO]₀ = 50 μ M, [H₂O₂]₀ = [PDS]₀ = 1 mM, [TBA]₀ = 15 mM for UV/PDS treatment, pH = 7, and reaction time of 30 min. Asterisks represented the direct photolysis products of PMSO.

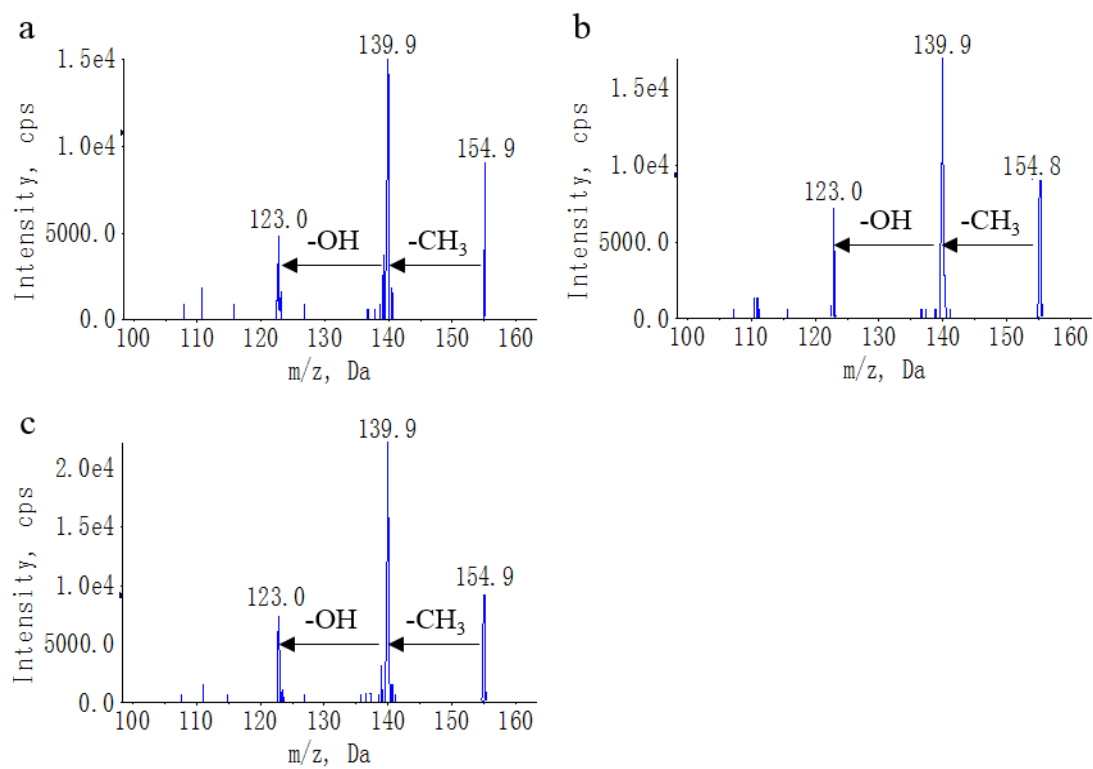
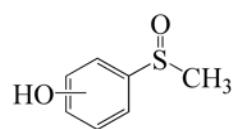


Figure S2. Product ion mass spectra of m/z 155.0 detected at retention times of 15.88 (a), 17.52 (b), and 21.76 min (c).

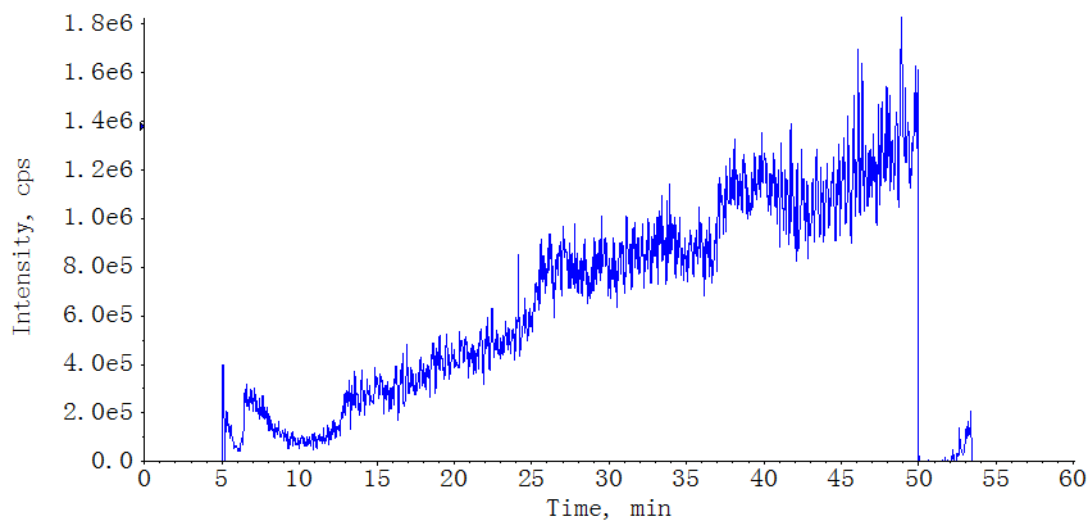


Figure S3. HPLC/ESI-QqQMS SIM (m/z 155.0) chromatogram in negative ESI of PMSO treated by thermal activation of PDS. Experimental conditions: $[PDS]_0 = 1$ mM, $[PMSO]_0 = 50$ μ M, $T = 60$ $^{\circ}$ C, pH = 3, and reaction time of 3 h.

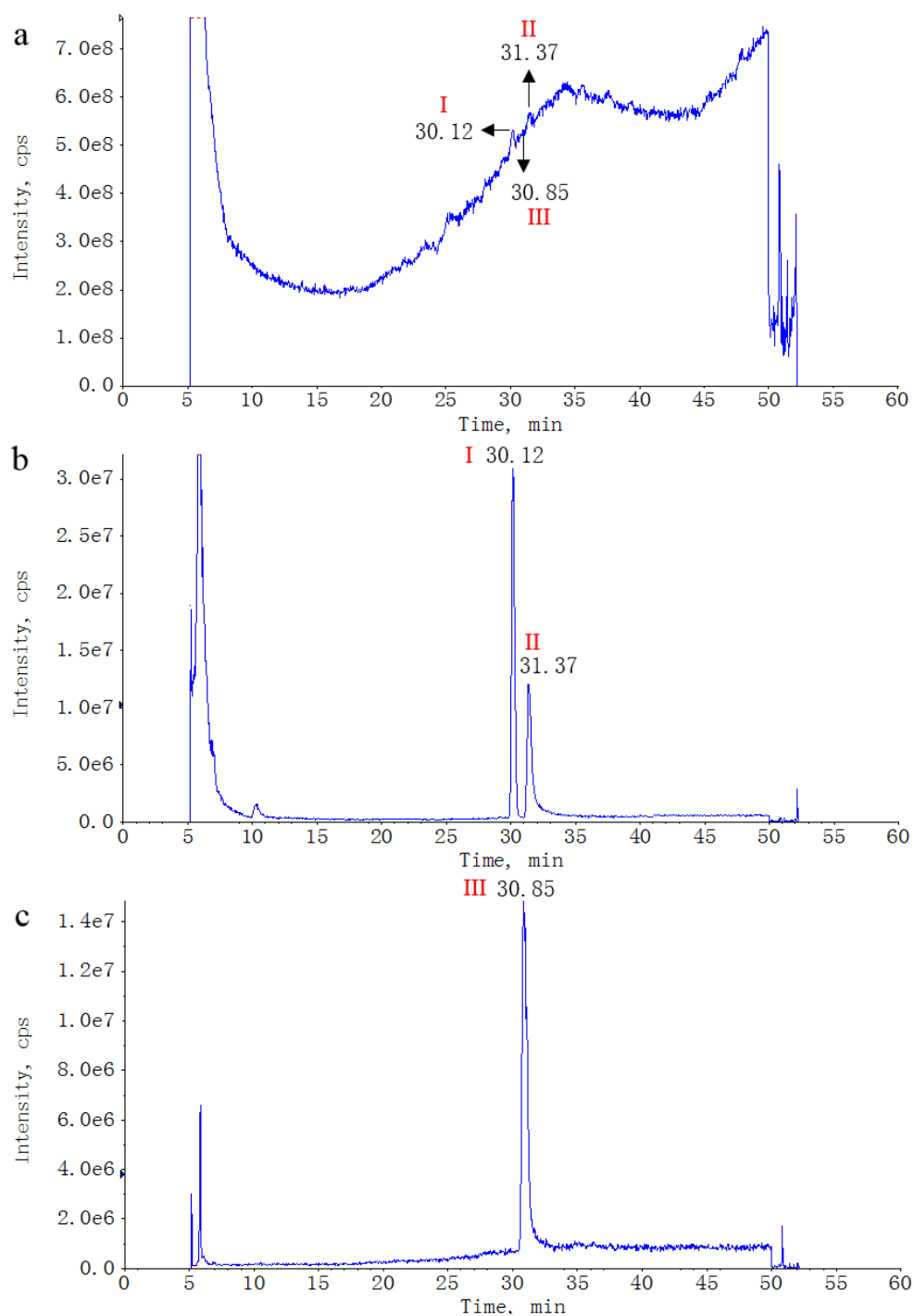


Figure S4. HPLC/ESI-QqQMS full scan (negative ESI) chromatogram of a sample containing PMSO treated by UV/PDS (a), and extracted chromatograms of specific products with m/z 217.0 (b) and m/z 341.0 (c). Experimental conditions: $[PDS]_0 = 1$ mM, $[PMSO]_0 = 50$ μ M, pH = 3, and reaction time of 30 min.

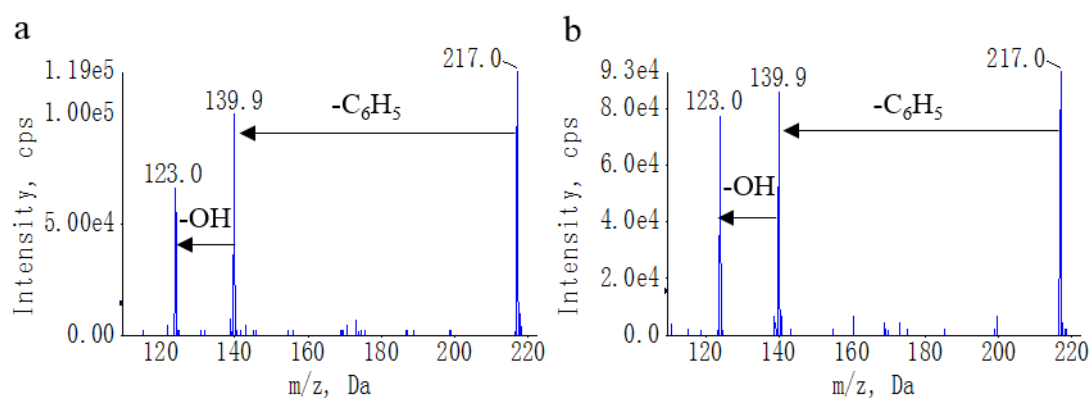
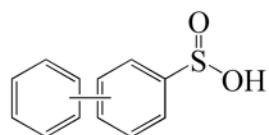


Figure S5. Product ion mass spectra of m/z 217.0 detected at retention times of 30.12 (a) and 31.37 min (b).

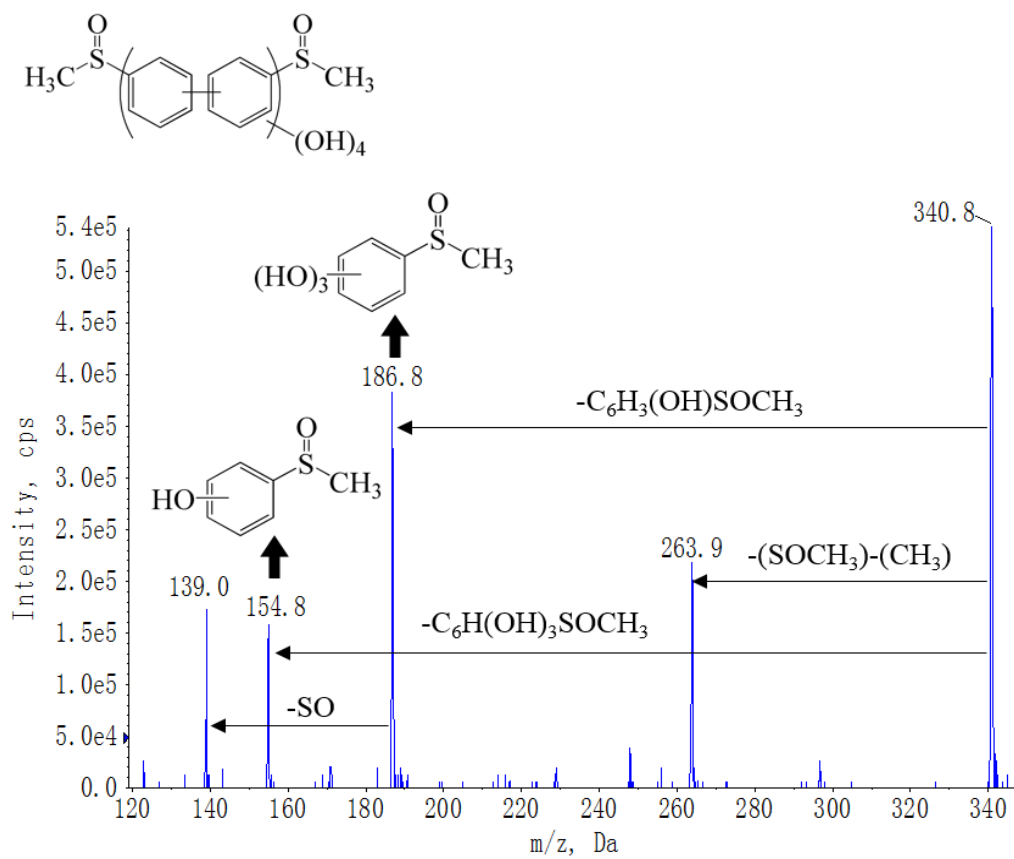


Figure S6. Product ion mass spectrum of m/z 341.0 detected at retention time of 30.85 min.

Text S3. Competition kinetic experiments for determination of second-order rate constants for the reactions of PMSO and PMSO₂ with [•]OH and SO₄^{•-}

The second-order rate constants of PMSO and PMSO₂ with [•]OH and SO₄^{•-} were determined by competition kinetics.² [•]OH and SO₄^{•-} were also produced by UV/H₂O₂ and UV/PDS, respectively.

The concentrations of substrates (S) and reference compounds (R) before and after the oxidation by [•]OH or SO₄^{•-} were measured by HPLC. Atrazine (ATZ) was selected as a reference compound, and the second-order constant of ATZ with [•]OH and SO₄^{•-} were $k_{\bullet\text{OH,ATZ}} = 2.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $k_{\text{SO}_4^{\bullet-},\text{ATZ}} = 2.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively.³ Experiments were conducted at pH 3 and 20 ± 2 °C.

In UV/H₂O₂ system, the substrate and reference compound were degraded not only by photolysis-induced [•]OH, but also by direct photolysis, as described by eq. S1 and S2:

$$-\frac{d[S]}{dt} = k_{\bullet\text{OH,S}}[S] + k_{d,S}[S] \quad (\text{S1})$$

$$-\frac{d[R]}{dt} = k_{\bullet\text{OH,R}}[R] + k_{d,R}[R] \quad (\text{S2})$$

where $k_{\bullet\text{OH,S}}$ and $k_{\bullet\text{OH,R}}$ are the second-order rate constants of the substrate and reference compound ($\text{M}^{-1}\text{s}^{-1}$) with [•]OH, respectively, and $k_{d,S}$ and $k_{d,R}$ are their direct photolysis rate constant (s^{-1}).

Combining Eq. S1 and S2 led to eq. S3:

$$\ln\left(\frac{[S]_t}{[S]_0}\right) - k_{d,S}t = \left(\ln\left(\frac{[R]_t}{[R]_0}\right) - k_{d,R}t\right) \frac{k_{\bullet\text{OH,S}}}{k_{\bullet\text{OH,R}}} \quad (\text{S3})$$

As shown in eq. S3, $k_{\bullet\text{OH,S}}/k_{\bullet\text{OH,R}}$ represents the slope of competition kinetic plot ($\ln\left(\frac{[S]_t}{[S]_0}\right) - k_{d,S}t$ vs. $\ln\left(\frac{[R]_t}{[R]_0}\right) - k_{d,R}t$). The rate constant $k_{\bullet\text{OH,S}}$ can be calculated from the obtained

slope value.

In the same way, the rate constant of the substrate with $\text{SO}_4^{\bullet-}$ ($k_{\text{SO}_4^{\bullet-},\text{S}}$) can be derived from the slope of the competition kinetic plot (eq. S4) and the known $k_{\text{SO}_4^{\bullet-},\text{R}}$ value.

$$\ln\left(\frac{[\text{S}]_t}{[\text{S}]_0}\right) - k_{\text{d},\text{S}}t = \left(\ln\left(\frac{[\text{R}]_t}{[\text{R}]_0}\right) - k_{\text{d},\text{R}}t\right) \frac{k_{\text{SO}_4^{\bullet-},\text{S}}}{k_{\text{SO}_4^{\bullet-},\text{R}}} \quad (\text{S4})$$

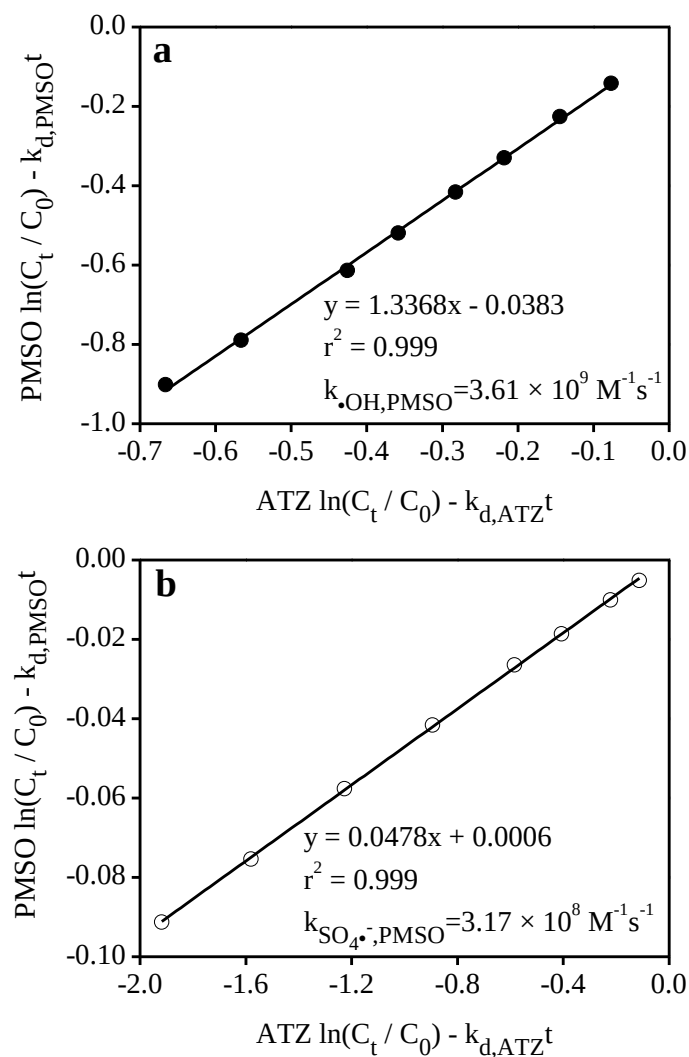


Figure S7. Competition kinetic plots and the calculated second-order rate constants for the reaction of (a) PMSO with $\bullet\text{OH}$, $[\text{PMSO}]_0 = 5 \mu\text{M}$, $[\text{ATZ}]_0 = 5 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$; (b) PMSO with $\text{SO}_4^{\bullet-}$, $[\text{PMSO}]_0 = 50 \mu\text{M}$, $[\text{ATZ}]_0 = 5 \mu\text{M}$, $[\text{PDS}]_0 = 1 \text{ mM}$. Experiments were conducted at pH 3.

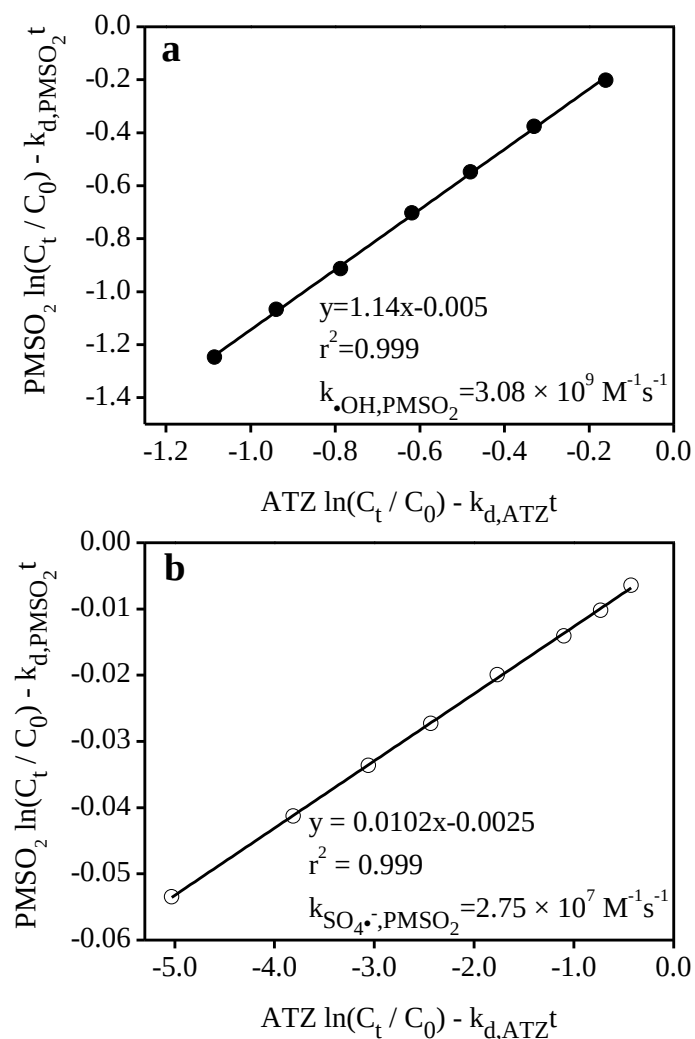


Figure S8. Competition kinetic plots and the calculated second-order rate constants for the reaction of (a) PMSO₂ with $\cdot\text{OH}$, $[\text{PMSO}_2]_0 = 5 \text{ } \mu\text{M}$, $[\text{ATZ}]_0 = 5 \text{ } \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$; (b) PMSO₂ with $\text{SO}_4^{\cdot-}$, $[\text{PMSO}_2]_0 = 100 \text{ } \mu\text{M}$, $[\text{ATZ}]_0 = 2.5 \text{ } \mu\text{M}$, $[\text{PDS}]_0 = 1 \text{ mM}$. Experiments were conducted at pH 3.

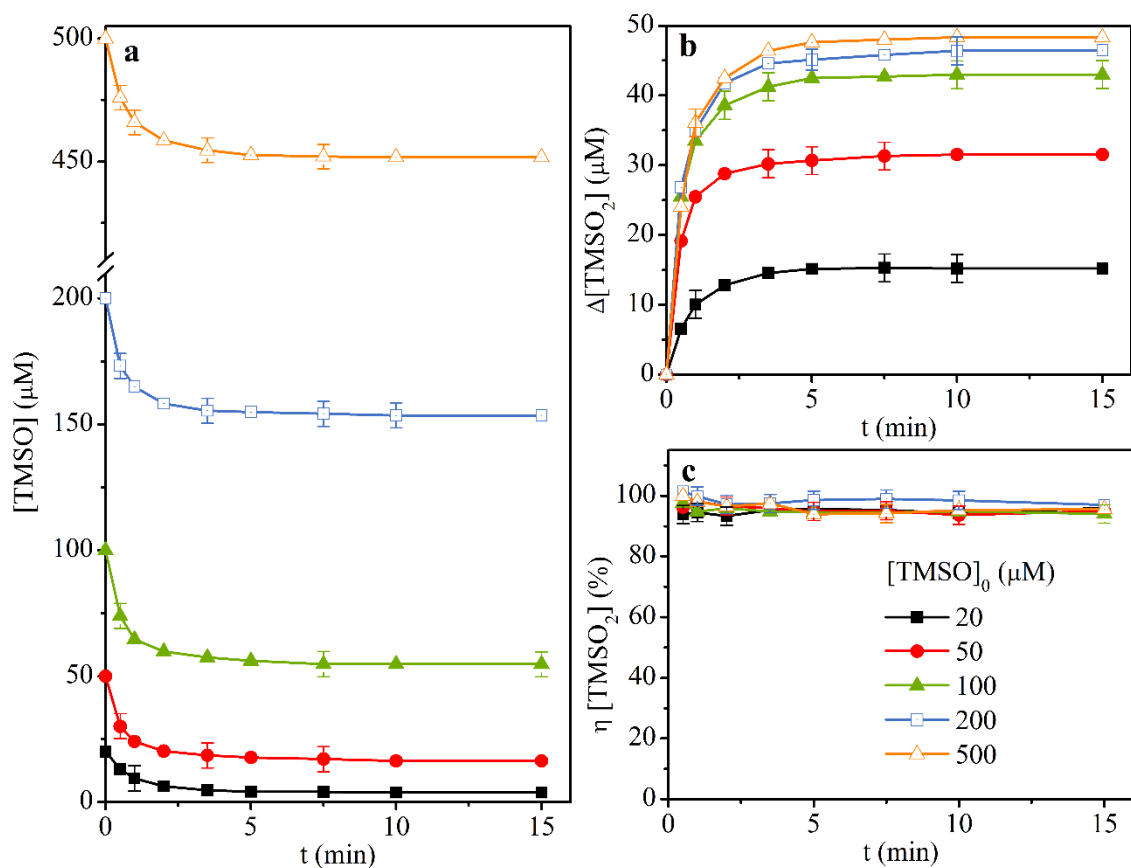


Figure S9. TMSO loss (a) and TMSO₂ production (b) by the Fe(II)/PDS system at different initial concentrations of TMSO, as well as calculated $\eta(\text{TMSO}_2)$ values (c). Experimental conditions: $[\text{Fe(II)}]_0 = 100 \mu\text{M}$, $[\text{PDS}]_0 = 500 \mu\text{M}$, $[\text{TMSO}]_0 = 20\text{-}500 \mu\text{M}$, and $\text{pH} = 3$.

Table S2. Second-order rate constants for the reactions of alcohol scavengers with $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$ and Fe(IV)

Alcohol	$k_{\cdot\text{OH},S} / \text{M}^{-1}\text{s}^{-1}$	$k_{\text{SO}_4^{\cdot-},S} / \text{M}^{-1}\text{s}^{-1}$	$k_{\text{Fe(IV)},S} / \text{M}^{-1}\text{s}^{-1}$
Ethanol	$(1.2\text{-}2.8) \times 10^9$	$(1.6\text{-}7.7) \times 10^7$	2.51×10^3
Tert-butyl alcohol	$(3.8\text{-}7.6) \times 10^8$	$(4.0\text{-}9.1) \times 10^5$	6.0×10^1

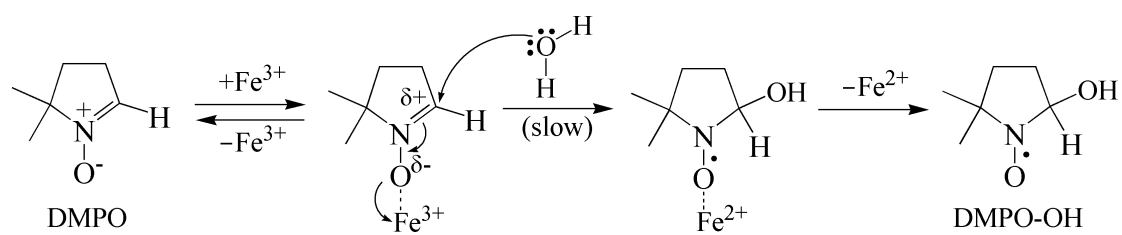


Figure S10. Possible pathway for the formation of DMPO-OH derived from the oxidation of DMPO by Fe(III)^6 .

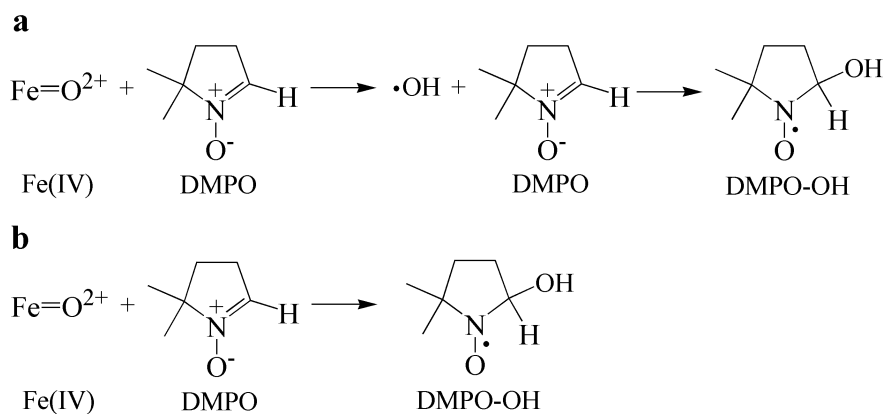


Figure S11. Possible pathways for the formation of DMPO-OH derived from the oxidation of DMPO by Fe(IV) through: $\cdot\text{OH}$ intermediate induced reaction (a) and direct oxidation (b).⁷

Table S3. Reactions involved in PMSO oxidation by the Fe(II)/PDS system^a

No.	Reactions	Rate Constants
Fe(IV) Production and Subsequent Oxidation of PMSO		
A1	$\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \rightarrow \text{Fe}^{\text{IV}}\text{O}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$	$2.0 \times 10^1 \text{ M}^{-1}\text{s}^{-1}$ ⁸
A2	$\text{PMSO} + \text{Fe}^{\text{IV}}\text{O}^{2+} \rightarrow \text{PMSO}_2 + \text{Fe}^{2+}$	$1.23 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ (pH = 1) ⁹
Fe(IV) Consumption in Side Reactions		
B1	$\text{Fe}^{\text{IV}}\text{O}^{2+} + \text{Fe}^{2+} + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O}$	$1.40 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ (pH = 1) ¹⁰
B2	$\text{Fe}^{\text{IV}}\text{O}^{2+} + \text{H}^+ \rightarrow \text{Fe}^{3+} + 1/4 \text{ O}_2 + 1/2 \text{ H}_2\text{O}$	$1.0 \times 10^{-1} \text{ s}^{-1}$ (pH = 1) ⁵
B3	$\text{Fe}^{\text{IV}}\text{O}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-}$ (unbalanced)	$1.0 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ (pH = 1) ^b
Fe(IV) Consumption by Scavengers		
C1	$\text{C}_2\text{H}_5\text{OH} + \text{Fe}^{\text{IV}}\text{O}^{2+} \rightarrow \text{Fe}^{3+}$ (unbalanced)	$2.51 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ (pH = 1) ⁵
C2	$(\text{CH}_3)_3\text{COH} + \text{Fe}^{\text{IV}}\text{O}^{2+} \rightarrow \text{Fe}^{3+}$ (unbalanced)	$6.0 \times 10^1 \text{ M}^{-1}\text{s}^{-1}$ (pH = 1) ⁵
C3	$\text{DMSO} + \text{Fe}^{\text{IV}}\text{O}^{2+} \rightarrow \text{DMSO}_2 + \text{Fe}^{2+}$	$1.26 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ (pH = 1) ⁹

^a Species in italics were written to keep equations balanced but were not taken into account in the model.

^b The rate constant of the reaction between Fe(IV) and PDS (eq. B3) was optimized in this study as described in Text S4.

Text S4. Rate constant optimization of the reaction between Fe(IV) and PDS

The effect of k_{B3} (the second-order rate constant of eq. B3 in Table S3) variation on the simulation results of PMSO loss and PMSO₂ production by the Fe(II)/PDS (100/500 μ M) system at pH 1 was shown in Figure S12. Based on the kinetic simulations, an increase of k_{B3} from 1.0×10^3 to 2.0×10^4 M⁻¹s⁻¹ significantly reduced PMSO loss and PMSO₂ production. The best agreement between the experimental data and the modeling results was obtained at $k_{B3} = 1.0 \times 10^4$ M⁻¹s⁻¹.

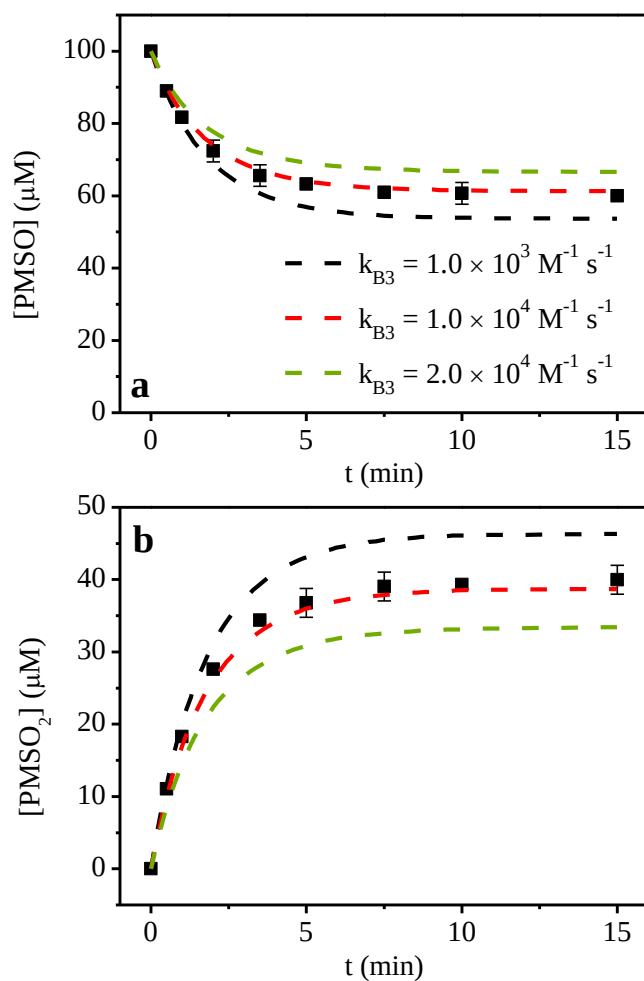


Figure S12. Influence of k_{B3} variation on the simulation results of PMSO loss (a) and PMSO₂ production (b) by the Fe(II)/PDS system (symbols: experimental data; dashed lines: model simulations). Experimental conditions: $[PDS]_0 = 500 \text{ } \mu M$, $[Fe(II)]_0 = 100 \text{ } \mu M$, $[PMSO]_0 = 100 \text{ } \mu M$, and $pH = 1$.

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