

## Supporting Information

### **Activating peroxymonosulfate by halogenated and methylated benzoquinones: Performance and mechanism**

Hong Zhang<sup>a,b</sup>, Lina Qiao<sup>b</sup>, Jing He<sup>a,b</sup>, Na Li<sup>a,b</sup>, Dongmei Zhang<sup>a,b</sup>, Kai Yu<sup>a,b</sup>, Hong You<sup>a,b</sup>, Jie Jiang<sup>a,b\*</sup>

<sup>a</sup> School of Marine Science and Technology, Harbin Institute of Technology at Weihai, Weihai, Shandong 264209, P. R. China

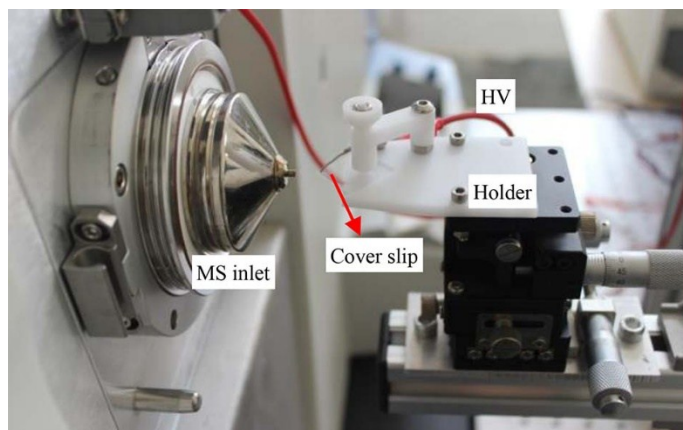
<sup>b</sup> State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, Heilongjiang 150090, P. R. China

\*Correspondence to: Jie Jiang; E-mail: [jiejiang@hitwh.edu.cn](mailto:jiejiang@hitwh.edu.cn);

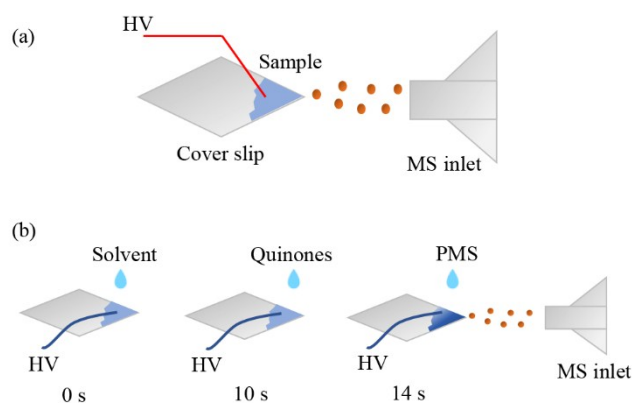
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## TABLE OF CONTENTS

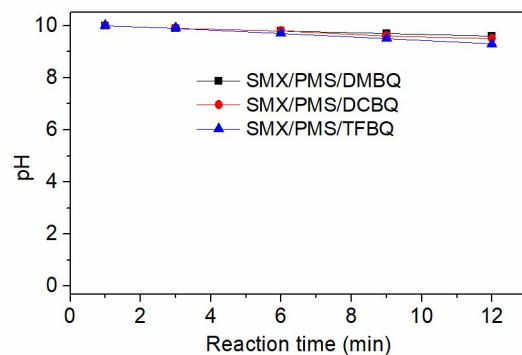
Fig. S1. Photograph of DSI-MS .....	3
Fig. S2. Experimental setup.....	3
Fig. S3. pH variation in experiment of pH 10. ....	4
Fig. S4. Residual PMS after the degradation of SMX under different pH. ....	4
Fig. S5. Effect of scavengers on SMX degradation. ....	5
Fig. S6. Degradation of BA in PMS/different quinones system.....	5
Fig. S7. Theoretical simulation and detected isotopic envelope of $m/z$ 180.98. ....	6
Fig. S8. Theoretical simulation and detected isotopic envelope of $m/z$ 89.98. ....	6
Fig. S9. MS/MS results of $m/z$ 180.98 and 89.98. ....	7
Fig. S10. Theoretical simulation and detected isotopic envelope of $m/z$ 168.04. ....	7
Fig. S11. Intermediates identification in PMS activated by DCBQ. ....	8
Fig. S12. Intermediates identification in PMS activated by TFBQ. ....	8
Table S1. The chemical characteristics of quinones. ....	9
Table S2. Pseudo-first-order rate constants for SMX degradation. ....	9
Table S3. Rate constant of selected quenchers with $^1O_2$ , $\cdot OH$ and $SO_4^{\cdot -}$ . ....	9
Table S4. Identified products of PMS activated by DMBQ derived from Figure 5a. ....	10
Table S5. Identified products of PMS activated by DCBQ derived from Figure 5b. ....	10
Table S6. Identified products of PMS activated by TFBQ derived from Figure 5c. ....	10



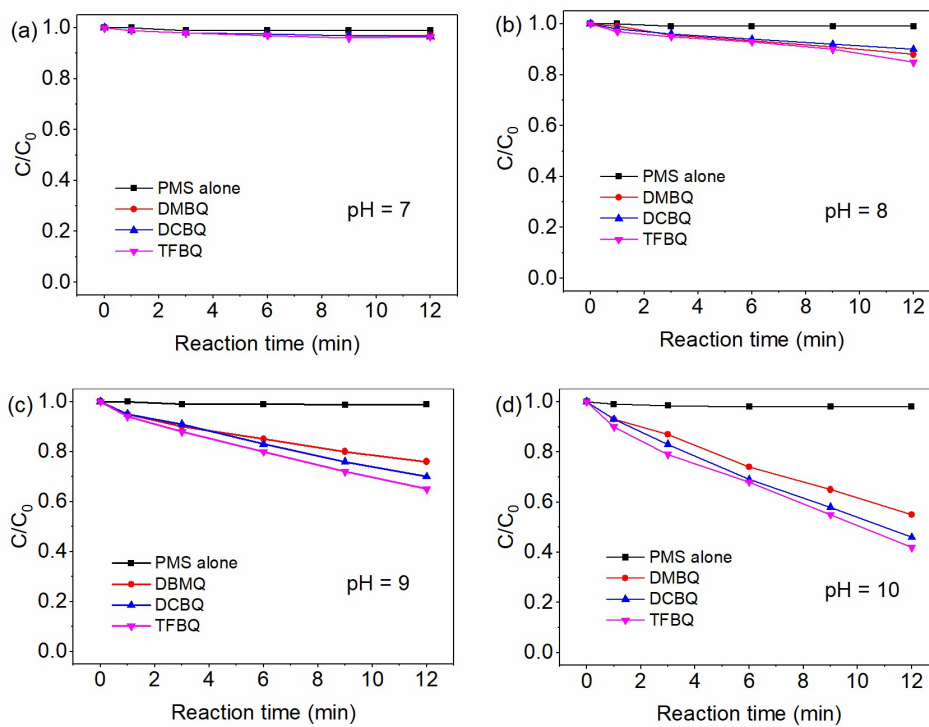
**Fig. S1.** Photograph of droplet spray ionization mass spectrometry (DSI-MS).



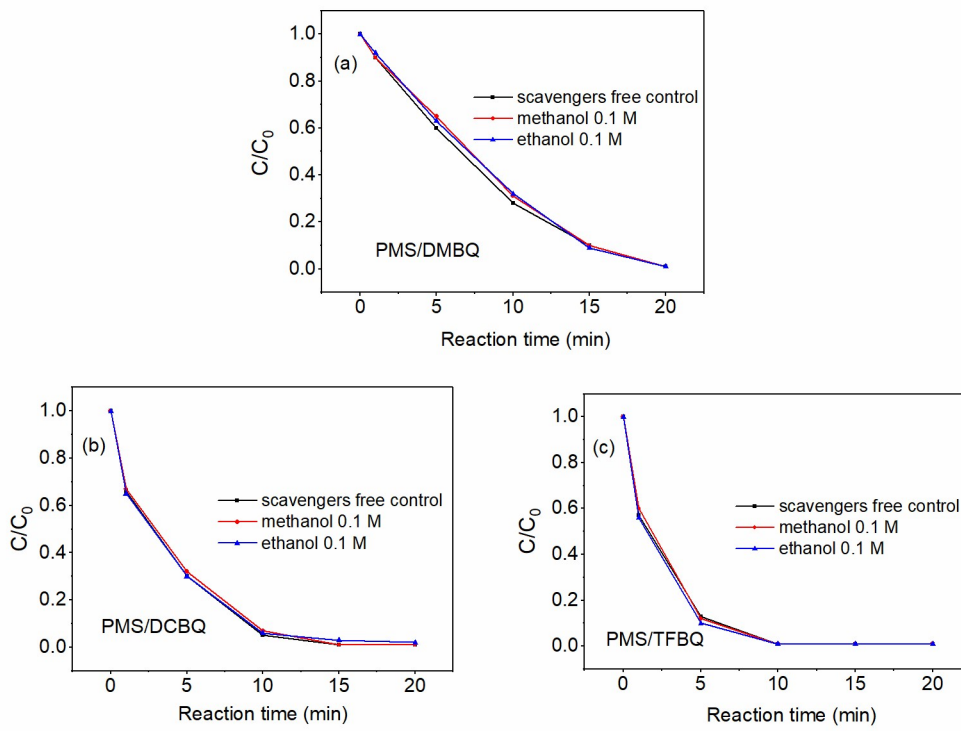
**Fig. S2.** Experimental setup. (a) Schematic of DSI-MS; (b) workflow of in situ analysis and real-time monitoring of PMS activated by different quinines (DMBQ, DCBQ, and TFBQ). The slip tip-end was 5 mm from the MS inlet. The angle between the corner and the MS inlet was 4 °.



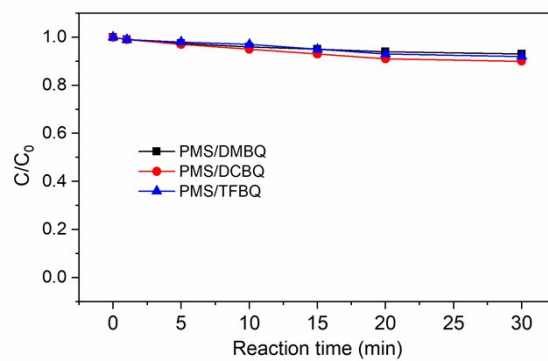
**Fig. S3.** pH variation in experiment of pH 10.



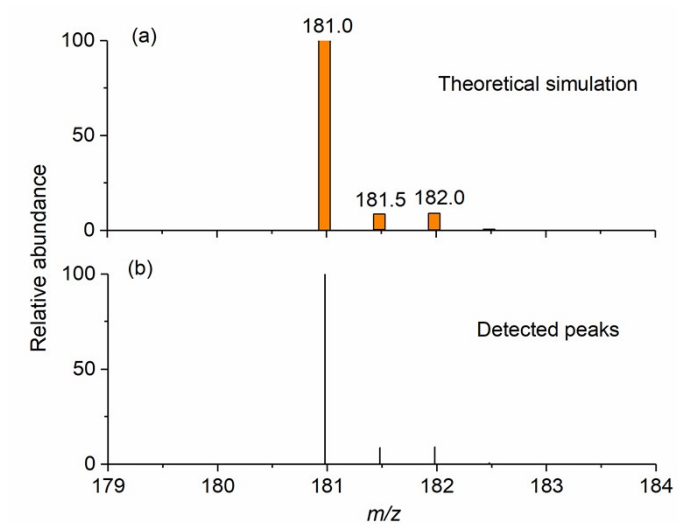
**Fig. S4.** Residual PMS after the degradation of SMX under different pH. (a) 7; (b) 8; (c) 9; (d) 10.



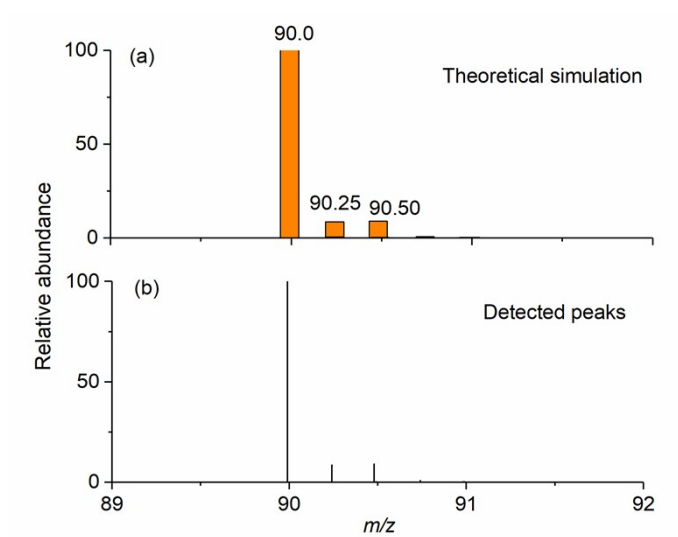
**Fig. S5.** Effect of scavengers on SMX degradation. (a) DMBQ; (b) DCBQ; (c) TFBQ.



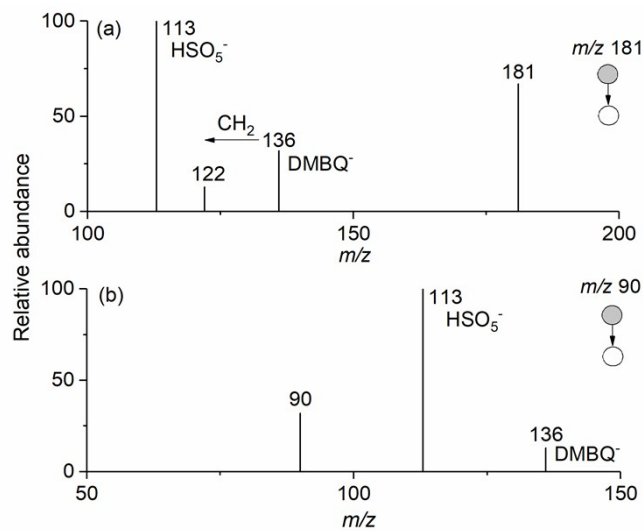
**Fig. S6.** Degradation of BA in PMS/different quinones system.



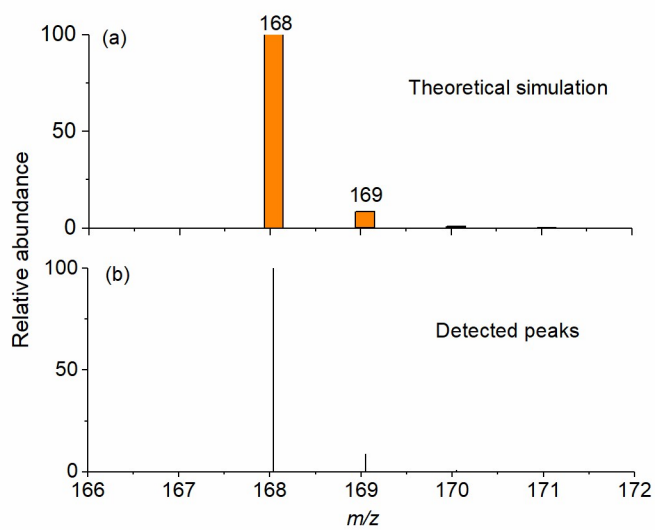
**Fig. S7.** Theoretical simulation and detected isotopic envelope of  $m/z$  180.98.



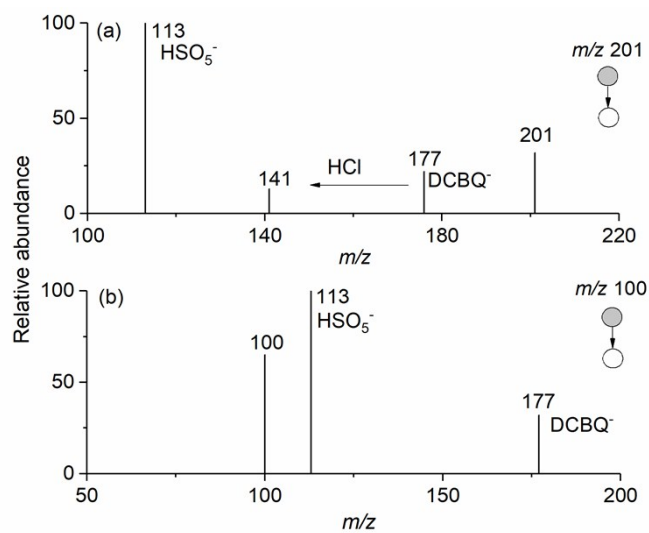
**Fig. S8.** Theoretical simulation and detected isotopic envelope of  $m/z$  89.98.



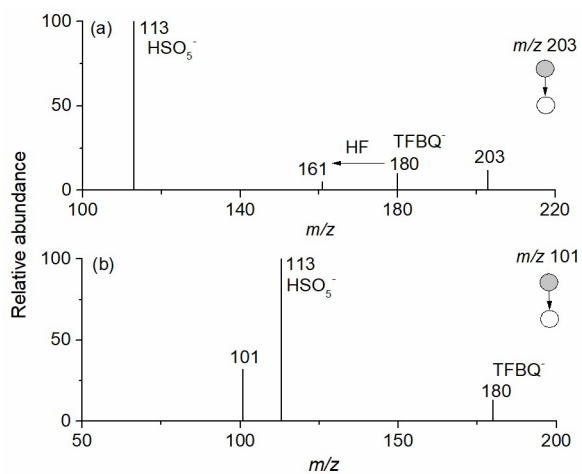
**Fig. S9.** MS/MS results of (a)  $m/z$  180.98 and (b) 89.98.



**Fig. S10.** Theoretical simulation and detected isotopic envelope of  $m/z$  168.04.



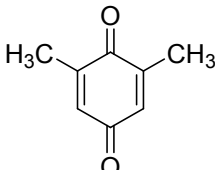
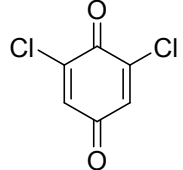
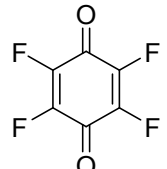
**Fig. S11.** Intermediates identification in PMS activated by DCBQ.



**Fig. S12.** Intermediates identification in PMS activated by TFBQ.



**Table S1.** The chemical characteristics of quinones.

Compound	Structure	Molecular formula	Molecular mass
2,6-dimethyl-1,4-benzoquinone		C <sub>6</sub> H <sub>6</sub> O <sub>4</sub>	136.05
2,6-dichloro-1,4-benzoquinone		C <sub>6</sub> H <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub>	175.94
tetrafluoro-1,4-benzoquinone		C <sub>6</sub> O <sub>2</sub> F <sub>4</sub>	179.98

**Table S2.** Pseudo-first-order rate constants for SMX degradation.

BQs	pH = 7	pH = 8	pH = 9	pH = 10
	$k_{obs}$ (min <sup>-1</sup> )	$k_{obs}$ (min <sup>-1</sup> )	$k_{obs}$ (min <sup>-1</sup> )	$k_{obs}$ (min <sup>-1</sup> )
DMBQ	0.0101	0.0136	0.074	0.0958
DCBQ	0.0185	0.0382	0.2310	0.3054
TFBQ	0.0277	0.0702	0.3042	0.6323

**Table S3.** Rate constant of selected quenchers with <sup>1</sup>O<sub>2</sub>, ·OH and SO<sub>4</sub><sup>·-</sup>.

quenchers	reaction rate constant (M <sup>-1</sup> s <sup>-1</sup> )		
	SO <sub>4</sub> <sup>·-</sup>	·OH	<sup>1</sup> O <sub>2</sub>
methanol	2.5×10 <sup>7</sup>	9.7×10 <sup>8</sup>	--
ethanol	1.0 × 10 <sup>7</sup>	1.0 × 10 <sup>9</sup>	--
NaN <sub>3</sub>	2.5 × 10 <sup>9</sup>	1.2 × 10 <sup>10</sup>	1.0 × 10 <sup>9</sup>

**Table S4.** Identified products of PMS activated by DMBQ derived from Figure 5a.

Compound	Molecular formula	Assignment	Theoretical $m/z$	Measured $m/z$	Mass Diff. (ppm)
bisulfate	$\text{HSO}_4^-$	$\text{M}^-$	96.9590	96.9592	2.1
peroxymonosulfate	$\text{HSO}_5^-$	$\text{M}^-$	112.9539	112.9542	2.6
DMBQ	$\text{C}_8\text{H}_8\text{O}_2$	$\text{M}^-$	136.0519	136.0522	2.2
Hydro-DMBQ	$\text{C}_8\text{H}_{10}\text{O}_2$	$[\text{M}-\text{H}]^-$	137.0597	137.0600	2.2
DMBQ-OH	$\text{C}_8\text{H}_8\text{O}_3$	$[\text{M}-\text{H}]^-$	151.0390	151.0393	2.0
Intermediate I	$\text{C}_8\text{H}_{12}\text{O}_{12}\text{S}_2$	$[\text{M}-2\text{H}]^{2-}$	180.9801	180.9803	1.1
Intermediate II	$\text{C}_8\text{H}_{12}\text{O}_{12}\text{S}_2$	$[\text{M}-4\text{H}]^{4-}$	89.9859	89.9862	3.3
Intermediate III	$\text{C}_8\text{H}_8\text{O}_4$	$\text{M}^-$	168.0417	168.0420	1.8

**Table S5.** Identified products of PMS activated by DCBQ derived from Figure 5b.

Compound	Molecular formula	Assignment	Theoretical $m/z$	Measured $m/z$	Mass Diff. (ppm)
DCBQ	$\text{C}_6\text{H}_2\text{O}_2\text{Cl}_2$	$\text{M}^-$	175.9426	175.0429	1.7
Hydro-DCBQ	$\text{C}_6\text{H}_4\text{O}_2\text{Cl}_2$	$[\text{M}-\text{H}]^-$	176.9505	176.9508	1.6
Intermediate I	$\text{C}_6\text{H}_6\text{O}_{12}\text{S}_2\text{Cl}_2$	$[\text{M}-2\text{H}]^{2-}$	200.9255	200.9257	1.0
Intermediate II	$\text{C}_6\text{H}_6\text{O}_{12}\text{S}_2\text{Cl}_2$	$[\text{M}-4\text{H}]^{4-}$	99.9586	99.9588	2.0
Intermediate III	$\text{C}_6\text{H}_2\text{O}_4\text{Cl}_2$	$\text{M}^-$	207.9325	207.0328	1.4

**Table S6.** Identified products of PMS activated by TFBQ derived from Figure 5c.

Compound	Molecular formula	Assignment	Theoretical $m/z$	Measured $m/z$	Mass Diff. (ppm)
TFBQ	$\text{C}_6\text{O}_2\text{F}_4$	$\text{M}^-$	179.9829	179.9832	1.6
Hydro-TFBQ	$\text{C}_6\text{H}_2\text{O}_2\text{F}_4$	$[\text{M}-\text{H}]^-$	180.9907	180.9909	1.1
Intermediate I	$\text{C}_6\text{H}_4\text{O}_{12}\text{S}_2\text{F}_4$	$[\text{M}-2\text{H}]^{2-}$	202.9456	202.9459	1.5
Intermediate II	$\text{C}_6\text{H}_4\text{O}_{12}\text{S}_2\text{F}_4$	$[\text{M}-4\text{H}]^{4-}$	100.9686	100.9688	2.0
Intermediate III	$\text{C}_6\text{F}_4\text{O}_4$	$\text{M}^-$	211.9727	211.9730	1.4