Supplementary Materials

for

Removal of contaminants by activating peroxymonosulfate using zero valent iron based bimetallic particles (Fe/Cu, Fe/Co, Fe/Ni, Fe/Ag)

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Test S1

Micron zero valent iron powder (ZVI, Fe⁰, \geq 99.9 %), Micron zero vatent copper powder (Cu⁰, \geq 99.9 %), Micron zero vatent cobalt powder (Co⁰, \geq 99.9 %), Micron zero vatent nickel powder (Ni⁰, \geq 99.5 %), Micron zero vatent silver powder (Ag⁰, \geq 99.9 %), 2,4-dichlorophenol (2,4-DCP, \geq 99 %), bisphenol A (BPA), bisphenol F (BPF), levofloxacin (LFX), chloramphenicol (CAP), methanol (HPLC grade) and acetonitrile (HPLC grade) were purchased from Aladdin Industrial Corporation. Oxone (PMS, KHSO₅·0.5KHSO₄·0.5K₂SO₄, \geq 99.5 %) was purchased from Sigma-Aldrich. Methyl phenyl sulfoxide (PMSO, \geq 98.0 %), methyl phenyl sulfone (PMSO₂, \geq 98.0 %) were purchased from Shanghai Macklin Biochemical Co., Ltd. Rhodamine B (RB, \geq 99%), copper sulfate, cobaltous sulfate, nickel sulfate, silver nitrate, formic acid, sulfuric acid, sodium hydroxide, ethanol, tert-butyl alcohol, phenol, nitrobenzene (NB) and sodium nitrite were all supplied by Chengdu Kelong chemical reagent factory.

Test S2

The HPLC chromatography (Waters, e2695) was equipped with a 2489 UV-vis detector and the detection wavelength and binary phase composition were as follows: 286 nm and methanol/0.1% formic acid (70:30, v/v) for 2,4-DCP; 276 nm and methanol/0.1 % formic acid (70:30, v/v) for BPA; 230 nm and methanol/0.1 % formic acid (65:35, v/v) for BPF; 293 nm and acetonitrile /0.1 % formic acid (13:87, v/v) for LFX and 277 nm and acetonitrile /0.1 % formic acid (30:70, v/v) for CAP. The flow rate of these binary phases was 1 mL/min and the temperature of liquid chromatographic column was 35 °C.

Test S3

The bimetallic particles' surface topography and chemical composition before and after reaction were characterized by scanning electron microscopy (SEM, JSM-7500F (JEOL, Japan)) and X-ray diffraction (XRD, X'Pert Pro MPD diffractometer (Panalytical, Holland)), respectively. The surface element distribution and valence state of the pristine bimetallic particles were characterized by energy dispersive spectrometer (EDS, JSM-7500F (JEOL, Japan)) and X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD (Kratos, Britain)).

Test S4

The EPR spectrum was measured under the following conditions: a center field of 3505.40 G; a sweep width of 150.00 G, a microwave frequency of 9.84 GHz, a microwave attenuator of 20.00 dB, a microwave power of 2.00 mW, and a sweep time of 10.53 seconds.

Test S5

In this study, the existence of PMSO₂ were examined with ultrahigh performance liquid chromatograph (Shimazu, LC-30AD) coupled with a SCIEX TRIPLE QUAD 4500 mass spectrometry in a negative electrospray ionization mode (UPLC/ESI-MS/MS). A mixture of (A) ultrapure water and (B) acetonitrile were used as mobile phases in a binary gradient with a flow rate of 0.3 mL/min. The gradient was set as follows: B increased from 10 % to 90 % within 1.5 min and remained unchanged for 1.5 min. Then, a decreased from 90 % to 10 % within 0.1 min. Finally, it stayed for 1.9 min at the current rate. Sample injection volume was 1uL. The MS parameters were set as follows: ionspray voltage = -4500 V; source temperature = 500 °C; collision energy (CE) for ion fragments of *m*/*z* 79.1 was -22 V, and for ion fragments of *m*/*z* 63.5 was -41 V; declustering potential (DP) for ion fragments of *m*/*z* 79.1 was -44 V, and for ion fragments of *m*/*z* 63.5 was -53 V.



Fig. S1. The reaction rates of different systems (M: Fe = 1: 10). $[RB]_0 = 20 \text{ mg } L^{-1}$, $[PMS]_0 = 1 \text{ mM}$, [PMS]: [RB] = 15.4:1, $[catalyst]_0 = 100 \text{ mg } L^{-1}$, initial $pH = 3 \pm 0.2$, $T = 25\pm1$ °C.



Fig. S2. Various organics compounds degradation in different systems. (a) $[2,4-DCP]_0 = (b) [BPA]_0 = (c) [BPF]_0 = (d) [CAP]_0 = (e) [LFX]_0 = 20 \text{ mg } \text{L}^{-1}, [PMS]_0 = 1 \text{ mM}, [PMS]$: [Organic contaminations] =15.4:1, [catalyst]_0 =

100 mg L⁻¹, initial pH = 3 ± 0.2 , T = 25 ± 1 °C.



Fig. S3. The TOC (reaction time 3 h) of various organics compounds degradation in different systems. (a) [2,4-

 $DCP]_0 = (b) [BPA]_0 = (c) [BPF]_0 = (d) [CAP]_0 = (e) [LFX]_0 = 20 mg L^{-1}, [PMS]_0 = 1 mM, [PMS]: [Organic contaminations] =15.4:1, [catalyst]_0 = 100 mg L^{-1}, initial pH = 3 \pm 0.2, T = 25\pm1 °C.$

Organics	Abbreviations	Relative	Structural formula	Chemical
		molecular		formula
		mass		
Rhodamine B	RB	479.01	H ₃ C OH H ₃ C CH ₃	C ₂₈ H ₃₁ ClN ₂ O ₃
2, 4- dichlorophenol	2,4-DCP	163.00	СІОН	C ₆ H ₄ Cl ₂ O
Bisphenol A	BPA	228.29	HO CH3	$C_{15}H_{16}O_2$
Bisphenol F	BPF	200.24	но он	$C_{13}H_{12}O_2$
Chloramphenicol	CLP	323.14	OH O2N OH HN OH CI CI	C ₁₁ H ₁₂ Cl ₂ N ₂ O 5

Table. S1. Characteristics of various organics.



Fig. S4 SEM and EDS spectra of Fe/Cu bimetallic particles with the molar ratio (Cu: Fe) is 1: 5, 1: 10 and 1: 50.



Fig. S5 SEM and EDS spectra of Fe/Co bimetallic particles with the molar ratio (Co: Fe) is 1: 5, 1: 10 and 1: 50.



Fig. S6 SEM and EDS spectra of Fe/Ni bimetallic particles with the molar ratio (Ni: Fe) is 1: 5, 1: 10 and 1: 50.



Fig. S7 SEM and EDS spectra of Fe/Ag bimetallic particles with the molar ratio (Ag: Fe) is 1: 5, 1: 10 and 1: 50.







Fig. S8. XPS full-scan spectra of (a) Fe, (b) Fe/Cu, (c) Fe/Co, (d) Fe/Ni and (e) Fe/Ag.

Test S6

As we all know, Fe(IV) could oxidize PMSO to its oxygen transfer product PMSO₂ ¹. As shown in Fig. S9 to Fig. S12, compared with the UPLC/ESI-MS/MS chromatograms of standard PMSO₂ (Fig. S8), the unlabled PMSO₂ by oxidizing PMSO were all observed in our four systems and the intensities of the four unlabled PMSO₂ were practically little difference. In principle, if Fe(IV) was the dominant reactive species in our four systems, then, the removal ratio of contaminants should be similar, nevertheless, it's worth noting that the contaminants degradation efficiency in four systems were almost completely different. So according to the above results, during the process, the iron leaching was the main contributor for PMS activation in our systems and the reactive radicals (*OH, SO_4^{--} and O_2^{--}) are possible the main reactive species.

$$HSO_5^- + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{IV}O^{2+} + H^+$$
 (S1)

$$\overset{O}{\underset{CH_{3}}{\overset{+}{\xrightarrow{}}}} Fe^{IV}O^{2+} \xrightarrow{\overset{O}{\underset{R}{\xrightarrow{}}}} \overset{O}{\underset{CH_{3}}{\overset{O}{\xrightarrow{}}}} Fe^{2+}$$
(S2)



Fig. S9. UPLC/ESI-MS/MS chromatograms of standard PMSO₂.



Fig. S10. UPLC/ESI-MS/MS chromatograms of unlabled PMSO₂ produced by oxidizing PMSO in the ZVI/Cu-PMS system. $[PMS]_0 = 1 \text{ mM}$, $[catalyst]_0 = 100 \text{ mg L}^{-1}$, $[PMSO]_0 = 0.1 \text{ mM}$, initial $pH = 3 \pm 0.2$, $T = 25 \pm 1 \text{ °C}$.



Fig. S11. UPLC/ESI-MS/MS chromatograms of unlabled PMSO₂ produced by oxidizing PMSO in the ZVI/Ni-PMS system. $[PMS]_0 = 1 \text{ mM}$, $[catalyst]_0 = 100 \text{ mg L}^{-1}$, $[PMSO]_0 = 0.1 \text{ mM}$, initial $pH = 3 \pm 0.2$, $T = 25 \pm 1 \text{ °C}$.



Fig. S12. UPLC/ESI-MS/MS chromatograms of unlabled PMSO₂ produced by oxidizing PMSO in the ZVI/Co-PMS system. $[PMS]_0 = 1 \text{ mM}$, $[catalyst]_0 = 100 \text{ mg L}^{-1}$, $[PMSO]_0 = 0.1 \text{ mM}$, initial $pH = 3 \pm 0.2$, $T = 25 \pm 1 \text{ °C}$.



Fig. S13. UPLC/ESI-MS/MS chromatograms of unlabled PMSO₂ produced by oxidizing PMSO in the ZVI/Ag-PMS system. $[PMS]_0 = 1 \text{ mM}$, $[catalyst]_0 = 100 \text{ mg L}^{-1}$, $[PMSO]_0 = 0.1 \text{ mM}$, initial $pH = 3 \pm 0.2$, $T = 25 \pm 1 \text{ °C}$.



Fig. S14. Open-circuit potential curves on the glassy carbon electrodes in different systems.



Fig. S15. The reaction rate with different M: Fe ratio using the catalyst as (a) Fe/Cu, (b) Fe/Co, (c) Fe/Ni and (d) Fe/Ag. $[RB]_0 = 20 \text{ mg } \text{L}^{-1}$, $[PMS]_0 = 1 \text{ mM}$, [PMS]: [RB] = 15.4:1, $[catalyst]_0 = 100 \text{ mg } \text{L}^{-1}$, initial pH = 3 ± 0.2 , T = $25 \pm 1 \text{ °C}$.



Fig. S16. RB degradation when the bimetallic ratio (M: ZVI) is 1: 50, 1: 10 and 1: 5 using the catalyst as (a) ZVI/Cu, (b) ZVI/Co, (c) ZVI/Ni and (d) ZVI/Ag within 20 min. $[RB]_0 = 20 \text{ mg L}^{-1}$, $[PMS]_0 = 1 \text{ mM}$, [PMS]: [RB]

=15.4:1, [catalyst]₀ = 100 mg L⁻¹, initial pH = 3 ± 0.2 , T = 25 ± 1 °C.



Fig. S17. The reaction rate with different catalysts dosages using the catalysts as (a) Fe, (b) Fe/Cu, (c) Fe/Co, (d) Fe/Ni and (e) Fe/Ag. $[RB]_0 = 20 \text{ mg L}^{-1}$, $[PMS]_0 = 1 \text{mM}$, [PMS]: [RB] = 15.4:1, initial $pH = 3 \pm 0.2$, $T = 25 \pm 1$ °C.

Water	DW	JAW	LW	MYW	RW
рН	5.77	8.01	7.51	7.79	8.16
TOC	-	1.13±0.10	1.78 ± 0.05	1.80 ± 0.42	$0.60{\pm}0.04$
F ⁻ (mg L ⁻¹)	-	0.143	0.445	0.204	0.256
Cl ⁻ (mg L ⁻¹)	-	3.778	8.077	6.936	7.111
NO ₂ - (mg L ⁻¹)	-	5.300	4.075	5.240	4.380
NO ₃ ⁻ (mg L ⁻¹)	-	3.246	0.792	0.930	2.521
Na ⁺ (mg L ⁻¹)	-	5.004	8.566	7.594	3.308
$NH_4^+ (mg L^{-1})$	-	1.419	1.082	1.607	1.054
K ⁺ (mg L ⁻¹)	-	5.289	2.455	2.229	3.770
Mg ²⁺ (mg L ⁻¹)	-	8.180	11.161	10.963	7.185
Ca ²⁺ (mg L ⁻¹)	-	34.566	21.341	32.976	31.488
Sr ²⁺ (mg L ⁻¹)	-	7.437	6.868	7.440	0.570

Table. S2. Characteristics of various water matrices.

Note: "-" stands for undetected.

References

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