Supplementary material

Ca(OH)₂-mediated activation of peroxymonosulfate for the degradation of bisphenol S

Leliang Wu^a, Yiting Lin^a, Yimin Zhang^a, Peng Wang^a, Mingjun Ding^a, Minghua Nie^{*} ^{a b} and Caixia Yan^{* a}

^a School of Geography and Environment, Key Laboratory of Poyang Lake Wetland and Watershed Research, Ministry of Education, Jiangxi Normal University, Nanchang 330022, China

^b Key Laboratory of Eco-geochemistry, Ministry of Natural Resource, Beijing 100037, China

* Corresponding author email: <u>mhnie@jxnu.edu.cn</u> (M. Nie); <u>wysycx@foxmail.com</u> (C. Yan)

Water matrixes	Degradation	Cl-	F ⁻	NO_2^-	SO4 ²⁻	NO ₃ -	<i>k</i> _{obs}	Half-life ^a	D ?
	of BPS (%)	$(mg \bullet L^{-1})$	(\min^{-1})	(min)	Λ^2				
Ultrapure water	100	n.d. ^b	n.d.	n.d.	n.d.	n.d.	0.2010	4.595195	0.995
River water	85.03	16.4728	1.3848	n.d.	33.4097	14.1677	0.0829	6.366535	0.997
Lake water	81.47	13.3090	0.7952	n.d.	15.7176	6.2020	0.0729	6.623628	0.997
Domestic water	77.94	15.1818	0.8712	0.3201	15.7535	8.5110	0.0626	6.928274	9.996

Table S1. Basic physical and chemical characteristics of different water matrices and removal of ACE in these matrices.

^a Calculated from the pseudo-first order kinetics law where $1 / (2t) = \ln 2 / k_{obs}$.

^b n.d.: not detected

Compounds	Mobile phase and proportion (%)	Flow rate (mL•min ⁻¹)	Detector	Detection wavelength (nm)	Temperature of column incubator (°C)	Injection volume (µl)
BPA	Water: Methanol 20: 80	0.2	DAD	220	40	2
BPS	Water: Methanol 40: 60	0.2	DAD	258	40	2
FFA	Methanol: Trifluoroacetic acid (0.5‰) 30: 70	0.2	DAD	214	40	2
ТАР	Methanol: Trifluoroacetic acid (0.5‰) 25: 75	0.3	FLD	$\lambda_{ex} = 224$ $\lambda_{em} = 290$	40	2
NOF	Methanol: Trifluoroacetic acid (0.5‰) 25: 75	0.3	FLD	$\lambda_{ex} = 278$ $\lambda_{em} = 445$	40	2
ENR	Methanol: Trifluoroacetic acid (0.5‰) 28: 72	0.3	FLD	$\lambda_{ex} = 280$ $\lambda_{em} = 450$	40	2
LOM	Methanol: Trifluoroacetic acid (0.5‰) 30: 70	0.3	FLD	$\lambda_{ex} = 338$ $\lambda_{em} = 425$	40	2

 Table S2. Detail information of HPLC analysis.

Table S3. Removal of BPS by $Ca(OH)_2/PMS$ system in the presence of varioussubstances. Experiment conditions: $[BPS]_0 = 20 \ \mu m$, $[PMS]_0 = 1.5 \ mM$, $[Ca(OH)_2]_0 =$

Coexisting	Concentrations	Removal of	k_{obs}	R^2	Initial-final
No addition -		100%	2.01×10 ⁻²	0.995	9.83-7.03
	1 mM	98.01	1.57×10^{-2}	0.963	10.77-9.17
Cl ⁻	5 mM	100	2.53×10 ⁻²	0.900	10.82-9.09
	10 mM	100	2.78×10 ⁻²	0.777	10.89-8.97
	1 mM	89.71	9.70×10 ⁻³	0.999	10.16-9.01
HCO_3^-	5 mM	67.57	4.80×10 ⁻³	0.991	9.64-9.02
	10 mM	63.82	4.30×10 ⁻³	0.981	9.5-9.16
	1 mM	100.00	2.03×10 ⁻²	0.993	9.86-7.61
NO_3^-	5 mM	100.00	1.95×10 ⁻²	0.995	10.07-7.80
	10 mM	99.35	2.09×10 ⁻²	0.987	10.16-7.88
	1 mM	99.23	2.04×10 ⁻²	0.994	9.9-7.75
SO_4^{2-}	5 mM	100.00	1.94×10 ⁻²	0.991	10.52-8.33
	10 mM	99.40	2.09×10 ⁻²	0.974	10.28-8.19
НА	$5 \text{ mg} \cdot \text{L}^{-1}$	98.62	1.79×10 ⁻²	0.992	9.93-7.56
	$20 \text{ mg} \cdot \text{L}^{-1}$	96.83	1.49×10 ⁻²	0.996	9.74-7.55
	$50 \text{ mg} \cdot \text{L}^{-1}$	96.31	1.42×10^{-2}	0.993	10.4-7.70

1 mM, [substances]₀ = 0-10 mM, [HA]₀ = 0-50 mg•L⁻¹.



Fig. S1. Degradation of NBT (a), and FFA (b)in the Ca(OH) ₂/PMS system,

 $[Ca(OH)_2]_0 = 1 \text{ mM}, [PMS]_0 = 1.5 \text{ mM}, [NBT]_0 = [FFA]_0 = 20 \mu M.$



Fig. S2 Effect of PMS adding modes on the degradation of PMS. $[Ca(OH)_2]_0 = 1 \text{ mM}, [PMS]_0 = 1.5 \text{ mM}, [BPS]_0 = 20 \mu M.$

Oxidation methods	BPS dosages	Experimental conditions	Reaction time	BPS degradati on rate	Degradatio n mechanism	References
α-Fe ₂ O ₃ nanosheets, visible light	80 µM	$\begin{array}{c} 0.2 \ g \bullet L^{-1} \\ catalyst, \\ 0.2 \ g \bullet L^{-1} \ H_2 O_2, \\ pH{=}5.6 \pm 0.2, \\ 25^{\circ}C \end{array}$	160 min	91%	h^+ and $\bullet OH$	Shao et al., 2017 ¹
Heat, PS	25 μΜ	0.5 mM PS, pH=7.0, 60°C	180 min	91%	$SO_4^{\bullet-}$	Wang et al., 2017 ²
Spinel sulfide, PMS	10 µM	0.01 g•L ⁻¹ catalyst, 0.1 mM PS, 25°C	30 min	100%	SO₄•−	Xu et al., 2018 ³
Ferrate	5 μΜ	0.05 mM Ferrate, 25°C	10 min	90%	HFeO ₄ ⁻	Yang et al., 2019 ⁴
visible light, BIOI/B4C, PMS	20 μΜ	$100 \text{ mg} \cdot \text{L}^{-1}$ BIOI/B ₄ C, 0.05 mM PMS, pH = 7.0 ± 0.5, 25°C	45 min	90.4%	h ⁺ , •OH, SO ₄ • ⁻ , O ₂ • ⁻	Lv et al., 2021 ⁵
Ca(OH) ₂ , PMS	20 µM	1.5 mM PMS, 1 mM Ca(OH) ₂ , 25°C	240 min	100%	$O_2^{\bullet-}$ and 1O_2	Present study

Table R1. Removal of BPS by different oxidation methods

Mologular structure	Molecular	Molecular	Denisity	n V a	Melting	
Molecular structure	formula	weight	(g/cm^3)		point (°C)	
но	$C_{12}H_{10}O_4S$	250.2	1.433	8.2	240	

Table R2 The structures and basic properties of BPS.

Coexisting	Concentration	Removal	<i>k</i> _{obs}	P 2	Initial-final
substance	Concentration	of BPS(%)	(min^{-1})	Λ	pН
	only PMS	3.57	1.17×10^{-4}	0.742	3.96-3.38
1.00	only Ca(OH) ₂	1.05	1.74×10^{-5}	0.033	11.12-10.97
different	PMS+Ca(OH) ₂	100	2.01×10^{-2}	0.995	9.69-8.20
systems	PS+Ca(OH) ₂	0	6.64×10^{-5}	0.346	-
	H ₂ O ₂ +Ca(OH) ₂	0	9.88×10 ⁻⁵	0.723	-
	0.00 mM	1.05	1.17×10^{-4}	0.742	3.45-3.26
	0.25 mM	3.70	1.38×10^{-4}	0.855	3.66-3.61
1	0.50 mM	6.42	1.92×10^{-4}	0.652	8.03-5.28
$C_{\alpha}(OH)_{\alpha}$	0.75 mM	89.32	1.01×10^{-2}	0.988	9.24-6.06
	1.00 mM	100	2.01×10^{-2}	0.995	9.69-8.20
	1.50 mM	82.17	7.53×10 ⁻³	0.953	10.89-10.97
	2.00 mM	38.16	1.94×10 ⁻³	0.852	10.96-10.94
	0.00 mM	1.05	1.74×10^{-5}	0.032	11.12-10.97
	0.50 mM	12.79	5.40×10 ⁻⁴	0.934	10.92-10.79
	1.00 mM	61.23	4.09×10 ⁻³	0.978	10.41-10.13
initial DMC	1.25 mM	88.03	9.27×10 ⁻³	0.986	10.02-9.31
iniliai PMS	1.50 mM	100	2.01×10^{-2}	0.995	9.69-8.20
	1.75 mM	98.21	1.76×10^{-2}	0.995	9.31-8.59
	2.00 mM	98.39	1.80×10^{-2}	0.993	9.14-8.10
	3.00 mM	77.63	6.87×10^{-3}	0.928	7.65-7.50
	10 µM	98.74	1.79×10^{-2}	0.986	9.71-8.70
	20 µM	100.00	2.01×10^{-2}	0.995	9.69-8.20
initial BPS	40 µM	91.94	1.14×10^{-2}	0.971	10.36-7.85
	60 µM	84.63	8.60×10 ⁻³	0.898	9.71-7.23
	80 µM	77.08	6.60×10 ⁻³	0.863	9.57-7.21
temperatur e	4°C	43.12	2.40×10 ⁻³	0.997	10.44-9.44
	25°C	100	2.01×10^{-2}	0.995	9.69-8.20
	40°C	100	2.11×10^{-2}	0.994	9.33-7.24
	50°C	100	5.92×10 ⁻²	0.972	9.64-7.43

Table R3. Removal of BPS by Ca(OH)₂/PMS system in the presence of various substances. Experiment conditions: $[BPS]_0 = 20 \ \mu m$, $[PMS]_0 = 0-3 \ mM$, $[Ca(OH)_2]_0 = 0-2 \ mM$, $[HA]_0 = 0-50 \ mg \cdot L^{-1}$.

References:

- X. Wang, J. Ma, H., Z. Wang, R. Guo, and X. Hu, Aqueous phototrans-formation of bisphenol S: The competitive radical-attack pathway to p-hydroxybenzene-sulfonic acid. *Water Sci. Technol.*, 2014, 70(3), 540-547.
- 2 P. Shao, Z. Ren, J. Tian, S. Gao, X. Luo, W. Shi and F. Cui, Silica hydrogelmediated dissolution-recrystallization strategy for synthesis of ultrathin a-Fe₂O₃ nano-sheets with highly exposed (110) facets: A superior photocatalyst for degradation of bisphenol S. *Chem Eng. J.*, 2017, 323, 64-73.
- 3 Q. Wang, X. Lu, Y. Cao, J. Ma, J. Jiang, X. Bai and T. Hu, Degradation of Bisphenol S by heat activated persulfate: Kinetics study, transformation pathways and influences of co-existing chemicals. *Chem Eng. J.*, 2017, 328, 236-245.
- 4 H. Xu, D. Wang, J. Ma, T. Zhang, X. Lu, and Z. Chen, A superior active and stable spinel sulfide for catalytic peroxymonosulfate oxidation of bisphenol S, *Appl. Catal.*, *B*, 2018, 238, 557-567.
- 5 T. Yang, L. Wang, Y. Liu, Z. Huang, H. He, X. Wang, J. Jiang. D. Gao and J. Ma, Comparative study on ferrate oxidation of BPS and BPAF: Kinetics, reaction mechanism, and the improvement on their biodegradability, *Water Res*, 2019, 148, 115-125.
- 6 Y. Lv, Y. Liu, J. Wei, M. Li, D. Xu and B. Lai, Bisphenol S degradation by visible light assisted peroxymonosulfate process based on BiOI/B₄C photocatalysts with Z-scheme heterojunction, *Chem Eng. J.*, 2021, 417, 129188.