

Supporting Information

**Performance of the solar/peroxymonosulfate process in (waste)water
treatment: Abatement of micropollutants, roles of reactive oxygen
species, and formation of disinfection by-products**

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Table S1 Abbreviations

Full name	Abbreviation	Full name	Abbreviation
peroxymonosulfate	PMS	peracetic acid	PAA
nitrobenzene	NB	total organic carbon	TOC
flunixin meglumine	FMME	natural organic matter	NOM
aspirin	ASA	the energy consumption of the solar device	EE/O _{Solar}
benzoic acid	BA	the cost of the oxidant	EE/O _{Oxidant}
hydroxyl radical	·OH	the total energy consumption	EE/O _{total}
sulfate radical	SO ₄ ^{·-}	the oxidizer production	Oxidant _{energy}
reactive oxygen species	ROS	Trichloromethane	CHCl ₃
disinfection by-products	DBPs	Bromodichloromethane	BDCM
trihalomethanes	THMs	Dibromochloromethane	DBCM
haloacetic acids	HAAs	Tribromomethane	CHBr ₃
Pharmaceutical and personal care products	PPCPs	Chloroacetic acid	CAA
wastewater treatment plant	WWTP	Bromoacetic acid	BAA
advanced oxidation processes	AOPs	Dichloroacetic acid	DCAA
ultraviolet	UV	Dibromoacetic acid	DBAA
free available chlorine	FAC	Trichloroacetic acid	TCAA
hydrogen peroxide	H ₂ O ₂	the United States Environmental Protection Agency	USEPA

Table S2 Water quality parameters of actual water samples

Parameters	Yangtze River	Effluent of wastewater treatment plant
pH	7.88	7.23
TOC (mg/L)	4.22	8.07
TN (mg/L)	1.84	6.18
TP (mg/L)	0.18	0.16
NH ₃ -N (mg/L)	0.59	0.15

Table S3 HPLC methods of the concentration of ASA, FMME, NB, and BA

Material	Mobile phase (v:v)	Detection wavelength (nm)	Flow rate (mL·min ⁻¹)	Column temperature (°C)
ASA	Water : Acetonitrile : 2% phosphoric acid = 40 : 30 : 30	230	0.3	40
FMME	Water : Acetonitrile : 2% phosphoric acid = 40 : 30 : 30	280	0.3	40
NB	Methanol : 2% phosphoric acid = 45: 55	270	0.2	40
BA	Methanol : 2% phosphoric acid = 45: 55	225	0.2	40

Table S4 Calculation of k_{obs} and ROS contributions of ASA, FMME, NB, and BA degradation in solar/PMS system at varying pH values

pH	Material	$k_{\text{obs,contaminant}}$ (min^{-1})	$[\cdot\text{OH}]_{\text{ss}}$ $\times 10^{-13}$	$k'_{\cdot\text{OH}}$ Contaminant (10^{-4} s^{-1})	$\cdot\text{OH}$ (%)	$k'_{\text{SO}_4^{\cdot-}}$ Contaminant (10^{-4} s^{-1})	$[\text{SO}_4^{\cdot-}]_{\text{ss}}$ $\times 10^{-13}$	$\text{SO}_4^{\cdot-}$ (%)	Other active ROS (%)
5.5	NB	0.032	1.13					/	/
	BA	0.093		6.00	38.9%	9.43		61.1%	/
	ASA	0.058		2.86	29.4%	4.13	7.86	42.4%	28.2%
	FMME	0.059		3.96	40.6%	5.50		56.3%	3.1%
7.0	NB	0.040	1.43					/	/
	BA	0.112		7.57	40.6%	11.09		59.4%	/
	ASA	0.067		3.61	32.1%	4.85	9.24	43.1%	24.8%
	FMME	0.063		5.00	47.3%	5.33		50.3%	2.4%
8.5	NB	0.051	1.81					/	/
	BA	0.159		9.59	36.2%	16.93		63.8%	/
	ASA	0.074		4.58	37.2%	7.41	14.1	60.2%	2.6%
	FMME	0.077		6.33	49.1%	6.39		49.5%	1.4%

$\cdot\text{OH}$ (%), $\text{SO}_4^{\cdot-}$ (%), and other active ROS (%) represents the contribution of $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, and other active ROS, respectively.

Table S5 Production of THMs ($\mu\text{g/L}$) with and without solar/PMS pre-oxidation at varying pH values

Condition	pH	CHCl_3	BDCM	DBCM	CHBr_3	Total THMs
Without pre-oxidation	5.5	2.6	3.0	0.5	ND*	6.2
	7.0	4.6	2.1	0.6	ND	7.2
	8.5	4.9	5.7	0.8	ND	11.4
With pre-oxidation	5.5	3.8	3.2	0.6	ND	7.6
	7.0	4.5	3.0	0.7	ND	8.2
	8.5	7.6	5.8	0.8	ND	14.2

*ND represents not detected.

Table S6 Production of HAAs ($\mu\text{g/L}$) with and without solar/PMS pre-oxidation at -varying pH values

Condition	pH	CAA	BAA	DCAA	TCAA	DBAA	Total HAAs
Without pre-oxidation	5.5	ND	ND	2.1	5.9	ND	8.0
	7.0	ND	ND	3.5	8.4	ND	11.9
	8.5	ND	ND	2.5	3.2	ND	5.8
With pre-oxidation	5.5	5.6	ND	47.2	28.6	ND	81.3
	7.0	4.8	ND	29.1	33.3	ND	67.2
	8.5	5.8	ND	58.5	47.0	ND	111.0

*ND represents not detected.

Table S7 Characteristics of the DBPs selected in this study

Compound	Molecular Formula	Abbreviation	Cytotoxicity LC₅₀ (M)^{1, 2}	CAS No.
Trichloromethane	CHCl ₃	CHCl ₃	9.62×10 ⁻³	67-66-3
Bromodichloromethane	CHCl ₂ Br	BDCM	1.15×10 ⁻²	75-27-4
Dibromochloromethane	CHClBr ₂	DBCM	5.36×10 ⁻³	124-48-1
Tribromomethane	CHBr ₃	CHBr ₃	3.96×10 ⁻³	75-25-2
Bromoacetic acid	CH ₂ BrCOOH	BAA	1.0×10 ⁻⁵	79-08-3
Dibromoacetic acid	CHBr ₂ COOH	DBAA	5.9×10 ⁻⁴	631-64-1
Chloroacetic acid	CH ₂ ClCOOH	CAA	8.1×10 ⁻⁴	79-11-8
Dichloroacetic Acid	CHCl ₂ COOH	DCAA	7.3×10 ⁻³	79-43-6
Trichloroacetic acid	CCl ₃ COOH	TCAA	2.4×10 ⁻³	76-03-9

Table S8 Alteration of the algae density with incubation time (0–96 h) in different systems

System	Algal density ($\times 10^6$ per mL)				
	0 h	24 h	48 h	72 h	96 h
Control	3.652 \pm 0.008	4.07 \pm 0.004	4.989 \pm 0.004	5.516 \pm 0.007	6.299 \pm 0.007
Pollutants	3.649 \pm 0.007	4.322 \pm 0.031	4.921 \pm 0.006	5.252 \pm 0.017	5.760 \pm 0.006
PMS	3.658 \pm 0.008	3.882 \pm 0.012	3.987 \pm 0.061	3.984 \pm 0.043	4.053 \pm 0.035
Pollutants+ solar/PMS	3.646 \pm 0.000	3.850 \pm 0.004	3.942 \pm 0.016	3.969 \pm 0.037	4.059 \pm 0.072

Text S1 Chemicals and materials

Chemicals were prepared with analytical standard grade chemical reagents and deionized water. Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\geq 99.0\%$), benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$, $\geq 99.0\%$), phosphoric acid (H_3PO_4 , $\geq 95\%$), sodium bicarbonate (NaHCO_3 , $\geq 99.7\%$), sodium carbonate anhydrous (Na_2CO_3 , $\geq 99.7\%$), acetic acid (CH_3COOH , $\geq 99.7\%$) and sodium acetate (CH_3COONa , $\geq 99.7\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Aspirin ($\text{C}_9\text{H}_8\text{O}_4$, $\geq 99.7\%$), potassium peroxydisulfate ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, $\text{KHSO}_5 \geq 47\%$), nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$, $\text{NB} \geq 99\%$), hydrogen peroxide (H_2O_2 , 30 wt. %) and ABTS ($\text{C}_{18}\text{H}_{24}\text{N}_6\text{O}_6\text{S}_4$, $\geq 99.7\%$) were purchased from Aladdin Industrial Co., Ltd. (Shanghai, China). Sodium phosphate dibasic dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99.5\%$) and sulfuric acid (H_2SO_4 , 98 wt. %) were purchased from Chengdu Chron Chemicals Co., Ltd. (Chengdu, China). Flunixin Meglumine ($\text{C}_{14}\text{H}_{11}\text{F}_3\text{N}_2\text{O}_2\text{C}_7\text{H}_{17}\text{NO}_5$, FMME $\geq 98.0\%$) was purchased from Shanghai yuanye Bio-Technology Co., Ltd. (Shanghai, China). Sodium dihydrogen phosphate anhydrous (Na_2HPO_4 , $\geq 99.7\%$) was purchased from Energy Chemical Co., Ltd. (Shanghai, China). Sodium hypochlorite solution (NaOCl , 12~15 wt. %) was purchased from 9ding Chemical Co., Ltd. (Shanghai, China). Potassium iodide (KI , $\geq 99.7\%$) was purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Methanol (CH_4O , HPLC), acetonitrile ($\text{C}_2\text{H}_3\text{N}$, HPLC) and *tert*-Butyl methyl ether ($\text{C}_5\text{H}_{12}\text{O}$, HPLC) were purchased from Sigma-Aldrich Chemical Co., Ltd. (Shanghai, China). trichloromethane (CHCl_3 , HPLC), bromodichloromethane (CHCl_2Br , HPLC), dibromochloromethane (CHClBr_2 , HPLC), tribromomethane (CHBr_3 , HPLC), chloroacetic acid (CH_2ClCOOH , HPLC), dichloroacetic acid (CHCl_2COOH , HPLC), trichloroacetic acid (CCl_3COOH , HPLC), bromoacetic acid (CH_2BrCOOH , HPLC) and dibromoacetic acid (CHBr_2COOH , HPLC) were purchased from Organic Standards Solutions International LLC (the United States). Natural organic matter (NOM, No.2R101N) was purchased from International Humic Substances Association (IHSS). 0.22- μm mixed cellulose ester (MCE) membrane filters (50 mm diameter) were purchased from Xinya Purification Device Factory (Shanghai, China).

Text S2 Experimental devices and procedures

The photochemical experiments were conducted with high brightness parallel light source system to simulate solar light (500 W, Perfect Light Co., China). The light illuminates into a 50.0 mL sample magnetically stirred within a cylindrical glass dish with a quartz cover, and the reaction temperature was controlled at ambient temperature ($25 \pm 1^\circ\text{C}$) by a constant low-temperature circulator. The experiments were conducted in a black-box to avoid the disturbances from external light sources, and a fan was installed on top to maintain the temperature in the entire reaction device at room temperature. Under natural sunlight irradiation, the reaction was performed using a magnetic stirrer and a 50 mL quartz beaker containing four pollutants (NB ($1.22 \text{ mg}\cdot\text{L}^{-1}$), FMME ($4.92 \text{ mg}\cdot\text{L}^{-1}$), ASA ($1.80 \text{ mg}\cdot\text{L}^{-1}$), and BA ($1.23 \text{ mg}\cdot\text{L}^{-1}$)) and 2 mM PMS. And the solution temperature was up to nearly 50°C .

Before experiments, lamps were turned on for preheating and stabilizing for 20 min. A total volume of 50 mL of the reaction solutions was added to the reactor. Tests started with the addition of water sample (phosphate buffer, river or wastewater) spiked with the mixture of target pollutants (at an initial concentration of $10 \mu\text{M}$). After adding the required amount of oxidant, the reaction was started. At the predetermined time intervals, 0.9 mL of the reaction solution was sampled and added to the liquid phase vial containing 0.1 mL of $0.474 \text{ g}\cdot\text{L}^{-1}$ sodium thiosulfate (to quench radicals and residual oxidant). Samples were preserved in the refrigerator for subsequent testing.

Phosphate buffer (PB) solution: The phosphate buffer solutions (pH 5.5, 7.0, and 8.5) at a concentration of 10 mM composed of Na_2HPO_4 and $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ in deionized water were prepared.

Natural organic matter (NOM) solution: NOM was obtained from the International Humic Substance Society (batch number 2R101N). the NOM stock solution was obtained by dissolving NOM powder in ultrapure water followed with filtration by $0.7 \mu\text{m}$ pore size glass fiber membrane (GF/F, waterman). Then concentration of the NOM stock solution was calibrated by measuring the total organic carbon (TOC) content. The mineralization of target pollutants was evaluated through measuring the TOC of the reaction solution.

Chlorination experiments were conducted based on USEPA-551 and USEPA-552. 20 mL of water samples with and without solar/PMS pre-oxidation were collected into the brown colorimetric tube that contained NaClO solutions with a concentration 5 times TOC concentration in the solution. After dark reaction for 24h, $200 \mu\text{L}$ of L-ascorbic acid ($88.06 \text{ g}\cdot\text{L}^{-1}$) was added to quench the residual chlorine in the system.

Text S3 Toxicity assays

Toxicity assays on algae: Microalgae were incubated for 96 h with an initial algae density of 4×10^6 cell/mL when those in culture solution served as the control group. Samples were collected periodically (0, 24, 48, 72, and 96 h, respectively) to measure algae density. After 96 h of exposure, 4 mL of algal solution was taken and centrifuged at 6000 rpm for 15 min, then 4 mL of 95% methanol (v:v) was added to the precipitate. Samples were vortexed, heated in a water bath at 60 °C for 5 min and then centrifuged for 15 min at 6000 rpm. The supernatant was aspirated to determine the photosynthetic pigments of algae by UV-Vis spectrophotometry.

Determination of pigments: The absorbance of chlorophyll a, b, and carotenoid at wavelengths 470, 649, 652 and 665 nm was determined by UV-Vis spectrophotometry and content of pigments was calculated according to the Eqs. (2–4).³

$$\text{Chlorophyll a (mg/L)} = 16.29 \times A_{665} - 8.54 \times A_{652} \quad (2)$$

$$\text{Chlorophyll b (mg/L)} = 24.95 \times A_{649} - 7.32 \times A_{665} \quad (3)$$

$$\text{Carotenoid (mg/L)} = 1000 \times A_{470} - 2.05 \times Ca - 114.8 \times Cb \quad (4)$$

The growth inhibition rates were calculated as Eq. (5).

$$I_R = \left(1 - \frac{N}{M}\right) \times 100\% \quad (5)$$

where I_R is growth inhibition rates (%), N represents density of algae at incubation time t h in experimental groups and M represents that in control groups. The growth of algae was considered to be inhibited at $I_R > 0$ with statistical significance.

Text S4 DBPs cytotoxicity analysis

The cytotoxicity of formed DBPs were assessed by dividing measured molar concentrations of each kind of DBPs by concentrations determined in chlorination after solar/PMS pretreatment and their lethal concentration to 50% (LC₅₀) values (Table S7). 1.0 mL of solution was added into meteorological testing bottles to determine THMs and HAAs productions by using a gas chromatograph coupled with an electron capture detector (ECD).

The cytotoxicity of the DBPs was calculated using Eq. (6):

$$\text{Cytotoxicity} = \frac{c(\text{DBP})/M(\text{DBP})}{LC_{50}} \quad (6)$$

where $c(\text{DBP})$ and $M(\text{DBP})$ represent the concentration (mol L⁻¹) and relative molecular mass of the DBP, respectively, and LC₅₀ is the concentration at which the DBP induces a 50% decrease in ovarian cell density in Chinese hamsters over 72 h.

Fig.S1 Degradation of (a) NB, (b) FMME, (c) ASA, and (d) BA in solar irradiation alone, PMS alone, or solar/PMS system at pH 7.0.

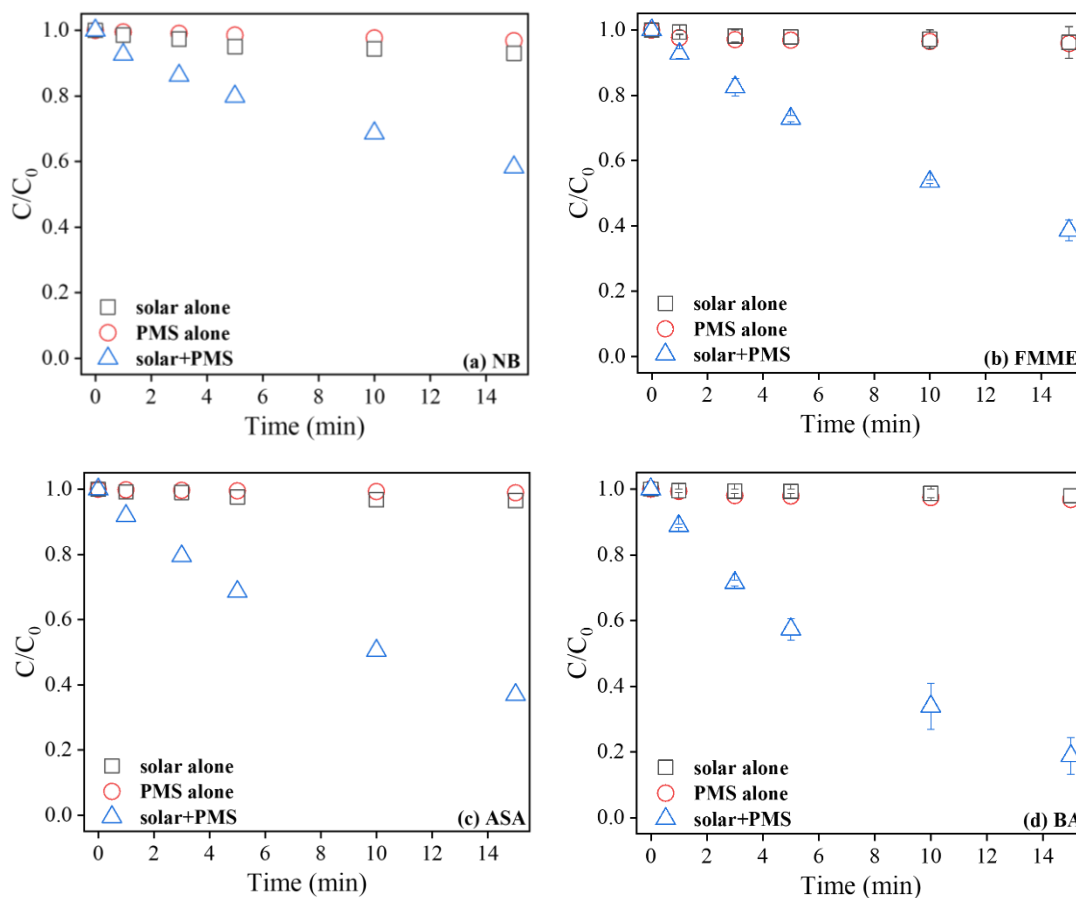


Fig.S1 Degradation of (a) NB, (b) FMME, (c) ASA, and (d) BA in solar alone, PMS alone, or solar/PMS system at pH 7.0. $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, pH 7.0 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$.

Fig.S2 Degradation of NB, FMME, ASA, and BA in (a) sunlight alone and (b) sunlight/PMS system at pH 7.0.

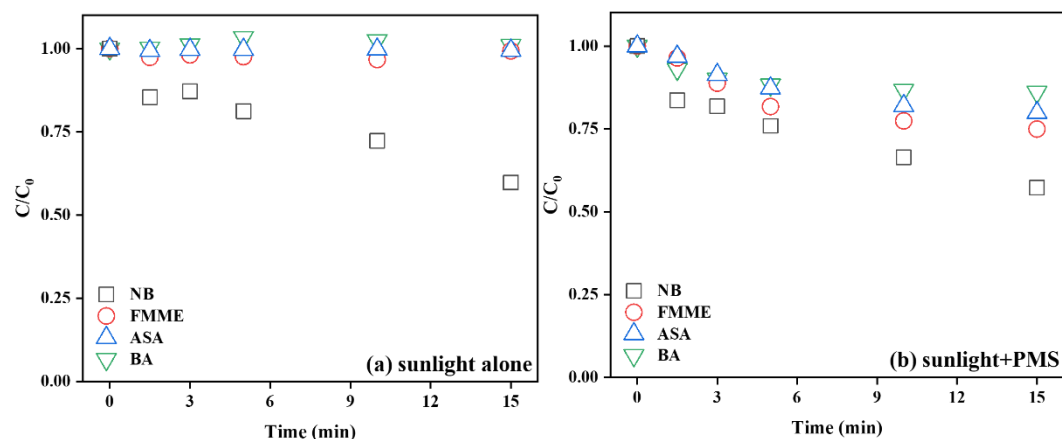


Fig.S2 Degradation of NB, FMME, ASA, and BA in (a) sunlight alone and (b) sunlight/PMS system at pH 7.0. $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, pH 7.0 phosphate buffer, $T = 30 \text{ }^\circ\text{C}$ (measured at the end of treatment for water samples; ambient temperature of the outdoor experiments was $37\pm 3 \text{ }^\circ\text{C}$).

Fig.S3 Degradation of four pollutants in PMS alone system at different pH values.

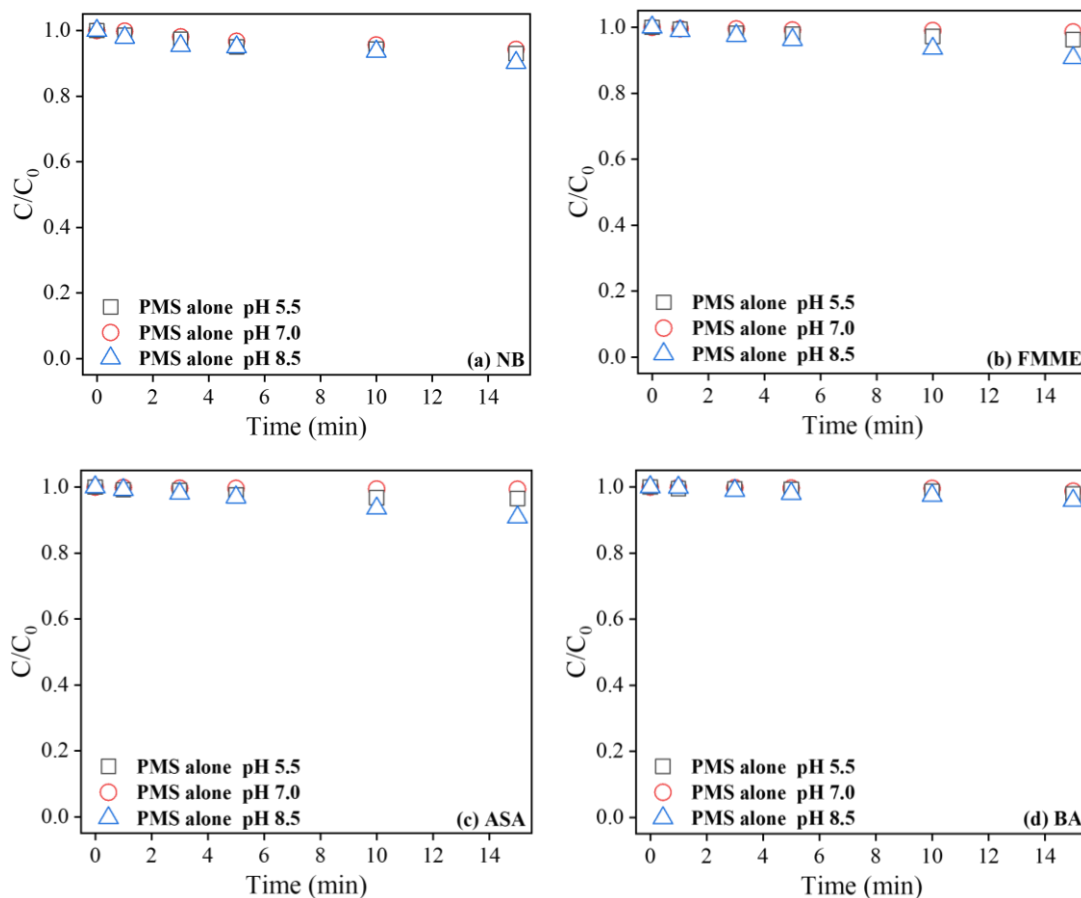


Fig.S3 Degradation of (a) NB, (b) FMME, (c) ASA, and (d) BA in PMS alone system at different pH values. $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, pH 5.5, 7.0 and 8.5 phosphate buffer, $T = 25 \text{ }^\circ\text{C}$.

Fig.S4 Effect of pH on the degradation rate (k_{obs}) of pollutants.

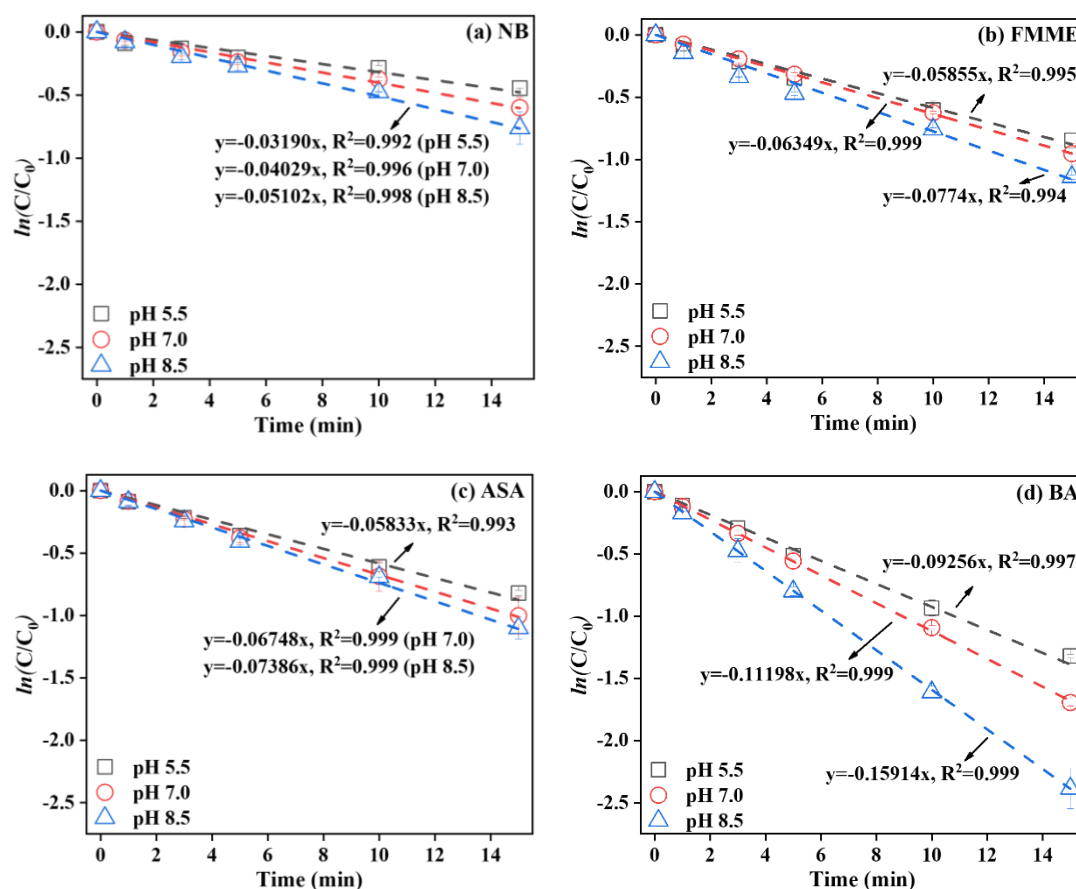


Fig.S4 Effect of pH on the degradation rate (k_{obs}) of pollutants: (a) NB, (b) FMME, (c) ASA, and (d) BA. $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, pH 5.5, 7.0 and 8.5 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$.

Fig.S5 Effect of pH on degradation of ASA, FMME, NB, and BA in solar/PMS system.

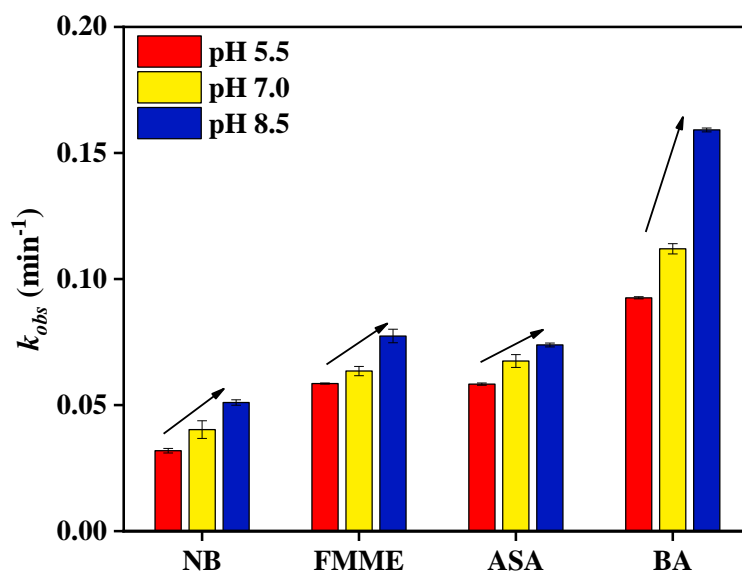


Fig.S5 Effect of pH on degradation of ASA, FMME, NB, and BA in solar/PMS system. $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, reaction time = 15 min, pH 5.5, 7.0, and 8.5 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$.

Fig.S6 Degradation kinetics and determination of observed rate constant of (a) NB and (b) BA in solar/PMS system.

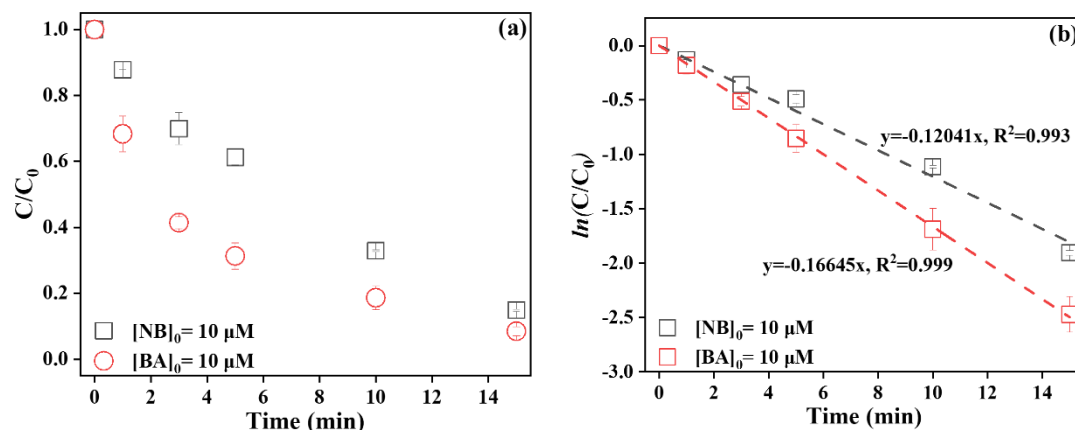


Fig.S6 Degradation and determination of observed rate constant of (a) NB and (b) BA in solar/PMS system. $[\text{NB}]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[\text{BA}]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[\text{PMS}]_0 = 1.0 \text{ mM}$, pH 7.0 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$. NB and BA were regarded as probe contaminants to demonstrate the production of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ here.

Fig.S7 The contributions of ROS for the degradation of I) NB, II) FMME, III) ASA, IV) BA in solar/PMS system.

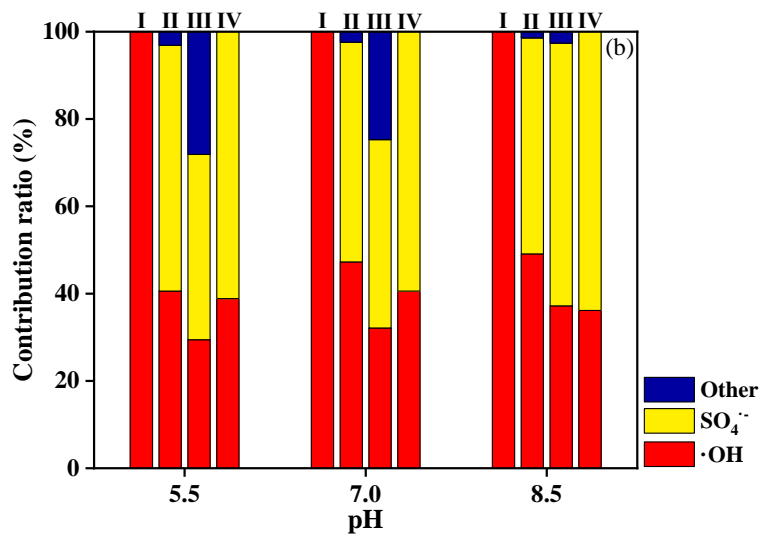


Fig.S7 The contributions of ROS for the degradation of I) NB, II) FMME, III) ASA, IV) BA in solar/PMS system. Conditions: [NB]₀ = 1.22 mg·L⁻¹, [FMME]₀ = 4.92 mg·L⁻¹, [ASA]₀ = 1.80 mg·L⁻¹, [BA]₀ = 1.23 mg·L⁻¹, [PMS]₀ = 2.0 mM, pH 5.5, 7.0, and 8.5 phosphate buffer, simulated sunlight intensity = 6.06 W·cm⁻², T = 25 °C.

Fig.S8 Effect of temperature on the degradation of pollutants.

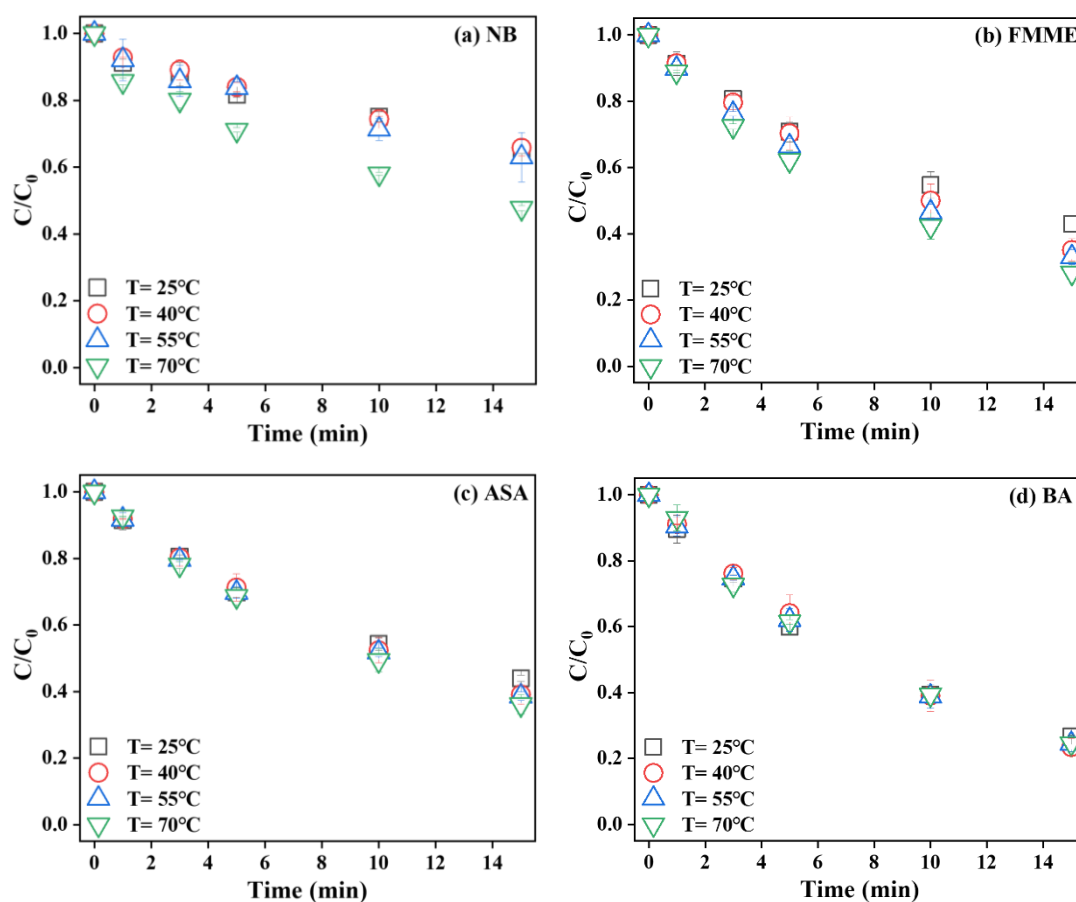


Fig.S8 Effect of temperature on degradation of (a) NB, (b) FMME, (c) ASA, and (d) BA in solar/PMS system. $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, pH 7.0 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25, 40, 55$ and $70 \text{ }^\circ\text{C}$.

Fig.S9 Removal of pollutants in (a) PMS alone and (b) solar alone system in presence of NOM.

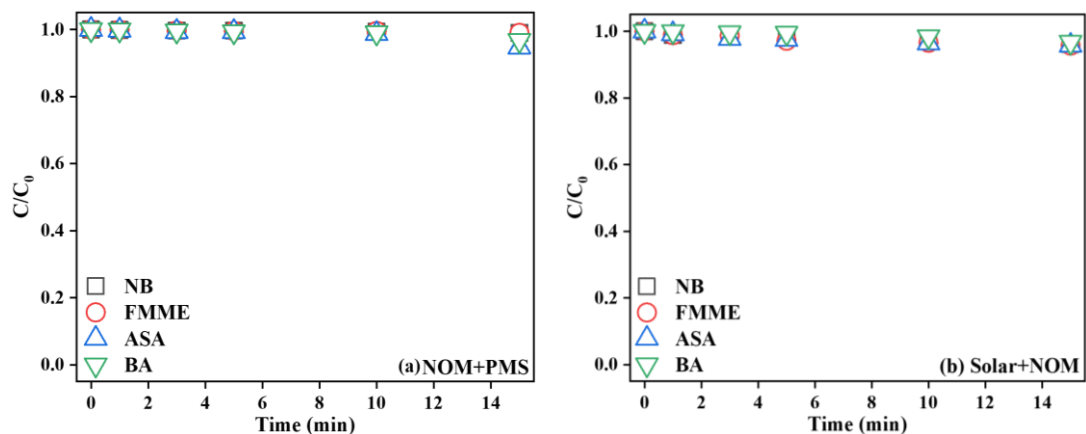


Fig.S9 Removal of contaminants in (a) PMS alone and (b) solar alone system in presence of NOM. $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[NOM]_0 = 6.0 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, pH 7.0 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$.

Fig.S10 Absorbance value of solutions containing pollutants with or without NOM.

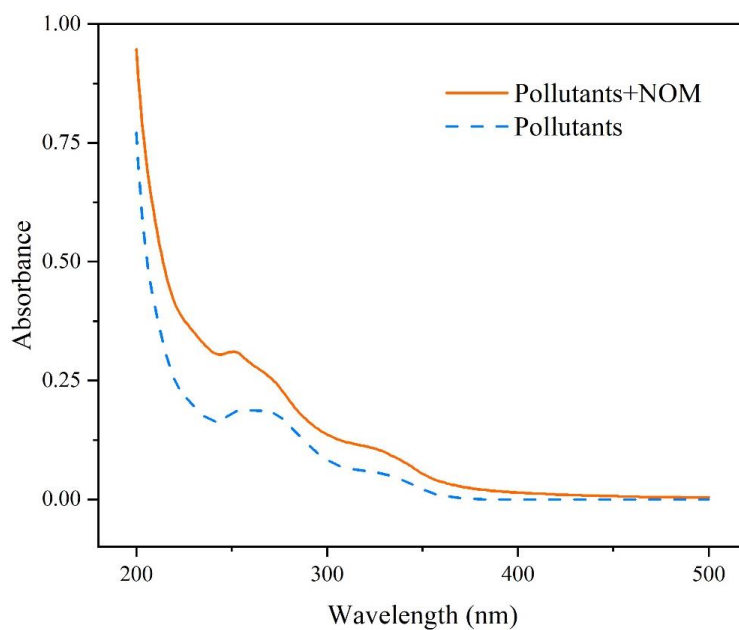


Fig.S10 Absorbance value of solutions containing pollutants with or without NOM. $[\text{NB}]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[\text{FMME}]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[\text{ASA}]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[\text{BA}]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[\text{NOM}]_0 = 6.0 \text{ mg}\cdot\text{L}^{-1}$, pH 7.0 phosphate buffer, $T = 25 \text{ }^\circ\text{C}$.

Fig.S11 Effect of NOM concentration on the degradation of (a) NB, (b) FMME, (c) ASA, and (d) BA in solar/PMS system.

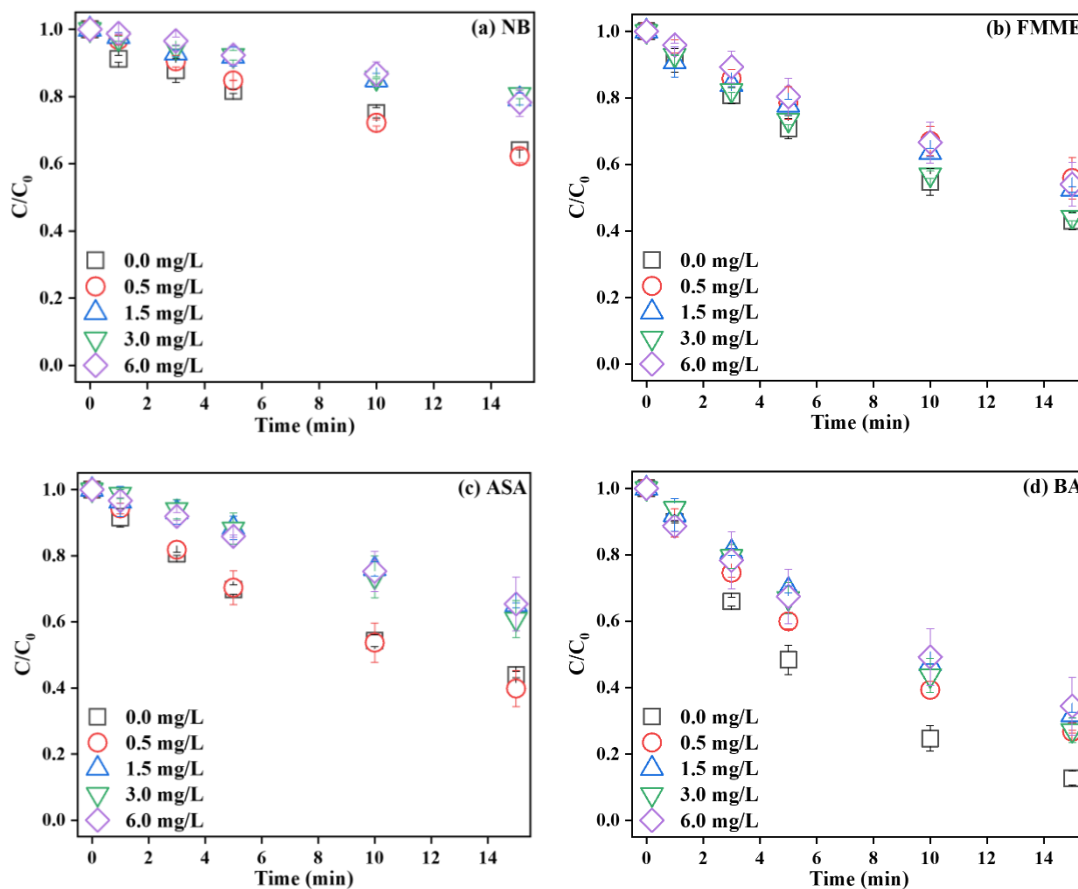


Fig.S11 Effect of NOM concentration on the degradation of (a) NB, (b) FMME, (c) ASA, and (d) BA in solar/PMS system. $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, $[NOM]_0 = 0.0\sim 6.0 \text{ mg}\cdot\text{L}^{-1}$, pH 7.0 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$.

Fig.S12 The k_{obs} of NB, FMME, ASA, and BA degradation as a function of NOM concentration in solar/PMS system.

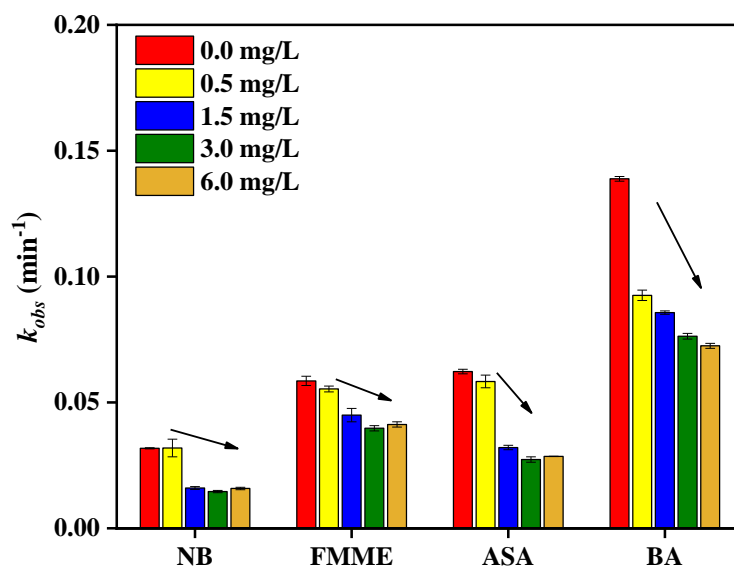


Fig.S12 The k_{obs} of NB, FMME, ASA, and BA degradation as a function of NOM concentration in solar/PMS system. $[NOM]_0 = 0.0\sim 6.0 \text{ mg}\cdot\text{L}^{-1}$, $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, pH 7.0 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$.

Fig.S13 Effect of natural water samples on the degradation of (a) NB, (b) FMME, (c) ASA and (d) BA in solar/PMS system.

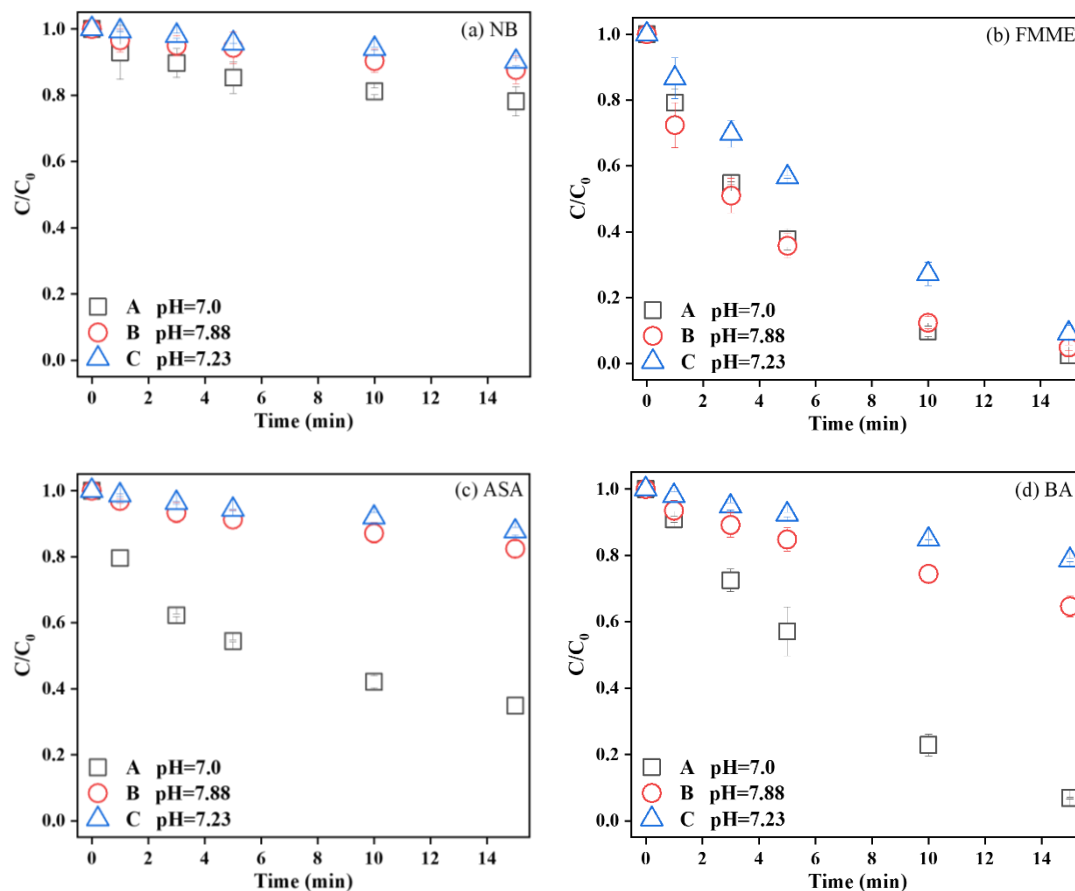


Fig.S13 Effect of natural water samples on the degradation of (a) NB, (b) FMME, (c) ASA and (d) BA in solar/PMS system (A, B, and C represent for PB system, Yangtze River water system, and WWTP effluent system, respectively). $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$.

Fig.S14 TOC abatement of actual water samples in solar/PMS system.

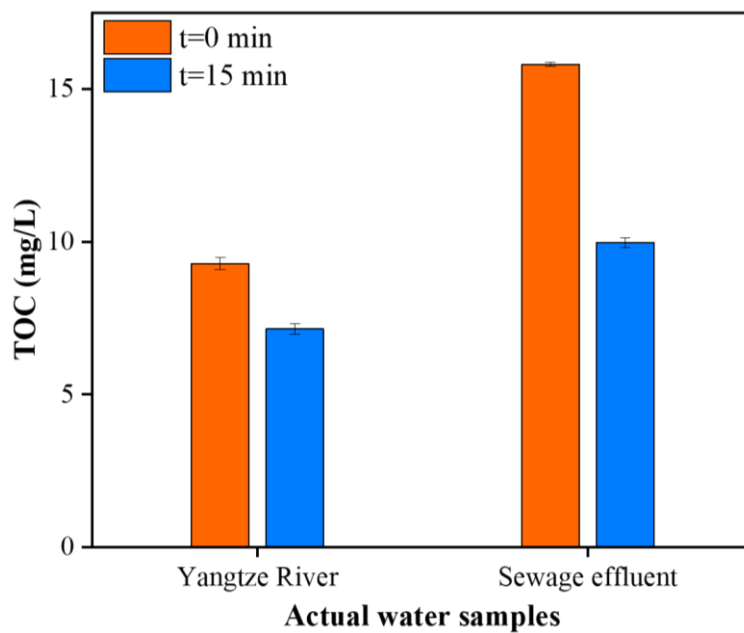


Fig. S14 TOC abatement of actual water samples in solar/PMS system. $[\text{NB}]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[\text{FMME}]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[\text{ASA}]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[\text{BA}]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[\text{PMS}]_0 = 2.0 \text{ mM}$, Yangtze River pH = 7.9, WWTP pH = 7.2, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$.

Fig.S15 Effect on yields of (a) THMs and (b) HAAs during post-chlorination with (shaded section) and without (non-shaded section) solar/PMS pretreatment.

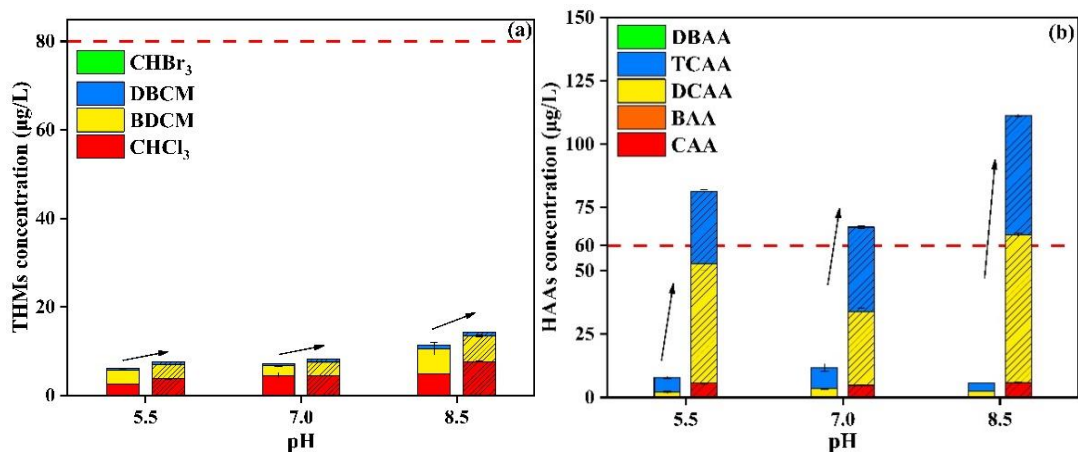


Fig.S15 Effect on yields of (a) THMs and (b) HAAs during post-chlorination with (shaded section) and without (non-shaded section) solar/PMS pretreatment. [NB]₀ = 1.22 mg·L⁻¹, [FMME]₀ = 4.92 mg·L⁻¹, [ASA]₀ = 1.80 mg·L⁻¹, [BA]₀ = 1.23 mg·L⁻¹, [PMS]₀ = 2.0 mM, intensity of simulated sunlight = 6.06 W·cm⁻², T = 25 °C, pH 5.5, 7.0, and 8.5 phosphate buffer, chlorination reaction time = 24 h.

Fig.S16 Variation of total organic carbon (TOC) concentration in solar/PMS system at different pH values.

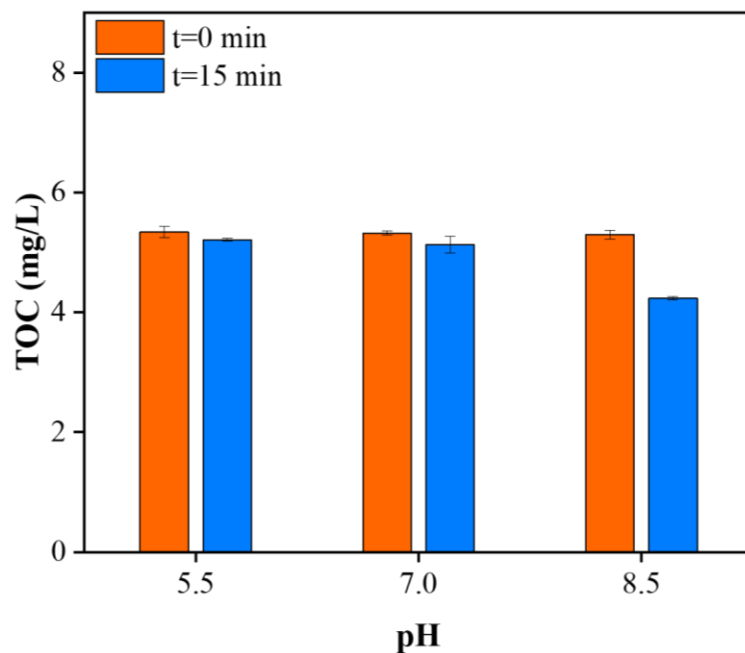


Fig.S16 Variation of total organic carbon (TOC) concentration in solar/PMS system at different pH values. $[\text{NB}]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[\text{FMME}]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[\text{ASA}]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[\text{BA}]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, pH = 5.5, 7.0, and 8.5 phosphate buffer, $[\text{PMS}]_0 = 2.0 \text{ mM}$, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$.

Fig. S17 The proportions of six DBPs on calculated cytotoxicity with (shaded) and without (unshaded) solar/PMS pre-oxidation in 15 min.

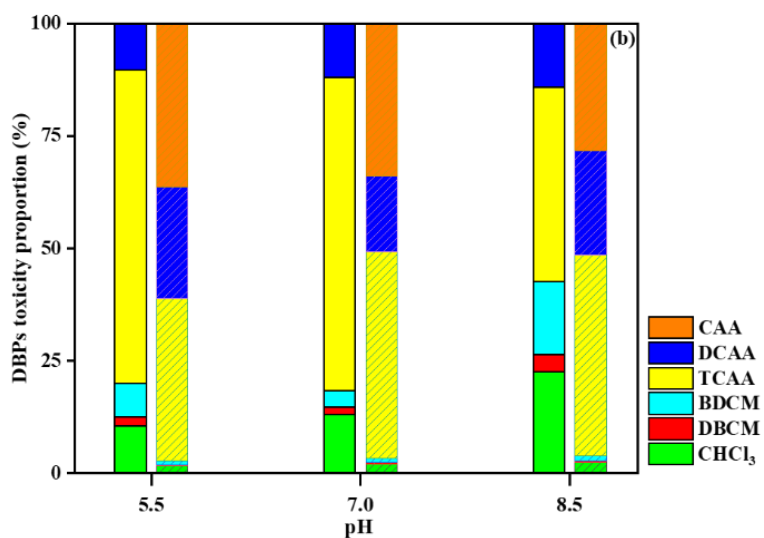


Fig.S17 The proportions of six DBPs on calculated cytotoxicity with (shaded) and without (unshaded) solar/PMS pre-oxidation in 15 min. $[\text{NB}]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[\text{FMME}]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[\text{ASA}]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[\text{BA}]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[\text{PMS}]_0 = 2.0 \text{ mM}$, $T = 25 \text{ }^\circ\text{C}$, pH 5.5, 7.0, and 8.5 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$.

Fig.S18 Comparison of the effect of pre-oxidation with (shaded) and without (unshaded) solar/PMS system on the generation of (a) THMs and (b) HAAs during chlorination at pH 7.0 with the addition of NOM solution.

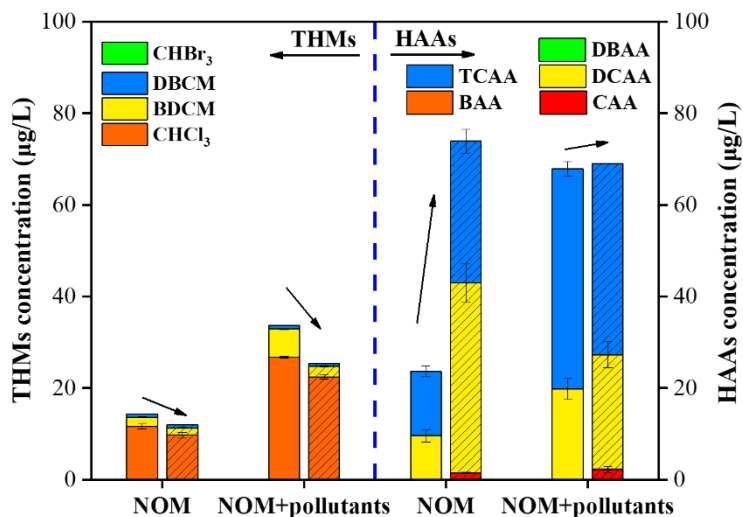


Fig.S18 Comparison of the effect of pre-oxidation with (shaded) and without (unshaded) solar/PMS system on the generation of (a) THMs and (b) HAAs during chlorination at pH 7.0 with the addition of NOM solution. $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, $[PMS]_0 = 2.0 \text{ mM}$, $[NOM]_0 = 3.0 \text{ mg}\cdot\text{L}^{-1}$, pH 7.0 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, $T = 25 \text{ }^\circ\text{C}$, $t = 15 \text{ min}$, chlorination reaction time = 24h.

Fig.S19 Effect of solar/PMS system (shaded) on the generation of (a) THMs and (b) HAAs during the chlorination of actual water bodies.

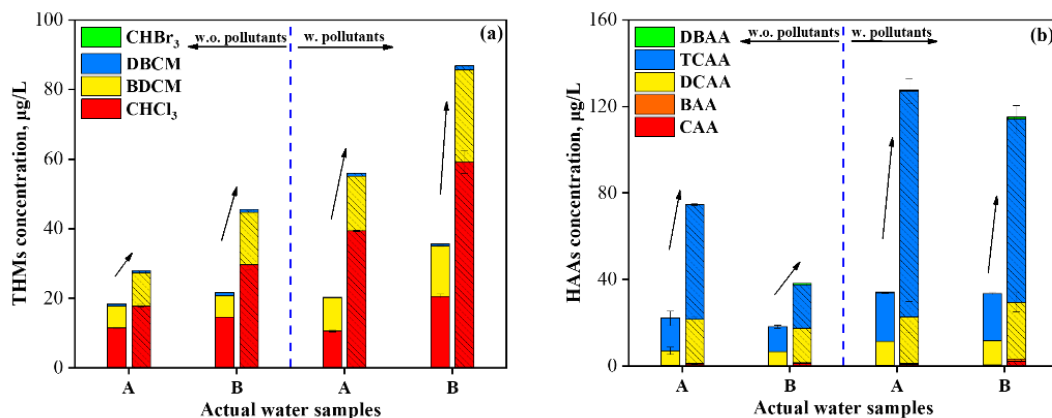


Fig.S19 Effect of solar/PMS system (shaded) on the generation of (a) THMs and (b) HAAs during the chlorination of actual water bodies A represents water samples from Yangtze River water (initial pH 7.9), and B represents WWTP (initial pH 7.2). $[\text{PMS}]_0 = 2.0 \text{ mM}$, $T = 25 \text{ }^\circ\text{C}$, $[\text{NB}]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[\text{FMME}]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[\text{ASA}]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[\text{BA}]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$, pH not buffered, $t = 15 \text{ min}$, chlorination reaction time = 24 h.

Fig.S20 PMS consumption in solar/PMS system at different pH values.

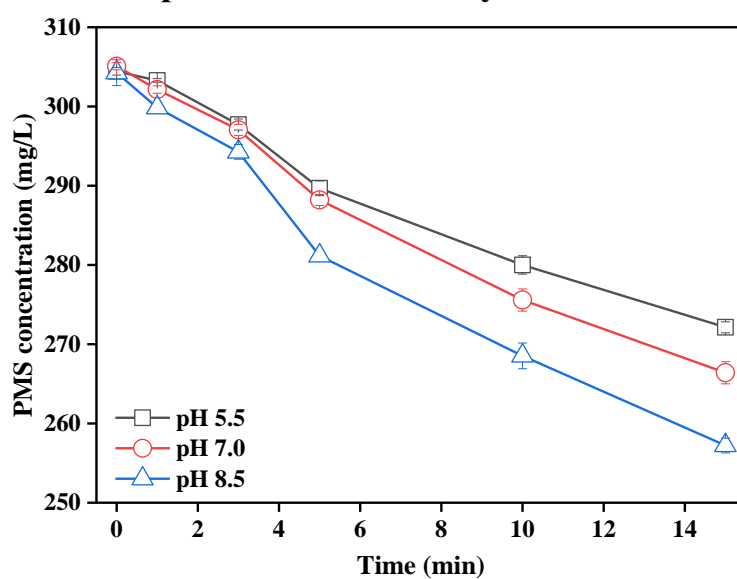


Fig.S20 PMS consumption in solar/PMS system at different pH values. $[PMS]_0 = 2.0 \text{ mM}$, $T = 25 \text{ }^\circ\text{C}$, $[NB]_0 = 1.22 \text{ mg}\cdot\text{L}^{-1}$, $[FMME]_0 = 4.92 \text{ mg}\cdot\text{L}^{-1}$, $[ASA]_0 = 1.80 \text{ mg}\cdot\text{L}^{-1}$, $[BA]_0 = 1.23 \text{ mg}\cdot\text{L}^{-1}$, pH 5.5, 7.0, and 8.5 phosphate buffer, intensity of simulated sunlight = $6.06 \text{ W}\cdot\text{cm}^{-2}$.

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