

Elimination of humic acid in water: Comparison of UV/PDS and UV/PMS

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Paragraph S1: calculation of EE/O

The definition of EE/O is “the consumption energy (kWh) needed to remove the pollutant by an order of magnitude concentration in 1 m³ of wastewater”. At low concentration (<100 mg L⁻¹) for contaminate in water, the EE/O can be computed by the following formula:

$$EE/O = \frac{P \times t}{60 \times V \times \log(C_0/C)}$$

Where P is the illumination power (W), t is the treatment duration (min), V is the treated water bulk (L), C_0 and C are the HA original and end concentrations (mg L⁻¹), respectively.

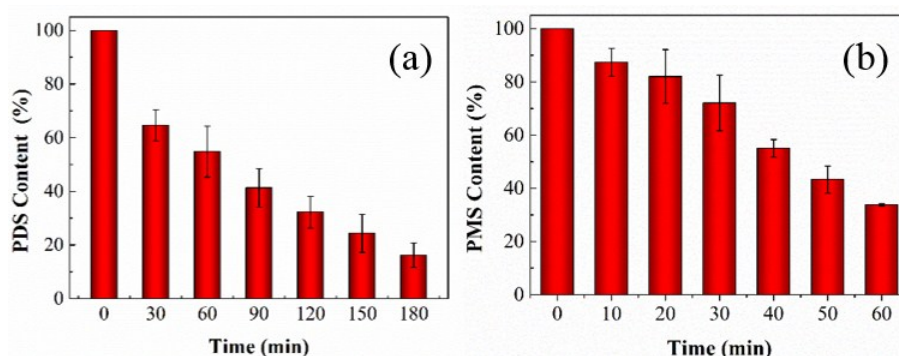


Figure S1 PDS and PMS determinations in UV/PDS (a) and UV/PMS (b). Conditions: $[HA]_0 = 15$ mg L⁻¹, $[PDS]_0 = [PMS]_0 = 3$ mmol L⁻¹, $[pH]_0 = 6$ and 3 for UV/PDS and UV/PMS, respectively.

Table S1 Effect of oxidant dosage on rate constants of UV/PDS and UV/PMS. Conditions: $[HA]_0 = 15$ mg L⁻¹, $[pH]_0 = 6$ and 3 for UV/PDS and UV/PMS, respectively.

System	UV/PDS			UV/PMS		
	Value	Rate constants (min ⁻¹)	R ²	Value	Rate constants (min ⁻¹)	R ²
oxidant dose (mmol L ⁻¹)	1	0.0162	0.94	0.5	0.0272	0.95
	3	0.0355	0.95	1	0.0461	0.96
	6	0.0366	0.91	2	0.0576	0.98
	10	0.0258	0.90	4	0.0976	0.96

Table S2 Effect of initial HA concentration on rate constants of UV/PDS and UV/PMS. Conditions: $[PDS]_0 = 3 \text{ mmol L}^{-1}$, $[PMS]_0 = 1 \text{ mmol L}^{-1}$, $[pH]_0 = 6$ and 3 for UV/PDS and UV/PMS, respectively.

System	UV/PDS			UV/PMS		
	Value	Rate constants (min^{-1})	R^2	Value	Rate constants (min^{-1})	R^2
Initial HA concentration (mg L^{-1})	5	0.0378	0.93	5	0.0870	0.94
	15	0.0366	0.99	15	0.0461	0.96
	35	0.0116	0.93	45	0.00628	0.90

Table S3 Effect of initial pH on rate constants of UV/PDS and UV/PMS. Conditions: $[HA]_0 = 15 \text{ mg L}^{-1}$, $[PDS]_0 = 3 \text{ mmol L}^{-1}$, $[PMS]_0 = 1 \text{ mmol L}^{-1}$.

System	UV/PDS			UV/PMS		
	Value	Rate constants (min^{-1})	R^2	Value	Rate constants (min^{-1})	R^2
Initial pH	3	0.0408	0.99	3	0.0461	0.98
	6	0.0366	0.99	5	0.0083	0.98
	9	0.0241	0.98	7	0.0062	0.94
	11	0.0217	0.99	9	0.0157	0.93
				11	0.0234	0.91

Paragraph S2 Effect of inorganic anions

Various inorganic anions are common components of the water matrix, which would impact organics decontamination in water body. The effect of anions on the HA elimination was investigated in the UV/PDS and UV/PMS, respectively, the results are presented in Figure S2 and S3 of SM. Diverse concentrations of CO_3^{2-} , HCO_3^- , Cl^- , NO_3^- , SO_4^{2-} , and H_2PO_4^- were introduced to the UV/persulphate systems, respectively. Overall, except for H_2PO_4^- , the impacts of other five inorganic ions on the HA removal were consistent under the two coupling systems.

In Figure S2a and S3a, the addition of CO_3^{2-} inhibited the HA removal with its amount augmented from 5 to 20 mmol L^{-1} the UV/PDS and UV/PMS, respectively. This could be due to the formation of $\text{CO}_3^{\cdot-}$ through the behavior between CO_3^{2-} and $\text{SO}_4^{\cdot-}$ (Eq. 1), whereas the oxidant

capacity of $\text{CO}_3^{\cdot-}$ (1.59 V) is lower than that of $\text{SO}_4^{\cdot-}$ [1]. Besides, CO_3^{2-} is known as an effective scavenger for $\cdot\text{OH}$, and CO_3^{2-} could transform to HCO_3^- (Eq. 2)[1]. Especially, the generation of $\text{CO}_3^{\cdot-}$ in presence of HCO_3^- is more than that of $\text{SO}_4^{\cdot-}$ by up to two orders of magnitude[2]. On the other hand, Figure S2b and S3b show that the HCO_3^- addition presented a masking effect for the HA decomposition as well. HCO_3^- would buffer the solution pH to alkalinity, and then influence the HA removals under the UV/PDS and UV/PMS systems. First, HCO_3^- would react with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ to generate $\text{CO}_3^{\cdot-}$ (Eqs. 3-4)[2]. Second, under the alkaline condition, $\text{SO}_4^{\cdot-}$ is easy to transform into $\cdot\text{OH}$ in the UV/PDS; besides, OH^- ions would accelerate the decomposition of PMS to generate more $\cdot\text{OH}$ in the UV/PMS. Due to the difference between $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, which also led to the decrease of HA degradation in the two coupling systems.

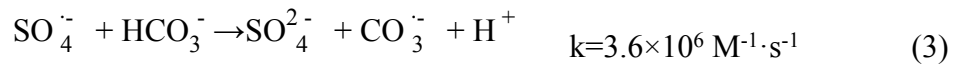
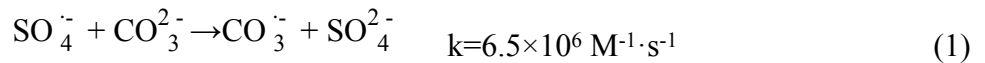


Figure S2c and S3c display the influence of Cl^- introduction for the HA degradation in the two UV/persulphate systems. The HA removals were suppressed marginally by Cl^- in both the two systems, respectively. Cl^- would consume $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ to generate some chloric matters, such as $\text{Cl}\cdot$, $\text{ClOH}^{\cdot-}$, and $\text{Cl}_2^{\cdot-}$ (Eqs. 5-7)[3]. They also have relatively strong redox potentials ($\text{Cl}\cdot$ 2.4 V and $\text{Cl}_2^{\cdot-}$ 1.36 V)[4], thereby the HA decontamination was slightly declined even the Cl^- concentration augmented to 30 mmol L^{-1} in the two cooperative systems.

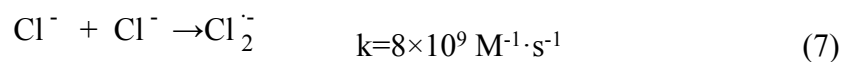
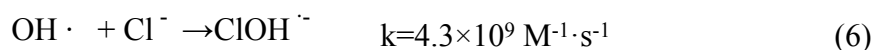
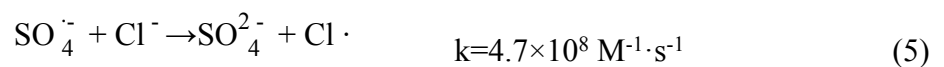


Figure S2d and S3d present the influence of NO_3^- amount on the HA removal in the two synergies. It seems that the HA elimination declined with the raising of NO_3^- quantity, and the more obvious effect was observed in the UV/PMS. NO_3^- can absorb UV light to form $\text{NO}_2\cdot$ (Eq. 8)[5]. Hence, the production of $\text{NO}_3\cdot$ with lower oxidation performance could inhibit the HA decomposition. For the UV/PMS, the more acidic solution is propitious to $\text{NO}_3\cdot$ formation, which would further impair the oxidation ability of the UV/PMS system.

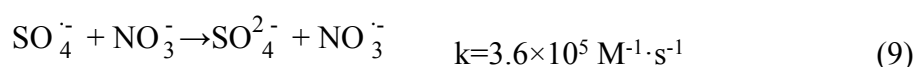


Figure S2e and S3e indicate that the existence of SO_4^{2-} had no significant effect on the HA removal in the two cooperative methods. Because SO_4^{2-} is the theoretical byproduct of persulphate activation, and it would not consume $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, analogous results were reported by other researchers (Eq. 9)[6].

Figure S2f shows that adding H_2PO_4^- showed no influence for the HA removal in the UV/PDS, but a distinct effect was emerged in the UV/PMS system (Figure S3f). H_2PO_4^- could react with $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ by the chain reactions and generate $\text{H}_2\text{PO}_4^{\cdot-}$ (Eqs. 10-11)[6], and its oxidation capability is weaker than $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, hence the HA removal decreased with the increased H_2PO_4^- addition in the UV/PMS. However, these side reaction rates would decline in the weak acidic circumstance of UV/PDS, so there was almost no effect on the HA decomposition after the introduction of H_2PO_4^- .



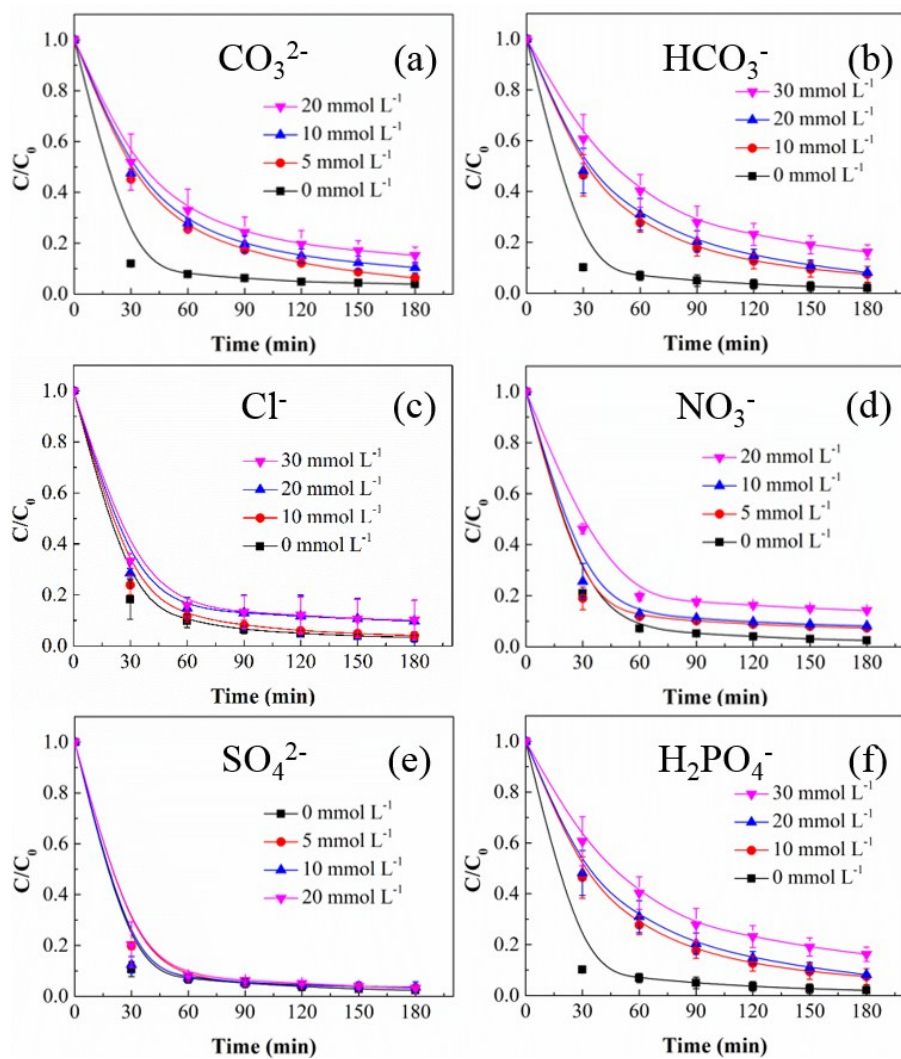


Figure S2 Effect of anions on HA removal in UV/PDS system: (a) CO_3^{2-} , (b) HCO_3^- , (c) Cl^- , (d) NO_3^- , (e) SO_4^{2-} , (f) H_2PO_4^- . Conditions: $[\text{HA}]_0 = 15 \text{ mg L}^{-1}$, $[\text{PDS}]_0 = 3 \text{ mmol L}^{-1}$, $[\text{pH}]_0 = 6$.

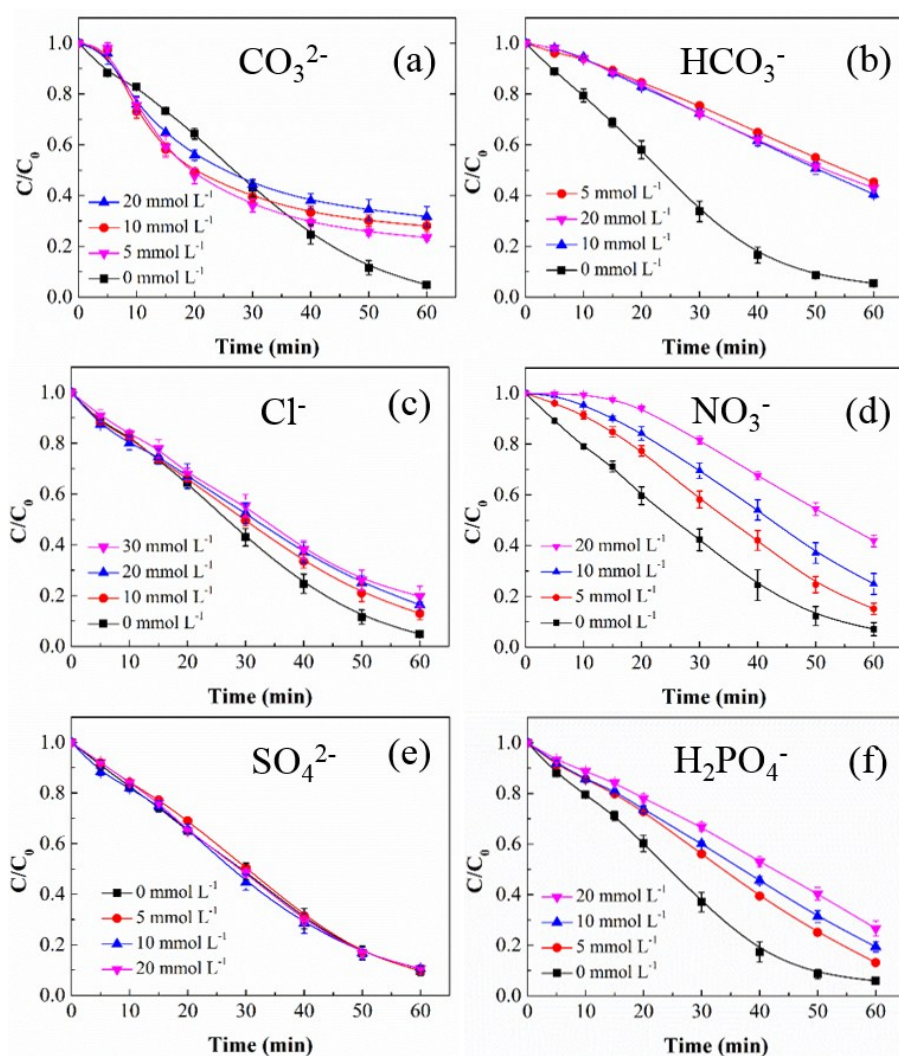


Figure S3 Effect of anions on HA removal in UV/PMS system: (a) CO_3^{2-} , (b) HCO_3^- , (c) Cl^- , (d) NO_3^- , (e) SO_4^{2-} , (f) H_2PO_4^- . Conditions: $[\text{HA}]_0 = 15 \text{ mg L}^{-1}$, $[\text{PMS}]_0 = 1 \text{ mmol L}^{-1}$, $[\text{pH}]_0 = 3$.

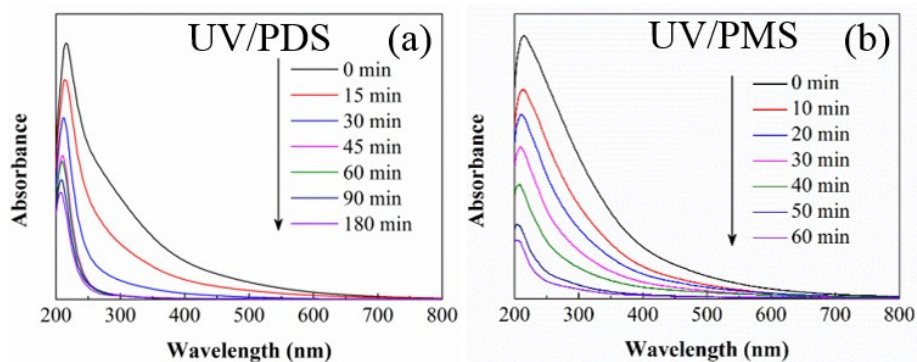


Figure S4 Evolution of UV-Vis spectra and specific absorbance parameters of HA sample in UV/PDS (a) and UV/PMS (b). Conditions: $[HA]_0 = 15 \text{ mg L}^{-1}$, $[PDS]_0 = [PMS]_0 = 3 \text{ mmol L}^{-1}$, $[pH]_0 = 6$ and 3 for UV/PDS and UV/PMS, respectively.

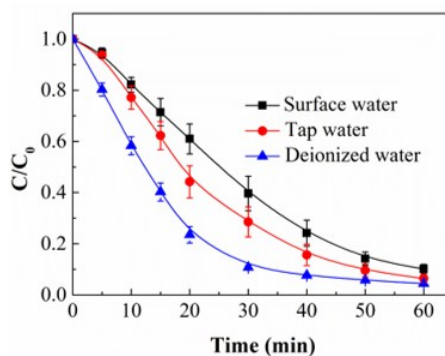


Figure S5 HA removal of different water sources by UV/PMS. Conditions: $[HA]_0 = 15 \text{ mg L}^{-1}$, $[PMS]_0 = 4 \text{ mmol L}^{-1}$, $[pH]_0 = 3.0, 7.4,$ and 7.8 for deionized water, surface water, and tap water, respectively.

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