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Supplementary Information

Potential of the colloidal removal from petrochemical secondary effluent by coagulation-flocculation coupled with persulfate process

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Factors of PS oxidation treatment

The main reasons for the decrease of c(Fe^{2+}) excess system efficiency are as follows: (1) Excess Fe^{2+} can catalyze the generation of more SO_4^{-}• (Eq.1), and the sulfate radicals will self-scavenge (terminate the chain reaction, Eq.2);[1] (2) The rapid formation of •OH and SO_4^{-}• tends to react with Fe^{2+} (Eq.3 and Eq.4), which reduces the effective utilization of SO_4^{-}• and •OH;[2] (3) It has been reported that excess Fe^{2+} was oxidized to Fe^{3+} and then transformed to various Ferric oxyhydroxides through hydrolysis (Eq.5-7).[3] Rao et al. found that Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^{+}$, and $Fe_2(OH)_2^{4+}$ activated PS with low efficiency.[4]

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{-}\bullet + SO_4^{2-} \qquad (1)$$

$$SO_4^{-}\bullet + SO_4^{-}\bullet \rightarrow S_2O_8^{2-} \qquad k = 8.9 \times 10^8\ M^{-1}s^{-1} \qquad (2)$$

$$Fe^{2+} + SO_4^{-}\bullet \rightarrow Fe^{3+} + SO_4^{2-} \qquad k = 4.6 \times 10^9\ M^{-1}s^{-1} \qquad (3)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^{-} \qquad (4)$$

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^{+} \qquad k = 2.3 \times 10^7\ M^{-1}s^{-1} \qquad (5)$$

$$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2^{+} + 2H^{+} \qquad k = 4.7 \times 10^3\ M^{-1}s^{-1} \qquad (6)$$

$$2Fe^{3+} + 2H_2O \rightarrow Fe_2(OH)_2^{4+} + 2H^{+} \qquad k = 1.1 \times 10^7\ M^{-1}s^{-1} \qquad (7)$$

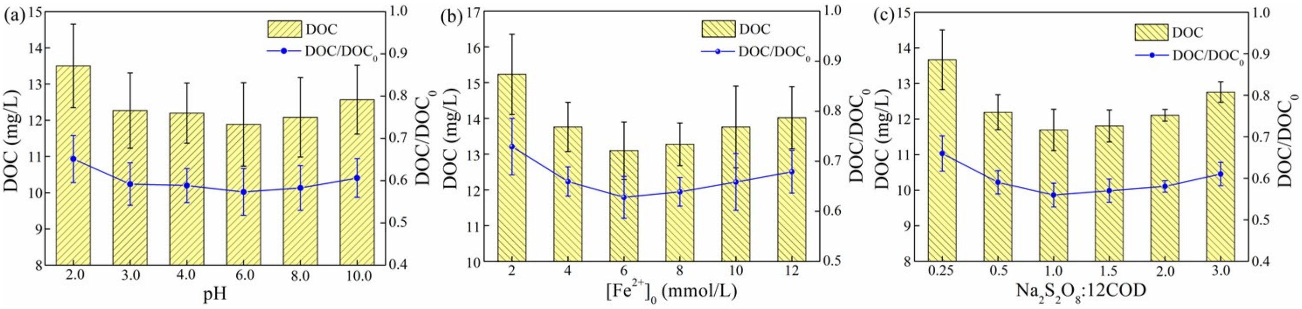


Fig. S1 Factors of DOC removal in PS process. (a) different initial pH value. Conditions: $[Fe^{2+}]0 = 6.0$ mmol/L, $[Na_2S_2O_8]_0 = 6.0$ mmol/L; (b) different $[Fe^{2+}]_0$ at $[Na_2S_2O_8]_0 = 6.0$ mmol/L; (c) different ratio of initial $Na_2S_2O_8$:12COD at $[Fe^{2+}]_0 = 6.0$ mmol/L.

Excess $Na_2S_2O_8$ reduces the degradation efficiency for the following three reasons: (1) Excess $S_2O_8^{2-}$ leads to elimination of SO_4^{-}• (Eq.1 and Eq.2);[5] (2) Excess $S_2O_8^{2-}$ will produce more SO_4^{-}•, and its hydrolysis will be further converted to •OH (Eq.2 and Eq.8);[6] (3) Excess $S_2O_8^{2-}$ inhibits SO_4^{-}• and •OH (Eq.9 and Eq.10).[7] Compared with SO_4^{-}• and •OH, the $S_2O_8^{-}$• has a lower REDOX potential.[8] Therefore, the optimal c($Na_2S_2O_8$):12COD ratio was 1.0, that is, the dosage of PS was 1020 mg/L.

$$SO_4{}^{-}\bullet + H_2O \rightarrow \bullet OH + SO_4{}^{2-} + H^{+} \qquad (8)$$

$$S_2O_8{}^{2-} + SO_4{}^{-}\bullet \rightarrow S_2O_8{}^{-}\bullet + SO_4{}^{2-} \qquad (9)$$

$$S_2O_8{}^{2-} + \bullet OH \rightarrow S_2O_8{}^{-}\bullet + OH^{-} \qquad (10)$$

Effect of coagulation pretreatment on initial pH

As shown in Fig. S2, the optimal pH value of coagulation pretreatment was 8.0, and the removal reached 52.0%, which was 9.0% higher than that of single PS oxidation process (when the optimal pH value was 6.0). With the change of pH, the DOC removal did not change much, indicating that the pH has almost no effect on the DOC removal of the wastewater in the CF-PS process.

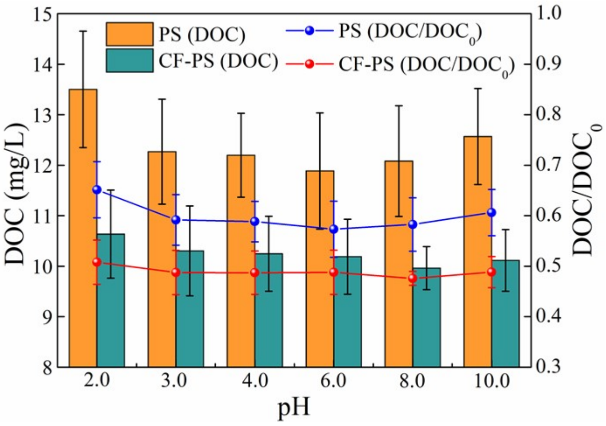


Fig. S2 The effect of initial pH on DOC removal in the PS and CF-PS processes. Conditions: $[PAC]_0 = 20.0$ mg/L; $[Fe^{2+}]_0 = 6.0$ mmol/L; $[Na_2S_2O_8]_0=6.0$ mmol/L

Variation of colloidal content with different MWs

The formula of X removal is:

$$X\% = (A_t - A_0)/A_t * 100\% \quad (11)$$

where the A_0 (mg/L) and A_t (mg/L) represents the value of DOC/UV_{254} at the initial and time t (min), respectively.

Table.S1 DOC degradation contribution of each MW fraction with CF, PS, and CF-PS processes

MWs		DOC degradation (%)		
		CF	PS	CF-PS
High-MWs	>100 K	-64.2	-31.3	46.3
	50~100 K	28.6	-47.6	33.3
medium-MWs	30~50 K	85.1	59.8	97.6
	10~30 K	96.2	57.3	79.4
	3~10 K	84.3	85.4	19.1
low-MWs	<3 K	-4.3	40.3	40.6

Table.S2 UV_{254} degradation contribution of each MW fraction with CF, PS, and CF-PS processes

MWs		UV_{254} degradation (%)		
		CF	PS	CF-PS
High-MWs	> 100 K	-700.0	0.0	0.0
	50~100 K	0.0	100.0	0.0
Medium-MWs	30~50 K	77.0	88.9	100.0
	10~30 K	100.0	60.0	-100.0
	3~10 K	75.0	75.0	0.0
Low-MWs	< 3 K	-8.7	33.0	36.2

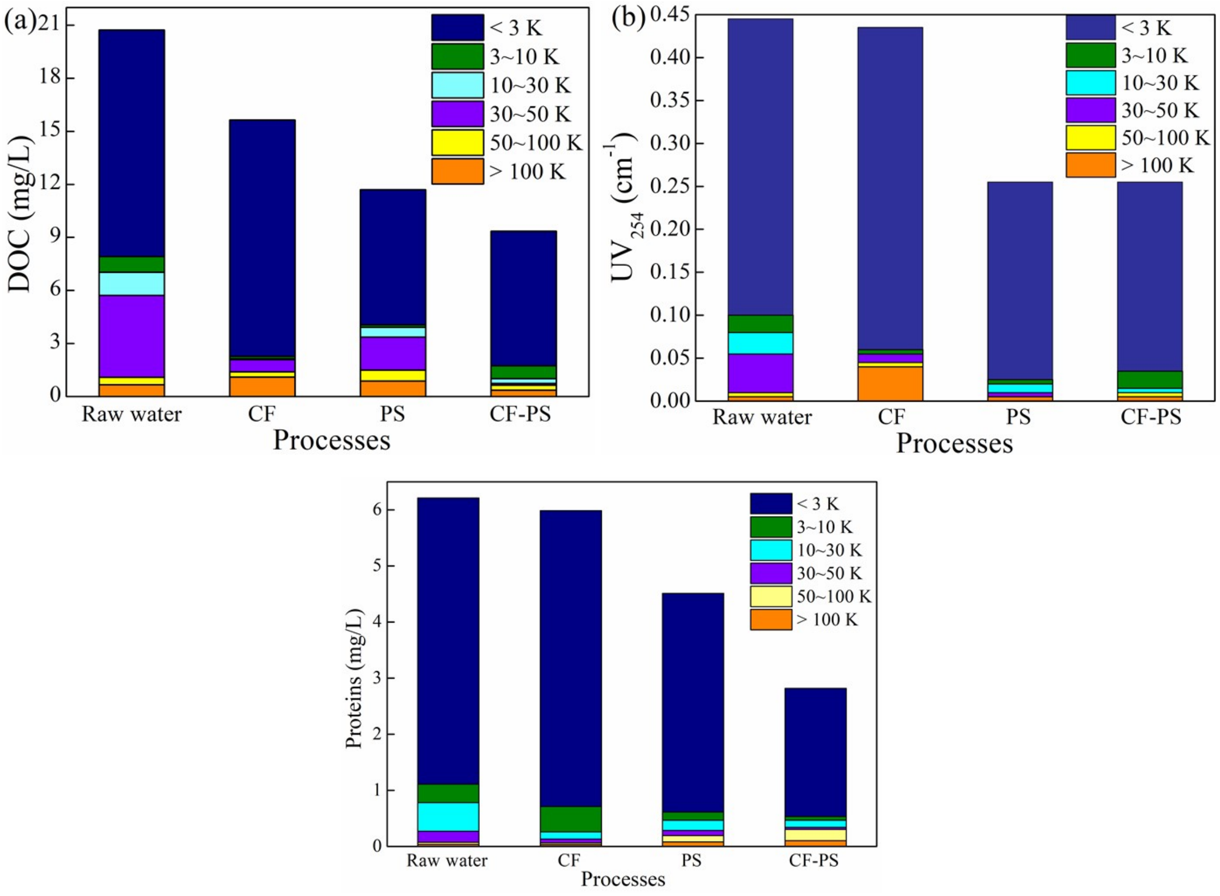
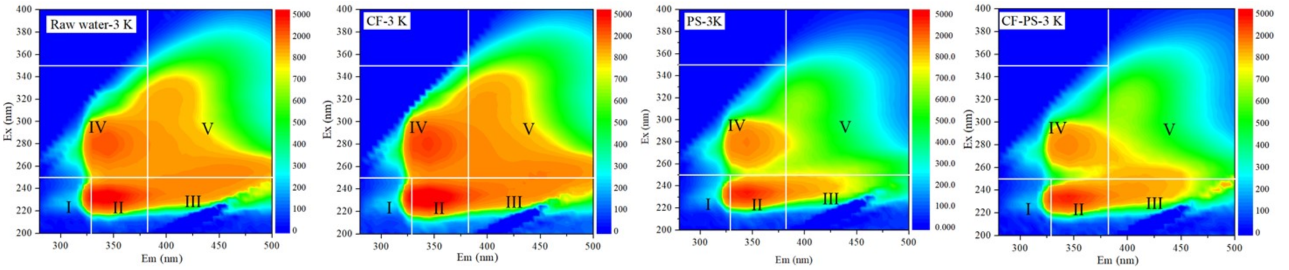
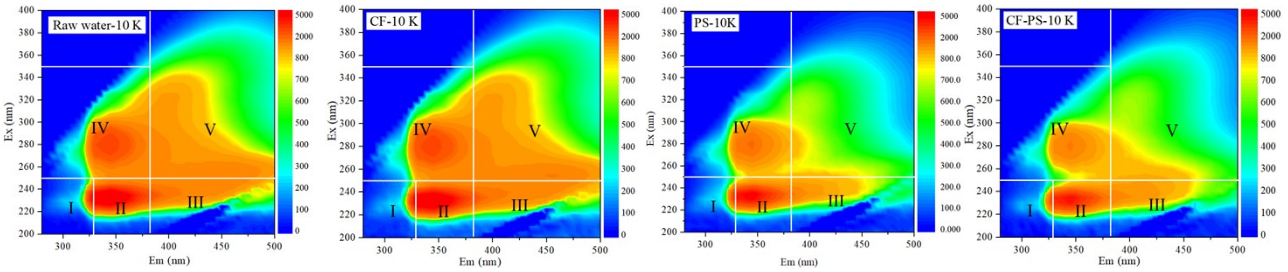


Fig. S3. MW distribution of organic matter under different processes. (a) DOC; (b) UV_{254}; (c) Proteins.

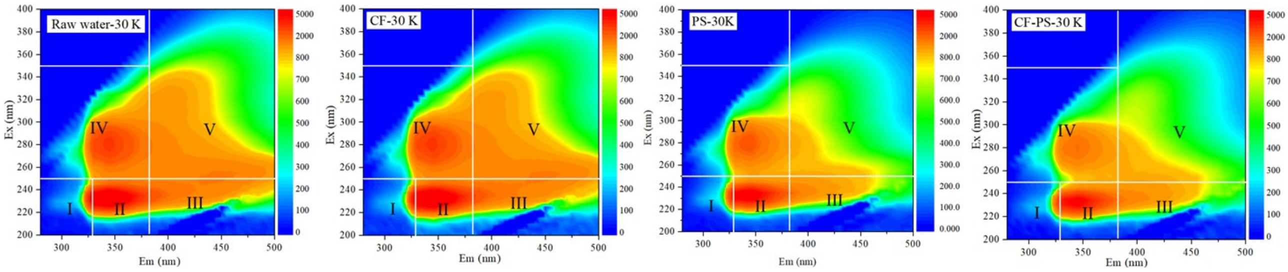
Fluorescent organics with different MWs



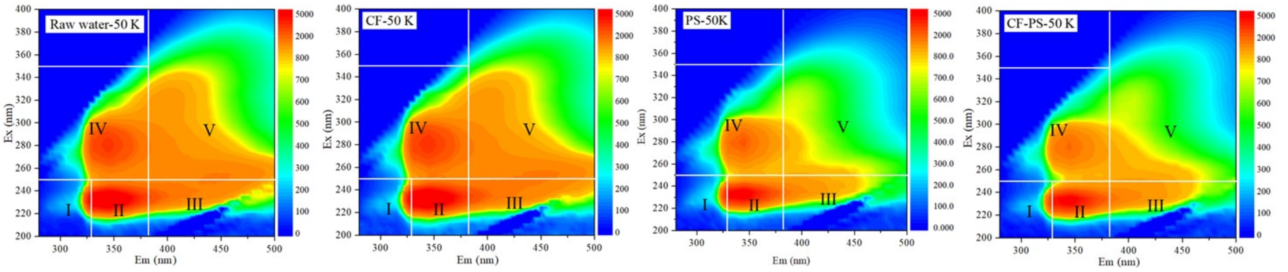
(a) <3 K



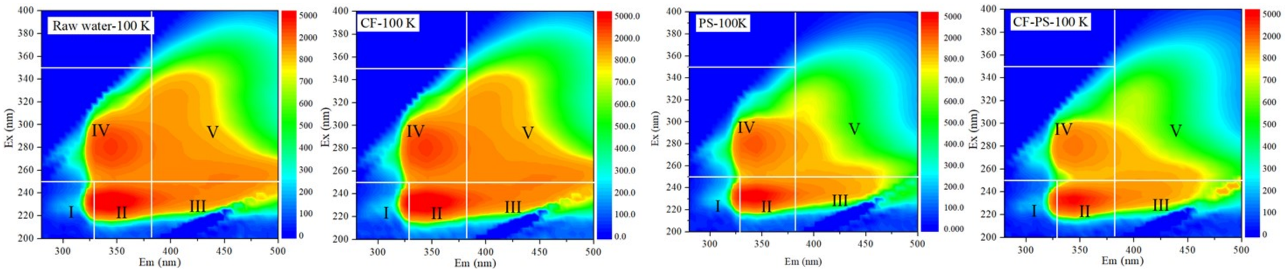
(b) < 10 K



(c) < 30 K



(d) < 50 K



(e) < 100 K

Fig. S4 3D-EEM spectra of organic components with different MWs

Table.S3 Regional fluorescence integral standard volume with different MWs

Processes	MWs	Regional fluorescence integral standard volume, $\Phi_{i,n}$/×10^4					
		I	II	III	IV	V	Total
Raw water	>100 K	5.40	36.22	5.28	13.50	2.51	62.92
	50~100 K	3.45	20.32	6.90	7.62	1.09	39.38
	30~50 K	8.50	26.23	6.01	11.97	1.26	53.96
	10~30 K	2.37	26.04	5.67	12.48	2.73	49.28
	3~10 K	5.22	44.82	7.30	23.62	7.73	88.69
	<3 K	53.41	258.02	88.23	129.63	87.01	616.31
	Total	78.36	411.65	119.38	198.81	102.34	910.53
CF	>100K	2.38	56.26	9.59	25.89	6.28	100.4
	50~100 K	0.56	11.04	2.04	12.47	1.70	27.82
	30~50 K	3.16	8.45	1.81	5.01	0.58	19.00
	10~30 K	0.76	11.80	2.56	-10.85	3.13	7.41
	3~10 K	3.51	29.09	4.79	14.94	-0.93	51.40
	<3 K	62.28	305.72	99.93	151.71	94.92	714.56
	Total	72.66	422.37	120.73	199.17	105.68	920.60
PS oxidation	>100 K	4.28	47.41	11.9	17.13	6.49	87.21
	50~100 K	3.90	20.81	4.40	7.68	5.25	42.04
	30~50 K	3.44	18.87	4.45	7.82	0.81	35.38
	10~30 K	1.17	12.32	0.90	2.57	1.03	17.99
	3~10 K	8.16	38.53	7.48	12.51	5.26	71.93
	<3 K	37.15	163.45	52.02	86.02	46.47	385.11
	Total	58.10	301.39	81.14	133.72	65.30	639.66
CF -PS oxidation	>100 K	2.30	38.75	1.56	9.72	3.79	56.14
	50~100 K	2.99	15.61	4.09	3.93	0.82	27.43
	30~50 K	2.99	15.61	4.09	3.93	0.82	27.43
	10~30 K	1.04	15.98	1.87	5.34	1.87	26.10
	3~10 K	1.86	13.21	0.59	6.94	1.65	24.25
	<3 K	33.78	159.71	61.94	81.21	54.12	390.75
	Total	43.52	249.69	70.88	115.75	61.78	541.62

Table. S4 Degradation of Φ*i,n* (%) with different MWs

Processes	MWs	Removal of $\Phi_{i,n}$/%

		I	II	III	IV	V	Total
CF	>100 K	55.87	-55.32	-81.66	-91.83	-150.35	-59.60
	50-100 K	83.73	45.66	70.36	-63.78	-55.08	29.37
	30-50 K	62.85	67.80	69.90	58.12	53.85	64.78
	10-30 K	67.85	54.67	54.74	186.95	-14.49	84.97
	3-10 K	32.81	35.09	34.38	36.76	111.97	42.04
	<3 K	-16.60	-18.49	-13.26	-17.03	-9.08	-15.94
	Total	7.28	-2.60	-1.13	-0.18	-3.26	-1.11
PS oxidation	>100 K	20.88	-30.88	-125.34	-26.93	-158.68	-38.61
	50-100 K	-12.98	-2.37	36.17	-0.87	-380.53	-6.76
	30-50 K	59.55	28.05	25.95	34.65	36.08	34.43
	10-30 K	50.44	52.67	84.18	79.44	62.31	63.50
	3-10 K	-56.18	14.03	-2.45	47.04	31.99	18.89
	<3 K	30.44	36.65	41.04	33.65	46.60	37.51
	Total	25.86	26.78	32.03	32.74	36.19	29.75
CF -PS oxidation	>100 K	57.36	-6.98	70.42	27.96	-51.18	10.77
	50-100 K	13.42	23.22	40.69	48.45	25.13	30.35
	30-50 K	64.83	40.50	31.92	67.19	35.17	49.17
	10-30 K	56.05	38.63	67.03	57.22	31.46	47.04
	3-10 K	64.32	70.53	91.91	70.63	78.59	72.65
	<3 K	36.76	38.10	29.80	37.35	37.81	36.60
	Total	44.46	39.35	40.62	41.78	39.63	40.52

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