Supporting information for *RSC Advances*

Coupling pretreatment of ultraviolet/ferrate (UV/Fe(VI)) for improving ultrafiltration of natural surface water

Fuwang Zhao[a], Zhiwei Zhou [b]*

[a]*School of Energy and Environment, Zhong Yuan University of Technology, Zhengzhou, 450007, China.*

[b]*College of Architecture & Civil Engineering, Faculty of Urban Construction, Beijing University of Technology, Beijing 100124, China*

*Author for correspondence: E-mail address: zhouzw@bjut.edu.cn;

Text S1. The details of Darcy's formula and model fitting of membrane fouling.

Darcy's law was adopted to calculate the fouling resistance, which was illustrated as Eqs. (1)-(2):

$$R_{rf} = \frac{\Delta P}{\mu J_1} - \frac{\Delta P}{\mu J_2} \tag{1}$$

$$R_{if} = \frac{\Delta P}{\mu J_2} - \frac{\Delta P}{\mu J_0} \tag{2}$$

where R_{rf} and R_{if} are reversible and irreversible membrane fouling resistance (m^{-1}), respectively. J_0, J_1 and J_2 are flux (m/s) for Milli-Q water of virgin membrane, water sample, and Milli-Q water of membrane after backwashing, respectively. ΔP represents transmembrane pressure (Pa) and μ is dynamic viscosity (Pa·s).

To be specific, four fouling models were employed to recognize the dominant mechanism during the UF process. According to Hermia's model, the fouling mechanisms are consistent with the characteristic curves between d^2t/dV^2 and dt/dV (Eq. (1)).

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{1}$$

where t is filtration time (s), V is filtration volume (m^3), and n is characteristic value for each fouling model (Table S1). The required d^2t/dV^2, dt/dV, and n can be calculated according to Eqs. (2)-(4).

$$\frac{dt}{dV}=\frac{1}{JA} \quad (2)$$

$$\frac{d^2t}{dV^2}=-\frac{1}{J^3A^2}\frac{dJ}{dt} \quad (3)$$

$$n=\frac{d\left[\log\left(\frac{d^2t}{dV^2}\right)\right]}{d\left[\log\left(\frac{dt}{dV}\right)\right]} \quad (4)$$

where J and A represent permeate flux (m/s) and filtration area (m^2), respectively.

Table S1. Four classical membrane fouling models.

Values of n	Fouling mechanism	Computational formula
2.0	Complete blocking	J_0 - J = C_1V
1.5	Standard blocking	1/t + C_2 = J_0/V
1.0	Intermediate blocking	lnJ_0 - lnJ=C_3V
0.0	Cake layer filtration	(1/J) - (1/J_0) = C_4V

Notes: J_0 is initial membrane flux; J is membrane flux; V is filtration volume; t is filtration time; C_1, C_2, C_3, and C_4 are constants.

Table S2. The changes of DOC under different pretreatment conditions.

Samples (Influent)	DOC (mg/L)
Feed water	7.553
0.02 mmol/L Fe(VI) with 30 minutes UV irradiation	5.994
0.04 mmol/L Fe(VI) with 60 minutes UV irradiation	5.524
0.06 mmol/L Fe(VI) with 90 minutes UV irradiation	5.223
0.08 mmol/L Fe(VI) with 90 minutes UV irradiation	5.407
0.06 mmol/L Fe(VI) with 120 minutes UV irradiation	5.396
0.08 mmol/L Fe(VI) with 120 minutes UV irradiation	5.461

Table S3. Summary of equations in the UV/Fe(VI) process.

Eq.	Reaction	Rate constant ($M^{-1}\cdot s^{-1}$)	Reference
(1)	Fe(VI)+H_2O → Fe(IV)+ H_2O_2	22	[1]
(2)	H_2O_2+UV ⇔ 2·OH	5.5×10^9	[2]
(3)	H_2O_2+$^{\bullet}$OH → $HO_2^{\bullet}$+H_2O	—	[3]
(4)	$HO_2^{\bullet}$ → H^++$O_2^{\bullet-}$	—	[4]

(5)	$Fe(VI)+H_2O_2 \rightarrow Fe(IV)+O_2$	10	5
(6)	$Fe(IV)+H_2O_2 \rightarrow Fe(II)+O_2+H_2O$	$\sim 10^4$	6
(7)	$Fe(II)+H_2O_2 \rightarrow Fe(III)+\cdot OH+OH^-$	63	7
(8)	$Fe(IV)+Fe(II) \rightarrow Fe(V)+Fe(III)$	$\sim 10^7$	1
(9)	$Fe(III)+H_2O_2 \rightarrow Fe(II)+HO_2^\bullet+H^+$	$\sim 10^{-3}$	7
(10)	$Fe(V)+H_2O \rightarrow Fe(III)+H_2O_2$	5.8×10^7	6
(11)	$Fe(V)+H_2O_2 \rightarrow Fe(III)+O_2$	5.6×10^7	8

Table S4. EEM spectrum volumes for reclaimed water.

	I	II	III	IV	V	Total
Feed water	454484.8	1092901.0	1473936.0	2163768.0	6699850.0	11884940.7
UV	313760.5	848627.2	1515434.0	1796971.0	7951880.0	12426672.9
Fe(VI)	680981.7	1634242.0	1834154.0	1329616.0	4883908.0	10362901.5
UV/Fe(VI)-1	584346.3	1049324.0	1546057.0	1435953.0	6122653.0	10738333.6
UV/Fe(VI)-2	373668.1	687577.0	1119804.0	1089391.0	4714690.0	7985130.7
UV/Fe(VI)-3	358527.9	678085.3	1004926.0	861628.1	3726265.0	6629432.5
Feed water-UF	395742.5	889558.0	1362587.0	1808721.0	6286827.0	10743435.0
UV-UF	384300.4	819801.3	1506045.0	1657578.0	7634961.0	12002685.7
Fe(VI)-UF	589085.5	1281834.0	1565213.0	1170434.0	4599610.0	9206176.67
UV/Fe(VI)-1-UF	435679.0	938212.2	1479270.0	1350966.0	5832885.0	10037012.8
UV/Fe(VI)-2-UF	315324.0	550372.4	1006746.0	946485.8	4467492.0	7286419.76
UV/Fe(VI)-3-UF	362353.3	599998.8	951266.8	866394.7	3713865.0	6493878.89

Table S5. 2D-COS results on the assignment and sign of each cross-peak.

Position (cm^{-1})	Assignment	Sign[a]					
		3600-3000	2965	1665	1420	1040	800
3600-3000	O-H	+	+(-)	+(+)	+(+)	+(+)	+(+)
2965	C-H		+	+(+)	+(+)	+(+)	+(+)
1665	C=O/NH_2			+	+(-)	+(-)	+(-)
1420	C-N				+	+(-)	+(-)
1040	C-O-C/C-O					+	+(+)
800	C-O						+

[a]Signs were obtained in the maps: +, positive; −, negative.

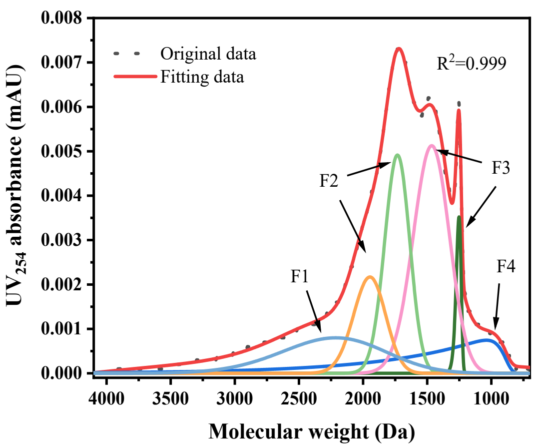

Fig. S1 Peakfit deconvolution results of the feed water.

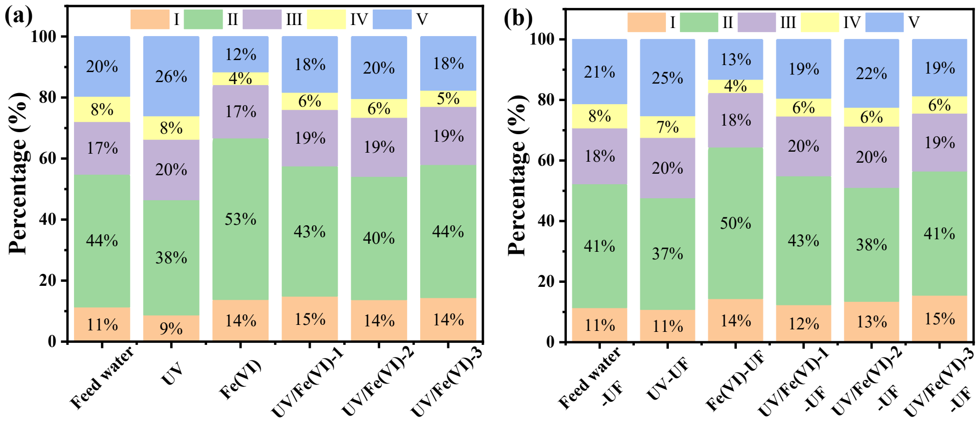

Fig. S2 The proportion of various fluorescent components: influent water (a) and effluent water (b).

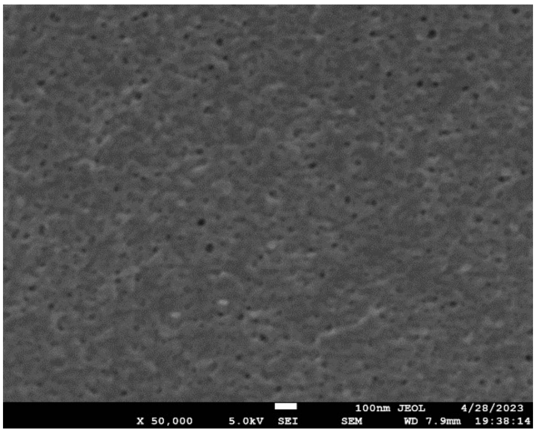

Fig. S3 SEM images of virgin membrane.

References

1. Z. Huang, L. Wang, Y. Liu, H. Zhang, X. Zhao, Y. Bai and J. Ma, *Water Res.*, 2021, **197**, 117094.
2. Y. Wan, P. Xie, Z. Wang, J. Ding, J. Wang, S. Wang and M. R. Wiesner, *Water Res.*, 2019, **158**, 213-226.
3. X. Tian, Y. Li, H. Xu, Y. Pang, J. Zhang and H. Pei, *J. Hazard. Mater.*, 2021, **412**, 125206.
4. X. Chang, T. Lin, J. Mo, H. Xu, H. Tao and W. Liu, *Chemosphere.*, 2021, **287**, 132049.
5. P. K. Rai, J. Lee, S. K. Kailasa, E. E. Kwon, Y. F. Tsang, Y. S. Ok and K. H. Kim, *Environ. Res.*, 2018, **160**, 420-448.
6. Y. Lee, R. Kissner and U. von Gunten, *Environ. Sci. Technol.*, 2014, **48**, 5154-5162.
7. K. Wei, X. Liu, S. Cao, H. Cui, Y. Zhang and Z. Ai, *Chem. Eng. J. Adv.*, 2021, **8**, 100165.
8. S. Wang, B. Shao, J. Qiao and X. Guan, *Front. Environ. Sci. Eng.*, 2020, **15**, 80.