Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.
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Supplementary information for:

Application of composite flocculant for removing organic matter and mitigating ultrafiltration membrane fouling in surface water treatment: The role of composite ratio

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Journal: Environmental Science: Water Research & Technology

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This document consists of 11 pages, 6 figures and 2 tables.

Corresponding to section *Raw water and flocculant* in the paper

Raw water

The properties of different water samples (HA-Kaolin water, FA-Kaolin water, Yellow River water and Yangtze River water) are listed in Table S1.

Table S1 Characteristics of different water samples

Items	HA	FA	Yellow river	Yangtze river
Turbidity/*NTU*	14.5~15.5	14.5~15.5	3.40±0.85	10.8±1.96
$UV_{254/278}/cm^{-1}$	0.211±0.003	0.114±0.002	0.032±0.009	0.084±0.021
DOC/$mg{\cdot}L^{-1}$	4.934±0.015	7.167±0.022	2.674±0.145	5.220±0.744
SUVA/$mg{\cdot}L^{-1}{\cdot}m^{-1}$	3.95	1.59	1.20	1.61
Zeta potential/*mV*	-18.633±0.49	-23.5±0.92	-11.303±0.87	-9.322±1.028

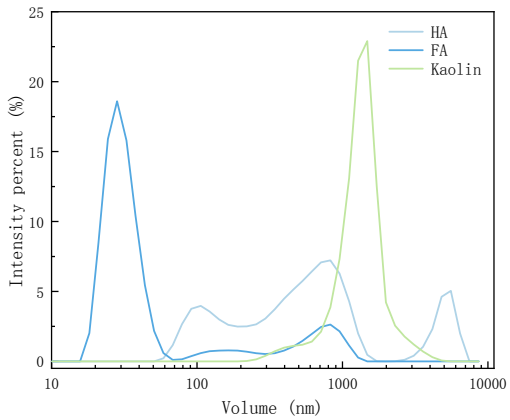

Fig. R1. The size distribution of the HA, FA and Kaolin.

Corresponding to section *Floc on-line monitoring* in the paper

Fractal dimension

The fractal dimension (D_f) was used to characterize floc structure and determined by the SALLS method. The scattered intensity, Q, as a function of the magnitude of the scattering wave vector is calculated by the equation:

$$Q = \frac{4\pi n \sin(\theta/2)}{\lambda} \tag{1}$$

The D_f was described by the following relationship between the total scattered light intensity I and the scattering vector Q by D_f [1]:

$$I \propto Q^{-Df} \tag{2}$$

where n, λ, and θ are the refractive index of the suspending medium, the wavelength of the radiation in vacuum and the scattering angle, respectively [2].

Corresponding to section *Other analysis methods* in the paper

Membrane resistance

In UF process, to reveal the membrane fouling behaviors, the resistance-in-series model was used. The detailed methods and equations were listed in Table S2 [3, 4].

Table S2 Detailed calculations and operations for various membrane resistances.

Membrane resistances	Methods	Equations
Intrinsic membrane resistance (Rm)	330 mL deionized (DI) water was filtrated through the clean membrane to record J_0.	$R_m = \frac{TMP}{\mu J_0}$
Loosely-attached resistance (R_{cl})	The coagulation effluent (1 L) was filtered with the same membrane to get J_1.	$R_{cl} = \frac{TMP}{\mu J_1} - \frac{TMP}{\mu J_2}$
Strongly-attached resistance (R_{cs})	DI (100 mL) was added with the stirring rate of 200 rpm to remove the loosely attached cake layer, and J_2 was obtained.	$R_{cs} = \frac{TMP}{\mu J_2} - \frac{TMP}{\mu J_3}$
Pore blocking resistance (R_p)	The strongly-attached cake/gel layer was wiped by a wet sponge, and DW (350 mL) was filtered to get J_3.	$R_p = \frac{TMP}{\mu J_3} - \frac{TMP}{\mu J_0}$

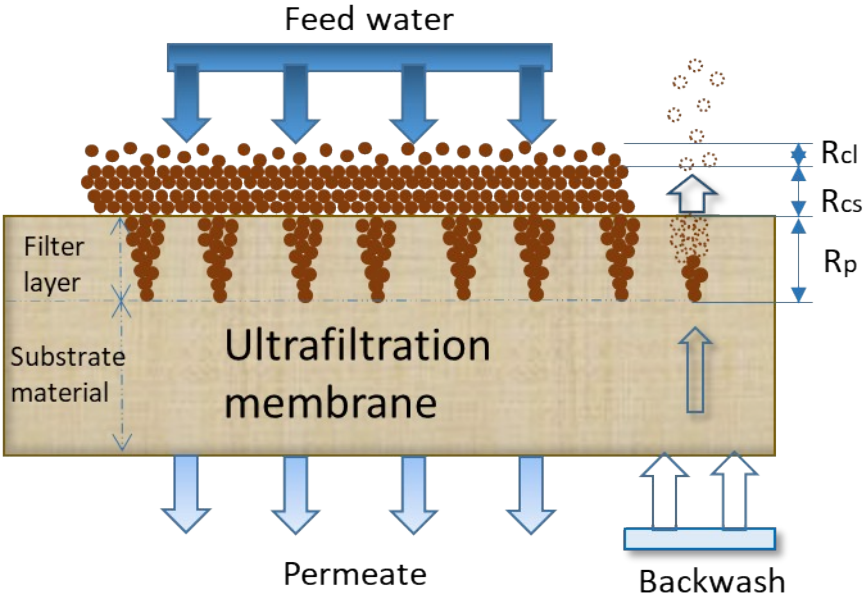

Fig. S2. Schematic diagram of membrane resistance model.

Corresponding to section *Comparison of Al-based flocculants and Fe-based flocculants* in the paper

Effect of different flocculants on coagulation performances

According to the consideration of both performances of pre-experiments and economy, the optimum dosage of PAC and PAC-PDMDAAC were chosen as 4.0 mg/L and that of PFC and PFC-PDMDAAC were chosen as 9.0 mg/L. From comparison of the four flocculants, it seems that PAC and PAC-PDMDAAC achieved better turbidity removal and DOC removal efficiencies than PFC and PFC-PDMDAAC. Meanwhile, compared with PAC and PFC, PAC-PDMDAAC and PFC-PDMDAAC as composite flocculant showed better performances for both simulated surface water and real surface water. And Fig. S2 showed that the removal of turbidity and DOC all decreased in the order of PAC-PDMDAAC>PAC>PFC-PDMDAAC>PFC. In addition, the removal efficiency of HA and FA by the same flocculant was better than that of the Yellow river and Yangtze river. That could be explained by that the Yellow river and Yangtze river had lower SUVA values (Table S1), that was to say, the Yellow river and Yangtze river contained more hydrophilic substances with small molecules which were difficult to be removed.

As shown in Fig. S3 (c), the changes in zeta potential of flocs were consistent with coagulation performances. The zeta potential of flocs generated in simulated surface water and real surface water were closest to 0 mV when PAC and PAC-PDMDAAC were used, this contributed to the better coagulation performance of PAC and PAC-PDMDAAC, especially PAC-PDMDAAC. According to Fig. S3 (d), PAC and PAC-

PDMDAAC as cationic flocculant had high charge density of 217000 μeq/l and 223000μeq/l, respectively, while the charge density of PFC and PFC-PDMDAAC were much lower than that of PAC and PAC-PDMDAAC (PFC: 34000 μeq/l, PFC-PDMDAAC: 29000 μeq/l). The difference in coagulation performance between Al-based flocculants and Fe-based flocculants could be explained by the higher charge density and higher charge neutralization ability of Al-based flocculants which can form more complex with negatively charge organic compounds, it indicated that charge neutralization played a dominant role in coagulation process for PAC and PAC-PDMDAAC. However, the coagulation performance of PAC-PDMDAAC was better than that of PAC although PAC and PAC-PDMDAAC had similar charge density. The improvement of NOM removal of PAC-PDMDAAC could be explained by that PAC-PDMDAAC trapped big particles which formed by small particles through charge neutralization to form aggregates easy to precipitate and be removed due to its charge neutralization ability and adsorption and bridging effect.

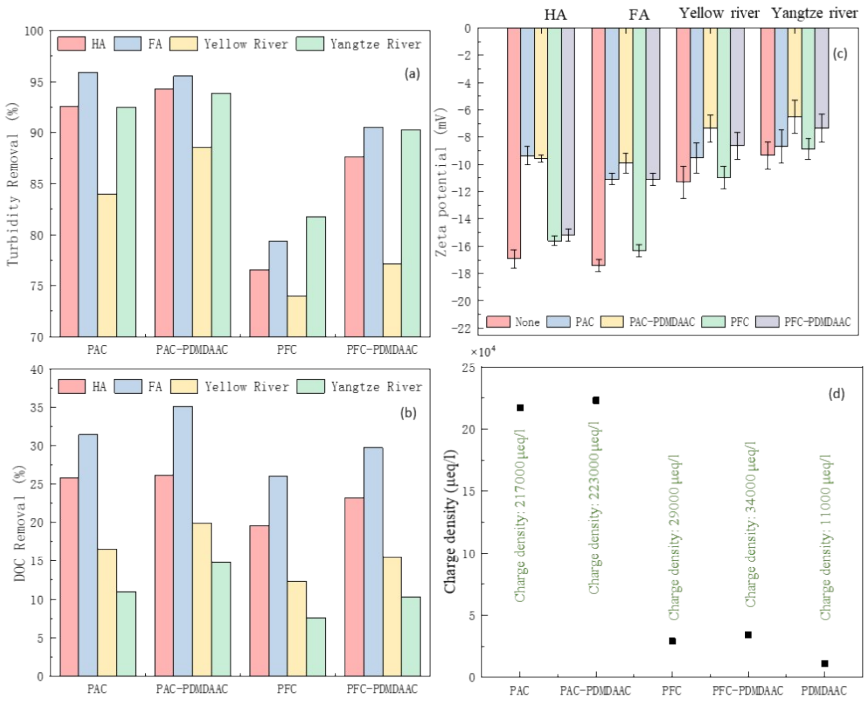

Fig. S3. Effect of different flocculants on coagulation performance: (a) turbidity removal, (b) DOC removal, (c) Zeta potential of flocs and (d) charge density. Conditions: PAC and PAC-PDMDAAC dosage=4.0 mg/L, PFC and PFC-PDMDAAC dosage=9.0 mg/L. the error bars represent the standard deviation from duplicate test.

Corresponding to section *Effects of composite ratio on coagulation performance of PAC-PDMDAAC* in the paper

Coagulation performance

As can be seen from Fig. S4, a common trend in all the cases was that the turbidity removal increased rapidly with the flocculant dosage firstly, and then the growth became negligible at the dose above 5 mg/L. With the dosage increasing, the turbidity removal even decreased because of the destabilization of flocs caused by excessive positive charge [5]. It could also be observed that PAC-PDMDAAC could augment the turbidity removal and FA removal. In addition, the higher content of PDMDAAC in PAC-PDMDAAC, the more obvious of augment in turbidity removal and FA removal.

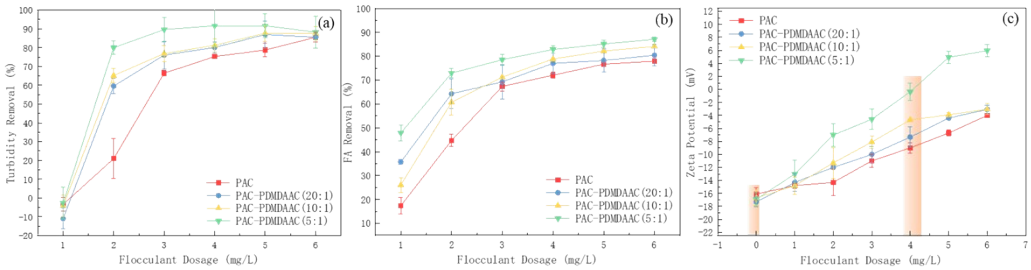

Fig. S4. Turbidity removal (a), FA removal (b) and zeta potential of flocs (c) as function of PAC-PDMDAAC dosage.

Corresponding to section *Floc characteristics at various composite ratio of PAC-PDMDAAC* in the paper

Floc size and structure

The growth curve of FA flocs and the D_f value of different periods were shown in Fig. S5.

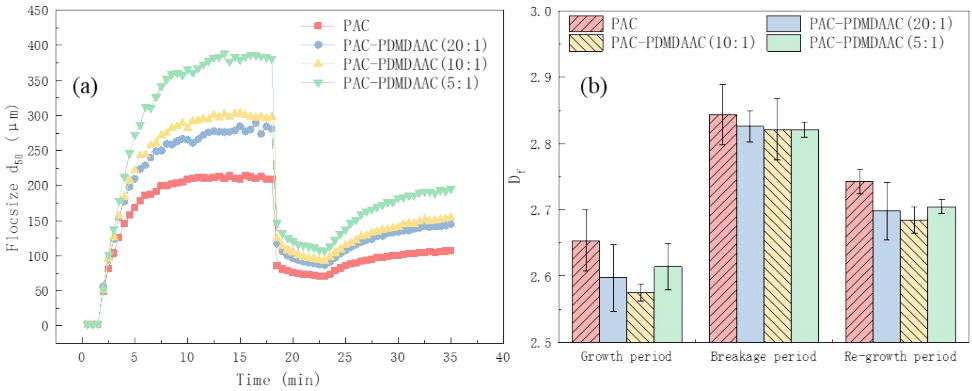

Fig. S5. The effects of the content of PDMDAAC in PAC-PDMDAAC on (a) floc size and (b) D_f value of FA flocs.

Corresponding to section *Membrane flux improvement by PAC-PDMDAAC with various composite ratio* in the paper

Membrane fouling

The effects of PAC-PDMDAAC with different content of PDMDAAC on membrane fouling of PES membrane and RC membrane caused by FA were investigated and the results were shown in Fig. S6.

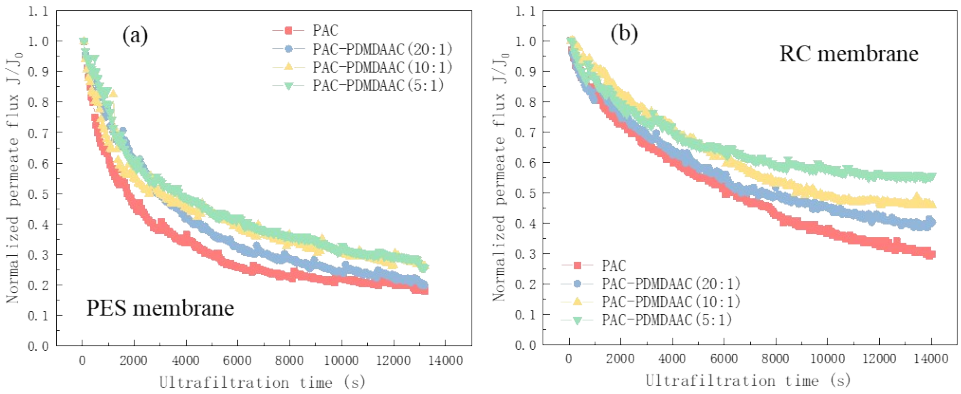

Fig. S6. The effects of the content of PDMDAAC in PAC-PDMDAAC on HA fouling mitigation on (a) PES membrane and (b) RC membrane.

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