Supplementary Information for: Quantitative temporal-based contribution of key foulants to fouling proceeding in direct membrane filtration for sewage pre-concentration

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Text S1. The definition of four kind of hydrophobic/philic foulants

In general, parts of foulants in raw sewage do not strictly belong to either hydrophobic or hydrophilic, but nominally moderate "hydrophobic/philic" fractions(Mu et al., 2019). The moderate hydrophilic foulants can be retained at low pH (≤2) with enriched hydrogen bonds (Thurman and Malcolm, 1981; Silva et al., 2017b), while moderate hydrophobic foulants can be filtered out with the DAX-8 resin at high pH (≥12) due to alleviated interaction (Thurman and Malcolm, 1981; Wang et al., 2014). As such, the moderate hydrophilic foulants that can be transformed at pH 2 are defined as "hydrophilic/phobic faction (HI/OF)" (Akio Imai, 2002), and the moderate hydrophobic foulants that can escape from the DAX-8 resin at pH 12 are defined as "hydrophobic/philic faction (HO/IF)" (Mu et al., 2019). Those in the filtrate of the resin column at pH 2 can be defined as "real hydrophilic faction (HIF)" (Thurman and Malcolm, 1979), comprising all hydrophilic components with HI/OF. Correspondingly, those retained in the resin column at pH 12 can accordingly be defined as "real hydrophobic faction (HOF)" (Imai et al., 2002), comprising all hydrophobic foulants with HO/IF.

In this study, pH was adjusted by adding HCl or NaOH solution to the samples. The DAX-8 resin column was eluted before use by rinsing with methanol, deionized water, 0.1 mol/L NaOH solution and 0.1 mol/L hydrochloric acid. PN and HA was measured by modified Lowry's method (Lowry et al., 1951), and PS was measured by the phenol-sulfuric acid colorimetric assay (Dubois et al., 1956).

Text S2. The experimental design for DMF

The dead-end filtration of sewage after pre-fractionation of key foulants were conducted in a stirred cell (Amicon Model 8400, Millipore USA) system containing polyvinylidene fluoride (PVDF) microfiltration (MF) flat sheet membranes with an average pore size of 0.45 μm (CATNO HVHP09050, Millipore, USA). The transmembrane pressure inside the dead-end cell was provided by a nitrogen cylinder (ZG special gases Science & technology, Beijing) and was controlled at 20.0 kPa during filtration. The real-time mass of the filtrate was weighed using an electronic balance, and the data were recorded by a laptop connected to the balance. All membranes were soaked with 3% NaClO solution and deionized water for 24 h before use and rinsed with deionized water for 3 times before filtration experiments. The stirred cell was also cleaned with above reagents before use.

Text S3. Fouling mode fitting for different stages of DMF

The classical constant pressure filtration model Eq. (S1) explains the relationship between filtration resistance (*R*) and the volume of filtrate (Hermia, 1982):

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^N or \frac{dR}{dV} = kR^N \#(S1)$$

where *t* is the filtration time, *V* is the volume of filtrate, *R* is the filtration resistance, and *N* is the constant of the filtration or blocking model. This equation can be transformed into the relationship between flux *J* and filtrate volume *V* in Eq. (S2):

$$\frac{dJ}{dV} =- kJ^{2-N}\#(S2)$$

By integrating Eq. (S2), the *J-V* relationship of each model can be described as Eq. (S3):

$$V - V_0 = \begin{cases} \frac{k_N}{N-1}\left(J_0^{N-1} - J^{N-1}\right), N = 0, 1.5, 2, 2.5 \\ k_N(lnJ_0 - lnJ), N = 1 \end{cases} \#(S3)$$

The applicable model for filtration can be determined through the parameter *N*. Different values of *N* (theoretically, *N* can be 0, 1, 1.5, 2 and/or 2.5) represent different filtration models from pore blocking to formation of the cake layer (Xu et al., 2020). The filtration data can be further fitted into a curve of *ln(dR/dV)-lnR*, where the membrane fouling filtration model can be determined based on the slope *N* (the same parameter *N*) of the curve at different time periods. By taking the logarithm of Eq. (S1) of the constant pressure filtration model, a linear function about *lnR* can be obtained in Eq. (S4):

$$ln\left(\frac{dR}{dV}\right) = NlnR + lnk\#(S4)$$

Text S4. The calculation of VPA and PLS

For the calculation of VPA, the absolute values of altered *R* ratio ($|R_0-R_i|/R_0$) in corresponding scenario were taken as the dependent variables, and the altered concentrations of PS, PN, and HA after each pre-fractionation were taken as the independent variables. The statistical analysis of VPA was implemented with the "vegan" package in the R Language (Lin et al., 2019).

For the calculation of PLS, the initial R_0 of raw sewage and its original foulant concentration c_0 were applied as reference points. The independent variables were defined as the ratio $(c_0-c_i)/c_0$, representing the difference between c_0 and the concentration c of corresponding key foulants in respective pre-fractionation scenarios. Meanwhile, the dependent variables were the ratio $(R_0-R_i)/R_0$, signifying the difference between R_0 and the R_i after respective pre-fractionation scenarios. In evaluation of the blocking coefficient N, the difference c_0-c_i served as the independent variables, while the blocking coefficient N in three stages of raw sewage DMF were regarded the dependent variables.

Table S1 Alternation of key foulants after different pre-fractionations

Scenario	Single-step	Two-step	Concentration (mg/L)			Pre-fractionation removal rate		
			PN	PS	HA	PN	PS	HA
Raw sewage	/	/	99.5~112.5	11.1~16.6	39.3~45.0	/	/	/
I	DAX-8	/	74.6~83.5	4.3~9.6	14.3~20.9	19.4~30.9%	42.0~61.4%	53.6~63.6%
IV		pH=2	13.4~22.6	4.9~8.6	8.7~13.5	79.9~86.5%	48.6~55.6%	70.0~77.9%
V		pH=12	4.9~13.3	4.2~9.6	3.6~7.9	88.2~95.1%	42.6~62.6%	82.4~91.7%
II	pH=2	/	46.5~54.5	14.7~18.6	20.7~26.4	51.5~53.3%	-31.8~-12.0%	41.3~51.1%
VI		DAX-8	14.1~26.6	10.7~14.5	5.7~9.9	76.3~86.9%	4.2~12.6%	78.0~85.5%
III	pH=12	/	47.2~56.5	12.0~16.6	20.5~25.9	49.7~52.5%	-8.8~-7.6%	42.3~48.8%
VII		DAX-8	21.2~30.6	3.6~8.4	19.5~24.5	72.8~78.7%	49.2~67.2%	45.3~51.1%

Table S2 Respective impacts on R growth after different pre-fractionations

Scenario	Single-step	Two-step	Staged R (10^{10} m^{-1})			R growth rate ($10^{10}m^{-1}/s$)			Altered R ratio		
			the initial stage	the middle stage	the final stage	the initial stage	the middle stage	the final stage	the initial stage	the middle stage	the final stage
Raw sewage	/	/	29.8±2.8	94.7±3.1	120.5±2.1	0.66~0.84	1.57~1.74	0.46~0.58	/	/	/
I	DAX-8	/	27.1±4.1	77.4±3.0	120.5±3.1	0.63~0.75	1.15~1.38	0.81~0.96	-13.8~ 20.4%	12.4~ 30.4%	-110.4~-39.5%
IV		pH=2	11.8±3.2	36.2±4.6	60.2±4.1	0.23~0.30	0.60~0.70	0.44~0.50	60.9~ 70.2%	56.2~ 62.0%	-8.4~ 14.2%
V		pH=12	6.2±2.1	6.7+4.2	/	0.14~0.18	-0.01~0.02	0	76.5~ 81.1%	98.5~ 100.3%	100.0%
II	pH=2	/	18.7±5.0	77.4±2.4	120.5±1.3	0.42~0.52	1.29~1.54	0.82~0.96	30.0~ 47.9%	3.7~ 25.7%	-96.0~-56.4%
VI		DAX-8	12.2±2.4	40.2+3.1	94.7+2.3	0.27~0.33	0.63~0.76	0.97~1.15	53.5~ 64.1%	53.2~ 59.8%	94.0~ 146.6%
III	pH=12	/	7.5±3.7	8.6±2.4	/	0.18~0.19	0~0.04	-0.01~0.02	71.5~ 77.6%	97.6~ 100%	95.6~ 102.0%
VII		DAX-8	6.5±2.9	8.0±4.2	/	0.16~0.22	-0.01~0.07	-0.05~0.04	71.6~ 81.2%	95.4~ 100.9%	93.4~ 111.3%

Table S3 The ln(*dR/dV*)-*lnR* slope (*N* values) of different stages in each scenario

Pre-fractionation	The initial stage N_1	The middle stage N_2	The final stage N_3
Raw sewage	2.26±0.20	1.26±0.18	0.68±0.50
Scenario I	2.12±0.18	1.25±0.72	0.55±0.48
Scenario II	2.39±0.21	1.74±0.10	0.35±0.20
Scenario III	0.55±0.19	0.55±0.19	0.56±0.19
Scenario IV	2.02±0.25	1.49±0.66	0.74±0.14
Scenario V	1.22±0.64	1.13±0.53	1.10±0.50
Scenario VI	1.84±0.36	1.14±0.53	0.98±0.33
Scenario VII	1.03±0.24	0.96±0.26	0.88±0.22

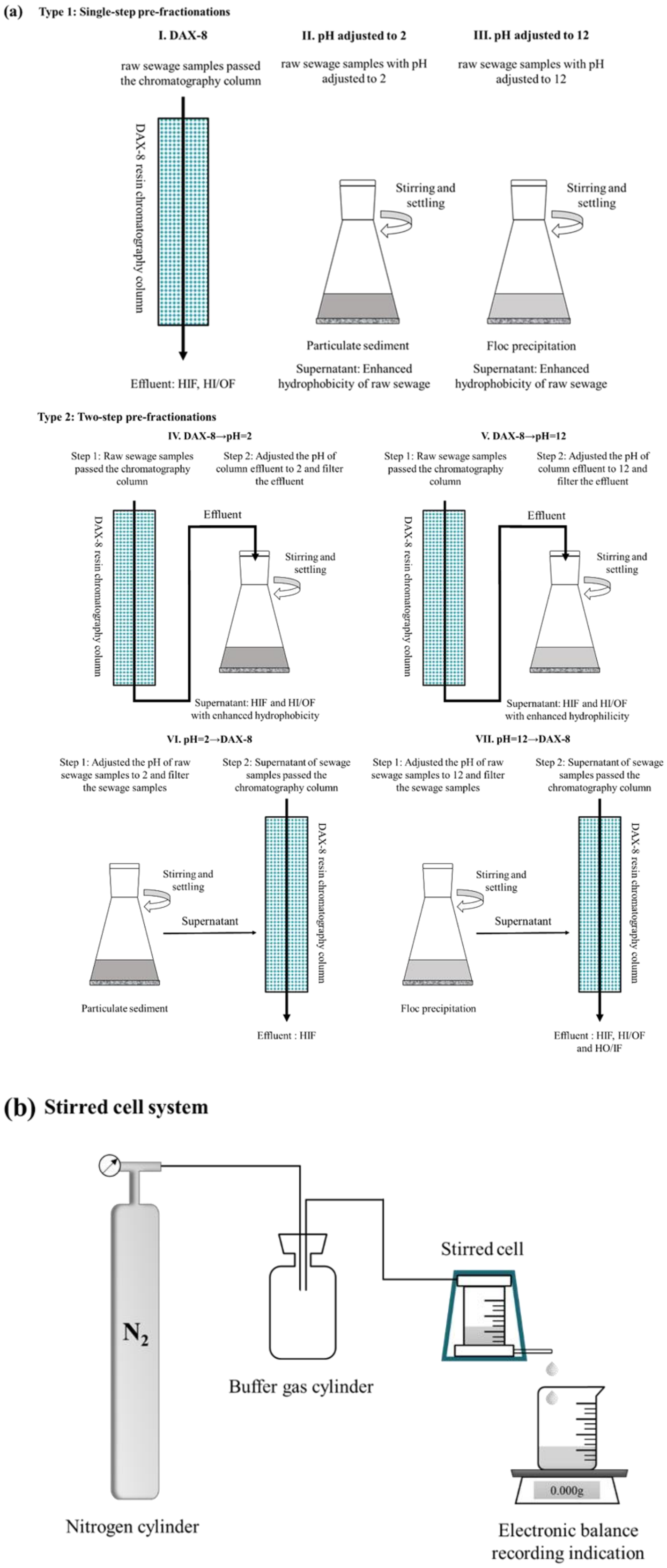

Fig. S1 (a) Schematic processes of different pre-fractionation scenarios; (b) Setup of stirred cell system.

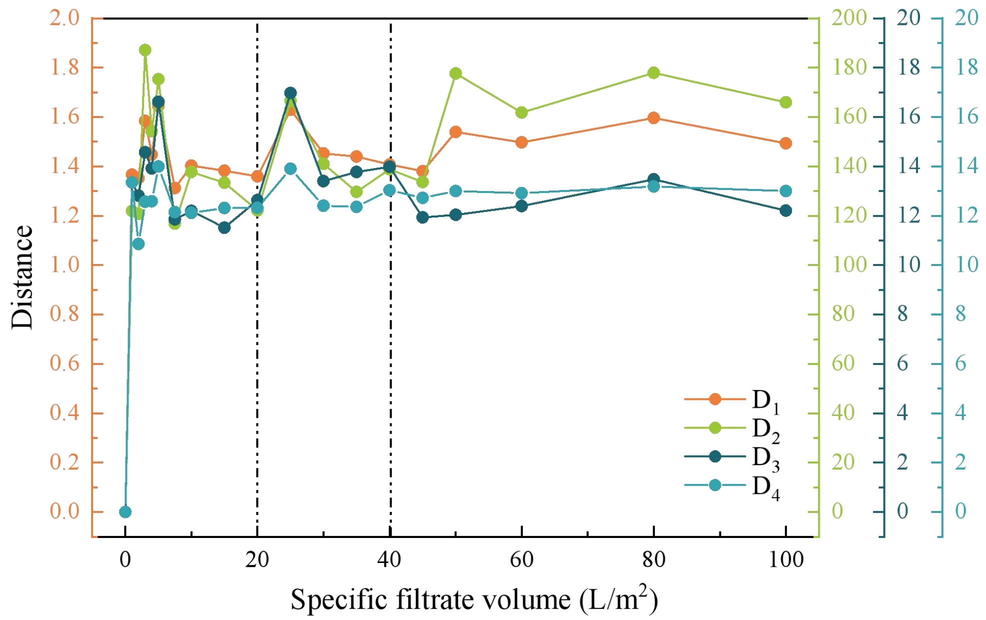

Fig. S2 The Euclidean distance(D_1), normalized Euclidian distance(D_2), Euclidean distance based on PCA(D_3) and Mahalanobis distance based on PCA(D_4) between fouled membranes (1~100 L/m^2) and virgin membrane based on FTIR spectra

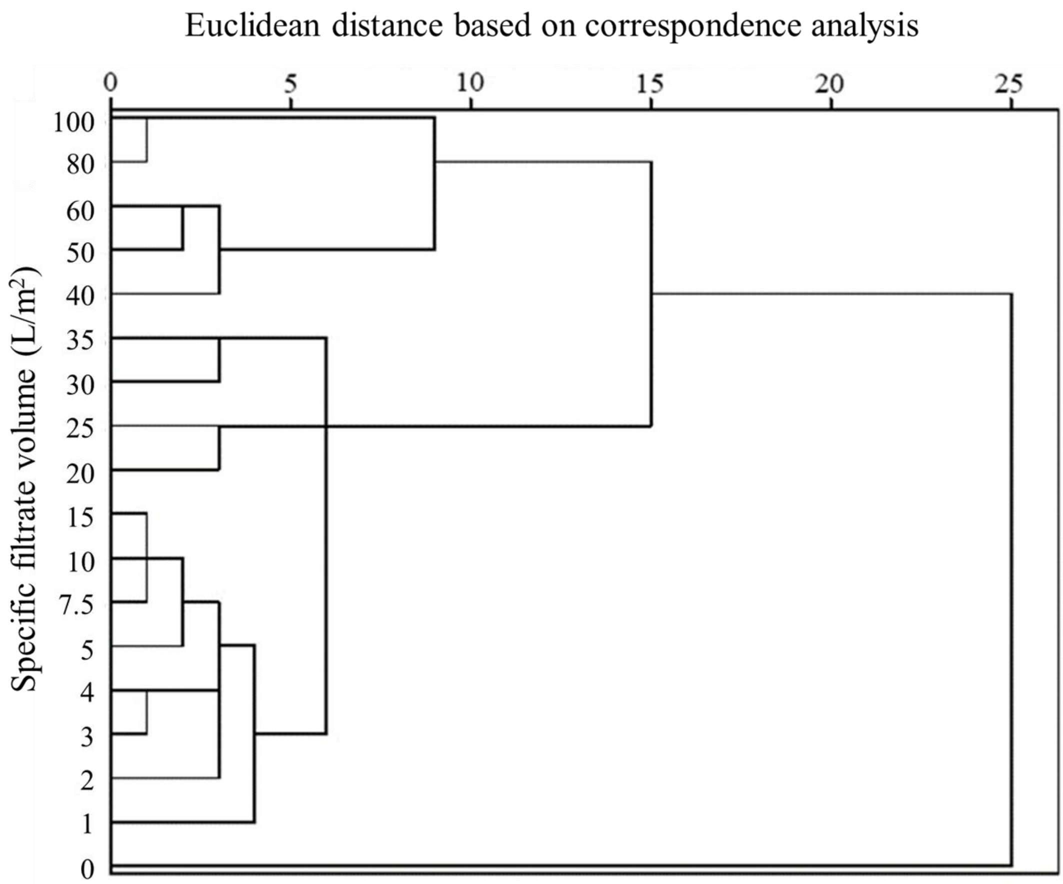

Fig. S3 The hierarchical clustering results of fouled membranes based on correspondence analysis

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