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Fractionating natural organic matter and evaluating the fouling potentials of its components

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ABSTRACT

This study was to fractionate natural organic matter (NOM) and evaluate the fouling potentials of its components in a pilot-scale microfiltration process. NOM in the feed water was fractionated into strongly hydrophobic acids (SHA), weakly hydrophobic acids (WHA), charged hydrophilic acids and neutral hydrophilic acids (NEU) fractions by resin adsorption; each fraction was then subdivided into low molecular weight (<1 kDa; LMW), medium molecular weight (1–10 kDa; MMW) and high molecular weight (10–10^4 kDa; HMW) components via high-performance size exclusion chromatography coupled with peak-fitting. Principal component analysis and Pearson correlation analysis demonstrated that hydraulically irreversible fouling index significantly correlated to NEU–MMW ($R^2 = 0.787$, p value = 0.001), SHA–LMW ($R^2 = 0.927$, p value < 0.0001) and WHA–LMW ($R^2 = 0.899$, p value < 0.0001). Fouling control strategy should be targeted at removing these foulants.

Keywords: MF; HIFI; MW distribution; Hydrophobicity

1. Introduction

Low-pressure membrane (LPM) filtration in surface water treatment has achieved enormous development in the past decades. However, membrane fouling, especially hydraulically irreversible fouling (HIF) is still a huge obstacle for the application of membrane as it decreases productivity, increases energy consumption and reduces membrane life span [1]. To settle the membrane fouling issues, many pre-treatment techniques, such as pre-coagulation, pre-adsorption, pre-oxidation and pre-filtration, have been developed and evaluated [2,3], which offered more options of improving membrane performance. Meanwhile, a fundamental knowledge of the potential irreversible foulants and their fouling mechanisms is essential in order to select a suitable pre-treatment technique. Researchers have long been devoted to the relevant foulants, such as colloidal organics, humic substances (HS), biopolymer (BP), polysaccharide (PS), proteins (PN), etc. [1,4–7]. Improvements in analytical techniques make it possible to characterize natural organic matter (NOM) more efficiently, among which resin adsorption fractionation and high-performance size exclusion chromatography (HPSEC) are the most optimistic measurements available for the determination of organic fractions in surface water. Via DAX-8/XAD-4/IRA-958 adsorbent resins, NOM could be fractionated into strongly hydrophobic acids (SHA), weakly hydrophobic acids (WHA), charged hydrophilic acids (CHA) and neutral hydrophilic acids (NEU) fractions [8]. The molecular weight (MW)

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distribution of NOM such as low MW (LMW) neutrals, LMW acids, building blocks, HS and BP could be identified and isolated by HPSEC in conjunction with a relatively new technique named peak-fitting [9–11]. Based on these analytical technologies, hydrophobic fractions (e.g., humic acid) [12], hydrophilic fractions [13], hydrophobic and hydrophilic compounds [14], SHA and NEU fractions [15], LMW compounds [16], macromolecules BP fractions [17] and PS-like organic matters [18] were all once believed to be responsible for irreversible fouling. In those researches, there were obviously contradictory results on the main foulants, which may be explained by: (1) NOM is complex, various and unstable, and thus difficult to control and predict; (2) the constituents of NOM were generally classified by adsorbent resins or HPSEC in previous studies; however, limited studies subdivided NOM into different components with a combination of these two methods; and (3) some results for observing irreversible fouling were obtained based on bench-scale/short-time experiments, which were not so persuasive and could not truly represent the pilot-/full-scale and long-time operation.

The objective of this study was, therefore, to fractionate NOM by resin adsorption in conjunction with HPSEC and identify critical MW range and hydrophobicity of NOM that was responsible for HIF during long-time operating of a pilot-scale microfiltration (MF) process for surface water treatment. NOM of water samples were fractionated into different hydrophilic/hydrophobic fractions by resin adsorption, and each fraction was further subdivided into different MW components via HPSEC coupled with peak-fitting. The results were expected to give practical suggestions for selecting suitable strategy to predict and control HIF during the MF process.

2. Materials and methods

2.1. MF operation and chemical cleaning

The pilot experiments were conducted in Chongshan Water Plant located in Wuxi City. The raw water sample was collected from Taihu Lake, with the elementary parameters for source water qualities listed in Table S1.

The raw water samples were filtrated through 300 μm screens to remove large suspended matters before entering the pre-treatment tank where pre-treatment was performed by dosing polyaluminium chloride (PACl), powdered activated carbon (PAC) and potassium permanganate ($KMnO_4$) there, allowing mixing and sedimentation by slope plate. The dosing of pre-treatments is illustrated in Table S2. Polyvinylidene fluoride hollow fiber MF membrane (pore size 0.1 μm; filtration area 20 m^2; Dow Corporation) was used in this study to filtrate the pre-treated water. The submerged membrane module was operated in a dead-end, constant-flow filtration mode with a fixed permeation flux of 50 $L/m^2/h$ (LMH). Each filtration cycle lasted 30 min, including 2 min of filling water, 25 min of filtrating at 50 LMH, 2 min of hydraulically backwashing by air scrubbing in a flow rate of 1 m^3/h and water washing in a flow rate of 2.25 m^3/h, 1 min of water draining.

When the TMP value reached the limit of 0.07 MPa, chemical cleaning was conducted to remove the irreversible foulants. There were totally 10 chemical cycles in the name of I–X. Alkaline agents (sodium hypochlorite, 0.2 wt% and sodium hydroxide, 0.2 wt%) and acidic agent (hydrochloric acid, 0.4 wt%) were prepared to successively clean fouled membranes.

2.2. Hydraulically irreversible fouling index

Fouling index was adopted for fouling evaluation. As expounded in relevant literature [19,20], hydraulically irreversible fouling index (HIFI) can be determined for multiple hydraulic cleaning cycles between two chemical cleanings. Briefly, HIFI could be calculated by using Eq. (1):

$$\frac{1}{J_s'} = 1 + \text{HIFI} \times V_s \tag{1}$$

where J_s' is the normalized specific flux defined as $J_s' = J/J_0$; J_0 is the initial flux for filtering DI water (LMH/bar); J is the specific flux for filtering feed water sample with hydraulic cleaning (LMH/bar); HIFI is the hydraulically irreversible fouling index (m^2/L); V_s is the specific volume of the permeate (L/m^2).

2.3. Fractionation and HPSEC with peak-fitting

NOM of water samples were isolated into SHA, WHA, CHA and NEU by adsorbent resins (Supelite DAX-8, Amberlite XAD-4 and Amberlite IRA-958) according to the previous method [21].

MW distribution of dissolved organic carbon (DOC) was characterized by HPSEC system (Waters e2695, USA; UV254 detector, Waters 2489, USA; total organic carbon (TOC) analyzer, Sievers 900 Turbo, USA). The column consisted of methyl acrylate copolymer (TSKgel G3000PWXL) with a size of 0.78 cm × 30 cm. The pre-column was a TSKgel guard column PWXL (0.6 cm× 4.0 cm). Polystyrene sulfonate (PSS) materials with MWs of 3.6 kDa, 4.3 kDa, 6.8 kDa, 15.4 kDa and 31 kDa were used as a standard MW substance. As the PSS materials did not contain a LMW, polyethylene glycols (PEGs) with MWs of 0.21 and 1.4 kDa were used as the standard LMW substances. The whole detection took 35 min in total. Therefore, the MW distribution of the water samples could be calculated according to the emerging time of their peaks. The MW distribution of the raw water samples is presented in Fig. 1. Three distinct peaks (in terms of the TOC

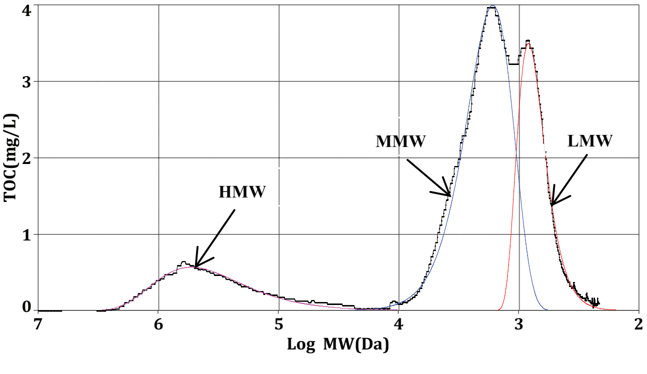

Fig. 1. Determination of source water by HPSEC–TOC chromatogram with peak-fitting.

response) were observed: high MW (HMW), medium MW (MMW) and LMW with MW range of 10^4–10^7 kDa, 1–10 kDa and <1 kDa, respectively. LMW and MMW showed remarkable TOC response, manifesting their domination in the raw water composition. In contrast, a weak TOC response of HMW suggested its small content in the raw water sample. It was reported that LMW, MMW and HMW were related to LMW acids and neutrals, HS matters including fulvic-/humic-acid-like substances, and BP such as PN and PS, respectively [10,11,16,22]. A peak-fitting software (Version 4.12, Systat Software Inc., USA) was used in chromatogram analysis to distinguish the overlapping peaks and to integrate the peak areas according to the method explained by Lai et al. [11]. Based on these data, the MW distribution in the raw water sample was separated into three peaks by peak-fitting.

2.4. Analytical methods

Turbidity was measured using a Turbidimeter (2100N, Hach, USA). Chemical oxygen demand (COD_{Mn}) was analyzed according to the Chinese State Environmental Protection Agency Standard Methods. UV_{254} of the water samples were determined by a UV-Vis spectrophotometer (Hach DR5000, USA). DOC was measured by a TOC analyzer (Shimadzu TOC-L, Japan). The PS were measured based on the phenol-sulfuric acid method with glucose as the standard matter [23]. The lowest limit of the detection is 1.0 mg/L. Principal component analysis (PCA) and Pearson correlation analysis were adopted via the XLSTAT2015 software to expound the relationship of HIFI in association with these subdivided components.

3. Results and discussion

3.1. MF performance and HIFI

The changes of the TMP value during MF of surface water are depicted in Fig. 2. As a constant membrane flux was maintained, TMP increased with the extension of the operating time. When the TMP reached the limiting value of 0.07 MPa, chemical cleaning was conducted to remove the irreversible foulants. The HIFIs were determined using the operational performance data from the 10 successive filtration cycles. Table 1 presents the HIFI results for this study. As the cycle repeated, the HIFI value changed in an irregular manner, probably related to the pre-treatments and the characteristics of the feed water sample.

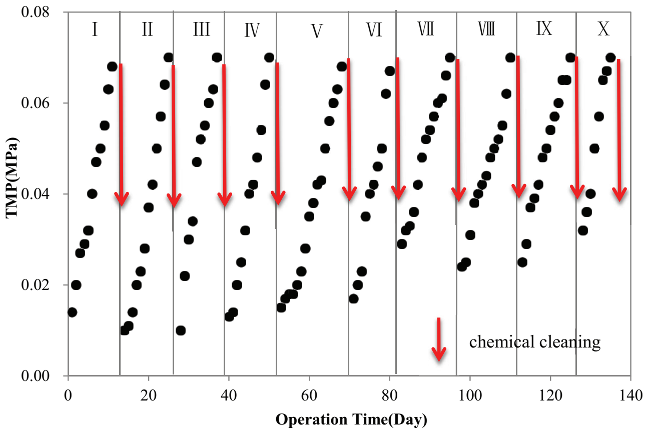

Fig. 2. TMP changes during MF of surface water with chemical cleaning cycles from I to X.

Pre-treatment would reduce membrane fouling due to the removal of NOM, thus resulting in prolonged membrane life span and induced long-term performance. Different pre-treatment techniques such as coagulation [24,25], oxidation [26–28] and adsorption [2,29–31] before LPM filtration have been widely used to mitigate membrane fouling for drinking water treatment. In this study, hybrid pre-treatment reagents, i.e., PACl, PAC and $KMnO_4$, were dosed into reaction tank, with their respective effect to remove NOM listed in Table 1. The coagulation technology is the traditional water treatment technology, which has been widely used in the water treatment field because of its low cost and easy to operate [32]. The TOC removal efficiency was increasing with the addition of PACl from cycle I to cycle IV. However, HIFI was not decreasing with the increasing dosage of PACl, indicating that the addition of PACl coagulation could not positively mitigate irreversible fouling. Nevertheless, the HIFI was obviously decreased when the oxidizing agent of $KMnO_4$ was added from cycle V. That is, $KMnO_4$ pre-oxidation had a better effect for the control of irreversible fouling. Through oxidation, macromolecular organics could be oxidized into small molecules and small molecules into inorganic matters [2]. Compared with those without $KMnO_4$ addition, pre-treatments with $KMnO_4$ could increase the removal efficiency of NOM and radically reduce membrane fouling from cycle V to cycle X (except the cycle VI). The combined technology of PAC–LPM is considered as the "crystal technology" in the membrane water treatment field [32]. In this study, when PACl and $KMnO_4$ maintained constant dosages of 40 and 1 mg/L, respectively, the TOC removal efficiency was increasing from 56.4% to 65.2% as the dosing of PAC increased from 10 mg/L(cycle VI) to 20 mg/L (cycle V), yet the TOC removal efficiency was not increasing too much when the dosing was extended to 30 mg/L (cycle VIII) and 40 mg/L (cycle X). Nevertheless, PAC had a positive effect for alleviating irreversible fouling since the HIFI was decreased from 0.326 to

Table 1
Removal efficiency of pre-treatments and HIFI values of MF process for surface water treatment

Cycle	TOC removal efficiency by pre-treatments, %	HIFI	R^2
I	53.2	0.294	0.992
II	59.8	0.578	0.979
III	60.8	0.633	0.967
IV	61.3	0.450	0.988
V	65.2	0.250	0.971
VI	56.4	0.326	0.975
VII	64.7	0.121	0.985
VIII	63.2	0.143	0.968
IX	64.5	0.122	0.988
X	63.8	0.187	0.974

0.143 (cycle VIII) and 0.187 (cycle X). This result is unsurprising, because TOC content is only a measurement of the total amount of DOM and thus cannot provide any quantitative or qualitative information concerning its fractions. In our previous research, we found that PAC could mitigate membrane fouling by reducing the foulants, especially the "LMW fractions", approach to the membrane surface and pores [33]. Since the pre-treatments were not the main topic of this study, we simply illustrated its performance for NOM removal and HIFI control.

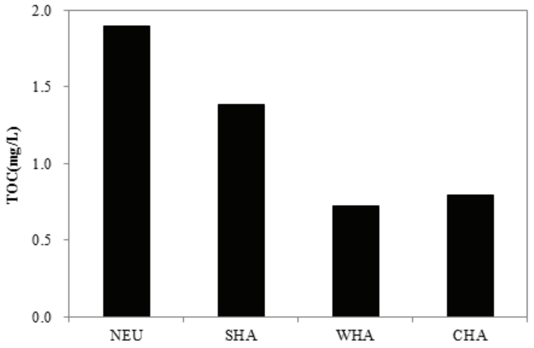

Fig. 3. Fractionation of source water by adsorbent resins.

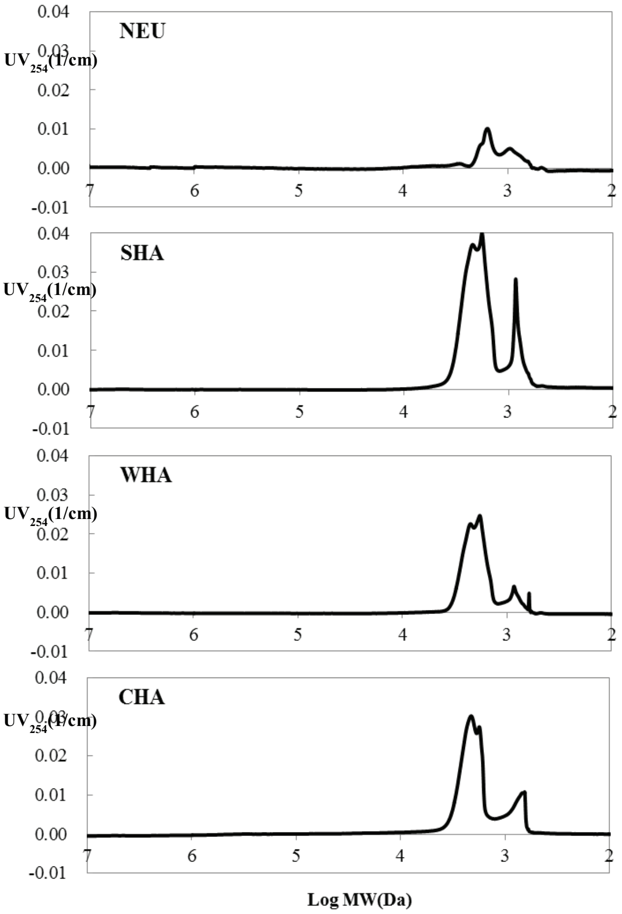

Fig. 4. HPSEC–UV_{254} chromatogram of isolated fractions.

3.2. Subdivision of NOM

Source water sample was fractionated by resin adsorption, and the result is shown in Fig. 3, from which large quantities of NEU and SHA fractions could be observed, while the WHA and CHA fractions accounted for a small portion.

Fractionation in conjunction with HPSEC was applied to subdivide each fraction of the NOM into LMW, HMW and HMW components, as shown in Figs. 4 and 5.

- HMW: This component was not responding in the UV_{254} (Fig. 4) but showed weak response in the TOC (Fig. 5). This fraction was related to BP such as colloid, PS, and PN according to the previous researches [11,22]. There were only two peaks emerging in the HPSEC–TOC chromatogram, which was defined as NEU–HMW and SHA–HMW, respectively.

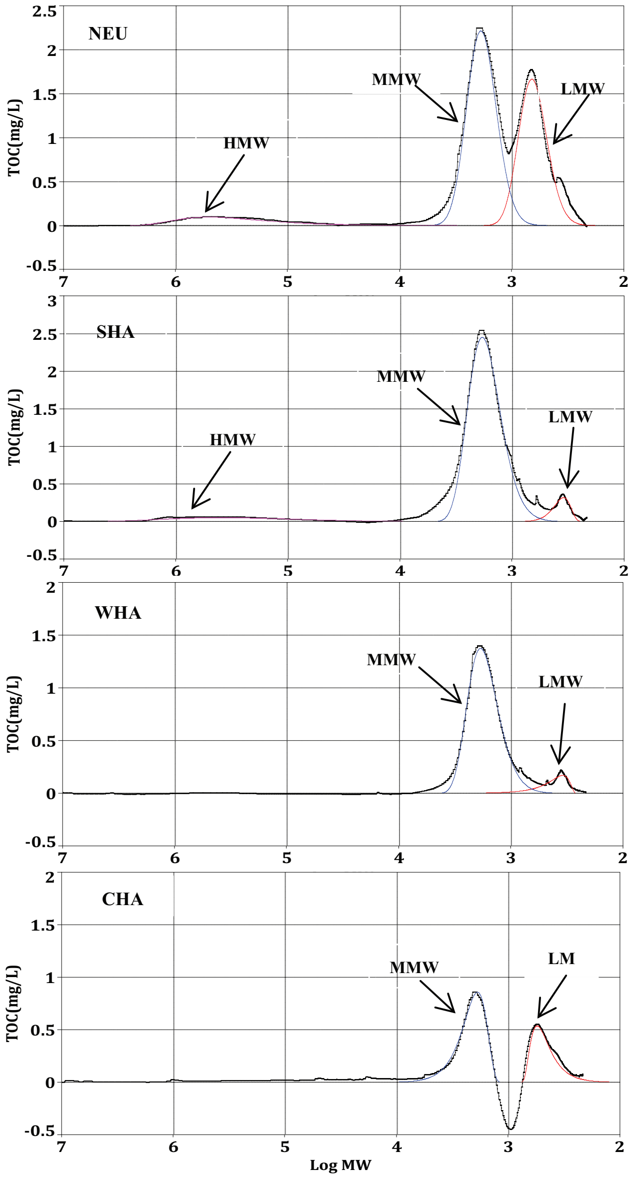

Fig. 5. Subdivision of isolated fractions by HPSEC–TOC chromatogram with peak-fitting.

- MMW: The MMW namely SHA–MMW, WHA–MMW and CHA–MMW exhibited strong absorption of both TOC and UV_{254}, indicating that aromatic compounds (unsaturated carbon) such as humic acid, fulvic acid and tannin acid, were the main components [21,22]. In contrast, the components of NEU–MMW had a strong TOC response but a very weak UV_{254} response, probably because NEU contained too much PS-like organics with no UV_{254} absorbance. We also determined the content of PS in each fraction and found that NEU contained more than half of the total PS substances (Fig. S1).
- LMW: This component was associated with LMW humics, LMW acids and LMW neutrals based on relevant reports [11,22,33]. In HPSEC–TOC chromatogram, the hydrophobic fractions namely SHA–LMW and WHA–LMW exhibited a weaker TOC signal than hydrophilic fractions, which was assigned as NEU–LMW and CHA–LMW. That is to say, LMW was mainly made up of hydrophilic fractions, especially NEU–LMW (Fig. 5). This fraction was associated with acidic PS, carboxylic acids, amino acids, carboxyl, ester and amide carbon, which were identified through ^{13}C nuclear magnetic resonance (^{13}C NMR) in the study of Wong et al. [8].

3.3. Correlation of HIFI with NOM components

An attempt was made to evaluate the HIFI in relation to water components. First, the content of the subdivided fractions in feed water sample were calculated (Table S3), and then PCA and Pearson correlation analysis were employed to match the subdivided components with HIFI, as shown in Fig. 6 and Table 2.

Humic- and fulvic-acid-like substances have long been believed to be one of the major fouling components in membrane performance, and many efforts have been made to assess its fouling behavior [7,34–36]. In this study, significant correlations were not observed between HS (MW > 1 kDa) in the feed water sample and HIF for the MF membrane. The values of R^2 were 0.118 (p value = 0.331) and 0.296 (p value = 0.104) for SHA–MMW vs. HIFI, and WHA–MMW vs. HIFI, respectively. These results implied that HS (MW > 1 kDa) were not critical in the evolution of HIF, but the SHA–LMW and WHA–LMW components clustered together with the HIFI instead (Fig. 6) for remarkable positive correlations were found between HIFI and SHA–LMW (R^2 = 0.927, p value < 0.0001), and HIFI and WHA–LMW (R^2 = 0.899, p value < 0.0001). SHA and WHA were associated with aliphatic species, aromatic compounds, unsaturated carbon, phenolic, etc. [8]. This result revealed that hydrophobic LMW components (SHA–LMW and WHA–LMW) had a high fouling potential. Since the size of these molecules were considerably smaller than the nominal pore size of the MF membrane (0.1 µm), hydrophobic interaction [36] and electrostatic interaction [37] were the possible explanations for the linking between hydrophobic small NOM and membrane fouling.

Correlation between the hydrophilic component of NOM and HIF was investigated. Unexpectedly, NEU–HMW was discriminated by PAC and located at the opposite direction, highlighting the lowest fouling potential; furthermore, poor correlation between NWU–HMW and HIFI was observed (R^2 = 0.196, p value = 0.199), indicating the insignificant contribution of the NEU–HMW of NOM to the evolution of HIF. These results differed from previous studies where macromolecules BP fractions (i.e., PS and PN) were mainly responsible for irreversible membrane fouling [17]. In addition, HIFI has very weak correlation to hydrophilic small MW, i.e., NEU–LMW (R^2 = 0.005) and CHA–LMW (R^2 = 0.150), respectively. In previous studies, some scholars found that the characteristics rather than the amount of BP were more important for irreversible fouling [5]; the quantity of PS could not explain the variations in the fouling but the quality of PS mattered [38]. In other words, it is the nature rather than the amount of the BP that induced HIF. The size of hydrophilic small MW (NEU–LMW and CHA–LMW) was <1 kDa, and the hydrodynamic size of organic molecules with an MW of 1 kDa was approximately 1 nm according to previous method [39,40]; thus, these organic molecules could easily pass through the membrane pores during MF process as their size was much smaller than the pore size of the membrane (0.1 µm). As to the hydrophilic macro MW (NEU–HMW), the peak value of the MW was up to 1,000 kDa (Fig. 5), which may be retained by MF membrane and washed out by hydraulic backwash.

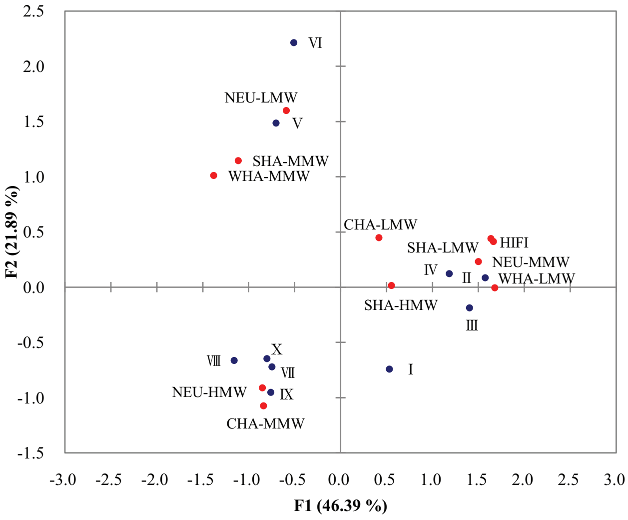

Fig. 6. PCA of HIFI with subdivided fractions in feed water.

Table 2
Pearson correlation results between HIFI and subdivided fraction

Variable	R^2	p
NEU–LMW	0.005	0.848
NEU–MMW	**0.787**	**0.001**
NEU–HMW	0.196	0.199
SHA–LMW	**0.927**	**<0.0001**
SHA–MMW	0.118	0.331
SHA–HMW	0.029	0.641
WHA–LMW	**0.899**	**<0.0001**
WHA–MMW	0.296	0.104
CHA–LMW	0.150	0.269
CHA–MMW	0.213	0.180

Note: Values in bold with a significance level alpha < 0.05.

In contrast, a strong correlation was observed between HIFI and NEU–MMW ($R^2 = 0.787$, p value = 0.001), likely due to the fact that the adsorption of small molecules, i.e., SHA–LMW and WHA–LMW, onto pore channels minified the pore size, which facilitated NEU–MMW to plug the pores (i.e., irreversible fouling), or the adsorbed small MW substances could work as the "glue" to capture the NEU–MMW on/in membranes conditioned by the hydrophobic components [14]. In addition, very poor correlation existed between HIFI and CHA–MMW ($R^2 = 0.213$, p value = 0.180). This could be ascribed to the small amount of PS in CHA led to less fouling than NEU (Fig. S2). Based on the above analysis, the reasons for the HIF are believed to be the narrowing of the membrane pores by SHA–LMW and WHA–LMW components and the blocking of the narrowed pores by NEU–MMW components. It must be pointed out that these results were taken as "convincing", considering that the investigation was performed from summer (July) to winter (December) and that significant seasonal changes in water qualities occurred. Given that SHA–LMW, WHA–LMW and NEU–MMW were expected to be the main membrane foulants for the water of this source, it was logical to speculate that the concentrations of these components should be high in chemical cleaning solutions. In order to further testify this conclusion, irreversible foulants were extracted via acidic and alkaline cleaning analysis. Fractionation of these foulants showed that NEU and SHA were predominant irrespective of the different cleaning agents (Fig. S2). HPSEC determination of the foulants revealed that LMW and MMW components were prevalently involved in the irreversible foulants (Fig. S3). The results from the fractionation, in conjunction with HPSEC, further confirmed the conclusion obtained above.

It was reported that inorganic particles could aggravate membrane fouling [41]. An attempt was therefore made to evaluate the fouling potential in relation to inorganic particles, and the result was shown in Fig. S4. No obvious correlation was observed between HIFI and turbidity. This was expected since inorganic particles were mainly responsible for reversible fouling rather than irreversible fouling [1,42,43].

4. Conclusion

In this study, a pilot-scale MF process was performed for surface water treatment. Source water sample was subdivided into different components via resin adsorption and HPSEC with peak-fitting. PCA and Pearson correlation analysis were employed to correlate the subdivided components with HIFI. It was found that NEU–MMW, SHA–LMW and SHA–LMW in the feed water sample were largely responsible for HIF. The results were useful and meaningful because on the one hand, the identification of foulants could be used as a useful indicator for predicting HIF; on the other hand, fouling control strategy should be targeted at removing these foulants.

Acknowledgments

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Supporting information

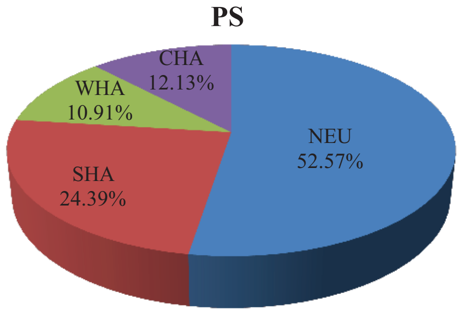

Fig. S1. Proportion of PS of isolated fraction in source water.

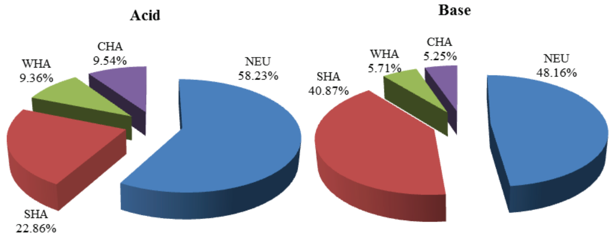

Fig. S2. Fraction percentage of extracted foulants via chemical cleaning.

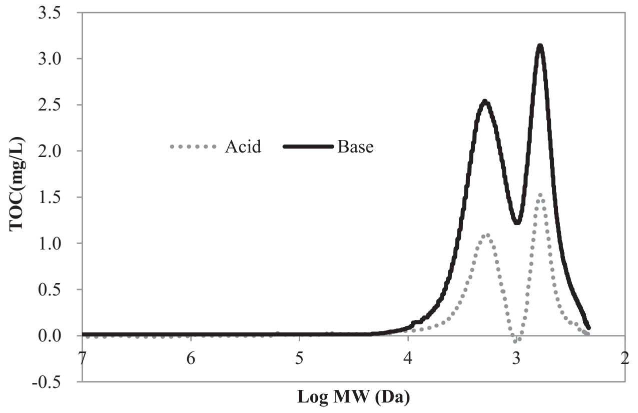

Fig. S3. HPSEC–TOC chromatogram of extracted foulants via chemical cleaning.

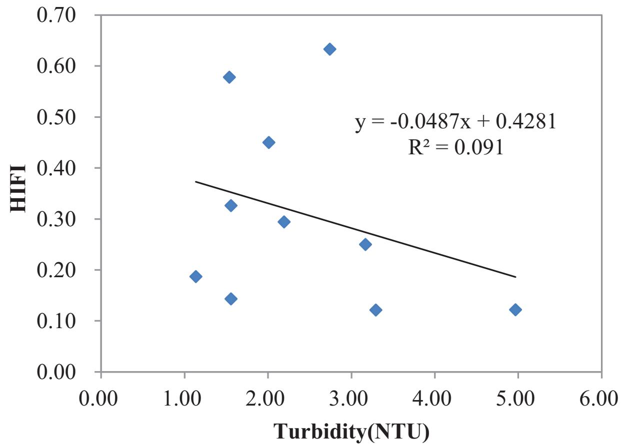

Fig. S4. HIFI vs. turbidity.

Table S1
Source water qualities

Parameter	Value
Temperature (°C)	5.6–32.4
pH	7.19–8.83
Turbidity (NTU)	16.6–174
COD_{Mn} (mg/L)	5.41–14.2
UV_{254} (cm^{-1})	0.065–0.106
TOC (mg/L)	3.64–7.73

Table S2
Dosing of pre-treatments prior to MF

Cycle	Dosing of pre-treatments: (A) PACl + (B) PAC + (C) $KMnO_4$
I	A 20 mg/L + B 20 mg/L
II	A 30 mg/L + B 20 mg/L
III	A 40 mg/L + B 20 mg/L
IV	A 50 mg/L + B 20 mg/L
V	A 40 mg/L + B 20 mg/L + C 1 mg/L
VI	A 40 mg/L + B 10 mg/L + C 1 mg/L
VII	A 30 mg/L + B 30 mg/L + C 1 mg/L
VIII	A 40 mg/L + B 30 mg/L + C 1 mg/L
IX	A 50 mg/L + B 40 mg/L + C 1 mg/L
X	A 40 mg/L + B 40 mg/L + C 1 mg/L

Table S3
Contents of subdivided fractions in feed water

Component	I	II	III	IV	V	VI	VII	VIII	IX	X
NEU–LMW	0.04	0.12	0.07	0.13	0.31	0.31	0.09	0.16	0.07	0.10
NEU–MMW	0.68	0.99	0.84	0.83	0.63	0.68	0.47	0.62	0.61	0.71
NEU–HMW	0.07	0.06	0.07	0.03	0.02	0.07	0.08	0.15	0.08	0.12
SHA–LMW	0.43	0.67	0.83	0.64	0.15	0.42	0.02	0.03	0.09	0.01
SHA–MMW	0.39	0.24	0.44	0.24	0.90	1.10	0.31	0.75	0.51	0.67
SHA–HMW	0.11	0.03	0.04	0.07	0.07	0.02	0.00	0.01	0.03	0.05
WHA–LMW	0.17	0.26	0.38	0.22	0.05	0.07	0.04	0.03	0.02	0.02
WHA–MMW	0.15	0.06	0.19	0.15	0.53	0.58	0.31	0.35	0.33	0.40
CHA–LMW	0.27	0.55	0.70	0.26	0.36	0.61	0.66	0.25	0.36	0.33
CHA–MMW	0.25	0.14	0.45	0.14	0.34	0.09	0.39	0.47	0.50	0.45