Identification of irreversible UF membrane foulants by fluorescence excitation–emission matrix coupled with parallel factor analysis

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ABSTRACT

In this work, a total of nine water samples were taken from different water sources at different seasons for UF membrane fouling experiments, with the purpose to find out if there were common foulant components responsible for the irreversible membrane fouling. It was found that the increase in DOC and UV_{254} in raw water caused a corresponding increase in the developing rate of irreversible membrane fouling, demonstrating NOM as the major membrane foulants. Using the fluorescence excitation–emission matrices coupled with parallel factor analysis, four fluorescence components in NOM were identified, i.e. microbial-derived and terrestrial-derived humic-like substances (C1 and C3), tryptophan-like and tyrosine-like proteins (C2 and C4). The C2 exhibited a strong correlation with the irreversible fouling of UF membrane, while no correlation between C4 and irreversible membrane fouling was observed. The humic-like substances were shown to be weakly correlated to the irreversible membrane fouling. By multivariate linear regression, synergistic fouling effect was identified between the C2 and C3, but a comparison of their coefficients revealed that C2 made a considerably larger contribution to the irreversible membrane fouling than C3. The results may provide insights into the development of appropriate fouling control strategies for sustainable UF operation.

Keywords: Ultrafiltration; Irreversible membrane fouling; Natural organic matter; Fluorescence excitation-emission matrix; Parallel factor analysis

1. Introduction

Over the past few decades, ultrafiltration (UF) membrane technology has become increasingly popular as an alternative or supplement to conventional drinking water treatment, due to more stringent water quality regulations and decreased costs of membrane materials. UF technology has exhibited many advantages over conventional water treatment processes, including excellent product water quality, less chemical dosing, reduced footprint requirements, and the reliability associated with the efficacy in removing pathogenic micro-organisms such as *Giardia*, *Cryptosporidium*, viruses, etc. [1–5].

However, membrane fouling, especially the irreversible fouling, still remains as a critical challenge to overcome in the practical applications of UF

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technology [6–9]. The irreversible membrane fouling results in severe decline in UF performance eventually leading to the failure of normal UF operation, and thus, chemical cleaning procedures with the use of acids, alkalis, and oxidants have to be applied to restore the membrane permeability. However, the chemical cleaning with the rigorous chemicals can lead to the shortage of membrane lifetime, increase in the operation costs, and the difficulties in post treatment of the used chemicals [10–12].

For better control of the membrane fouling in UF process, it is important to understand which components in water are the major components for the formation of membrane fouling. In drinking water treatment, natural organic matter (NOM) has been considered as the major membrane foulants [13–15]. However, the NOM is composed of various organic compounds such as humic acids, fulvic acids, polysaccharides, and proteins with different molecular size and chemical functional groups [16,17]. To exactly identify the subfractions of NOM that are responsible for the membrane fouling, several advanced characterization techniques have been employed. For example, using the high-performance liquid chromatography with online organic carbon detection (LC-OCD), the biopolymer fraction in NOM has shown to be strongly correlated with both the reversible and irreversible membrane fouling [18–22]. However, the biopolymers in NOM are still comprised several hydrophilic macromolecules such as polysaccharides and proteins [16,19].

Recently, fluorescence excitation–emission matrix (EEM) spectroscopy has emerged as another powerful technique for precisely distinguishing the different subfractions of NOM. By EEM, the components such as humic-like substances, fulvic-like substances, and protein-like substances can be differentiated with high sensitivity due to their respective fluorescence properties in ultraviolet and visible range. Principal components analysis and parallel factor analysis (PARAFAC) have also been developed for quantifying the relative concentration of each component present in water.

The EEM technique has been widely used in the identification of major membrane foulants during UF processes [23–28]. However, inconsistent conclusions have been drawn by different researchers. Peldszus et al. [27] found a strong correlation between protein-like substances and the irreversible fouling of UF membrane, while the humic-like substances cannot be correlated with the irreversible fouling. This observation had been consolidated by Yamamura et al. [16] who suggested the hydrophobic NOM did not cause any irreversible membrane fouling. On the contrary, the studies by Peiris et al. [29,30] indicated that both humic-like and protein-like substances made contributions to the irreversible membrane fouling. Shang et al. [31] also found that both humic substances and the biopolymers led to irreversible fouling on ceramic MF/UF membranes.

To better elucidate the contribution of different NOM fractions to irreversible membrane fouling during UF process, a total of nine water samples were collected from different water sources at different seasons in this work. Then, UF experiments were carried out in the presence of periodical hydraulic backwashing to determine the potential of irreversible fouling of different water samples. The fluorescence EEM coupled with PARAFAC analysis was employed to characterize the major NOM components in different waters, and their correlations with the irreversible fouling of UF membrane were systematically discussed.

2. Materials and methods

2.1. Raw water qualities

In this work, nine water samples were collected from different water sources and in different seasons for identification of major components causing the irreversible fouling on UF membrane, using the fluorescence EEM coupled with PARFAC analysis. The water qualities of the raw waters are given in Table 1. The turbidity in the waters was measured by a turbidimeter (TURBO550, WTW, Germany). The DOC (pre-filtered through 0.45 mm membrane) was determined by a TOC analyzer (TOC-VCPH, Shimadzu, Japan). The UV absorbance at 254 nm (UV_{254}) was determined using a spectrometer (T6, PUXI, China). The conductivity was measured with a conductivity meter (DDSJ-308A, LEICI, China). The zeta potential was determined by a zeta potential analyzer (ZETASIZER, Malven, England).

Among these samples, No. a and c were taken from Lake Longhupao (the water source for Daqing city), No. e was taken from the Zhushuntun section of Songhua River, while the others were taken from North 14th Street section of Songhua River in Harbin. All the water samples were stored under 4℃ before use, and the UF experiments with these water samples would be finished in 72 h since the samples were transported to the laboratory.

2.2. UF experiments

All UF experiments were performed on a bench scale, submerged membrane filtration setup. Tiny membrane modules were prepared in the laboratory

Table 1
Water qualities of the raw waters

No.	Date	pH	Turbidity (NTU)	Conductivity (μS/cm)	Zeta potential (mV)	UV$_{254}$ (cm^{-1})	DOC (mg/L)	SUVA (mg/L m)
a	7 June 2014	8.17	20.1	672	−27	0.101	10.24	0.99
b	10 July 2014	7.96	51.7	173	−27.5	0.132	15.31	0.86
c	10 August 2014	8.03	43.0	680	−24.22	0.113	13.09	0.86
d	29 September 2014	8.18	43.1	443	−29.5	0.137	22.46	0.61
e	20 November 2014	8.1	18.2	164.7	−30.04	0.079	8.20	0.96
f	14 December 2014	7.96	15.8	148.3	−26.4	0.095	8.87	1.07
g	29 December 2014	7.9	16.9	275	−23.86	0.103	10.72	0.96
h	10 January 2015	8.06	15.7	441	−32.8	0.112	10.72	1.05
i	22 April 2015	7.92	26.3	170	−22.5	0.136	17.98	0.76

using the commercially available PVDF hollow-fiber UF membranes with a nominal pore size of 0.01 μm (Litree, China). Three membrane fibers with a length of 25 cm were assembled into the modules, resulting in an effective membrane area of 34.15 cm². A new membrane module was used in each of the UF experiments. The module was immersed in a cylindrical filtration tank and operated in outside-in mode. The multi-cycle UF experiments with the raw waters were carried out under a constant permeation flux of 45 L/m² h. Periodic backwashing (59 min of filtration followed by 1 min of backwashing at 90 L/m² h with the permeate water) was performed automatically in the experiments. During the experiments, trans-membrane pressure (TMP) was continuously measured and recorded using an online pressure transducer. Before use, the membrane was thoroughly cleaned with deionized water to remove the organic residuals remained on the membrane. All the UF experiments were carried out under constant temperature of ~20℃ in the laboratory.

2.3. Determination of irreversible membrane fouling

The membrane fouling behavior can be described by the resistance-in-serial model, as shown below:

$$R_t = R_m + R_f = R_m + R_{rev} + R_{irr} = \frac{TMP}{\eta J} \qquad (1)$$

where R_t is the total filtration resistance (m^{-1}); R_m is the intrinsic membrane resistance (m^{-1}); R_f is the membrane fouling resistance (m^{-1}); R_{rev} is the reversible fouling resistance; R_{irr} is the irreversible fouling resistance (m^{-1}); TMP is the trans-membrane pressure (Pa); η is the dynamic viscosity of water (Pa s); J is the membrane flux (m^3/m^2 s).

In this work, hydraulic backwashing was periodically performed for the UF membrane during the multi-cycle filtration experiments, and it was assumed that only the irreversible fouling still remained on the membrane after the backwashing. Thus, the irreversible fouling resistance at the end of each UF experiment was calculated by:

$$R_{irr} = \frac{TMP_{final} - TMP_{initial}}{\eta J} \qquad (2)$$

where TMP_{final} is the TMP at the end of filtration experiments after hydraulic backwashing; $TMP_{initial}$ is the TMP at the initial of the filtration experiments (i.e. the TMP caused by the intrinsic membrane resistance).

It should be noted that although most of the UF experiments were performed for at least 24 filtration cycles (i.e. 24 h), some of which had to be terminated earlier due to the failure of the experimental setup. Thus, to make the irreversible fouling resistances with different raw waters comparable to each other, the filtration time-normalized irreversible fouling resistance was used, which can be taken as the developing rate of R_{irr} (DR – R_{irr}, m^{-1} min^{-1}) during the UF process.

2.4. Fluorescence EEM measurements

Fluorescence EEM was measured in a 1 cm cuvette using a fluorescence spectrophotometer (F7000, Hitachi, Japan) at the photomultiplier tube voltage of 700 V. To avoid the Raman scatter by colloids and particles in the water, the water samples were pre-filtered with 0.45 μm membranes. However, it should be noted that some fouling components attached to colloids/particles may be removed during the pre-filtration, which was not further considered in this work due to that the same pre-filtration procedure was

applied to all the water samples. The EEMs were obtained by scanning over an excitation wavelength of 220–450 nm at a step of 5 nm and an emission wavelength of 250–550 nm at a step of 1 nm. Both the excitation and emission slit widths were set at 5 nm and the scanning speed was set at 2,400 nm/min. To minimize the inner filter effect and the Raman scatter effect, dilution of the water samples and calibration of the data with an EEM of Milli-Q water were conducted for all the measurements, as reported in previous studies [24,28].

The PARAFAC modeling was performed following the procedures described by Stedmon and Bro [32]. In brief, a data-set of 81 fluorescence EEMs were modeled with the DOMFluor Toolbox in Matlab®. A series of PARAFAC models consisting of 3–7 components were generated. The validation judgment for the models was conducted using the residual analysis, spectral properties examination, split-half analysis and random initialization, and the number of fluorescence components was identified accordingly. The relative concentrations of the fluorescent components were indicated by their score values generated from the PARAFAC model, while the excitation and emission spectral characteristics were indicated by their excitation and emission loadings [33].

The 81 fluorescence EEMs include: 9 raw waters as the feed for UF membrane, with 9 retentates and 9 permeates, respectively; 12 raw waters that pretreated with different coagulants (polyaluminum chloride and ferric trichloride, at the dosages of 2, 4, 6, 8, 10, and 12 mg/L, respectively), with the corresponding 12 retentates and 12 permeates, respectively; 6 raw waters that pretreated with powered activated carbon (at 5, 10, 20, 30, 40, and 50 mg/L, respectively), with the corresponding 6 retentates and 6 permeates, respectively. It is noted that the coagulated and adsorbed water samples were only used to constitute a sufficient database of the fluorescence EEMs for subsequent parallel factor analysis, which was not included in the further discussion in the work.

3. Results and discussion

3.1. Water qualities of the raw waters

Due to that the raw waters were collected from different water sources, a significant variation in the water qualities was observed. Even for the same water source of Songhua River, a substantial seasonal change in the water qualities was also witnessed (Table 1). For example, the turbidity, DOC, UV_{254}, and SUVA were found to vary in a wide range of 15.7–51.7 NTU, 8.20–22.46 mg/L, 0.079–0.137 cm^{-1}, and 0.61–1.07 mg/L m,

respectively. The NOM in water has for a long time been identified as the major membrane foulants on UF membrane, while the particulate and colloidal matters can lead to a synergistic fouling effect together with NOM during the UF process [34,35]. Therefore, by considering the significant variation of water qualities, it is wondered if there exist the common irreversible fouling-causing components in different water samples, which might be especially important for developing suitable fouling control strategies for sustainable UF operation.

3.2. NOM removal by UF membrane

Multi-cycle UF experiments were carried out with the different raw waters for identification of the major components causing irreversible fouling on the UF membrane. The TMP increase patterns are shown in Fig. 1. As NOM had been suggested to play an exclusively important role in UF membrane fouling, the effect of surrogate NOM parameters (DOC and UV_{254}) on membrane fouling was first analyzed. As shown in Fig. 2, the UF membrane exhibited removal efficiencies ranged from 8.2 to 21.3% for DOC and from 15.8 to 33.8% for UV_{254}, respectively. With the increase in concentration in raw water, a corresponding increase in the removal efficiency was also observed. Especially for DOC, the R^2 of 0.78 ($p = 9.82 \times 10^{-4}$) for the correlation was obtained. It should be noted that only the NOM that was retained by the membrane during UF process can cause the membrane fouling. Thus, the observation suggested that higher the NOM concentration in raw water, more severe the membrane fouling would be. This speculation was confirmed by the remarkable correlations between the surrogate NOM parameters and the developing rate of R_{irr} as shown in Fig. 3, which demonstrated that an increase in DOC and UV_{254} concentrations in raw water resulted in a nearly proportional increase in the developing rate of R_{irr}.

However, although the surrogate NOM parameters of DOC and UV_{254} were strongly correlated with the irreversible membrane fouling, it would not be possible to remove all the NOM from water for effective membrane fouling control. Therefore, it might be highly expected to find some specific NOM components that are responsible for the irreversible fouling on UF membrane. In the following, the fluorescence EEM coupled with PARAFAC analysis was employed for this purpose.

3.3. Fluorescence EEM measurements and PARAFAC modeling

The fluorescence EEM spectra for the nine water samples taken from different water sources at differ-
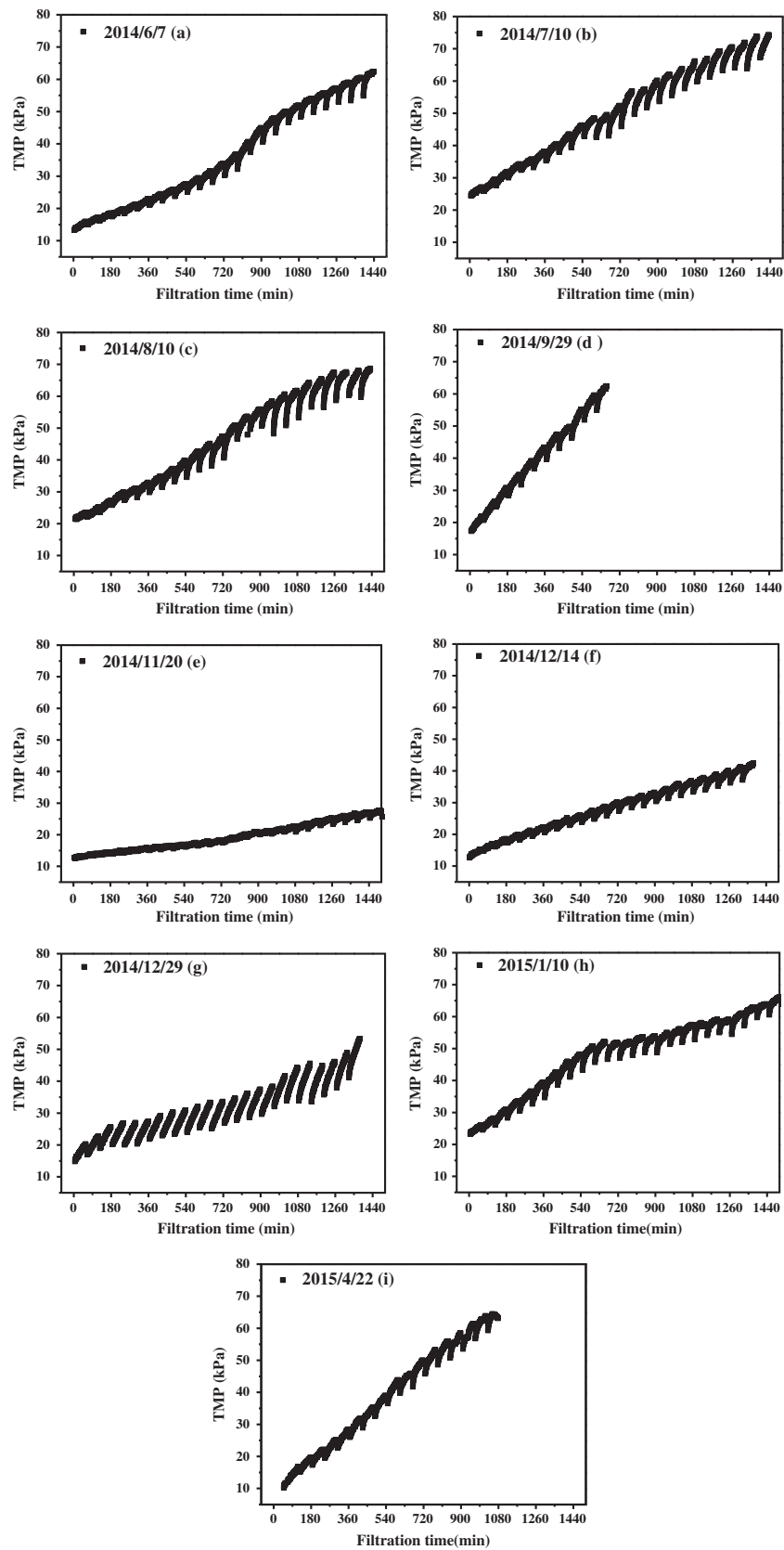
Fig. 1. TMP increase patterns during UF of the nine water samples.
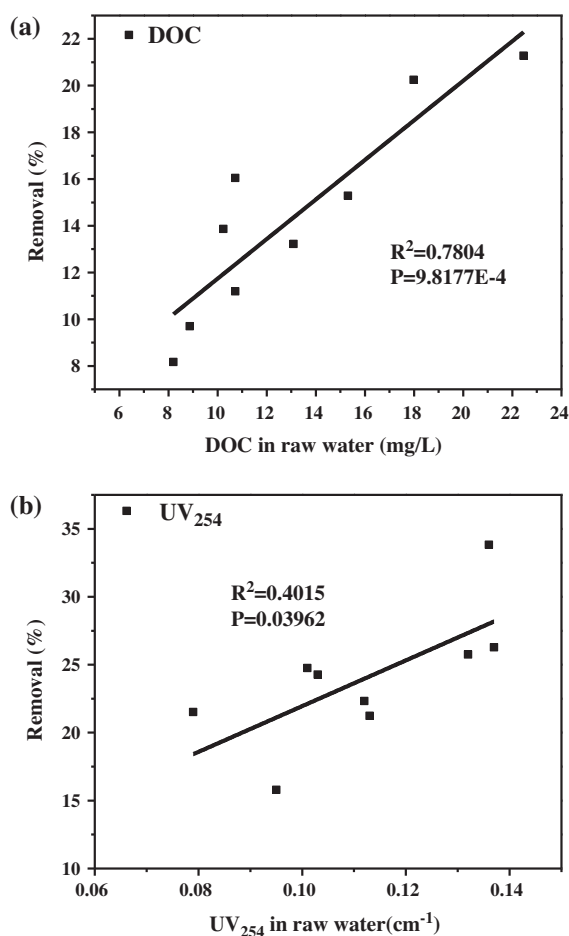Note: No. a-i corresponds to the water sample ID in Table 1.

Fig. 2. Effect of initial concentration of DOC (a) and UV_{254} (b) on their removal by UF membrane.

Fig. 3. Correlations of DOC (a) and UV_{254} (b) with irreversible fouling of UF membrane.

ent seasons are shown in Fig. 4. It can be seen that the fluorescence properties of NOM exhibited significant variation in different waters, implying the presence of different fluorescent components at different concentrations. To obtain quantitative information on the fluorescent components, PARAFAC modeling was implemented according to the procedures recommended by Stedmon and Bro [32]. Three- to seven-component models were tested in the work, and only the four-component model passed the validation judgment, which was used for further PARAFAC analysis.

The EEM contour, excitation, and emission loadings of the four fluorescent components were shown in Figs. 5 and 6. As can be seen, component 1 (C1) displayed two excitation (Ex) peaks centered at 240 and 310 nm with a broad emission (Em) band of 390–450 nm; component 2 (C2) also had two Ex peaks at 225 and 280 nm, with a single Em peak at 340 nm; component 3 (C3) showed a strong Ex at 270 nm and a weak Ex at 365 nm, respectively, while the Em peak
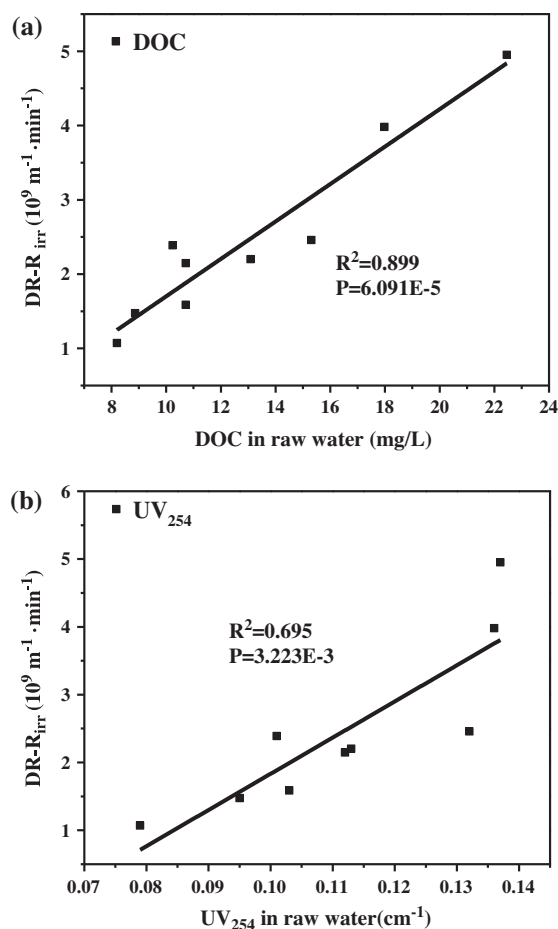
centered at around 480 nm; component 4 (C4) exhibited two Ex peaks at 225 and 275 nm, and one Em peak at 305 nm. The four components obtained in this work showed similar spectral characteristics to that reported in previous studies [23–25,28,36]. By comparison, C1 was identified as microbial-derived humic-like substances; C2 was identified as tryptophan-like proteins; C3 was identified as terrestrial-derived humic-like substances; and C4 was identified as tyrosine-like proteins. The relative concentrations of the four fluorescence components can be indicated by the score value of each component generated from the PARAFAC model.

3.4. Correlations of the fluorescence components with irreversible membrane fouling

To find out if there was the major component in NOM responsible for irreversible fouling of UF membrane, the correlations between the four fluorescent
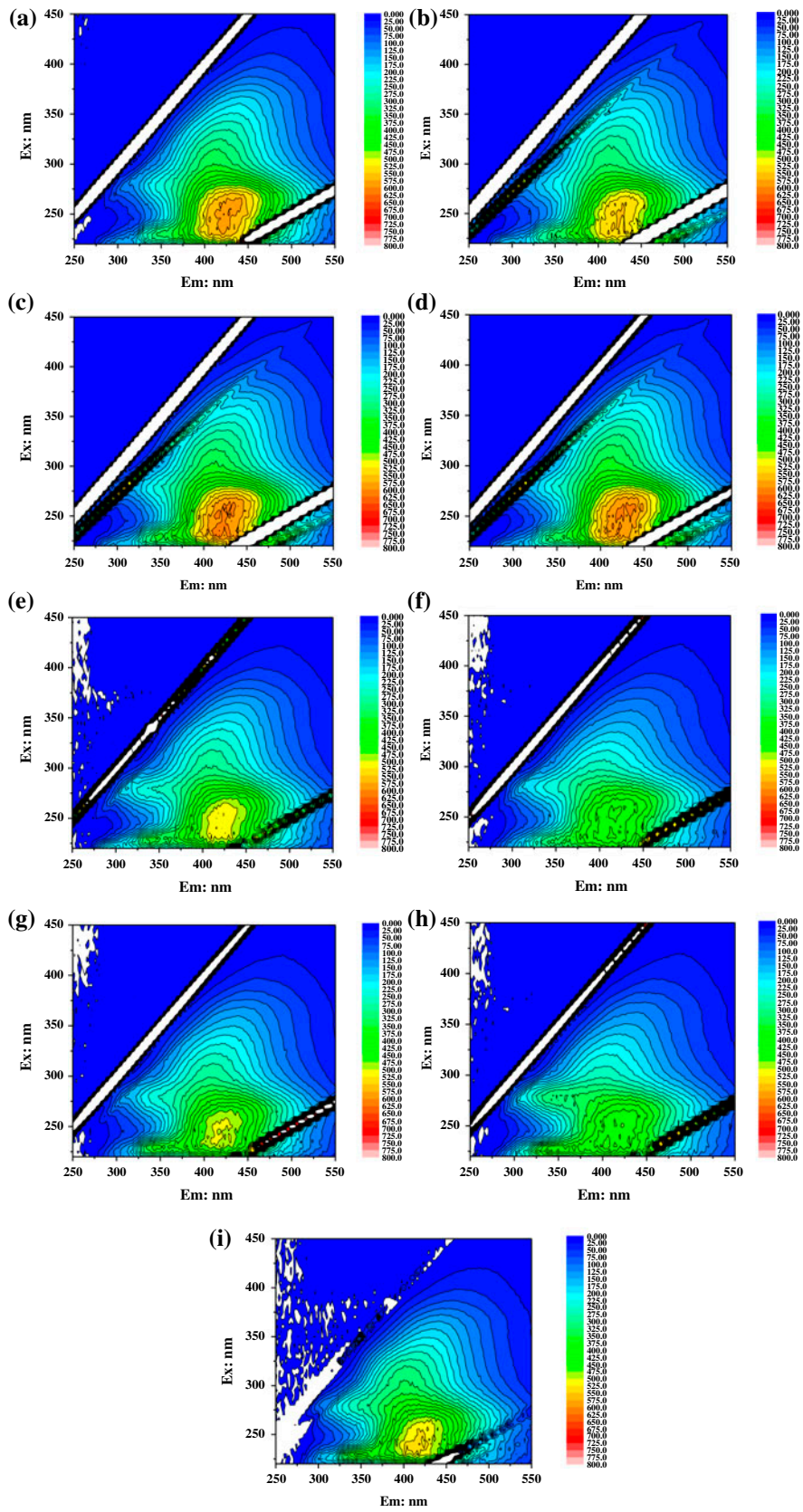
Fig. 4. Fluorescence EEM spectra of the nine water samples.
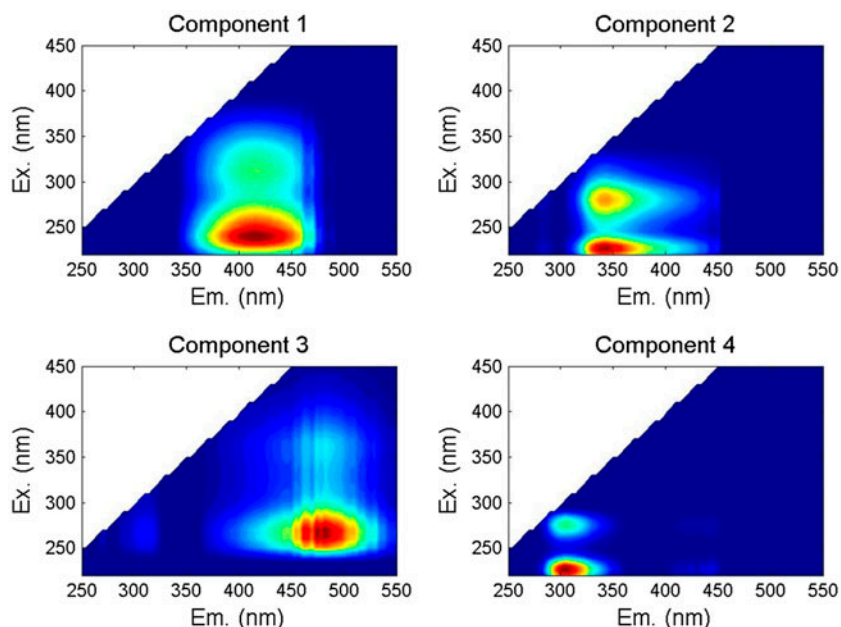Note: No. a-i corresponds to the water sample ID in Table 1.

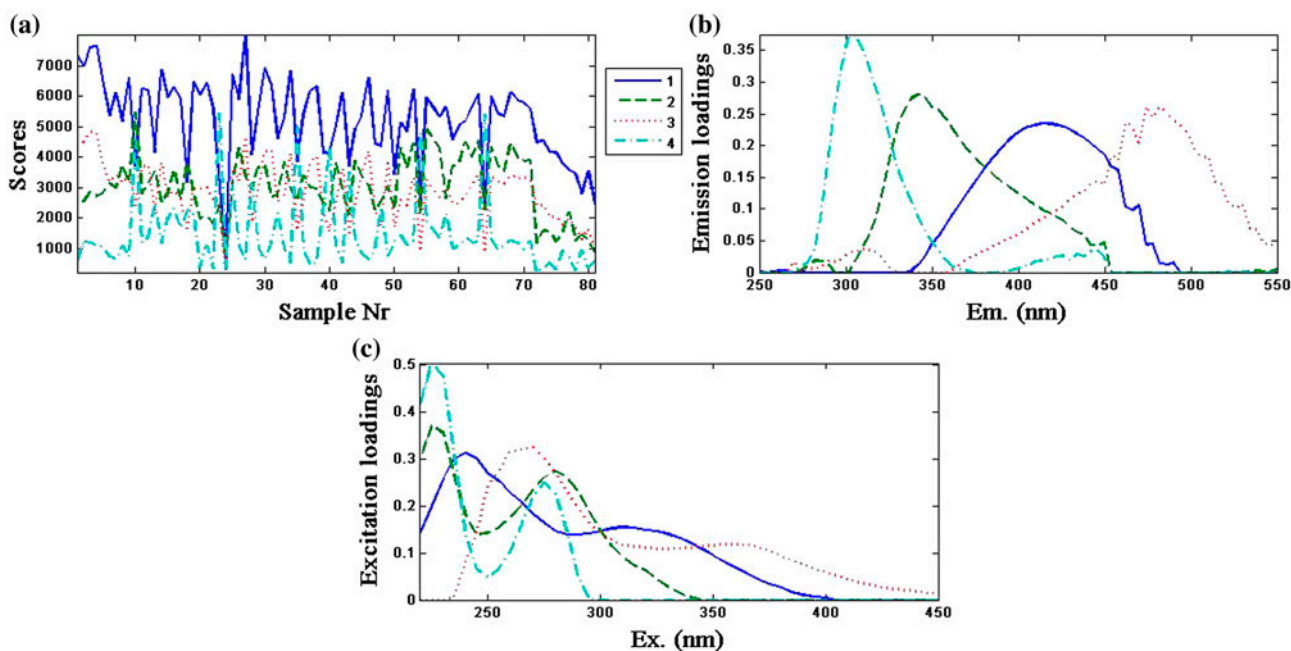Fig. 5. EEM contour of the four components obtained by PARAFAC analysis.

Fig. 6. Score values (a), emission (b), and excitation (c) loadings of the four fluorescent components.

components and developing rate of R_{irr} were examined. As shown in Fig. 7, only a weak correlation with the irreversible membrane fouling was observed for both the microbial-derived (C1, $R^2 = 0.301$) and the terrestrial-derived humic-like substances (C3, $R^2 = 0.542$). This was beyond expectation because it had been demonstrated in Section 3.2 that the increase of UV_{254} in raw water led to a corresponding increase in the irreversible membrane fouling. To the contrary, a much stronger correlation was identified between the tryptophan-like proteins (C2) and irreversible fouling of the UF membrane ($R^2 = 0.786$). This observation

was in consistence with the studies by Peldszus et al. and Shao et al. [27,28] who suggested that the protein-like substances should be responsible for the development of irreversible fouling during UF process. However, as could be seen in Fig. 7(d), the tyrosine-like proteins (C4) did not exhibit any relationship with the irreversible membrane fouling, with a poor R^2 of 0.143 obtained. The results suggests that it is not all the protein-like substances in NOM causing the irreversible fouling on UF membrane, but only a specific component can be taken as the major irreversible foulant.

On the other hand, it was still uncertain if the single component of tryptophan-like proteins (C2) contributed exclusively to the irreversible membrane fouling, because there were some kind of correlations between the humic-like substances, especially the terrestrial-derived humic-like substances (C3, $R^2 = 0.542$) with the irreversible fouling observed. Thus, the multivariate linear regression was conducted to assess the contributions of different fluorescent components to the irreversible fouling of UF membrane [25,28,30]. Due to that the two humic-like substances, C1 and C3, were strongly correlated to each other (Fig. 8(a)), only the C3, which showed a relatively high correlation with irreversible membrane fouling, was considered in the following as the representative of humic-like substances.

Firstly, the multivariate linear regression with the fluorescence components C2 and C3 was conducted, the result was shown below:

$$DR - R_{irr} = 2.354E6 \times \text{Score of C2} + 0.504E6 \\ \times \text{Score of C3} - 6.481E9 \quad (3) \\ (R^2 = 0.809, \, p = 0.003)$$

It can be seen that as compared with the single-component linear regression, the two-component linear regression exhibited a better fitting, with the R^2 value increased to 0.809 from the 0.542 for C3 alone and 0.786 for C2 alone. This implied that synergistic effect existed between C3 and C2 for the formation of irreversible fouling on UF membrane. However, by comparing the coefficients of C3 and C2, it was indicated that the C2 made a considerably larger contribution to irreversible membrane fouling than the C3. ANOVA analysis was conducted to examine the significance of the coefficients of C2 and C3 in the multi-linear regression model. A p-value of 0.017 (<0.05) was exhibited for the regression coefficient of C2, clearly indicating the significance of this model parameter. On the other hand, the p-value for coefficient of C3 was shown to be 0.222 (>0.05), thus it cannot be taken
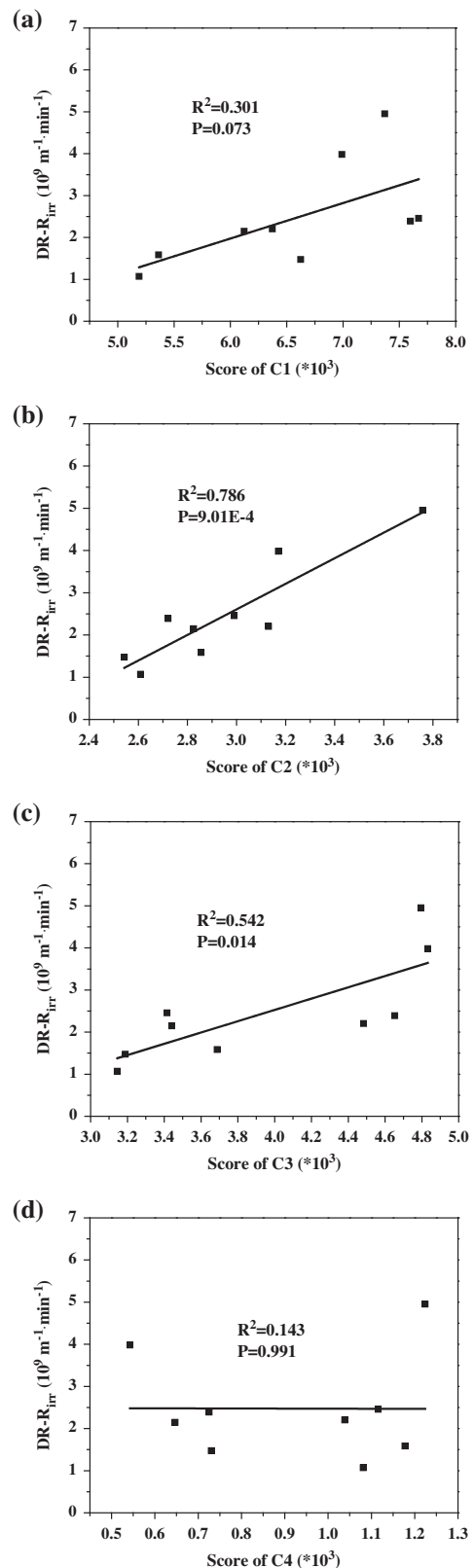

Fig. 7. Correlations between irreversible membrane fouling and the four fluorescent components (a) C1, (b) C2, (c) C3, and (d) C4.
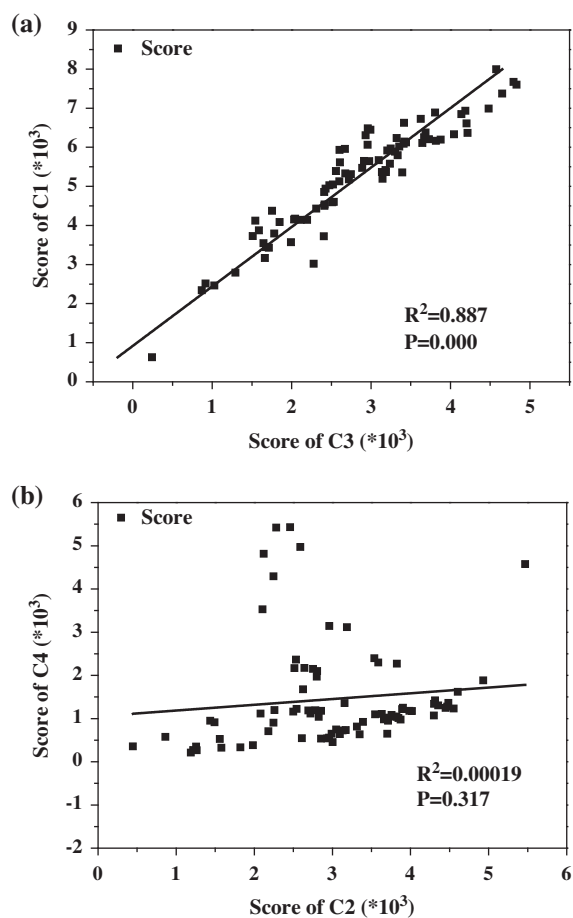
Fig. 8. Correlations between (a) C1 and C3, (b) C2 and C4 identified using the 81 fluorescence EEXs dataset for the PARAFAC modeling.

as "significant" in the model. The analysis results further consolidated the above-mentioned discussion.

Because the two protein-like substances C2 and C4 cannot be correlated to each other (Fig. 8(b)), the multiple linear regression by simultaneously considering C2, C3, and C4 was also conducted, the result was as follows:

$$
\begin{aligned}
DR - R_{irr} =\ & 3.311E6 \times \text{Score of C2} + 0.944E5 \\
& \times \text{Score of C3} - 1.674E6 \times \text{Score of C4} \\
& - 6.148E9
\end{aligned}
$$
$$
(R^2 = 0.892,\ p = 0.002)
$$

(4)

As could be seen, although an even higher R^2 value (0.892) was observed when incorporating C4 into the multiple linear regression, the coefficient of C4 was found to be minus. Thus, it was not appropriate to speculate that the C4 also caused a synergistic effect

together with C2 and C3 on the irreversible fouling of UF membrane. And by ANOVA analysis, only the regression coefficient of C2 was shown to be significant ($p = 0.004$); while that for C3 and C4 exhibited a much higher p-values (0.785 and 0.065 for the coefficients of C3 and C4, respectively). Further studies are still required to clarify the specific effect of different fluorescent components (e.g. C4) and their interactions on the membrane fouling behavior in UF process.

4. Conclusions

In this work, nine water samples were collected from different water sources at different seasons for UF membrane fouling experiments, and the major foulants causing the irreversible membrane fouling were identified. The following conclusions could be made:

(1) With the increase in DOC and UV_{254} as surrogate NOM parameters in raw water, higher removal efficiencies by UF membrane were obtained, which was accomplished by a corresponding increase in the developing rate of irreversible fouling.

(2) Four fluorescence components were identified in the nine water samples using the fluorescence EEM coupled with PARAFAC analysis: microbial-derived humic-like substances (C1), tryptophan-like proteins (C2), terrestrial-derived humic-like substances (C3), and tyrosine-like proteins (C4).

(3) C2 exhibited a strong correlation with the irreversible fouling of UF membrane ($R^2 = 0.786$); while no correlation between C4 and irreversible membrane fouling could be found. Both the humic-like substances (C1 and C3) were shown to be weakly correlated to the irreversible membrane fouling ($R^2 = 0.301$ for C1 and 0.542 for C3, respectively).

(4) By multivariate linear regression, the synergistic effect was identified between C2 and C3 on the irreversible fouling of UF membrane. The coefficients of C2 and C3 indicated that C2 made a considerably larger contribution to the irreversible membrane fouling than C3.

It should be noted that fluorescence EEM can only be used for characterizing the organic substances that are fluorescent, such as humic substances and protein-like substances. However, most of polysaccharides in NOM, which are also known to contribute to membrane fouling significantly, cannot be characterized by EEM properly. Therefore, further studies are still required to illuminate the contribution of

polysaccharides to UF membrane fouling, especially the irreversible membrane fouling.

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