



Identification of the fouling-caused foulants with different pretreatments during ultrafiltration in polluted raw water

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ABSTRACT

Different pretreatments, including coagulation, adsorption, and biofiltration, were used to identify the useful pretreatment for the ultrafiltration of polluted raw water. The following prefiltration investigation was conducted to identify foulants that were responsible for membrane fouling. Organic removal and particle size distribution of different pretreated samples were measured. The results indicated that the concentration of organic matter was not the critical factor that determined the extent of flux decline. The turbidity relevant materials, such as colloids and particles, were supposed to be important fouling-caused substances, and the particle size distribution also had a significant influence on flux decline. Moreover, the fouling resistance of different prefiltered samples showed that foulants sized over the membrane pore size caused the main part of the membrane fouling in raw water. Component analysis demonstrated that protein-like substances played a crucial role in membrane fouling; however, humic-like substances led to a weak membrane fouling.

Keywords: Ultrafiltration; Membrane fouling; Particles; Organics

1. Introduction

Ultrafiltration (UF), a low-pressure membrane filtration process, has significantly advanced in the treatment of drinking water by the removal of particles, turbidities, micro-organisms, and pathogens from surface water and groundwater [1,2]. However, membrane fouling is a critical issue that inhibits a wider application. Membrane fouling decreases the membrane permeability and increases the energy consumption due to the constriction and/or blocking of

membrane pores and the accumulation of foulants on membrane surface [3]. Natural organic matter is often identified as the major foulant in UF of surface water [4–6], since it contains organic particulate/colloid, a complex mixture of humic and fulvic acids, proteins, and carbohydrates of various molecular sizes.

Various strategies were conducted to control the membrane fouling, including conventional water treatment processes (coagulation, sedimentation and filtration). The conventional water treatment focuses on the particulate/colloid removal, although it can reduce some hydrophobic organics at the same time.

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Numerous studies concentrating on fouling mechanism and the characteristics of foulants in the treatment of drinking water and membrane bioreactor systems showed that dissolved extracellular polymer substances (EPS) or soluble microbiological products (SMPs), which normally measure as proteins and polysaccharides, were major fouling-caused contaminants [5,7–9]. Conventional drinking water treatment processes showed a limited ability on the removal of these mentioned contaminants for their hydrophilic property. Therefore, the selection of a proper pretreatment (such as coagulation, adsorption and biofiltration) for UF process is critical. Coagulation has been the most successful pretreatment for fouling control [10,11], although it was helpless for the EPS and SMPs. It could preferentially remove higher MW, hydrophobic, and acidic constituents [12]. Moreover, adsorption was also usually used as a pretreatment method. Liu et al. [13] selected coagulation and adsorption to control the membrane fouling of UF process and they found that serious flux decline still existed after the adsorption pretreatment, although the adsorption could reduce more organics than the coagulation. Mozia et al. [14] also reported that no significant improvement was observed in the permeate flux, although the addition of powdered activated carbon (PAC) led to a significant removal of organics. Additionally, biological filtration was also thought to be effective on membrane fouling control for the removal of big particles and biodegradation function [15]. However, there is no systematic study conducted comparing the performance of these different pretreatments methods in membrane fouling control, especially that in drinking water treatment.

Size exclusion is commonly recognized as the core mechanism in membrane-based filtration [16]. Foulants smaller than the pore size of the membrane can be adsorbed into the pores and may lead to pore constriction, while relative larger foulants block pore entrance and/or deposited on membrane surface forming a cake layer. The occurrence of different modes of fouling is related to a colloid size relative to the membrane pore size [17]. A study conducted by Howe et al. [18] demonstrated that the majority of dissolved organic matter (DOM), by itself, does not cause membrane fouling; the actual foulants is a relatively small fraction of bulk organics. Consequently, it is necessary to identify the crucial foulants that are responsible for membrane fouling by particle size, or molecular weight classification. The objective of this study is to investigate the fouling-caused foulants with different pretreatments, including coagulation, adsorption, and biofiltration, in the UF process of polluted raw water.

2. Materials and methods

2.1. Raw water and pretreatment method

To simulate the polluted raw water, domestic sewage was added to the local (Beijing, China) tap water with a volumetric ratio of 3:50 to simulate a surface water supply slightly polluted by sewage discharge, and 2 mg/L of humic acid (Shanghai, China) was also added. Before using, the simulated raw water was stabilized at room temperature for 24 h. The raw water was firstly pretreated by coagulation, adsorption, and biofiltration, respectively. The details of different pretreatments are as follows.

Coagulation experiments were conducted in a jar test apparatus (ZR4–6, Zhongrun Water Industry Technology Development Co. Ltd, China). Poly-aluminum chloride was used as the coagulant in reagent grade (with 28% Al_2O_3 content, basicity was 72.3%, GongYi, China). Each water sample (1 L) was rapidly mixed at 300 rpm for 1.0 min, then slowly mixed at 120 rpm for 15 min, and was allowed to settle for 20 min. After flocculation, a supernatant sample (200 mL) was carefully withdrawn for the UF as the next step. An optimal alum dose of 0.15 mM (determined by preexperiments) was continuously added to the rapid mixing tanks.

Adsorption was performed with PAC addition with the dosage of 50 mg/L for 60 min. PAC, made of wood, was 180 mesh (Actview carbon technology Inc, China); carbon size 98% > 180 mesh. The preadsorption was also conducted in the jar test apparatus; it was slowly mixed at 120 rpm to keep the PAC particles suspended in the raw water.

The biofilter consisted of a 60 mm inner-diameter Plexiglas pipe with a height of 1.0 m. Coal-based granular active carbon (Ruineng, China) was used in the filter with the carbon bed depth of 0.5 m. The filtration rate was set at 1.0 m/h, and the empty bed contact time was 0.5 h. The filter was backwashed once a week with consistency for more than six months.

Removal of the components, which were larger than a specific size, was conducted by prefiltering the water through specific membranes. The fractionation membranes were 1.2 μm binder-free glass fiber (GF/C, Whatman), 0.45 μm blend cellulose membrane (Beihua Corp), and 100 and 10 kDa molecular weights cut-off regenerated cellulose membranes (Amicon YM100 and YM10, Millipore Corp).

2.2. UF experimental setup

An unstirred-cell test was employed to evaluate the flux decline of different pretreated samples. The schematic diagram of the UF experiment is shown in Fig. 1.

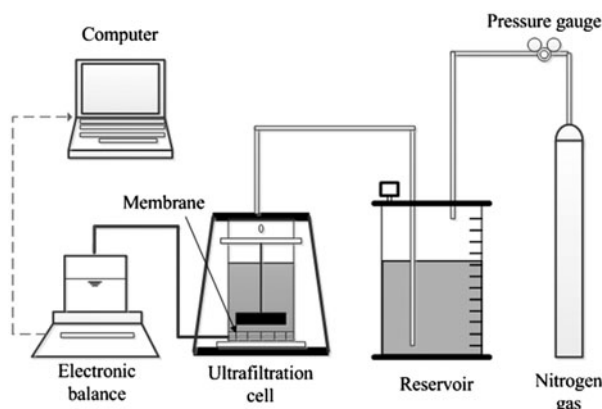


Fig. 1. Schematic diagram of UF experiment.

The cell (Amicon 8400, Millipore, USA), connects to an air-pressurized solution reservoir (2000 mL), has a volume of 400 mL and an effective filtration area of 45 cm². The filtration test was performed in a dead-end mode at room temperature (~24°C) with a constant pressure of 60 kPa controlled by a pressure gage. During the experiments, the permeate flux was recorded by an electronic balance connected to a computer.

For each UF experiment, a new hydrophilized poly-ethersulfone (PES) UF membrane (PALL, USA) with molecular weight cut-off (MWCO) of 100 kDa was used. Prior to the filtration test, each membrane was soaked in ultrapure water for 24 h and then rinsed thoroughly through a filter with at least 1,000 mL of ultrapure water to remove organic residues.

Prior to the filtration test, the pure water flux of the UF membrane was tested by filtration of 100 mL ultrapure water. Subsequently, 1,000 mL of the water sample was injected into the system and 900 mL of the sample was filtered. The data acquisition system automatically recorded this. After the filtration, the fouled membrane was removed from the cell and gently cleaned with a sponge to remove the cake layer formed on the membrane surface, and then 100 mL of ultrapure water was filtered to measure the fouling resistance constitution.

2.3. Fouling resistance

The resistance-in-series model, proposed by Choo and Lee [19], was used to analyze the fouling resistance in current studies. The filtration of ultrapure water with a new membrane was conducted to calculate R_m . At the end of every filtration experiment, the flux was used to estimate R_t . The $R_m + R_p$ was evaluated after removing the cake layer with a sponge. R_t , R_m , R_c , and R_p were estimated from Eqs. (1) to (4).

$$R_t = R_m + R_c + R_p \quad (1)$$

$$R_m = \frac{P}{\mu J_0} \quad (2)$$

$$R_t = \frac{P}{\mu J_e} \quad (3)$$

$$R_p = \frac{P}{\mu J_c} - R_m \quad (4)$$

where μ is fluid viscosity (Pa s), J is the permeate flux (m³/(m² s)), R_m is the intrinsic membrane resistance (m⁻¹), R_c is the cake fouling resistance (m⁻¹), R_p is the pore blocking resistance (m⁻¹), R_t is the total fouling resistance (m⁻¹), J_0 is the flux of the new membrane (m³/(m² s)), J_e is the flux at the end of the filtration (m³/(m² s)), and J_c is the flux after physical cleaning (m³/(m² s)).

2.4. Analytical methods

Excitation emission matrix fluorescence (EEM) measurements were conducted using a spectrofluorometer (F-4500, Hitachi, Japan) equipped with a 150 W xenon lamp at ambient temperature of 24°C. A 1 cm quartz cuvette with four optical windows was used for the analysis. Emission scans were performed from 220 to 550 nm at 5 nm steps, with excitation wavelengths from 220 to 450 nm at 5 nm intervals. The scanning speed was maintained at 1,200 nm/min; the slit widths for excitation and emission were both 5 nm. The fluorescence spectrum of Milli-Q water, obtained under the same conditions, was subtracted from all spectra to eliminate water Raman scattering and to reduce other background noise. According to Cobles [20] and Baker [21], there were four typical fluorescence peaks denoted as A, C, T1, and T2 commonly observed in natural water and sewage. Peaks A and C, which usually appeared at 320–350 nm and 230–260/400–500 nm of excitation/emission wavelengths, were related to humic-like substance derived from the plant breakdown. Peaks T1 and T2 were associated with tryptophan-like proteins, which normally occurred at 225–280 nm/310–340 nm of excitation/emission wavelengths.

UV₂₅₄ was evaluated by a UV/V spectrophotometer (T6, Puxi, China) with the absorbance measured at 254 nm, while dissolved organic carbon (DOC) was obtained by vario total organic carbon (TOC) (elementar, Germany) with the non-purgeable organic carbon (NPOC) method; samples for UV₂₅₄ and DOC were

both filtered through 0.45 μm cellulose acetate membrane before measuring. The distribution of nanometer particles was measured with a particle analyzer (DelsaNano S, Beckman Coulter, USA) having a size range of 0.6 nm–7 μm at 25°C, based on dynamic light scattering analysis. The analyses were performed in triplicate, and the representative result was shown.

2.5. Modeling for membrane fouling process

Four classic filtration models (complete blocking, standard blocking, intermediate blocking, and cake filtration) were applied to interpret the flux decline of the low-pressure membrane filtration in dead-end mode with constant pressure. The filtration models' assumptions are described by Tian et al. [22] and the equations are listed in Table 1. The fouling evolution of raw water and different pretreated waters were estimated using these equations.

3. Results and discussion

3.1. Effect of different pretreatments on fouling control

3.1.1. Flux decline and fouling resistance

In this study, the flux decline of raw water and that of pretreated water by coagulation, adsorption, and biofiltration, respectively, were conducted and compared. The normalized flux decline of different samples was shown in Fig. 2. It can be observed that the raw water caused the quick flux decline with a normalized flux of 0.19 after the UF of 900 mL sample. The adsorption effluent had similar profiles to that of the raw water throughout the period of filtration, which indicated that independent adsorption could not improve the flux of raw water. Similar results were also conducted by other researchers [13,14]. So, it was thus believed that an independent PAC pretreatment might not be a suitable way to fouling control in UF process. As compared with the flux decline of raw

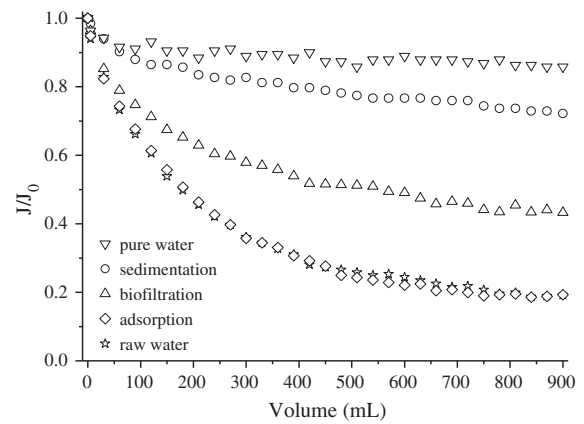


Fig. 2. Normalized flux decline of different pretreated samples.

water, relatively higher permeate fluxes were observed for the biofiltration and coagulation with the final normalized flux of 0.72 and 0.48, respectively. This phenomenon was mostly attributed to the reduction of foulants that might come into contact with the membrane [15], thus reduce the interaction between fouling-relevant materials and membrane surface. Biofiltration was able to removal particles that are greater than a few micrometers or smaller than 0.1 μm from water through physical sieving, chemical adsorption/deposition, and biological action [10]. As for coagulation, it showed the best fouling control behavior in this study, which was attributed to the fact that destabilized aquatic colloids and organics adsorptive to coagulant precipitates, were separated from the water in the presence of sedimentation.

In order to investigate the effects of pretreatment on the fouling resistance distribution, cake fouling and pore blocking resistance were calculated and compared. Fig. 3 showed that the pore blocking resistance

Table 1
Equation of different fouling mechanisms for dead-end filtration

Models	Equations
Complete blocking	$J_0 - J = AV$
Standard blocking	$1/t + B = J_0/V$
Intermediate blocking	$\ln J_0 - \ln J = CV$
Cake filtration	$(1/J) - (1/J_0) = DV$

Note: V, filtrated volume.

t, filtration time.

A, B, C, and D are all constants.

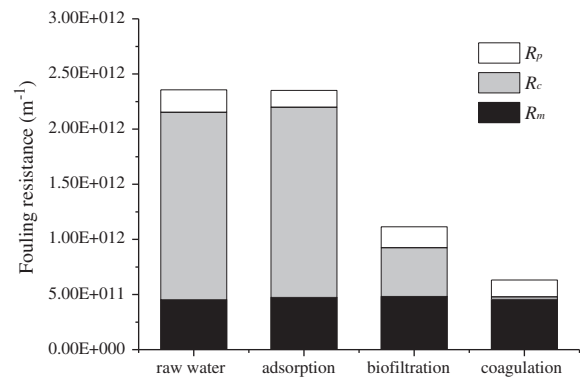


Fig. 3. Fouling resistance of different pretreated samples.

of raw water was similar to these pretreated samples, which indicated that these pretreatments had little influence on pore blocking. In other words, these pretreatments did not remove foulants that leads to pore blocking. Moreover, if the biofiltration and coagulation pretreatments reduced the cake fouling resistance of the raw water, then we can conclude that it was the reduction of cake fouling resistance leading to a mitigation of membrane fouling. The cake layer was usually formed by foulants sized larger than membrane pores, such as organics polymers, particles, and colloids. Therefore, the effective removal of foulants sized over membrane pores during the pretreatment will be an optional way to membrane fouling control.

3.1.2. Impurities removal

Impurities removal efficiencies of different pretreatments are listed and summarized in Table 2. DOM is one of the most important concerns in the drinking water treatment, since it is potentially hazardous and difficult to be eliminated [6], DOC and UV_{254} were used to show the concentration of DOM. As shown in Table 2, comparable DOC removal efficiencies were achieved with three pretreatment methods, which averaged to $34.0 \pm 4.2\%$, $35.4 \pm 4.2\%$ and $36.8 \pm 3.4\%$ for the adsorption, biofiltration and coagulation processes, respectively. However, the difference on organic removal was shown by UV_{254} , which averaged out to be $48.4 \pm 3.1\%$, $85.9 \pm 1.6\%$, and $65.6 \pm 4.7\%$ for the adsorption, biofiltration and coagulation, respectively. It seemed that no obvious correlation could be calculated between flux decline and the concentration of organics, especially the concentration of DOC. In other words, the concentration of organic matter is not the critical factor that determines the extent of flux decline. Tian et al. [1] also found that the DOC and UV_{254} did not show any distinct correlation with either the organic fouling resistance or total fouling resistance during the UF process of different samples. Additionally, the adsorption could not mitigate the flux decline, although some organics were removed in the raw water, which can be explained by

the phenomenon that organics removed by PAC had little influence on membrane fouling, as the result was also demonstrated by Howe et al. [18].

Colloids and particles, as ubiquitous components in natural water, have been increasingly emphasized in terms of membrane fouling. In this study, the characteristics of particles were illustrated by two parameters, turbidity and particle size distribution (shown in Fig. 4). For the water pretreated by adsorption, both the turbidity and the main peak of 5,700 nm in particle size distribution increased, which was mostly attributed to the influence of PAC particles. The peaks of 729 nm, 103 nm, and 0.7 nm in particle size distribution were removed to 544 nm, 82 nm, and 0.6 nm, respectively; the characteristic of colloids/particles did not show a significant change with/without adsorption pretreatment. So, the PAC addition had limited influence on the characteristic of particles and colloids [23]. In terms of other two samples, it could be seen that biofiltration and coagulation effectively decreased the turbidity, which was reduced from 4.40 ± 0.19 NTU to a level as low as 0.82 ± 0.08 NTU and 0.65 ± 0.10 NTU, respectively. Meanwhile, we can find that both biofiltration and coagulation mitigated the membrane fouling compared with the raw water. Therefore, it was thus believed that the turbidity relevant materials in raw water, such as particles and colloids, were supposed to be an important membrane fouling-caused substance. On the other hand, an obvious difference in flux decline (shown in Fig. 2) can be observed for biofiltration and coagulation effluents although they had similar turbidities, which implied that the particles number was not the unique factor for flux decline. As shown in Fig. 4, the main peak of sedimentation and biofiltration effluents was 1,540 and 308 nm, respectively. The particle size distribution indicated that particles in the sedimentation effluent were much bigger than that of biofiltration effluent. Huang et al. [10] found that colloids and particles closed to the size of membrane pores can cause serious pore blocking and form a compact cake layer, conversely, those particles much larger than membrane pores would lead to a porous cake layer. Therefore,

Table 2
Effect of pretreatments on the removal of impurities

	Turbidity/NTU	DOC/mgL ⁻¹	UV_{254}/cm^{-1}	SUVA/L mg ⁻¹ m ⁻¹
Raw water	4.40 ± 0.19	2.88 ± 0.14	0.064 ± 0.07	2.20
Adsorption	12.18 ± 0.59	1.90 ± 0.12	0.033 ± 0.02	1.73
Biofiltration	0.82 ± 0.08	1.86 ± 0.12	0.009 ± 0.01	0.48
Coagulation	0.65 ± 0.10	1.82 ± 0.10	0.022 ± 0.03	1.20

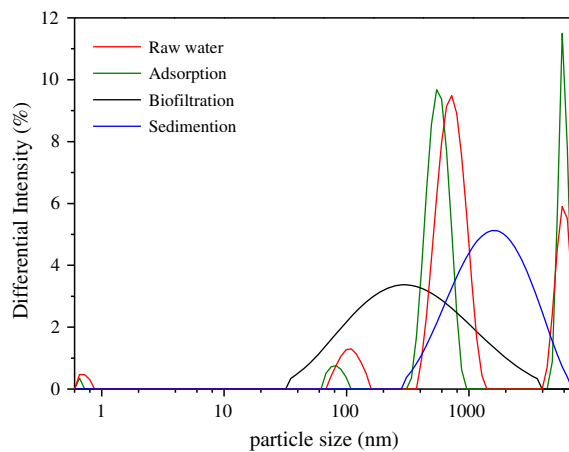


Fig. 4. Particles distribution of different pretreated samples.

the particle size distribution also had a significant influence on flux decline, and serious flux decline of biofiltration effluent compared with the coagulation effluent was attributed to the smaller particle size.

3.1.3. Modeling of filtration process

To investigate the fouling mechanism of the raw water and different pretreated samples, four classic filtration models were applied for further analysis of the fouling evolution, and the regression results using these models are given in Table 3. The R^2 values of raw water were 0.763, 0.999, 0.944 and 0.996 for complete blocking, standard blocking, intermediate blocking, and cake filtration, respectively. The results indicate that the mechanism for flux decline caused by raw water can be primarily ascribed to standard blocking and cake formation, allowing for the possibility that intermediate blocking was involved to some extent as well. The fouling mechanisms of standard blocking might be interpreted in terms of the foulants size. There was a large amount of foulants, sized smaller than pore size; such particles accumulated on the walls of straight cylindrical membrane pores causing

Table 3
 R^2 values of four regression analyses of different pretreated samples

	Complete blocking	Standard blocking	Intermediate blocking	Cake filtration
Raw water	0.763	0.999	0.944	0.996
Adsorption	0.772	0.999	0.949	0.991
Biofiltration	0.834	0.999	0.945	0.991
Coagulation	0.879	0.999	0.907	0.930

standard blocking. On the other hand, cake formation was the main fouling mechanism in the UF process because foulants sizes greater than the pore size were retained by the membrane and formed a cake layer.

The R^2 values from the regression analyses of the experimental results obtained with the treated water samples are shown in Table 3. It can be found that R^2 values of different water samples for standard blocking were all above 0.999, indicating that standard blocking was the major mechanism for flux decline independent of the pretreatment method. Particle size distribution in the water had significant influence on the fouling mechanism. Stoller et al. [24] found that the blocking of the pores occurs preferentially when the particles were similar to the pore size, and blocking may statistically be significant when $0.1 < \text{pore size/particle size} < 10$. The particle size distribution of four water samples showed numerous particles sized between 1 and 100 nm for the raw water adsorption, biofiltration, and coagulation samples, although it seem that no particles were distributed in the size comparable with the membrane pores in the coagulant sample. The phenomenon was attributed to the fact that big particles tend to mask the presence of smaller part [25].

3.2. Identification of the fouling-caused foulants

To understand the effect of different particle size foulants on membrane fouling, the same raw water was prefiltered through 1.2 μm , 0.45 μm , 100 kDa, or 10 kDa membrane, respectively, then the UF process of these prefiltered samples were conducted and the fouling resistance changes of these samples were shown in Fig. 5. It can be observed that the raw water caused the most serious membrane fouling with the final fouling

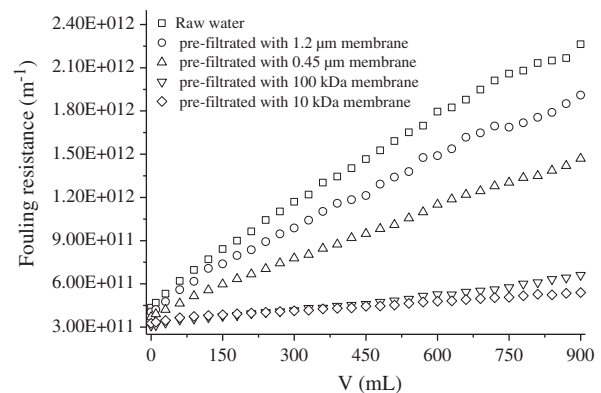


Fig. 5. Effect of prefiltration on fouling resistance of UF process.

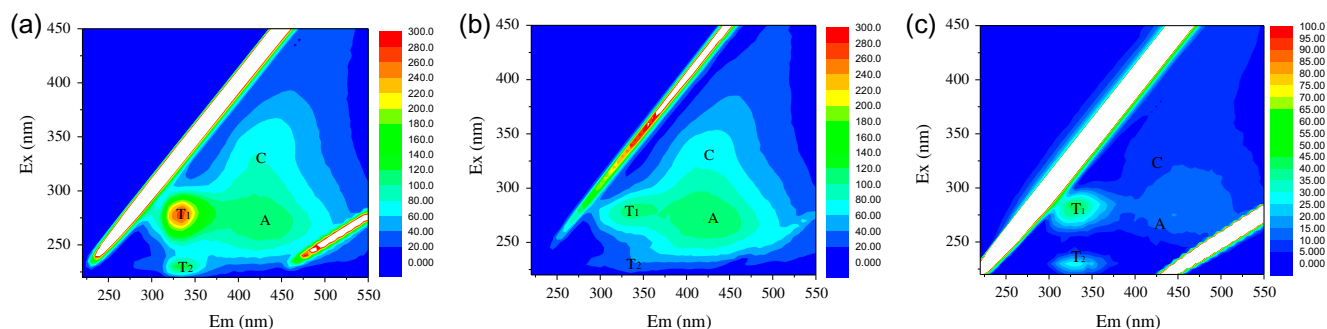


Fig. 6. EEM spectra of raw water (a) the permeate water (b) and the deposited foulants (c) on the membrane surface in raw water UF process.

resistance of $2.3 \times 10^{12} \text{ m}^{-1}$, while the prefiltration with different pore size membranes could alleviate the fouling resistance to some extent. At the end of UF process, the fouling of different foulants sized $< 10 \text{ kDa}$, $10\text{--}100 \text{ kDa}$, $100 \text{ kDa}\text{--}0.45 \mu\text{m}$, $0.45\text{--}1.2 \mu\text{m}$, $> 1.2 \mu\text{m}$ accounted for 10.9, 6.3, 41.8, 22.7, and 18.3% of the fouling resistance of the raw water (without intrinsic membrane resistance), respectively. This result indicated that all of foulants with different particle sizes could lead to membrane fouling during the UF process, but a significant difference was observed with different fractions. Size exclusion is the core mechanism in UF process [16], and foulants in water can be classified into two parts, including foulants bigger and smaller than membrane pore size. On one hand, foulants sized over membrane pore size caused the main part (82.8%) of the total fouling resistance of the raw water, which indicated that foulants retained by the membrane was the main fouling-caused material. The result was in accordance with other researchers in both drinking water treatment and reuse of secondary effluent from wastewater treatment plants. Generally, it was believed that these foulants would form a compact cake layer on membrane surface and leading to a barrier for the flow of the water. On the other hand, foulants sized smaller than the pore size only caused a small part (17.2%) of the total fouling resistance, although the majority of TOC (52%, data not shown) was concentrated in this part. Most of foulants in this part could permeate through the membrane, and leading to little membrane fouling. Moreover, this part showed a smaller fouling-tendency compared with the fraction bigger than 100 kDa.

In order to identify fouling-caused foulants, three-dimensional EEM fluorescence spectroscopy was utilized because of its ability to distinguish among certain classes of organic matter [26]. The EEM spectra of raw water, the permeate water, and the deposited foulants on membrane surface are presented in Fig. 6. It

was shown that protein-like substances (peak T_1 and T_2) and humic-like substances (peak A and C) were found to be dominant in raw water. Different variations were shown for the protein-like substances and humic-like substances during the UF process. On one hand, the intensity of peaks T_1 and T_2 for the permeate water dramatically decreased compared with the raw water, which were 63 and 79% lower than those of raw water, and the result suggests that a large percentage of the protein-like substances in raw water were of pretty high MW. The spectra of the deposited foulants (Fig. 6(c)) showed that the deposited part was mostly protein-like substances represented by peaks T_1 and T_2 , and low intensities of humic-like substances could be observed. As the main membrane fouling was owing to the deposited foulants; therefore, the main membrane fouling was attributed to the protein-like substances. Similar results were also obtained with other researchers. Filloux et al. [27] found that the protein-like substances were highly correlated with the total fouling of UF process of secondary effluents. Liu et al. [28] observed that the external foulants on membrane surface in membrane bioreactor were mostly protein-like substances. On the other hand, the intensities of both peaks A and C of the permeate water and raw water were almost identical, and it can be concluded that the humic-like substances in the raw water were mostly concentrated in low MW. So, most humic-like substances will penetrate through the membrane in UF process, leading to a weak membrane fouling.

4. Conclusion

Coagulation, adsorption, and biofiltration were used to identify fouling-caused foulants in treating polluted raw water. The following conclusions could be drawn:

- (1) The concentration of organic matter was not the critical factor that determined the extent of flux decline; organics removed by PAC had little influence on membrane fouling.
- (2) The turbidity relevant material, such as colloids and particles, was supposed to be an important fouling-caused substance, and the particle size distribution also had a significant influence on flux decline.
- (3) Foulants sized over the membrane pore size caused the main part of the fouling resistance of the raw water, and that smaller than membrane pore size only caused a small part.
- (4) Protein-like substances play a crucial role in membrane fouling; however, humic-like substances lead to a weak membrane fouling.

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