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Effects of natural organic matters molecular weight distribution on the immersed ultrafiltration membrane fouling of different materials

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ABSTRACT

Effects of natural organic matter molecular weight (MW) distribution in source water on the reversible and irreversible fouling of immersed ultrafiltration membranes of three different materials were systematically investigated using representative sources of natural waters. It was found from the bench-scale tests that the organic matters of the MW lower than 1 K and higher than 30 KDa were the main substances that induced reversible fouling regardless of the materials, and that of MW between 1 K and 5 KDa could cause reversible fouling for polyvinylidene fluoride (PVDF) and polysulfone (PS) membrane. As for the irreversible fouling, small organic molecules of the MW lower than 1 KDa were the main part due to the hydrogen bonds. In addition, the organic matters of MW between 1 K and 3 KDa can induce irreversible fouling for polyvinyl chloride and PVDF membrane. Results of long-term filtration tests showed that PVDF membrane was more vulnerable to small organic molecules due to its high electronegativity substances, and PS membrane had better resistance to organic fouling.

Keywords: Natural organic matter; Molecular weight; Membrane materials; Immersed UF; Membrane fouling

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1. Introduction

Recently microfiltration and ultrafiltration (UF), the low pressure membrane filtration processes, have received considerable attention. They have been increasingly used in drinking water treatment as alternative technology to conventional clarification and filtration processes, in order to remove particles, microorganisms and natural organic matters (NOM). Nevertheless, fouling of membrane materials represents a serious constraint for employing low-pressure membrane systems as a substitute for conventional treatment [1]. Membrane fouling is a universal phenomenon observed with membrane systems used in water treatment, which causes an increase in hyd raulic resistance and hence a reduction in filtration efficiency, leading to a substantial loss of capacity or higher pumping energy cost. Therefore, understanding fouling phenomena is critical for sustainable operation of membrane systems.

For membrane filtration of surface water, NOM is thought to be a primary contributor to membrane fouling including molecular size, hydrophobicity, charge and chemical functionality [2–9]. Significant progress has been made in understanding the qualitative effects

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of NOM on the performance of membrane systems (fouling and flux reversibility) [10–18], despite the fact that conflicting assessments are not rare. Different molecular weight (MW) fractions exhibit different fouling tendencies. Some studies showed that the larger MW fraction, fractionated by gel permeation chromatography, cause more significant fouling [7,19,20], while other studies indicated that only molecules in a certain size range (3–20 nm) are responsible for membrane fouling [21]. Because of the complex and unstable nature of NOM present in natural waters, the mechanisms how NOM contribute to fouling are still under debate.

Low-pressure membranes currently used in large-scale water treatment facilities are predominantly hollow-fiber membranes often made of polyvinylidene fluoride (PVDF) or polyether sulfone due to their superb chlorine and acid resistance. Structural modification of these membranes has also been a common practice for manufacturers to reduce membrane fouling. The concentration and property of NOM present in raw water can also influence the interaction of the NOM with a particular membrane. Studies have showed that humic acid adsorption on hydrophobic UF membranes was greater than that on hydrophilic UF membranes [13]. However, little information is available in the literature so far on the NOM that govern the fouling of low-pressure membranes with different materials. Therefore, the main objective of this study is to systematically investigate the effect of NOM MW on the fouling of immersed UF membrane with different materials. These results are expected to help us identify the causation of fouling in UF for surface water and improve membrane operation.

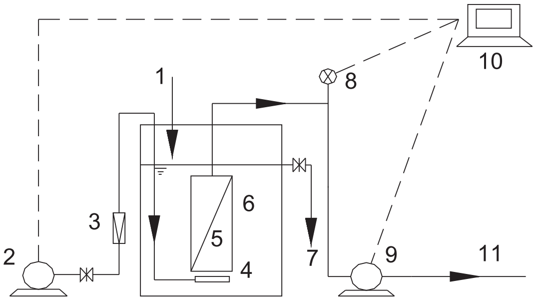

Fig. 1. Schematic diagram of the experimental set-up: (1) feed water; (2) air pump; (3) air flowmeter; (4) air diffuser; (5) UF membrane module; (6) UF tank; (7) overflow; (8) pressure sensor; (9) peristaltic pump; (10) computer and software; and (11) effluent.

2. Materials and methods

2.1. Experimental setup

Three identical bench-scale immersed UF membranes were employed in this study. A schematic illustration of the experimental set-up is shown in Fig. 1. The UF membrane modules with a nominal pore size of 0.01 μm and a total membrane area of 0.01 m^2 were made from three different materials. The effluent was drawn directly from the membrane module by using a peristaltic pump, which was also applied for backwashing. A pressure sensor was set between the membrane module and the suction pump to monitor and record the transmembrane pressure (TMP) automatically by software. Aeration was provided at the bottom of the membrane tank to reduce fouling. UF filtration was operated at a constant flux of 30 L/m^2h, and change of TMP was taken to express the extent of fouling. The flux of backwash was 50 L/m^2h with the time 5 min, and the intensity of aeration was 35 m^3/m^2h which was applied for all the filtration process. Backwash was applied when one filtration cycle finished. In the short-term fouling experiment there were three filtration cycles and the duration of one filtration cycle is 10 h.

2.2. UF membrane unit

Three UF hollow-fiber membranes with different materials were used in this study, the characteristics of which are shown in Table 1. The three UF membranes were made from polyvinyl chloride (PVC; Litree, Suzhou, China), PVDF (Litree, Suzhou, China)

Table 1
Physical characteristics of the UF membranes

Material	PVC	PVDF	PS
Type	Hollow fiber	Hollow fiber	Hollow fiber
Filtration mode	External pressure	External pressure	External pressure
Weight cut-off (KDa)	100	100	80–100
Contact angle (°)	67.0	56.5	75.5
Inner diameter (mm)	0.85	0.85	0.50
Outside diameter (mm)	1.45	1.45	1.00

and polysulfone (PS; Tri-High, Beijing, China), respectively. Although these UF membranes were made from different polymers, they had the same MW cut-off of 100 KDa.

2.3. Analytical methods

Water quality analysis was conducted following the standard methods [21]. UV_{254} was determined by using the spectrometer (UV754, CANY, China). DOC (prefiltration through 0.45 μm membrane) was measured by the TOC analyser (TOC-VCPH, Shimadzu, Japan). Turbidity was monitored by a turbidimeter (TURBO550, WTW, Germany).

2.4. Raw water supply

The raw water from the Songhua River in northeast of China represented a kind of typical surface water in China. The main water quality characteristics of the raw water used in the study are summarized in Table 2.

2.5. MW fractionation

The MW distribution of the organic matters in the raw water, UF effluent and the fouling substances were determined following the method of UF fractionation [22]. The organic matters washed down by backwash were fractionated to analyse the reversible fouling, and the absorbed organic matters by NaOH after backwash and sponge scrubbing were fractionated to analyse the irreversible fouling in this test. For the raw water and fouling matters sample, they were first filtered through a 0.45 μm membrane. The samples used for the MW distribution were filtered through a number of cellulose membranes in turn, which had nominal MW cut-offs of 30,000, 10,000, 5,000, 3,000 and 1,000 Da (YM30, YM10, YM5, YM3 and YM1, Amicon). For the filtration test, a membrane with a surface area of 63.6 cm^2 was laid in a stirred cell of 300 mL in volume and placed on a magnetic stirrer. The sample liquid filled inside the cell was stirred by a magnetic stir-bar at 120 rpm to prevent the membrane from fouling. Pressure was applied using a nitrogen gas cylinder at 1 bar at room temperature against the liquid enclosed in the stirred cell. The permeated liquid was analysed for TOC concentrations. The concentration of organic matter with different MW ranges was got by the subtraction method.

Table 2
Main characteristics of the raw water

Parameter	Results
Turbidity (NTU)	19.5–21.2
pH	7.62–7.72
DOC (mg/L)	7.718–7.832
UV_{254} (cm^{-1})	0.088–0.096
Total hardness ($CaCO_3$)(mg/L)	75.5–81.0
Total alkalinity (mg/L)	62.3–72.0

2.6. Standard flux rate (SFR) analysis

Standard flux rate (SFR) was calculated by the ratio of specific flux of raw water (SFR_t) to the specific flux of pure water (SFR_0), and was used to compare the fouling of membrane with different materials. Specific flux is defined as follows, in which J is the membrane flux ($L/m^2 h$), P_0 is the pressure in the process of membrane filtration with pure water (kPa), μ is viscosity coefficient (Pa s), R_m is the original resistance of UF membrane (m^{-1}), P_t is the pressure in the process of membrane filtration with raw water (kPa), and R_t is the total resistance (m^{-1}).

$$SFR_0 = \frac{J}{\Delta P_0} = \frac{1}{\mu R_m} \tag{1}$$

$$SFR_t = \frac{J}{\Delta P_t} = \frac{1}{\mu R_t} \tag{2}$$

3. Results and discussion

3.1. SFR development of UF membrane with three different materials in short-term filtration

The correlation between accumulated DOC passing through the membrane module (mgDOC/m^2 membrane area) and SFR was adopted for investigating fouling of different materials caused by natural organic matter in raw water. The SFR development of UF membrane with three different materials is shown in Fig. 2.

It could been observed that fouling of three UF membranes during three filtration cycles was quite different, i.e. the SFR of PVDF membrane decreased the most and the UF of PS membrane flux loss the least. It indicated that the fouling of PVDF membrane was the most serious by raw water, and the PS membrane had a better capacity to resist fouling compared to PVDF and PVC membranes. Considering the fact that the weight cut-off of three different UF membranes is almost identical, the different variations of membrane fouling could be attributed to the

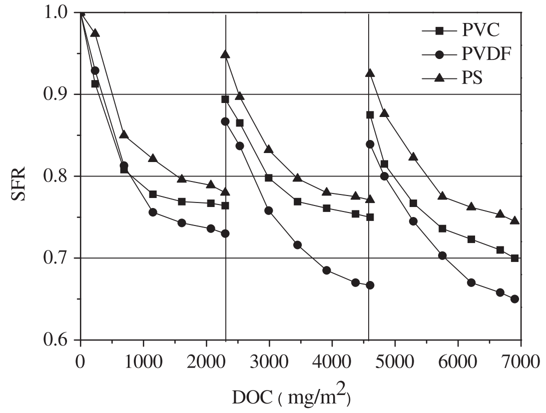

Fig. 2. SFR development of UF membrane with different materials in three filtration periods.

different membrane materials. In addition, the filtration performance of UF membranes could be recovered by backwash to some extent, but the degree of recovery varies. The SFR of PVC, PVDF and PS membrane was improved from 0.764, 0.73 and 0.78 to 0.894, 0.867 and 0.948 respectively by the first backwash, and from 0.75, 0.667 and 0.771 respectively to 0.875, 0.839 and 0.925 by the second backwash. The recovery capacity of PS membrane with fouling was better in view of the degree of recovery.

3.2. MW distribution of organic matters causing fouling

The MW distribution of organic matters in raw water and UF effluent was shown in Fig. 3. It could be seen that the organic matters in the raw water with the MW range of <1 K, 1–3 K and >30 KDa accounted for 56.2, 21.3 and 15.9%, respectively. The organic matters of the MW larger than 30 KDa were removed the most effectively by the UF membranes, and the removal efficiency was 51.9, 58.0 and 38.2% for PVC, PVDF and PS, respectively. Results also showed that the removal of organic matters of the MW lower than 1 KDa was 11.3, 19.1 and 16.4% for PVC, PVDF and PS, respectively, indicating that organic matters lower than 1 KDa may also have an important effect on membrane fouling.

The MW distribution of organic matters causing reversible fouling was shown in Fig. 4. Results showed that the organic matters of the MW >30 K and <1 KDa were the main parts of reversible foulants for PVC, PVDF and PS membrane, which accounted for 64.5 and 25.5%, 43.4 and 37.4%, 52.4 and 27.2%, respectively. As for the PVDF membranes, the organic matters of the MW 3–5 K were also another important fouling fraction, which accounted for 15.3 and 8.4% respectively, and for PS membrane the organic matters of the MW 1–3 K were also another important fouling fraction which accounted for 12.6%. Based on the above results, it might be indicated that the organic matters of the MW >30 K and <1 KDa were the main substances causing UF membrane reversible fouling regardless of the materials, though the degree of fouling by these matters was different for different membrane materials. The organic matters of the MW higher than 30 KDa may cause pore blockage directly or form a combination with small molecules to attach on the membrane pore for UF membranes [7]. Some small molecules, such as organic matters of the MW lower than 1 KDa, might be retained by the cake layer on the membrane surface or form a combination with large molecules to induce the reversible fouling.

As shown in Fig. 5, for all three different UF membranes, the main organic matters that could induce irreversible fouling were that of the MW lower than 1 KDa, with a proportion of 68.8, 72.8 and 71% for PVC, PVDF and PS membrane, respectively. In addi-

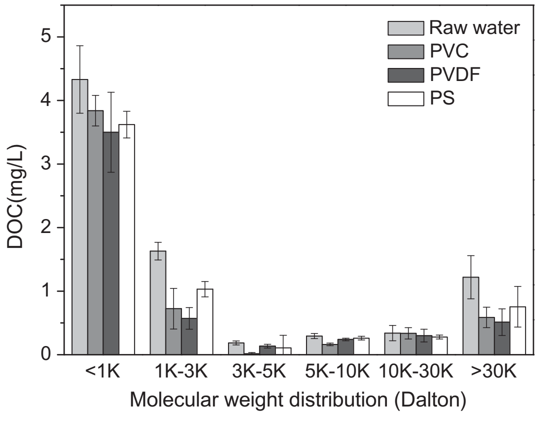

Fig. 3. MW distribution of organic matters in raw water and UF effluent.

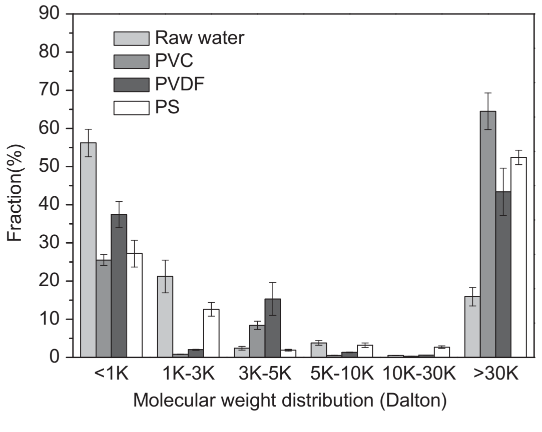

Fig. 4. MW distribution of organic matters causing reversible membrane fouling.

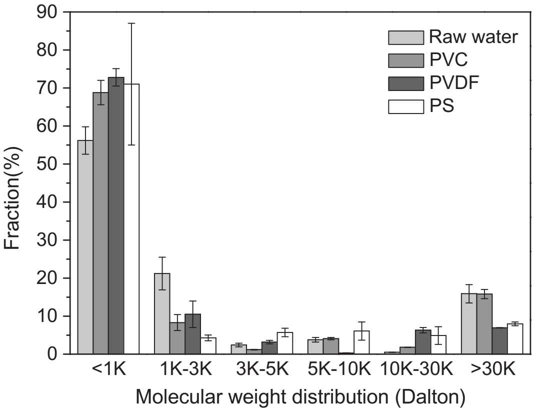

Fig. 5. MW distribution of organic matters causing irreversible membrane fouling.

tion, PVC, PVDF and PS membrane could be irreversibly fouled by the organic matters of the MW >30 KDa, which accounted for 15.8, 6.9 and 8%, respectively. PVDF membrane was more easily fouled by the organic matters of the MW between 1 K and 3 KDa, which accounted for 10.5%. Hydrophilic fractions of NOM (e.g. carbohydrate-like substances) are usually small molecules of the MW lower than 1 KDa [23]. These organic matters of small molecules could induce irreversible fouling due to their reaction with membrane materials through hydrogen bonds [24], but the degree of fouling was different depending on the membranes materials because different materials had quite different electronegative nature and hydrophobicity.

3.3. *Removal for organic matters of different MW distribution during long-term UF filtration*

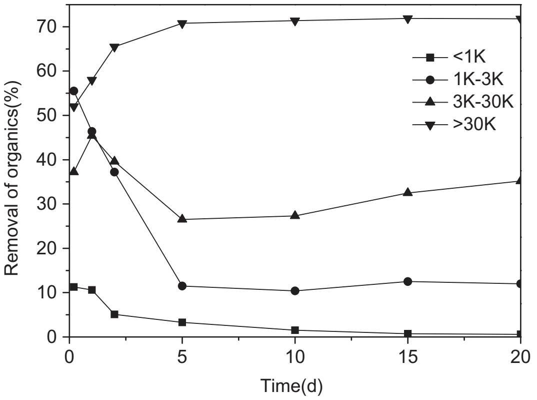

Fig. 6. Removal of organic matters with different MW distribution in the effluent of PVC membrane.

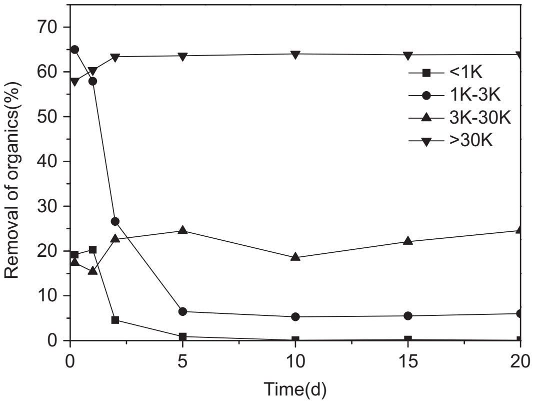

Fig. 7. Removal of organic matters with different MW distribution in the effluent of PVDF membrane.

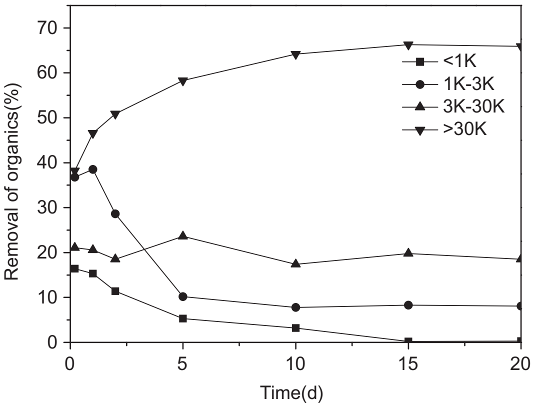

Fig. 8. Removal of organic matters with different MW distribution in the effluent of PS membrane.

The evolution of the removal for organic matters of different MW distribution during long-term UF filtration was investigated to compare the fouling for different UF membranes. Removal of organic matters with different MW distribution for PVC, PVDF and PS membrane is shown in Figs. 6–8, respectively. As shown in Fig. 6, the removal of the organic matters of the MW <1 K, 1–3 K, 3–30 K and >30 KDa was 11.3, 55.5, 37.2 and 52.0% respectively for PVC membrane at the beginning of filtration. As the filtration time increased, the organic matters removal of the MW <1 K and 1 K–3 KDa decreased and stabilized at around 12.1% after 15 days. There was no removal for the organic matters of the MW lower than 1 KDa after 15 days, which probably due to the gradually saturated adsorption by PVC membrane. The organic matters removal of the MW 3 K–30 KDa decreased to 26.5% after 5 days and increased to 35.2% after 20 days. In addition, the removal for the organic matters of the MW higher than 30 KDa was improved as the filtration time increased, which was stabilized at about 71.0% after 10 days. The retention of macromolecular organic matters could be improved by membrane as the pores were blocked by small molecules or particulates [25].

Fig. 7 showed that the removal of the organic matters of the MW <1 K, 1–3 K, 3–30 K and >30 KDa was 19.2, 65.0, 17.4 and 58.5% respectively for PVDF membrane at the beginning of filtration, which was higher than that for PVC membrane, indicating that the retention ability of organic matters was better for PVDF than for PVC membrane. After 10 days filtration, the removal for the organic matters of the MW between 1 K and 3 KDa was stabilized at about 5.5%, and there was no removal for the organic matters of the MW lower than 1 KDa. The organic matters removal of the MW 3 K–30 KDa slightly increased from 17.4 to 24.6% in 20 days. Similar to PVC membrane, the removal for the organic matters of the MW higher than 30 KDa was improved as the filtration time increased, and was stabilized at about 64.0% after 10 days.

As shown in Fig. 8, the removal of the organic matters of the MW <1 K, 1–3 K, 3–30 K and >30 KDa was 16.4, 36.8, 21.1 and 38.2% respectively for PS membrane in the beginning of filtration. After 15 days filtration, the removal for the organic matters of the MW 1 K–3 KDa and >30 KDa was stabilized at about 8.1 and 66.1%, respectively, and there was no removal for the organic matters of the MW lower than 1 KDa. The organic matters removal of the MW 3 K–30 KDa slightly decreased from 21.1 to 18.9% in 20 days.

It can be inferred from the above results that the adsorption of the organic matters of the MW <1 K and 1–3 K was more for PVDF membrane than for the two other membranes, and the adsorption rate was more fast. In 10 days filtration, the decrease rates of organic matters with the MW <1 K and 1–3 K removal by PVDF membrane were 1.91 and 4.97%/d, while 0.98 and 4.51%/d, and 1.32 and 2.9%/d for PVC and PS membrane respectively. All the three membranes were made from polymers containing atoms with electronegativity, and carbohydrate-like substances relatively easily accessed from the membrane surface because of their electrostatically neutral nature and formed the irreversible fouling. The higher electronegativity the membranes containing, the more easily the hydrogen bonds are formed. PVDF membrane used in this test contained high electronegativity substances of F, which could easily form hydrogen bonds with carbohydrate-like substances. The facts that hydrophilic NOM actually has a great binding power to the membrane due to hydrogen bonding partially explains why hydrophilic NOM was shown to be a major foulant in previous studies on fouling.

In the long-term filtration, for PS membrane, the evolution of removal for organic matters of different MW distribution was similar to other two membranes, but the adsorption rate was slower, indicating PS membrane had better resistance to organic fouling. Suitable material needs to be chosen for different water qualities because the organic matters in source water would have different effects on UF membranes with different materials.

4. Conclusion

The effects of NOM MW on fouling of immersed UF membrane with different materials were investigated in this study. The organic matters of the MW higher than 30 KDa were the main substances that could induce reversible membrane fouling regardless of the materials probably due to the direct pore blockage. Small organic molecules of the MW lower than 1 KDa were the main part that could induce irreversible fouling because of the hydrogen bonds, but the degree of fouling was different depending on the membranes materials. PVDF membrane was more vulnerable to small organic molecules due to its high electronegativity substances, and PS membrane had better resistance to organic fouling. The organic matters that could cause membrane fouling must be effectively removed when the UF filtration process is applied and suitable material needs to be chosen for different source water qualities.

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