Fouling analysis of polysulfone ultrafiltration membranes used for drinking water treatment

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ABSTRACT

Natural organic matter (NOM) plays a significant role in the fouling of ultrafiltration membranes in drinking water treatment processes. For a better understanding of the interaction between fractional components of NOM and polysulfone (PS) ultrafiltration membranes used for drinking water treatment, fouling and especially the physically irreversible fouling of natural organic matter were investigated. Resin fractionation, fluorescence excitation–emission matrix (EEM) spectroscopy, fourier transform infrared spectroscopy (FTIR), contact angle and a scanning electron microscope (SEM) were employed to identify the potential foulants. The results showed that humic acid and fulvic acid of small size were likely to permeate the membrane, while the hydrophobic fraction of humic and fulvic acid and aromatic proteins tended to be rejected and retained. Organic compounds such as proteins, humic substances, and polysaccharide-like materials, were all detected in the fouling layer. The physically irreversible fouling of the PS membrane seemed to be mainly attributed to the hydrophobic fraction of humic substances.

Key words | fouling, NOM, physically irreversible fouling, ultrafiltration

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INTRODUCTION

Membrane technology has rapidly become an efficient alternative to conventional drinking water treatment. The primary limitation encountered in the application of membrane technology is membrane fouling, which results in increases in hydraulic resistances, operational and maintenance costs, and deterioration of productivity and product quality (Aoustin *et al.* 2001; Yamamura *et al.* 2007). Much effort has been made to investigate the fouling mechanisms and foulant composition (Zularisam *et al.* 2007a). Several physical and chemical membrane cleaning methods such as hydraulic backwashing and NaOH or HCl solution cleaning have been developed and used routinely in many membrane plants to minimize membrane fouling. Usually, fouling that can be removed by physical cleaning is defined as physically reversible fouling, otherwise it is described as physically irreversible fouling (Yamamura *et al.* 2007).

Natural organic matter (NOM) consisting of a variety of nonbiodegradable organic compounds including humic substances has been widely reported as the major foulant

during surface water filtration (Yuan & Zydney 1999; Li & Elimelech 2004). However, presently there is still little agreement on the relative role of each NOM fraction in membrane fouling, especially on physically irreversible fouling. Previous researchers have suggested that the humic substances fraction of NOM is the major foulant which controls the rate and extent of fouling. Nilson & DiGiano (1996) investigated the influence of hydrophobic and hydrophilic NOM on nanofiltration; their work showed that the hydrophobic NOM fraction was responsible for nearly the entire flux decline. Aoustin *et al.* (2001) reported that the larger and more UV-absorbing fraction of humic acid was responsible for the irreversible pore adsorption and plugging. The fulvic acid and the hydrophilic fraction showed a smaller and mostly reversible flux decline.

More recently, as resin fractionation of NOM has been introduced into the investigation of potential fouling, hydrophilic NOM has been reported by several researchers to be a major foulant. Cho *et al.* (2000) reported that higher

molecular weight (MW) of the hydrophilic fraction was responsible for flux decline. Polypropylene MF filtration tests showed that small, neutral, hydrophilic compounds were the major NOM foulants for MF membranes. The NOM fractions comprised of humic and fulvic acid made only a minor contribution to membrane fouling (Carroll *et al.* 2000). Fan *et al.* (2001) identified the order of potential foulants as being hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. They further concluded that the low aromatic hydrophilic neutral compounds were the main determinant of the rate and extent of flux decline. Kennedy *et al.* (2005) suggested a similar order of fouling potential: hydrophilic > hydrophobic > transphilic. They found that a UF membrane showed almost no rejection for humic acids (20,000–1,000 Da). They also demonstrated that the reversibility of fouling caused by the hydrophilic fraction was very poor. However, Zularisam *et al.* (2007b) found the hydrophilic fraction of NOM exhibited a better flux recovery than the hydrophobic fraction despite its higher adsorption resistance and greater flux decline. Up to now, there is little agreement on which fraction of NOM is responsible for membrane fouling, especially for physically irreversible fouling.

In this study, fouling and physically irreversible fouling with natural organic matter source waters were investigated for a better understanding of the interactions between fractional components of NOM and a polysulfone (PS) UF membrane. Resin fractionation, fluorescence excitation–emission matrix (EEM) spectroscopy, Fourier transform infrared spectroscopy (FTIR), contact angle techniques and a scanning electron microscope (SEM) were employed to explore the nature of foulants and their reversibility, as well as looking at causes.

METHODS

Experiments were carried out at Baoshan water treatment plant (Hsinchu, Taiwan). Influent at the plant (raw water from Baoshan Reservoir) was on-line pretreated with 5 µm and 1 µm cartridge filters, and then delivered to a cross-flow membrane test unit (Sepa® CFII, GE Osmonics) as feed water at a flow rate of 0.8 L/min and at a

constant trans-membrane pressure (TMP) of 2 bar. The feed, concentrate and permeate were sampled, collected and analyzed every day during the whole operation period (200 hours).

The DOM fractions in the above water samples were further characterized by resin fractionation about which a detailed procedure has been reported by Wei *et al.* (2008). XAD-8 and XAD-4 resins (Amberlite, Sigma-Aldrich Co., USA) were used to fractionate DOM as follows: (1) the pre-filtered sample (by 0.45 µm membrane) was first passed through XAD-8 resin without any pH adjustment to isolate hydrophobic bases (HoB) and hydrophobic neutral (HoN). (2) HoB was obtained by back-washing the XAD-8 resin immediately with 10 bed-volumes of 0.1 mol/L H₃PO₄ at 15 bed-volumes/h. The hydrophobic neutral (HoN) could not be desorbed by H₃PO₄ and retained in the resin. H₃PO₄ was selected because of its minimal impact on the dissolved organic carbon (DOC) measurement compared to HCl or HNO₃. (3) The first effluent of the XAD-8 column was adjusted to pH 2 by 85% H₃PO₄ and then added into this XAD-8 resin column again. The hydrophobic acid (HoA) was adsorbed. (4) The second effluent from the XAD-8 column was passed through XAD-4 resin. The fraction adsorbed by this resin could be described as weakly hydrophobic acid (WHoA), which is also commonly defined as transphilic acid (THPA). (5) Organics contained in the XAD-4 effluent (not retained by either the XAD-8 or the XAD-4 resins) were named hydrophilic matter (HiM). The resins were cleaned and conditioned as described by Leenheer (1981) before use.

A flat sheet of PS membrane (GE Osmonics) with a MWCO of 30 kDa was used. It was soaked in methanol for 2 h before use. When the operation ended, the fouled membrane was taken out. A part of the membrane was cut and manually wiped with a sponge and thoroughly rinsed with DI water to remove the accumulated physically reversible cake layer. The original fouled membrane and the sponged wiped membrane were then analyzed using ATR-FTIR (Bomem, DA8.3, Canada), contact angle analysis techniques (MagicDroplet Model 100, USA) and an SEM (Hitachi S-4700, type II, Japan) after drying.

Analysis of DOC was performed by a TOC analyzer (TOC-5000A, Shimadzu, Japan). Measurements of

absorbance at the wavelength of 254 nm (UV_{254}) were carried out using a UV-Vis spectrophotometer (U3010, Hitachi, Japan) with a 1 cm quartz cell. Each EEM was generated by scanning excitation wavelengths from 200 to 400 nm with 10 nm steps, and detecting the emitted fluorescence between 250 and 550 nm with 1 nm steps. DI water was measured as a quality control for daily analysis. The pH value of water samples were controlled at 7.

RESULTS AND DISCUSSION

Membrane filtration

Figure 1 shows the flux behaviour of the PS membrane filtration. The flux declined fast during the first two days of the filtration and decreased to about 40% of the initial membrane flux. Severe fouling is observed with a flux decline of 70% at the end of the operation.

Characteristics of water streams

The average quality of the feed, permeate and concentrate was calculated based on daily analyses during the whole operation period and the results are shown in Table 1. It can be seen that the SUVA ($UV_{254}/DOC \times 100$) value of the permeates decreased as compared with the feed water. It was proposed that there was a larger amount of

Table 1 | Average amount of organic compounds and related parameters of three water streams: feed, permeate and concentrate

Samples	SUVA L/mg m	DOC mg/L	$UV_{254} \text{ cm}^{-1}$
Feed	3.00	0.97	0.029
Permeate	2.80	0.82	0.023
Concentrate	2.88	1.04	0.030

hydrophilic organic compounds in the permeate since the SUVA value represents the aromaticity of dissolved organic matter (Tian *et al.* 2009).

To investigate the specific fractional composition of each water stream, the resin fractionation analysis was conducted (shown in Figure 2). The permeate was found to have higher hydrophilic DOC (%) content and relative lower hydrophobic DOC (%) such as HoA, HoN and HoB fractions. This was consistent with the SUVA value trend.

To further study the organic matter, EEMs of feed, permeate and concentrate were measured and compared (Figure 3). As shown in Figure 3, three apparent peaks are observed. Chen *et al.* (2003) have reported that peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) were related to simple aromatic proteins such as tyrosine. Peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) were related to humic acid-like

Figure 1 | Flux decline profiles of PS ultrafiltration.

Figure 2 | Relative fraction of hydrophobic neutral (HoN), hydrophobic base (HoB), hydrophobic acid (HoA), weakly hydrophobic acid (WWhoA) and hydrophilic (HiM) DOM fractions in feed, permeate and concentrate.

Figure 3 | EEMs of (a) feed, (b) permeate and (c) concentrate.

organics. Peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) were related to fulvic acid-like materials. This implied that the feed water contained mainly simple aromatic proteins, humic acid and fulvic acid-like organics. While the aromatic proteins were effectively rejected, and the permeate contained mainly humic and fulvic acid-like organics.

Therefore, it was proposed that hydrophilic fractions of humic acid and fulvic acid of a small size permeated the membrane easier, while the hydrophobic fraction with relatively higher molecular weight or molecular mass were likely to be rejected and retained by the membrane. Their complex molecular structure also prevents components with an aromatic shape from easily passing through the membrane (Zularisam *et al.* 2007a, b).

ATR-FTIR analysis

Figure 4 illustrates the ATR-FTIR spectra of the fouled and sponge wiped PS membrane. Filtration of lake waters commonly results in the addition of carboxyl or amide groups to the clean membrane. For the fouled PS membrane, corresponding peaks were detected at wave-numbers 1,540 and 1,650 cm^{-1} (Ahn *et al.* 2008). Deprotonated carboxyl groups have two modes of vibration. Peaks arising from asymmetric stretching of $-(\text{C}=\text{O})-\text{O}-$ appear between 1,540 and 1,650 cm^{-1} , while peaks from symmetric stretching appear between 1,200 and 1,300 cm^{-1} (Cabaniss & McVey 1995). In addition, stretching of $-\text{C}-\text{O}$ group and OH deformation of COOH appear between 1,200 and 1,300 cm^{-1} in combination with the acid O-H stretching bond at $\sim 3,300 \text{ cm}^{-1}$.

Figure 4 | ATR-FTIR spectra of fouled and sponge wiped PS membranes: ATR-FTIR spectrum of clean PS membrane was digitally subtracted.

Figure 5 | Contact angles of virgin, fouled and sponge wiped PS membranes.

both of which suggest the presence of humic substances (Zularisam *et al.* 2006). Due to the similar structure of amide and deprotonated carboxyl groups, vibration frequencies are similar as well. Primary and secondary amide peaks are located at $\sim 1,580$ and $1,650\text{ cm}^{-1}$, respectively (Cho *et al.* 1998; Jarusutthirak *et al.* 2002). Other common peaks were detected at $1,130$ and $1,170\text{ cm}^{-1}$ for

the filtration of lakes waters, which was assigned to polysaccharide-like material (Jarusutthirak *et al.* 2002; Zularisam *et al.* 2006). The silicon oxide bond (i.e., $-\text{Si}-\text{O}$) of clay minerals is apparent at $1,080\text{ cm}^{-1}$ (Ahn *et al.* 2008). As described above, the foulant included proteins, humic substances, polysaccharide-like materials and silicon-contained minerals. By contrast, for the sponge wiped PS membrane, the main adsorption bands were $2,940\text{ cm}^{-1}$ (aliphatic C–H stretching), $1,720\text{ cm}^{-1}$ ($-\text{C}=\text{O}$ stretching band of carboxylic acid), $1,200\text{--}1,300\text{ cm}^{-1}$. The results suggest that the major constituents of the irreversible membrane fouling were humic substances.

Contact angle analysis

Contact angle analysis was used to investigate the hydrophobicity/hydrophilicity of the membrane surface. The angle of a water drop on the membrane surface was measured by a goniometer. Although it is not a very precise and quantitative methodology, it is still informative in explaining the relative changes of a membrane's properties by fouling (Lee *et al.* 2004). As shown in Figure 5, the contact angle of the fouled membrane was slightly higher than the virgin membrane. But the contact angle of sponge wiped PS increased to 79.7° . In general, the change in contact angle was primarily influenced by the deposition of organic foulants on the membrane surface, especially the composition of NOM. From this interpretation, these results were in accordance with the findings described above: more

Figure 6 | SEM images of membranes (magnification: $\times 50,000$): (a) fouled PS membrane and (b) sponge wiped PS membrane.

hydrophobic NOM was rejected by the membrane and the hydrophobic fraction of humic acid could be the potential physically irreversible foulant.

Scanning electron microscopy

The top surfaces of fouled and sponge wiped PS membranes were observed with an SEM. The images are shown in Figure 6(a) and (b), respectively. Comparing Figures 6(a) and (b), it can clearly be seen that membrane fouling was very serious after a 200 h filtration. A compact gel layer covered the surface and caused significant flux reduction while, after manually sponge wiping, most of the membrane surface pores could be clearly observed. This further confirmed that the physically irreversible fouling of the PS membrane was relatively weak with few foulants plugging in the membrane pores.

CONCLUSIONS

In this study, the fouling, and particularly the physically irreversible fouling, of a PS ultrafiltration membrane was investigated. It was found that the hydrophilic fractions of humic acid and fulvic acid of small size were likely to permeate the membrane, whilst it was easier to reject and retain the hydrophobic fraction of humic and fulvic acid and aromatic proteins. Through membrane autopsy, the organic compounds which contained proteins, humic substances and polysaccharide-like materials, were all detected in the fouling layer. But the physically irreversible fouling of the PS membrane seemed to be mainly the hydrophobic fraction of humic substances.

ACKNOWLEDGEMENTS

This work is supported by the NSF of China under 50908224, 50921064, the national 863 program under 2008AA06A414 and the special fund from the State Key Laboratory of Environmental Aquatic Chemistry (Project 08Y03ESPCR). The authors are grateful to Prof. D.J. Lee (National Taiwan University) for his help in EEM

measurement. The kind comments from anonymous reviewers are gratefully acknowledged.

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First received 1 June 2010; accepted in revised form 25 August 2010