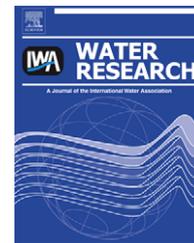


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Effects of mass retention of dissolved organic matter and membrane pore size on membrane fouling and flux decline

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ABSTRACT

Ultrafiltration (UF) fouling has been attributed to concentration polarization, gel layer formation as well as outer and inner membrane pore clogging. It is believed that mass of humic materials either retained on membrane surface or associated with membrane inner pore surface is the primary cause for permeate flux decline and filtration resistance build-up in water supply industries. While biofilm/biofouling and inorganic matter could also be contributing factors for permeability decline in wastewater treatment practices. The present study relates UF fouling to mass of dissolved organic matter (DOM) retained on membrane and quantifies the effect of retained DOM mass on filtration flux decline. The results demonstrate that larger pore membranes exhibit significant flux decline in comparison with the smaller ones. During a 24-h period, dissolved organic carbon mass retained in 10 kDa membranes was about 1.0 g m^{-2} and that in 100 kDa membranes was more than 3 times higher (3.6 g m^{-2}). The accumulation of retained DOM mass significantly affects permeate flux. It is highly likely that some DOMs bind or aggregate together to form surface gel layer in the smaller 10 kDa UF system; those DOMs largely present in inner pore and serving as pore blockage on a loose membrane (100 kDa) are responsible for severe flux decline.

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1. Introduction

Membrane application for water purification has gained much popularity in recent years. Water supply industries have successfully used nanofiltration (NF) or ultrafiltration (UF) technologies to remove natural organic matter (NOM) and simultaneously control disinfection byproduct precursors. The critical problem encountered in NF or UF of natural water containing dissolved organic matter (DOM) is membrane fouling which causes permeate flux decline and thus shortens the UF operation life, increases the maintenance cost and eventually adds additional capital cost for membrane replacement (Maartens et al., 1998). Publications on membrane fouling are quite abundant (e.g., Aoustin et al., 2001; Howe and

Clark, 2002; Zhang et al., 2003; Kimura et al., 2004; Kweon and Lawler, 2004; Lee et al., 2004). In general, UF fouling resulting due to NOM has been attributed to concentration polarization, gel or cake layer formation as well as outer and inner pore clogging. Aoustin et al. (2001) reported that internal deposition of NOM resulted in irreversible fouling with larger molecular fraction of humic materials responsible for pore clogging. Fouling due to concentration polarization is rather complex to quantify. Thorsen (2004) studied the concentration polarization caused by NOM in NF and UF and concluded that adsorption of NOM onto membrane surface played little role on membrane fouling.

Although membrane fouling can theoretically be rationalized with the physical and chemical phenomena, quantitative

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differentiation among concentration polarization, gel or cake layer formation and pore clogging is difficult. However, it is believed that mass of humic materials deposited on membrane surface associated with membrane inner pore surface or pore blockage are the primary reasons for permeate decline and filtration resistance build-up in water supply industries. While biofilm/biofouling and inorganic matter could also be contributing factors for permeability decline in wastewater treatment practices. Hong and Elimelech (1997) studied the interaction between divalent ions and NOM and concluded that NOM deposition on the membrane surface and the formation of fouling layer were due to the molecular associations between NOMs. At a deposited NOM less than 6 gm^{-2} , the membrane flux could be maintained at about $10 \times 10^{-6} \text{ m}^{-1} \text{ s}$. A similar work was conducted by Katsoufidou et al. (2005) on the effect of divalent ions on membrane fouling by humic acids. The amounts of humic acids deposited on membrane surface varied from 100 to 170 mgm^{-2} and depended on solution Ca^{2+} concentrations. Lee et al. (2004) used field waters to study the fouling of microfiltration (MF) and UF by DOM and reported that the dissolved organic carbon (DOC) at 250 mgm^{-2} would cause 11–71% of permeate flux decline, depending on the water chemistry of the feed waters. These studies elucidate that membrane fouling is consequence of NOM accumulation and deposition, but provided very little quantitative information on the fouling layer.

Consequently, the present work is intended to present quantitatively the effects of DOM on UF fouling through mass balance of humic materials on UF permeation. Specifically, two types of membrane size, operating pressure and feed DOC concentration were evaluated to quantify their effects on flux decline. The role of membrane pore size on surface gel layer formation and inner pore association or pore blockage was also evaluated.

2. Experimental section

Humic acid (sodium salt) from Aldrich was used to prepare stock humic acid feed solution (2 and 9 mgL^{-1} DOC) by dissolving 1 g of humic acid in 1 L deionized water (Milli-Q), and filtering through $0.45 \text{ }\mu\text{m}$ membrane filter. The feed solutions were supplemented with NaCl to maintain conductivity near $300 \text{ }\mu\text{S cm}^{-1}$ and pH was adjusted to 7 with 1 N NaOH and/or 1 N HCl . The stock humic acid solution and feed solutions were stored at $4 \text{ }^\circ\text{C}$ for subsequent UF experiments.

A single hollow fiber module (hydrophobic with negatively charged polysulfone: A/G Technology) with a length of 29 cm and an area of approximately 9 cm^2 was used. Two types of UF membranes with the nominal molecular weight cutoff (MWCO) of 10 and 100 kDa were employed. The crossflow mode in the UF system was operated without recirculating the concentrated retentate to avoid changes in feed solution composition. Fig. 1 shows the schematic of the crossflow experimental setup which includes high pressure N_2 gas chamber that provides the driving pressure to deliver feed solution, hollow fiber UF module, pressure gauges and fraction collector for flux measurement. The transmembrane pressure (TMP) was controlled at four different levels: near 70 kPa (10 psi), 105 kPa (15 psi), 140 kPa (20 psi) and 175 kPa (25 psi). In

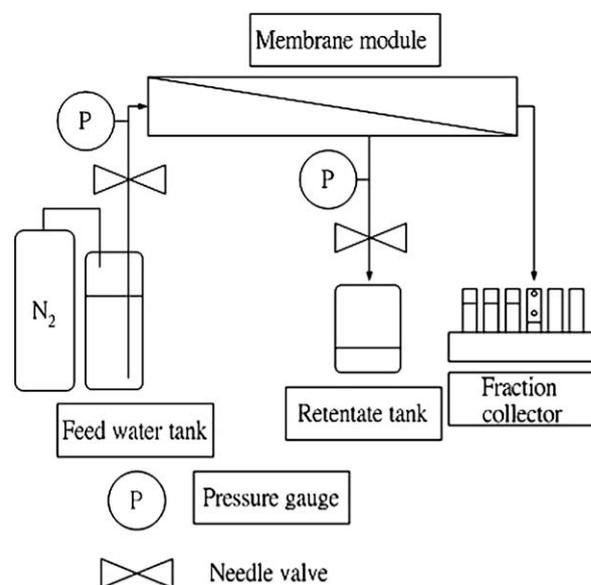


Fig. 1 – Schematic diagram of UF hollow fiber module employed in the permeation experiments.

all the UF operations, tangential flow velocity was controlled at 0.1 m s^{-1} . For each experiment, a new hollow fiber UF was used to ensure no interference of humic materials that were remaining from previous experiments. The hollow fiber was initially pre-washed with alcohol for 5 min and then flushed with Milli-Q water for 8 h before the designated experiments.

Throughout the experiments ($T = 25 \text{ }^\circ\text{C}$), the TMP was maintained constant and permeate flux monitored. The permeate was collected using a fraction collector at various time intervals: 3 (at the beginning), 10 , 15 , 30 , 45 – 60 min (after 6 h). Permeate volume was measured using electric balance with the detection level in mg . The DOC concentrations in retentate and permeate were measured at the pre-designated time intervals. The DOM mass (retentate and permeate) at time t_n was the average of time t_{n-1} and t_n . DOC concentration of feed solution for each experiment was quantified in an organic carbon analyzer (O.I. Corporation, model 700).

The mass retained on membrane was calculated based on the mass balance of humic materials in DOC. During the UF operation, the retained mass of humic materials on membrane is equal to humic material mass in feed minus humic material mass out in both retentate and permeate. The humic material mass is then summed throughout the entire permeation period to represent the accumulated DOM.

The membrane permeation resistance during operation is calculated based on resistance-in-series model which has originated from the hydraulic gradient theorem. It stipulates that the energy loss to maintain a constant fluid velocity is due to the friction on porous media as (Chiang and Cheryan, 1986):

$$J = \frac{P_T}{R_M + R_i + R_G} = \frac{P_T}{R_M + R_i + \phi P_T} \quad (1)$$

where J is permeate flux ($\text{m}^{-3} \text{ m}^{-2} \text{ s}^{-1}$), P_T TMP (Pa), R_M membrane intrinsic resistance ($\text{Pa s}^{-1} \text{ m}^{-1}$), R_i interaction resistance ($\text{Pa s}^{-1} \text{ m}^{-1}$) due to the interaction between DOC and inner membrane material, and R_G gel layer/concentration

polarization resistance ($\text{Pa s}^{-1} \text{m}^{-1}$). R_G is considered to be proportional to the mass of deposited DOC and the specific resistance of the gel layer. As the gel layer is compressed, the resistance tends to increase with applied pressure (McCarthy et al., 2002). Therefore R_G is expressed as a function of TMP with $R_G = \phi P_T$, where ϕ is dependent on the specific membrane system and can be determined from experimental data (Yeh and Wu, 1997).

The R_M can be easily determined in a deionized water UF system with a fresh hollow fiber module. By varying TMP and plotting $(1/J)$ versus $(1/P_T)$, the slope of the straight line yields the R_M . To determine R_i and ϕ , the flux as a function of TMP and feed DOC concentration was monitored. The plots of $(1/J)_t$ versus $(1/P_T)$ are constructed and the slope and the intercept yield $(R_M + R_i)$ and ϕ , respectively, as:

$$\left(\frac{1}{J}\right)_t = \phi + \frac{R_M + R_i}{P_T} \quad (2)$$

where t represents the filtration time. R_i is then obtained by subtracting R_M value from $R_M + R_i$ (Eq. (2)). Since R_G and R_i were not experimentally differentiable at this stage, we rather used fouling resistance, R_F (due to retained DOM mass on membrane) to represent the confounding results of both gel layer resistance and inner pore adsorption/clogging resistance. In this study, R_F refers to the resistance resulting from DOC retained during the filtration. Numerically, R_F is equated to the difference between total resistance and the membrane intrinsic resistance ($= (P_T/J) - R_M$).

3. Results and discussion

A typical UF permeate flux evolution at four TMPs with time is presented in Fig. 2. Two MWCO UF (10 and 100 kDa) were fed with 2 mg L^{-1} DOC to induce membrane fouling. The initial permeate flux ranged from 30 to $70 \mu\text{m s}^{-1}$ for 10 kDa UF and 60 to $160 \mu\text{m s}^{-1}$ for 100 kDa UF. Initial flux values are seen to be clearly dependent on membrane size as well as TMP. Permeate flux decline was faster and more severe in the loose

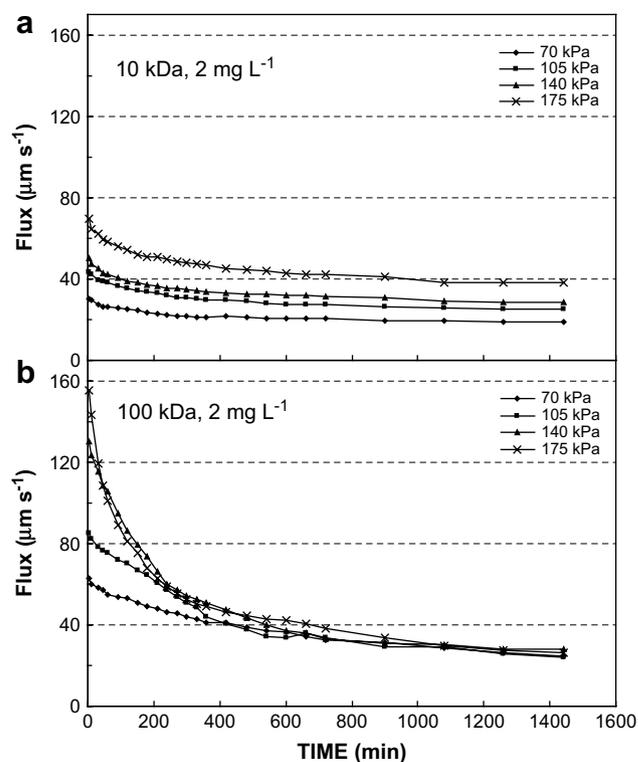


Fig. 2 – UF permeate flux evolution under four transmembrane pressures at feed DOC 2 mg L^{-1} . (a) 10 kDa UF, (b) 100 kDa UF.

pore UF system (100 kDa), particularly during the first 200 min filtration (Fig. 2b). On the other hand, there was only slight flux change within 24-h filtration period for 10 kDa UF system, or from 10 to $30 \mu\text{m s}^{-1}$ (Fig. 2a). Based on these results, it is justifiable to state that the loose pore membrane exhibits more significant flux decline than the tight pore membrane. In addition to MWCO size, the TMP also significantly affects the flux decline. For example, for 100 kDa system, flux dropped from 63 to $25 \mu\text{m s}^{-1}$ at TMP of 70 kPa after 24 h, whereas for an

Table 1 – DOM mass retention (g m^{-2}) on 10 kDa and 100 kDa membranes during 24-h operation.

Transmembrane pressure (kPa)	2 mg L^{-1}		9 mg L^{-1}	
	10 kDa	100 kDa	10 kDa	100 kDa
70	0.7 P (0.5–0.8) R (3.0)	3.33 P (1.0–1.4) R (2.6)	3.9 P (0.4–0.9) R (10.7)	7.97 P (4.4–5.5) R (10.1)
105	1.03 P (0.5–1.0) R (3.5)	3.58 P (1.0–1.5) R (2.4)	4.76 P (0.5–1.3) R (11.9)	9.33 P (4.2–6.3) R (10.2)
140	1.64 P (0.6–0.8) R (3.0)	3.87 P (1.0–1.5) R (2.5)	6.56 P (0.9–1.6) R (11.1)	9.70 P (4.5–6.0) R (10.4)
175	2.23 P (0.7–1.0) R (2.9)	4.18 P (1.2–1.5) R (2.3)	7.62 P (1.1–2.2) R (12.1)	11.1 P (4.4–6.0) R (10.1)

P (·): the range of permeate concentrations in mg L^{-1} . R (·): the averaged retentate concentration in mg L^{-1} .

increased TMP of 175 kPa the flux decline was from 155 to 26 $\mu\text{m s}^{-1}$. The quantitative results of flux evolution presented in Fig. 2 were converted to the mass of DOM retained on membrane for the entire 24-h operation as shown in Table 1. The permeate DOC and average DOC in retentate are also shown in Table 1. The data again reveal some common phenomena: (1) higher TMP results in more accumulated DOM on membrane, (2) higher DOC feed concentrations bring more DOM on membrane, and (3) larger pore size membrane retains more DOM during the same operation period. For example, the accumulated DOC on 10 kDa membrane at a feed DOC of 2 mg L^{-1} has increased from 0.7 to 2.2 g m^{-2} when TMP was increased from 70 to 175 kPa. For the 100 kDa UF with TMP of 175 kPa, DOC retained on membrane increased from 4 to 11 g m^{-2} as feed DOC concentration was increased from 2 to 9 mg L^{-1} . Under same operating conditions, 100 kDa membrane retained up to 4 times more humic materials than 10 kDa membrane. According to the work by McCarthy et al. (2002), gel layer thickness was considered to be affected by TMP. Therefore it was assumed in our study that surface gel layer would have same thickness for the same permeation area (i.e., same amount of DOC); the extra amount of retained DOC on 100 kDa membrane should be deposited inside the inner pores. In other words, most of the foulant (DOM) should be associated with inner pore surfaces.

The deposition of DOM on membrane causes permeation flux decline and also increases permeation resistance. Figs. 3 (10 kDa) and 4 (100 kDa) present the advancement of UF permeation resistances as a function of DOM mass retention. In both systems, the permeation resistances were relatively

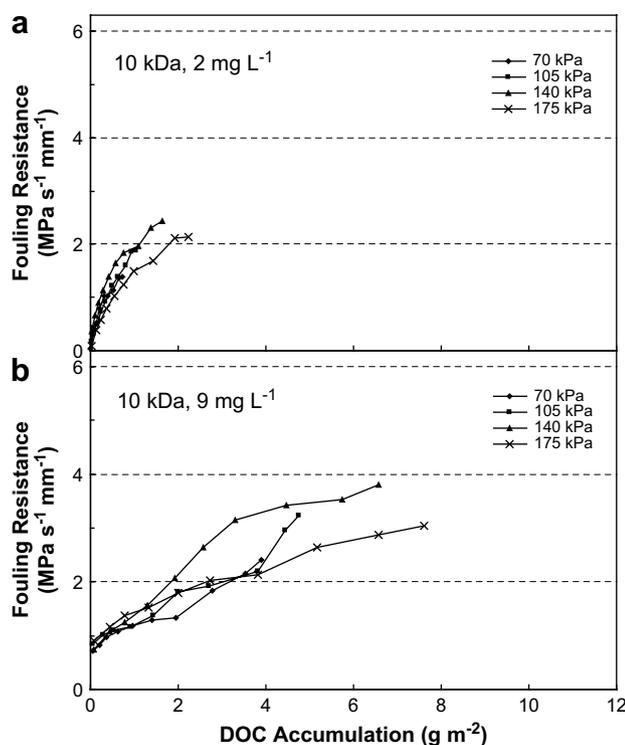


Fig. 3 – Advancement of UF permeation resistances as a function of DOC mass retention for 10 kDa UF. (a) Feed DOC 2 mg L^{-1} , (b) feed DOC 9 mg L^{-1} .

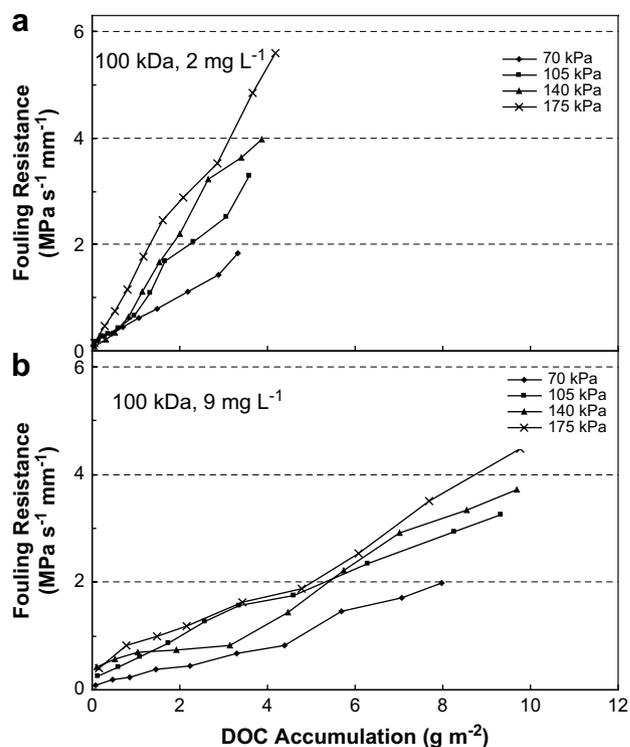


Fig. 4 – Advancement of UF permeation resistances as a function of DOC mass retention for 100 kDa UF. (a) Feed DOC 2 mg L^{-1} , (b) feed DOC 9 mg L^{-1} .

linearly dependent on DOC mass accumulation on membrane. The initial slopes of fouling resistances versus retained DOM (Figs. 3 and 4) were calculated with the regression method of least squares and the corresponding results are presented in Table 2. The correlation coefficients were always >0.94 . Interestingly, the slopes representing the resistance change per unit retained DOM mass are steeper in 2 mg L^{-1} systems than those in 9 mg L^{-1} systems, particularly for 10 kDa membranes. The higher humic acid concentration (9 mg L^{-1}) might favor molecular agglomeration which can result in the formation of larger molecules. It appears that larger molecules can easily get deposited on membrane surface rather than moving into the inner pores. Therefore it is believed that the effect of inner pore interaction on the fouling resistance per unit retained DOM mass at 2 mg L^{-1} feed concentration was less than 9 mg L^{-1} feed concentration.

Table 2 – Fouling resistances per unit retained DOM mass ($\text{MPa s}^{-1} \text{m}^{-1} \text{mm}^{-1} \text{g}^{-1} \text{m}^2$).

Transmembrane pressure (kPa)	2 mg L^{-1}		9 mg L^{-1}	
	10 kDa	100 kDa	10 kDa	100 kDa
70	1.73	0.48	0.4	0.24
105	1.69	0.87	0.46	0.32
140	1.19	1.11	0.48	0.36
175	0.89	1.29	0.27	0.39

The regression coefficients of the slopes (R^2) are >0.94 in all cases.

The effect of TMP on the fouling resistances per DOM mass retained was different for 10 and 100 kDa systems. For example, the fouling resistance per unit accumulated DOM decreased as TMP was increased from 70 to 175 kPa in the 10 kDa UF system, whereas it increased steadily with increasing TMP in the loose 100 kDa UF system (Table 2). TMP acts as the main driving force through membrane for permeate flux and leaves the DOM molecules on membrane either as gel layer or inner pore accumulation. For 100 kDa membrane, higher TMP might push and deliver more DOM molecules into membrane pores resulting in severe inner pore adsorption/clogging; therefore, the fouling resistance per unit mass of retained DOM increased as the operating TMP increased resulting in severe flux decline. As for the 10 kDa systems, fouling resistance decreased with increasing TMP. The totally contrast results observed in tight UF might be because of the size exclusive effect and the surface gel layer effect that prevent pushing of DOM molecules to cause the inner pore adsorption/clogging. Indeed, an earlier report shows that larger humic materials are responsible for the surface layer clogging (Aoustin et al., 2001). Quantitative effects of retained DOM on permeate flux decline over a 24-h filtration period are profiled in Figs. 5 and 6. Again, the influent with 2 mg L^{-1} DOC caused more severe flux decline per unit retained DOM mass than that of 9 mg L^{-1} systems, especially during the beginning of filtration stage. The slopes in Figs. 5 and 6 represent the effect of unit mass of retained DOM on changes of permeate flux. In Fig. 5, the trend of slopes of the curves was similar indicating that the effect of TMP on unit flux change per unit retained DOM was not significant in the

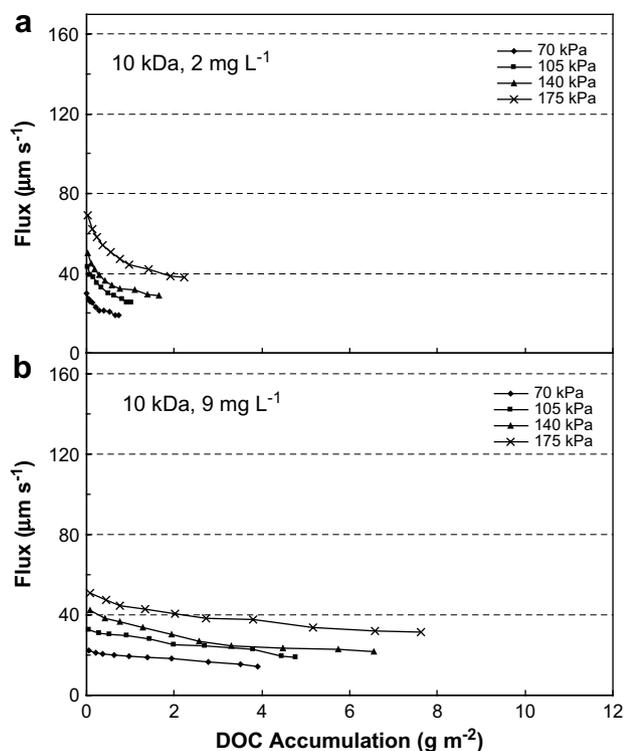


Fig. 5 – Effects of DOC mass retention on membrane flux decline of 10 kDa UF. (a) Feed DOC 2 mg L^{-1} , (b) feed DOC 9 mg L^{-1} .

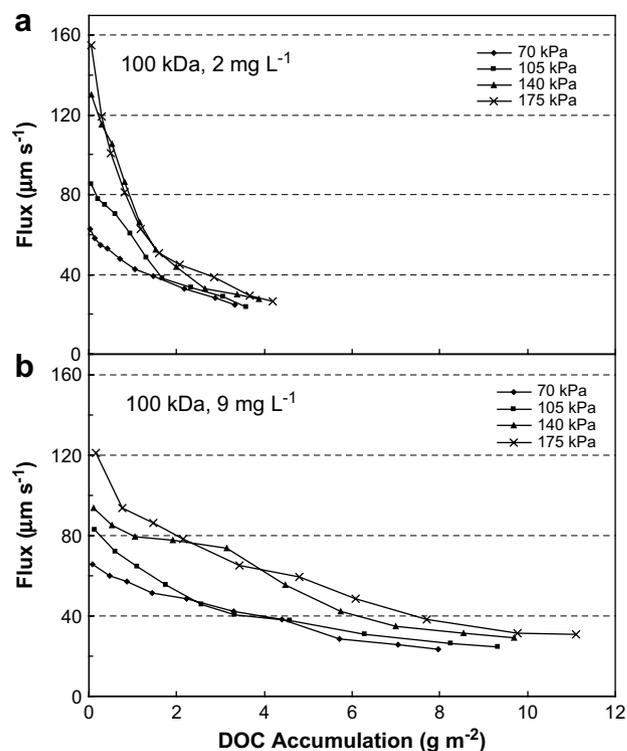


Fig. 6 – Effects of DOC mass retention on membrane flux decline of 100 kDa UF. (a) Feed DOC 2 mg L^{-1} , (b) Feed DOC 9 mg L^{-1} .

case of 10 kDa UF. Whereas for 100 kDa UF (Fig. 6), higher TMP (140 and 175 kPa in 2 mg L^{-1} system) appears to cause more flux decline by the retained DOM. The initial flux changes with the unit DOM mass retained were nonlinear and flux then gradually reached the steady-state fouling condition. The two-stage flux phenomenon was best illustrated for 100 kDa at 2 mg L^{-1} with higher TMP (Fig. 6a). The initial rapid drop of flux with unit DOM mass retained may be due to pore blockage for this loose membrane. Thereafter, DOM accumulation on the membrane surface may be responsible for gradual flux decline. It was construed that the retained DOM foulant indeed results in permeate flux decline. The effects of the retained DOM on permeate flux decline was further shown to be dependent on the membrane pore size in conjunction with the feed and the operational conditions. The observed condition for the most severe impact on permeate flux decline per unit retained DOM was low feed concentration and loose membrane with higher TMP.

Hypothetically, we have proposed two classes of fouling schemes as depicted in Fig. 7. Fouling on a tight pore membrane is primarily due to surface gel layer formation with very little inner pore adsorption or clogging (Fig. 7a). This is partially supported by the fact that the fraction of $<1 \text{ kDa}$ size humic materials is less than 25% of total DOC based on the gel filtration chromatography experiments of humic materials (Syafei, 2007). Membrane fouling in the 100 kDa UF, on the other hand, is believed to be inner pore adsorption/blockage (Fig. 7b). A large fraction of the humic materials having the molecular size $<100 \text{ kDa}$ is able to enter membrane pore and subsequently aggregate and stick together in the pore

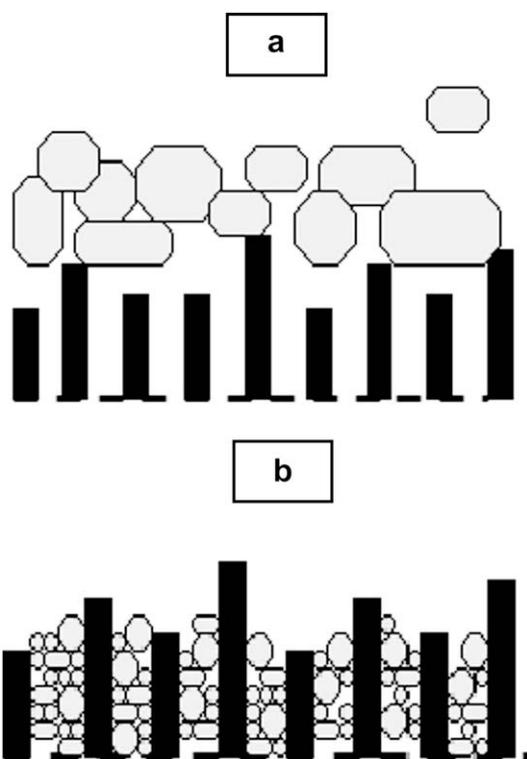


Fig. 7 – The proposed fouling mechanisms for (a) tight membrane (surface gel layer) and (b) loose membrane (inner pore adsorption and clogging).

channel. Indeed, study of Katsoufidou et al. (2005) supports this hypothesized fouling mechanism on tight and loose pore membranes. They further stated that the irreversible fouling was attributed to internal pore adsorption with fouling cake deposited on membrane surface that can easily be removed by backwashing. It is anticipated that the results of our experiments and the proposed hypothetical fouling mechanism will be of great help for the membrane modeling researches.

4. Conclusions

UF membrane is easily fouled by feed water containing DOM. The fouling is primarily originated from the gel layer formation and inner pore adsorption or pore blockage. A 10 kDa UF feeding with 2 mg L^{-1} DOC will accumulate $0.7\text{--}2.2 \text{ g m}^{-2}$ DOM in a 24-h operation period, while 9 mg L^{-1} DOC feed results in the accumulated $3.9\text{--}7.6 \text{ g m}^{-2}$ DOM. In the case of 100 kDa UF, the accumulated DOM is $3.3\text{--}4.2 \text{ g m}^{-2}$ (2 mg L^{-1}) and $8\text{--}11 \text{ g m}^{-2}$ (9 mg L^{-1}). We proposed that those DOMs are largely present in inner pore in a loose membrane resulting in severe flux decline. The membrane surface gel layer formation is more crucial in the tight pore membrane. The effects of retained DOM on permeate flux decline depend on the membrane pore size as well as the feed and operational conditions. Low feed concentration, loose membrane with higher TMP will cause stern impact on permeate flux decline

per unit retained DOM. Depending on the permeation conditions, membrane flux due to accumulation of DOM could be classified into an initial rapid decline and eventual gradual decrease before reaching steady-state condition.

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