



## Reduction of natural organic matter by nanofiltration process

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### ABSTRACT

The objectives of this investigation were to characterize natural organic matter (NOM) in Kin-men raw water, to evaluate the performance of the nanofiltration (NF) membrane process for NOM removal, and to determine the good engineering practice (GEP) of the NF 270 membrane filtration performance. Three different samples: (1) raw water collected from the Tai Lake in Kin-men, Taiwan; (2) ultrafiltration (UF) pre-treated water; and (3) sand filtration (SF) treated water after the coagulation and sedimentation processes were employed in this study.

The hydrophobic component (58%) was the predominant NOM fraction, and the NOM molecular weight was distributed broadly, i.e., lower than 1 kDa (30%), 1–5 kDa (32%) and larger than 5 kDa (38%). Hydrophobic NOM easily accumulated on the NF membrane surface and resulted in flux decline. The SF–NF was the proposed treatment process because it can reduce the NOMs effectively with lower energy consumption than UF–NF.

It was noted that the dissolved organic carbon (DOC) rejection ratio was not affected by changing cross-flow velocity. However, at lower cross-flow velocity ( $0.15 \text{ m s}^{-1}$ ), the reduction of organic matter in water sample was higher than that at higher cross-flow velocity ( $0.30 \text{ m s}^{-1}$ ). By integrating the experimental results, it was concluded that a transmembrane pressure of 690 kPa and a cross-flow velocity of  $0.30 \text{ m s}^{-1}$  exhibited the GEP, yielding about 94% of both DOC and  $\text{UV}_{254}$  reduction.

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### 1. Introduction

To prevent microbial contamination in drinking water, chlorination has been widely used as a disinfectant in water treatment plants. Free chlorine can react with natural organic matter (NOM) to form disinfection by-products (DBPs), which are considered carcinogenic and mutagenic (Rook, 1976). Effective removal of NOM has been a challenge for water utilities.

NOM is a heterogeneous mixture present in natural waters with a wide range of molecular weights (MW) and functional groups (Aiken et al., 1992; Kwon et al., 2005; Lee et al., 2005b; Zularisam et al., 2006). Because of the complex nature of NOM, surrogate parameters such as dissolved organic carbon (DOC),  $\text{UV}_{254}$ , and specific UV absorbance at 254 nm ( $\text{SUVA}_{254}$ ) are often used to represent its general properties. NOM may also be fractionated into hydrophobic acid, transphilic acid, and hydrophilic acid by XAD-8/XAD-4 resins (Aiken et al., 1992; Zularisam et al., 2007). Thurman (1985) reported that hydrophobic and hydrophilic acid fractions comprised approximately 40% and 25–40% of the NOM in surface water, respectively. This fractionation has been shown to provide

important information regarding the removal efficiencies of NOM by various water treatment processes.

NOM associated with suspended particles is also removed by coagulation, but the removal efficiency is variable, depending on the physical and chemical characteristics of the water and the operating conditions (Ratnaweera et al., 1999). Aquatic NOM consists of humic substance, which may carry weakly acidic functional groups, such as carboxylic and phenolic groups (Cook and Langford, 1998); furthermore, different molecular sizes of NOMs may have different contributions to trihalomethanes (THMs) formation (Plummer and Edzwald, 2001). The higher MW of NOM with the hydrophobic fraction was removed readily by coagulation (Collins et al., 1986; White, 1997). However, low MW organic matters, like resorcinol, phloroglucinol, and p-hydroxybenzoic acid, were considered to be major contributors to higher DBP formation (Chang et al., 2004), which has been proven to be unfavorable to conventional potable water treatment, like coagulation process (Bekbolet et al., 2005).

As a result, it is required to introduce membrane treatment processes, such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), after the conventional treatment processes, i.e., coagulation, sedimentation and filtration processes to remove residual NOM. Owen et al. (1995) proposed that NF with a relatively lower MWCO (molecular weight cut-off) of 400–800 Da is effective in controlling the formation of DBPs. Retentions of various

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micropollutants by NF membranes were also reported by several researchers (Wintgens et al., 2002; Nghiem et al., 2004; Kim et al., 2005). Some researchers have indicated that membrane costs are comparable to or lower than conventional treatment for small systems of  $< 20,000 \text{ m}^3 \text{ d}^{-1}$  (Wiesner et al., 1994; Jacangelo et al., 1995).

In order to optimize the NF process for reduction of NOMs, the appropriate pretreatment processes should be assessed and selected. For instance, if flocculation and adsorption are used for pretreatment prior to membrane filtration, membrane fouling could be significantly reduced. Most organic matters with a molecular weight of near or less than 1 kDa in source water are responsible for the formation of THM precursors in Taiwan (Chang et al., 2001; Chiang et al., 2002). Limited research focused on reduction of DBP precursors with different functional groups of small molecular aromatic compounds by NF.

The main goals of this study were to investigate the effectiveness of NF in NOM removal under different pretreatment processes prior to NF membrane process and to determine the good engineering practice (GEP) for removing NOMs from either raw water or pre-treated water. Three different water samples were employed in this study: (1) raw water collected from the Tai Lake in Kin-men, Taiwan; (2) UF pre-treated water; and (3) sand filtration (SF) treated water after the coagulation and sedimentation processes. The UF and SF pretreatments were performed to compare their effectiveness in removing NOMs from raw water prior to NF membrane treatment. The performance of NF process was assessed by measurements of the DOC and  $\text{UV}_{254}$ .

## 2. Materials and methods

The experiments of the membrane processes of this study were divided into two stages. In stage 1, the water sample was taken from the effluent of SF process in Tai Lake water treatment plant. In stage 2, samples were taken from the raw water of Tai Lake water treatment plant in Kin-men County for NOM analysis. All water used in the membrane process was pre-filtered with  $0.45 \mu\text{m}$  filters to remove particles. UF membrane was used for pre-treating water source and controlled at 350 kPa and  $0.3 \text{ m s}^{-1}$ . The SF and UF effluents were then treated by NF270 membrane which were operated under pressures of 515–1035 kPa and cross-flow velocity of  $0.15\text{--}0.45 \text{ m s}^{-1}$ .

This study employed the DOC and  $\text{UV}_{254}$  values to quantify the NOMs. Besides, the hydrophobic resins (DAX-8/XAD-4) were used to fractionate the NOMs into three categories, i.e., hydrophilic, transphilic and hydrophobic. Based on the MW standard solutions (polyethylene glycol, PEG). The MW distribution of NOMs was determined by gel filtration chromatography (GFC). In addition, the characteristics of NF270 membrane, such as MWCF, pore radius, roughness, contact angle, surface charge, thickness and pure water permeability were also investigated in this research work.

### 2.1. NOM fractionation by XAD-8/XAD-4 resin

NOM in the collected water samples was fractionated into hydrophilic, transphilic and hydrophobic acids using DAX-8 (Supelite)/XAD-4 (Amberlite) resin columns according to the procedures published by some authors (Peuravuori et al., 2002; Shon et al., 2005; Park et al., 2006; Zularisam et al., 2007).

Prior to use, the resins were washed by methanol and deionized water repeatedly to bring the DOC concentration below  $0.02 \text{ mg L}^{-1}$ . The column size was  $2.5 \text{ cm}$  (diameter)  $\times$   $60 \text{ cm}$  (height). Prior to fractionation, water samples were filtered by  $0.45 \mu\text{m}$  filters (Adventec MFS Inc., USA).

### 2.2. GFC molecular weight distribution

MW separation was performed by GFC using a 30-cm TSK-G2000SW<sub>XL</sub> column with an inner diameter of 7.8 mm. The HPLC (LCP 4100, ECOM) was coupled with a refractive index detector (LR 125, VISCOTEK). The mobile phase was deionized water (Milli-Q SP), and the flow rate was  $0.5 \text{ mL min}^{-1}$  with a sample injection volume of  $500 \mu\text{L}$ . The standard solutions for the construction of a MW calibration curve were made with PEG. Water samples were filtered by  $0.45 \mu\text{m}$  filters before being pumped into the column.

### 2.3. Membrane filtration setup

A cross-flow NF membrane module was used in this study. A plate form membrane (NF270 manufactured by Film-Tech) was employed. The surface area of the membrane was  $46.2 \text{ cm}^2$  ( $8.4 \text{ cm}$  (L)  $\times$   $5.5 \text{ cm}$  (W)), and the cross-sectional area of the membrane module was  $1.1 \text{ cm}^2$  ( $5.5 \text{ cm}$  (W)  $\times$   $0.2 \text{ cm}$  (Height)). Membrane sheets were stored in 1.5% sodium meta-bisulfite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) to prevent oxidation and dried. Prior to the experiment, the membrane sheet was cleaned with deionized water and compacted at operating conditions. After membrane compaction (indicated by a steady-state permeate flux), the deionized water flux was used to estimate the pure water permeability.

### 2.4. Analytical methods

#### 2.4.1. Contact angle measurement

Contact angle is an index of the hydrophobicity of the membrane surface. In this study, it was measured by a contact angle system (FTA 125) with water dropping on the membrane surface. It was repeated 10–12 times to examine the contact angle of the membrane surface, and the mean value was calculated as the analysis result.

#### 2.4.2. Spectroscopy (ATR-FTIR)

Analysis was performed using a Varian 800 Fourier transform infrared (FTIR) spectrometer equipped with an attenuated total reflection (ATR) element, and deuterated triglycine sulfate was employed as the detector. The ATR method was used to record the IR spectra of the sample, where a Zn–Se crystal was employed as an accessory. It was operated as a single-reflection element at a nominal angle of incidence of  $45^\circ$ . All the membrane samples, including virgin, clean and fouled membranes, were gently washed with deionized water and then dried overnight at room temperature. The ATR-FTIR spectrum for each membrane sample was collected from  $600$  to  $4000 \text{ cm}^{-1}$  wavenumbers.

#### 2.4.3. SEM

The surface and cross-section of the membranes were analyzed using a field emission scanning electron microscope (FE-SEM) (JSM-6500F, JEOL). Before analysis, all membrane samples were dried and coated with a thin layer of platinum.

#### 2.4.4. Atomic force microscope (AFM)

The AFM technique was employed to image the membrane surfaces at a nanometer-scale resolution. The instrument (CP series, Veeco) was operated in a contact mode ( $450 \mu\text{m}$  (L)  $\times$   $45 \mu\text{m}$  (W)  $\times$   $2.0 \mu\text{m}$  (thickness), force constant:  $0.2 \text{ N m}^{-1}$ ), and the images were obtained by scanning a sharp tip over the membrane surface. The scanning area was  $3 \times 3 \mu\text{m}^2$ , and the roughness of the membrane surface, which is defined as the average deviation of the peaks and the valleys from the mean plane by AFM, was estimated.

DOC and  $\text{UV}_{254}$  were measured in water samples. All analyses, unless otherwise noted, were performed according to the Standards Methods (APHA, 2005). Water samples for DOC and UV analyses were first filtered through a prewashed  $0.45 \mu\text{m}$  filter and

then determined by a TOC instrument (O.I. Corporation model 700) and UV spectroscopy (Hitachi U-2000), respectively. The rejection of NOM was determined as follows:

$$R = \left[ 1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}} \right] \times 100\%$$

where  $R$  is the rejection ratio,  $C_{\text{feed}}$  and  $C_{\text{permeate}}$  are the DOC or  $UV_{254}$  of feed and permeate, respectively.

### 3. Results and discussion

#### 3.1. Characteristics of NF membrane

In this study, one type of commercial thin-film polyamide NF membrane, NF 270, produced by DOW-Film Tech was examined. Further information regarding the characteristics of NF-270 membrane analyzed by the contact angle measurement, ATR-FTIR spectrum, SEM and AFM are also presented as the following.

The contact angles were measured immediately after water was dropped on the membrane surface to avoid errors owing to spreading of the drop caused by surface capillary forces, which are an indication of the membrane's hydrophobicity. The contact angle of the clean NF270 membrane was approximately  $64 \pm 11^\circ$ , which indicated that the NF270 membrane was relatively hydrophobic compared to the findings reported by Cho et al. (1998).

Typical structures for a thin-film composite polyamide NF270 membrane are illustrated by the SEM analysis; the total thickness of the NF270 membrane was approximately 135  $\mu\text{m}$ . In general, the membrane is composed of three layers, i.e., a dense layer composed of polyamide at the top, a non-woven fabric layer as the bottom support layer, and a microporous polysulfone layer between the two.

Roughness is one of the most important membrane surface properties. The roughness of the clean NF270 membrane, which was permeated by the deionized water, was obtained by AFM. The surface morphology of the clean NF membrane was reflected by the root mean square surface roughness ( $R_{\text{rms}}$ ) value. The dark areas in the image are depressions, and the light areas are peaks. The total scanning area was  $3 \times 3 \mu\text{m}^2$ . The image shows that the surface of the NF270 membrane is smooth, with  $R_{\text{rms}}$  of approximately 1.3 nm.

#### 3.2. Water quality and NOMs fractions

The qualities of raw water, SF effluent and UF membrane process effluent are shown in Table 1. The pHs of the selected samples

in this investigation were near neutral. The DOC concentration of raw water was  $6.54 \text{ mg L}^{-1}$ , which was higher than the national standard for the source water. The SUVA is an index of aromatics in humic substances. The SUVA values for the above selected samples ranged from 1.22 to  $1.70 \text{ L mg}^{-1} \text{ m}^{-1}$ . This suggests that the raw water needs to be treated by an advanced treatment process, for instance, using the membrane technology at the end of conventional processes to meet the drinking water quality standard.

The MW distribution of source water indicates that the MW fractions of raw water ranged from less than 1 to more than 100 kDa. The dominant category with MW less than 5 kDa was about 38%. With this observation, the UF membrane with MWCO 5 kDa was selected as a pretreatment process prior to the NF270 membrane treatment.

Table 1, which presents the NOM fraction and characterization of raw water, SF effluent and UF membrane process effluent, indicates that the fraction of hydrophobic component having strong acids, i.e., fulvic and humic acids was higher than that of the hydrophilic including neutrals and bases, i.e., polysaccharides with low MW alkyl amide and amino acids and transphilic components with hydroxyl acids and sulfonic acids (Lee et al., 2005a). The hydrophobic material percentages were 58%, 57%, and 62% in raw water and SF and UF effluents, respectively, which means that the hydrophobic component was the predominant NOM fraction. The fractionation of these two components is important since the hydrophobic and hydrophilic DOC may result in different membrane fouling potential, DOC removal efficiency and interaction on membrane surface.

In addition, it was observed that the components of hydrophobic and hydrophilic NOMs were reduced 20% by the SF treatment process and 54% by the UF membrane treatment process, respectively. This suggests that the UF membrane process could remove the hydrophilic NOM more readily than the hydrophobic NOM, in contrast to the SF treatment process. In addition, the removal efficiencies of transphilic and hydrophobic fractions by the UF process were 26% and 31%, respectively, which were higher than those by the SF process (14% and 20%). In general, the UF process exhibits better removal efficiency of NOM fraction than the SF process.

#### 3.3. Effect of operating parameters on flux and rejection performance

NF is a pressure-driven membrane treatment process in which the operating parameters, including operating pressure, cross-flow velocity, and pretreatment process, can affect the permeate flux and NOM rejection. Both DOC and  $UV_{254}$  were selected to monitor

**Table 1**  
NOM fractions and characteristics of water sample.

| Item         | pH   | DOC<br>( $\text{mg L}^{-1}$ ) | C<br>(mg) | Removal<br>(%) | Fraction<br>(%) | $UV_{254}$<br>( $\text{cm}^{-1}$ ) | SUVA<br>( $\text{L mg}^{-1} \text{ m}^{-1}$ ) |
|--------------|------|-------------------------------|-----------|----------------|-----------------|------------------------------------|---|
| Raw water    | 7.18 | 6.54                          | 1.63      | –              | –               | 0.111                              | 1.70  |
| Hydrophilic  | –    | 1.41                          | 0.35      | –              | 21              | 0.019                              | 1.31  |
| Transphilic  | –    | 0.88                          | 0.35      | –              | 21              | 0.011                              | 1.22  |
| Hydrophobic  | –    | 2.48                          | 0.99      | –              | 58              | 0.036                              | 1.45  |
| Recovery (%) | –    | –                             | 104       | –              | –               | –                                  | –   |
| SF effluent  | 7.22 | 5.45                          | 1.36      | –              | –               | 0.069                              | 1.27  |
| Hydrophilic  | –    | 1.23                          | 0.31      | 11             | 22              | 0.014                              | 1.11  |
| Transphilic  | –    | 0.74                          | 0.30      | 14             | 21              | ND <sup>a</sup>                    | –   |
| Hydrophobic  | –    | 1.97                          | 0.79      | 20             | 57              | 0.027                              | 1.39  |
| Recovery (%) | –    | –                             | 102       | –              | –               | –                                  | –   |
| UF effluent  | 6.72 | 2.78                          | 1.11      | –              | –               | 0.034                              | 1.22  |
| Hydrophilic  | –    | 0.39                          | 0.15      | 54             | 14              | ND <sup>a</sup>                    | –   |
| Transphilic  | –    | 0.66                          | 0.26      | 26             | 24              | ND <sup>a</sup>                    | –   |
| Hydrophobic  | –    | 1.69                          | 0.68      | 31             | 62              | 0.022                              | 1.32  |
| Recovery (%) | –    | –                             | 98        | –              | –               | –                                  | –   |

<sup>a</sup> ND means the UV absorbance was less than  $0.009 \text{ cm}^{-1}$ .

the feed and permeate water for determination of the rejection ratio by NF membrane.

### 3.4. Effect of operating pressure

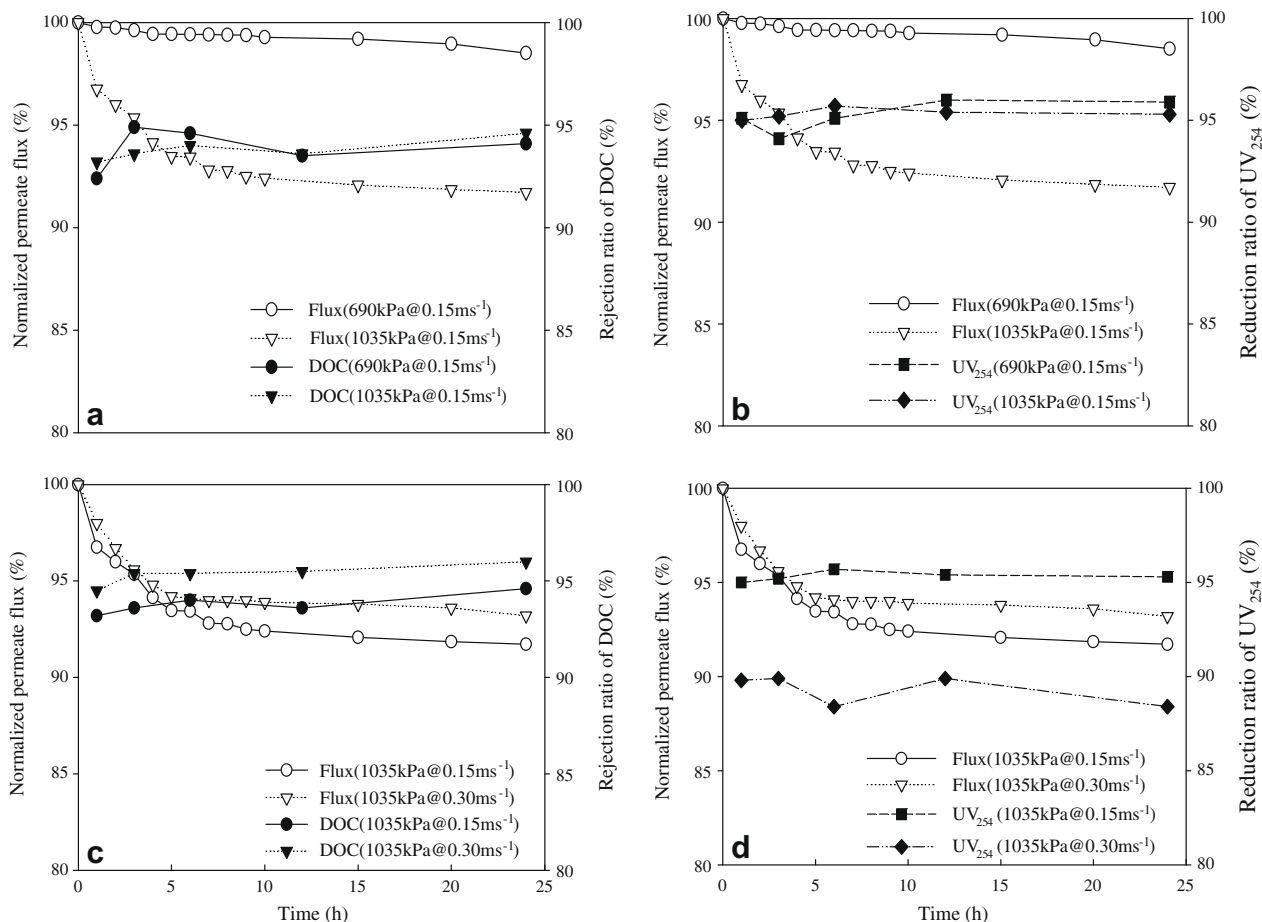
According to Darcy's Law, the permeate flux increases with increasing transmembrane pressure (TMP) while other operating conditions remain constant. The permeate flux and DOC/UV<sub>254</sub> rejection as a function of time using the SF effluent at a constant cross-flow velocity (0.15 m s<sup>-1</sup>) and two different TMPs (690 and 1035 kPa) are presented in Fig. 1a and b. The permeate flux decreased slightly at 690 kPa TMP, while it declined dramatically when the pressure increased to 1035 kPa. Regardless of the operating pressure, the permeate flux reached a relatively constant value after 10 h. The results suggest that flux decline was greater at higher pressures, which was possibly caused by the extensive cake layer formation on the membrane surface at higher TMP, and the constant flux may be due to equilibrium of the cake layer formation (Elmaleh and Ghaffor, 1996).

The rejection of DOC and UV<sub>254</sub> remained constant at approximately 92% and 96%, respectively, while the TMP and cross-flow velocities were operated from 690 to 1035 kPa and 0.15 to 0.30 m s<sup>-1</sup>, respectively. Because increasing TMP resulted in the membrane structure becoming more compact, the organic solute could barely pass through the membrane. In addition, the gel-type layer thickness increased with increasing applied pressure and resulted in concentration polarization phenomena. The above

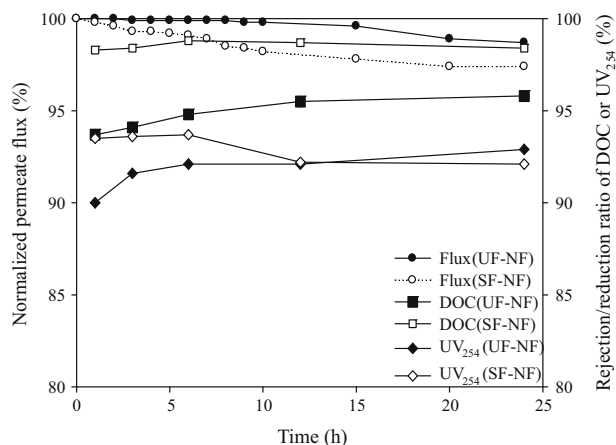
effects became more pronounced at lower cross-flow velocity. Therefore, the permeate qualities of NOMs (DOC or UV<sub>254</sub>) decreased with increasing TMP, which is similar to the findings reported by Benítez et al. (2006). While the applied pressure was higher than 690 kPa, the reduction ratio of NOM (DOC or UV<sub>254</sub>) tended to be stable, because the higher pressure would increase solvent permeability more rapidly than that of the solute. This might impede the organic solute passing through the membrane with increasing pressure, but the rejection ratio increased slightly (Visvanathan et al., 1998). In other words, the rejection ratio of DOC increased with increasing TMP until an upper limit was reached, when the application of higher pressure did not increase DOC rejection.

### 3.5. Effect of cross-flow velocity

The permeate flux and DOC/UV<sub>254</sub> rejection as a function of time using the SF effluent at a constant TMP (1035 kPa) and different cross-velocity rates (0.15–0.30 m s<sup>-1</sup>) are presented in Fig. 1c and d. Because of the very small pores of NF membrane, surface fouling caused by foulant accumulation (deposition) on the membrane surface is the dominant fouling mechanism in NF. The adhesion force between the foulant and the membrane surface and between the bulk foulant and the fouling layer were determined by AFM (Li and Elimelech, 2004). As a result, a higher permeate flux was observed when 0.30 m s<sup>-1</sup> cross velocity was employed. It suggests that increasing cross-flow velocity might increase the



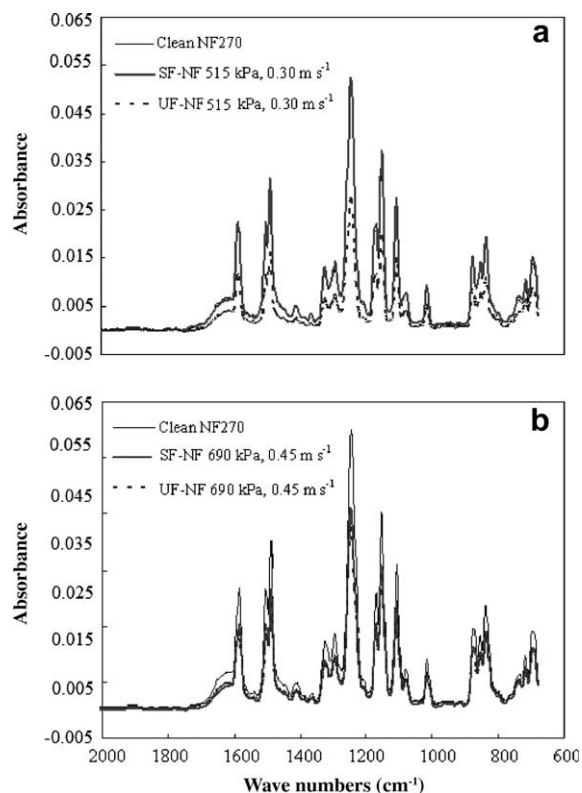
**Fig. 1.** Permeate flux and water quality (DOC and UV<sub>254</sub>) of SF effluent treated by NF270 at different operation conditions: (a) and (b) treated by NF270 at pressures of 690 and 1035 kPa and cross-flow velocity of 0.15 m s<sup>-1</sup>. The initial flux ( $J_0$ ) of NF270 membrane treatment operated at 690 kPa and 1035 kPa (at cross-flow velocity of 0.15 m s<sup>-1</sup>) were 8.2 and 12.4 cm<sup>3</sup> cm<sup>-2</sup> h<sup>-1</sup>, respectively; (c) and (d) treated by NF270 at pressure of 1035 kPa and cross-flow velocities of 0.15 and 0.30 m s<sup>-1</sup>. The initial flux ( $J_0$ ) of NF270 membrane treatment operated at 0.15 and 0.30 m s<sup>-1</sup> (at pressure of 1035 kPa) were 12.4 and 12.5 cm<sup>3</sup> cm<sup>-2</sup> h<sup>-1</sup>, respectively.



**Fig. 2.** Effect of pretreatment process (i.e., SF-NF and UF-NF) on permeate flux and water quality (DOC and UV<sub>254</sub>) for NF270 membrane at pressure of 690 kPa and cross-flow velocity of 0.45 m s<sup>-1</sup> (The initial flux ( $J_0$ ) of NF270 membrane treatment was 9.2 cm<sup>3</sup> cm<sup>-2</sup> h<sup>-1</sup>).

turbulence and shear stress that minimize NOM fouling on the membrane surface (Mohammadi and Esmaelifar, 2005).

The cross-flow velocity is an important parameter of membrane filtration, because it can reduce the potency of concentration polarization and fouling problems on the membrane surface. After operating for 1 h, the rejection ratio of DOC reached around 93%, regardless of the levels of the cross-flow velocity. In other words, the variation of the rejection ratio of DOC was not obvious during membrane filtration. As shown in Fig. 1c, the rejection ratio of DOC ranged from 94% to 96% with increasing cross-flow velocity. It was noted that the DOC rejection ratio was not affected by changing



**Fig. 3.** FTIR spectra comparison of the clean and fouled membranes at different pretreatment processes. (i.e. SF-NF and UF-NF): (a) pressure, 515 kPa; cross-flow velocity, 0.30 m s<sup>-1</sup>; (b) pressure, 690 kPa; cross-flow velocity, 0.45 m s<sup>-1</sup>.

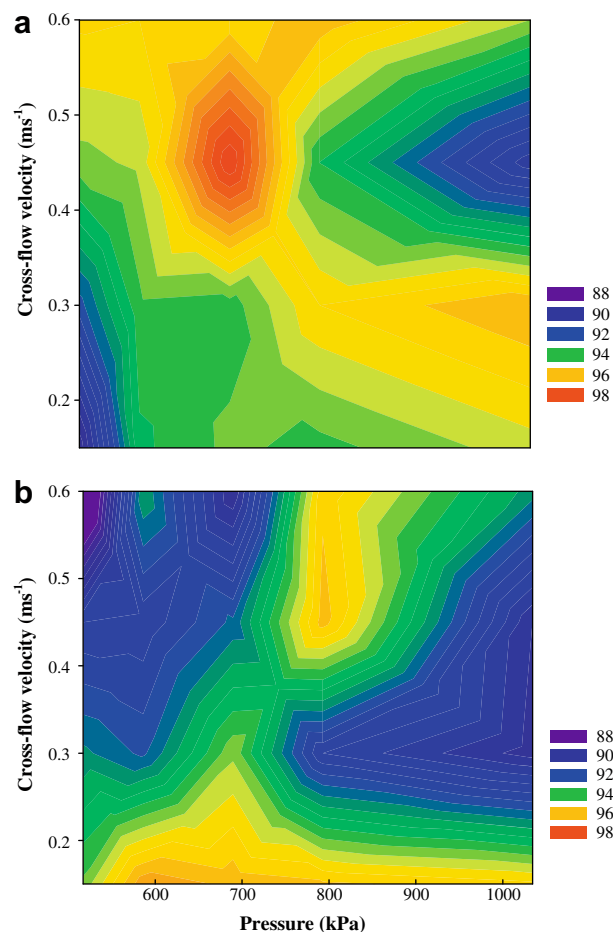
cross-flow velocity. The experimental results and speculations were fairly consistent with the findings suggested by Ratanatamskul et al. (1996).

With the use of the SF-NF 270 treatment process, UV<sub>254</sub> could be reduced by approximately 0.064 cm<sup>-1</sup>. After operating for 1 h, the reduction ratio of UV<sub>254</sub> exceeded 90% regardless of the levels of cross-flow velocity. However, at lower cross-flow velocity (0.15 m s<sup>-1</sup>), the reduction of organic matter in water sample was higher than that at higher cross-flow velocity (0.30 m s<sup>-1</sup>). It was speculated that at higher cross-flow velocity, the fouling component on the membrane surface was removed more effectively. Furthermore, the cake layer formation on the membrane surface ceased at higher operating pressure, resulting in a constant reduction ratio of DOC or UV<sub>254</sub>.

### 3.6. Effect of pretreatment process

In this, the applications of SF and UF membrane processes for NF270 membrane pre-treatment were discussed in this investigation. Fig. 2 present that the variations of the normalized permeate flux operated at constant TMP (690 kPa) and constant of cross-flow velocity (0.45 m s<sup>-1</sup>). Regardless of the pretreatment process, the normalized permeate flux declines very rapidly in the beginning, and the permeate flux tends to be constant after 15 h.

According to the results, the permeate flux declined more rapidly with SF-NF than with UF-NF, which might be ascribed to the fact that hydrophobic NOM can easily accumulate on the hydrophobic membrane (NF270) surface, resulting in a flux



**Fig. 4.** Contour plots for (a) rejection ratio of DOC and (b) reduction ratio of UV<sub>254</sub> of SF effluent treated by NF270.

decline. Besides, the UF membrane can reject more hydrophobic NOM than the SF treatment process (Table 1). The phenomenon could also be explained by the recent findings which suggest that combined fouling mechanism of colloids and NOM should be occurred simultaneously in these NF experiments (Lee et al., 2005a). Obviously, the different levels of colloids and NOM reduced by the two pretreatment processes, i.e., SF and UF would affect the performance of SF–NF and UF–NF, respectively. Consequently, the UF pretreatment offers better performance for reducing permeate flux decline than the SF pretreatment.

At about 12 h operation, the rejection ratio of DOC was apparently constant. Furthermore, the DOC rejection by SF–NF was higher than that by UF–NF. The UV<sub>254</sub> reduction capacity for SF–NF was also slightly higher than that for UF–NF after 12 h operation. According to the above experimental results, the SF–NF treatment processes demonstrate better performance for NOM rejection than the UF–NF treatment process, in spite of the permeate flux. It was thus concluded that the SF–NF was the proposed treatment pro-

cess because it can reduce the NOMs effectively with lower energy consumption than UF–NF.

The FTIR spectra of clean and fouled NF270 (operated at 515 (or 690) kPa and 0.30 (or 0.45) m s<sup>-1</sup>) membranes are shown in Fig. 3, which shows that the polyamide membrane exhibits the IR peaks associated with the aromatic double-bonded carbons, carboxylic groups, C–O bond of ethers or carboxylic acids, C–H aromatic rings, amides, and nitro compounds. Among all peaks associated with the virgin NF membrane, it possesses the highest peak, around 1246 cm<sup>-1</sup>, which corresponds to the carboxylic groups. The special spectrum of the NF270 membrane also reveals several functional groups, such as amides, ethers, and aromatic double-bonded carbons, which are the major components of a polyamide NF membrane with a thin-film composite.

It was observed that the absorbance intensity of the clean NF270 membrane was reduced while being filtrated water samples. This is because of the functional groups in the water samples were coated with foulants resulted in reducing their respective

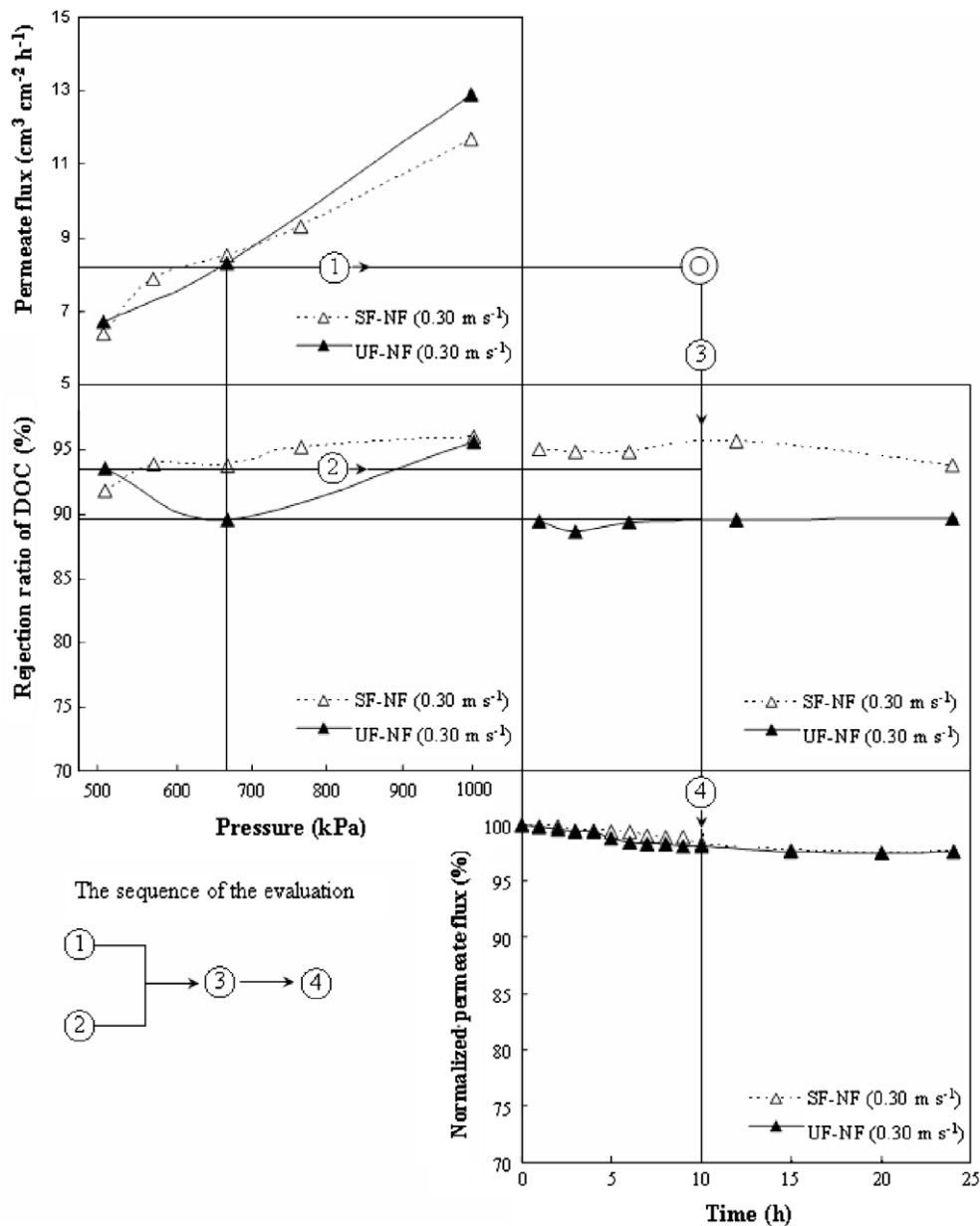


Fig. 5. Relationship among permeate quality, operating time, permeate flux and transmembrane pressure.

absorbance intensity or peak, shown in Fig. 3 which was similar to the findings reported by Cho et al. (1998). Prior to the NF270 membrane, parts of the adsorbable substances in the UF–NF processes were adsorbed on the UF membrane surface and reflected by the permeate flux for SF–NF and UF–NF, which were in consistent with the findings suggested by Song et al. (2004).

### 3.7. Relationship among permeate quality, cross-flow velocity and TMP

Fig. 4a demonstrates the 3-D relationship among the cross-flow velocity (0.15–0.60 m s<sup>-1</sup>), the TMPs (515–1035 kPa), and the rejection ratio of DOC of SF effluent treated by NF270 membrane throughout this investigation. The rejection ratio of DOC increased slightly with increasing cross-flow velocity (0.15–0.60 m s<sup>-1</sup>) at constant pressure (below 760 kPa). When the applied pressure was increased from 760 to 830 kPa, the rejection ratio of DOC changes in cross-flow velocity was not significant. However, if the TMPs were higher (over 830 kPa), the DOC rejection ratios decreased slightly with increasing cross-flow velocity. Generally, when the NF270 membrane filtrated at an applied pressure from 855 to 795 kPa and a cross-flow velocity from 0.15 to 0.60 m s<sup>-1</sup>, higher rejection ratios of DOC (over 94%) were obtained.

At lower cross-flow velocity (below 0.25 m s<sup>-1</sup>), the reduction ratios of UV<sub>254</sub> were over 92% regardless of TMPs in the range from 515 to 1035 kPa (Fig. 4b). At cross-flow velocity over 0.30 m s<sup>-1</sup>, the reduction ratio of UV<sub>254</sub> increased with increasing TMPs but tended to be constant at higher pressure (over 760 kPa), especially at higher cross-flow velocity (over 0.45 m s<sup>-1</sup>). In contrast, the UV<sub>254</sub> reduction ratio decreased with increasing cross-flow velocity at a constant TMP. When the TMP was held below 690 kPa, the reduction ratios of UV<sub>254</sub> decreased from 94% to 86% with increasing cross-flow velocity from 0.15 to 0.60 m s<sup>-1</sup>. The trend of the UV<sub>254</sub> reduction ratio at higher cross-flow velocity (0.15–0.60 m s<sup>-1</sup>) seems to be similar to the case at higher pressure (over 895 kPa). However, when the TMP was between 725 and 795 kPa, the reduction ratio of UV<sub>254</sub> changes in cross-flow velocity was not significant. Generally, when the NF270 membrane filtrated at an applied pressure from 690 to 965 kPa with cross-flow velocity from 0.40 to 0.60 m s<sup>-1</sup>, higher rejection ratios of UV<sub>254</sub> (over 92%) were obtained. Moreover, if the filtration conditions at the lower cross-flow velocity (0.15–0.30 m s<sup>-1</sup>), the rejection ratios of UV<sub>254</sub> were also over 92% regardless of the TMPs (515–1035 kPa).

### 3.8. Approach to determine good engineering practice (GEP)

By integrating the experimental results in this investigation, it is possible to determine the GEP for reducing the DOC and UV<sub>254</sub> in Kin-men raw water. Running the NF270 membrane filtration at lower cross-flow velocity (0.15–0.30 m s<sup>-1</sup>) was preferred, owing to the expected lower energy cost. In other words, the operating condition most conducive to efficiently reducing the UV<sub>254</sub> was cross-flow velocity from 0.15 to 0.30 m s<sup>-1</sup> regardless of the TMPs. Thus, the better rejection ratio of NOM (DOC and UV<sub>254</sub>) by NF270 were obtained when the TMP was increased from 620 to 795 kPa and the cross-flow velocity was from 0.15 to 0.30 m s<sup>-1</sup>. It was thus concluded that a TMP of 690 kPa and a cross-flow velocity of 0.30 m s<sup>-1</sup> comprised the better operating conditions, yielding about 94% of both DOC and UV<sub>254</sub> reduction ratios. In addition, if the NF270 membrane filtrated at this range of conditions, the permeate flux was obtained at around 8–10 cm<sup>3</sup> cm<sup>-2</sup> h<sup>-1</sup>.

Finally, a comparison of the reduction performance between the SF–NF and the UF–NF processes at a pressure of 690 kPa and a velocity of 0.45 m s<sup>-1</sup> was also made (Fig. 2) which reveals that SF–NF processes could obtain higher rejection ratios than the UF–NF processes. Moreover, whether using the UF–NF processes

or the SF–NF processes, the similar permeate flux and normalized permeate flux decline was obtained at around 10 h of operation, which was close to 8.4 cm<sup>3</sup> cm<sup>-2</sup> h<sup>-1</sup> (1.8%).

The above suggestions can be clearly observed by the diagram shown in Fig. 5, which demonstrates the systematic approach to determine the GEP based on the available information generated from this investigation.

## 4. Conclusions

The removal efficiencies of transphilic and hydrophobic fractions by the UF process were 26% and 31%, respectively, which were higher than those by the SF process (14% and 20%). The permeate flux declined more rapidly with SF–NF than with UF–NF, which might be ascribed to the fact that hydrophobic NOM can easily accumulate on the hydrophobic membrane (NF270) surface, resulting in a flux decline. The SF–NF treatment processes demonstrate slightly better performance for NOM rejection than the UF–NF treatment processes, in spite of the permeate flux. It was thus concluded that the SF–NF was the proposed treatment process because it can reduce the NOMs effectively with lower energy consumption than UF–NF.

The rejection of DOC and UV<sub>254</sub> remained constant at approximately 92% and 96%, respectively, while the TMPs and cross-flow velocities were operated from 690 to 1035 kPa and 0.15–0.45 m s<sup>-1</sup>, respectively. It was noted that the DOC rejection ratio was not affected by changing cross-flow velocity. However, at lower cross-flow velocity (0.15 m s<sup>-1</sup>), the reduction of organic matter with double bond in water sample was higher than that at higher cross-flow velocity (0.45 m s<sup>-1</sup>). It was speculated that at higher cross-flow velocity, the fouling component on the membrane surface was removed more effectively.

By integrating the experimental results, it was concluded that a TMP of 690 kPa and a cross-flow velocity of 0.30 m s<sup>-1</sup> comprised the GEP, yielding about 94% DOC and UV<sub>254</sub> reduction ratios.

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