COMPARISON OF NANOFILTRATION AND REVERSE OSMOSIS MEMBRANES PERFORMANCE SUBJECT TO CROSSFLOW VELOCITY EFFECT DURING FILTRATION OF HUMIC ACIDS

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EXTENDED ABSTRACT

Organic fouling of membrane is one of the barriers that limits the application of membrane in water separation. Study about the effect of crossflow velocity on fouling rate is important to ensure that the system is operating at optimal conditions. This paper investigates the influence of crossflow velocity on the permeate flux in crossflow configuration of nanofiltration (NF) and reverse osmosis (RO) processes by treating an organic compound in aqueous suspension. A commercial Aldrich humic acid (AHA) of 15 mg/L was used as the feed solution. The experiments were conducted at different crossflow velocities (i.e. 0.27, 0.39, and 0.60 m/s) under a constant driving pressure of 7 bar and operating temperature of 22 - 25°C. The permeate flux for both NF and RO membranes tested with AHA foulant increased slightly with time at the crossflow velocities of 0.39 and 0.60 m/s. Despite the organic rejections increased with the increased crossflow velocity, the rejection performance of AHA suspension was only marginally affected by the variation of crossflow velocity. Low permeate rates (flux) and strong repulsive forces were the reasons of no fouling result observed in the NF and RO membranes throughout the studied duration (i.e. 8 h). To study the fouling behaviour of these membranes, it is suggested that an AHA feed with higher concentration, an addition of calcium ions, a longer filtration duration, and a higher initial flux should be used.

Keywords: Crossflow velocity, humic acid, organic compound removal, nanofiltration, reverse osmosis

1. INTRODUCTION

Membrane technology is widely used in water treatment due to its consistent permeate water quality, considerably high recovery rate, capabilities of handling wide fluctuations in feed, and wide areas of application (Zularisam et al., 2006; Madaeni and Eslamifard, 2010). Reverse osmosis (RO) is a pressure driven membrane process. RO membrane is good in rejecting dissolved ionized salts and micromolecules. If they can be claimed to have pores, the pores should not be greater than 20 Å (Angstrom) in diameter. This is much lower than ultrafiltration (UF) which has the pores diameter of 20 – 100 Å (Harriott, 1973). Nanofiltration (NF) has similar functions as RO, but it is typically designed to reject only large divalent and multivalent ions. Transport mechanism in RO is solution-diffusion, while in NF the process is governed by sieving and solution-diffusion effects because the
pore sizes of NF lies between UF and RO (Hussain et al., 2007; Hussain and Al-Rawajfeh, 2009).

Natural organic matter (NOM) is usually found in surface waters such as river water and seawater (Kordel et al., 1997). The concentration level of NOM in natural surface waters is low in suspension (2 – 15 mg/L) (Ghous et al., 2010). The concentration of NOM is commonly expressed by dissolved organic carbon (DOC) and total organic carbon (TOC) in the unit of mg/L. Although NOM is fundamentally low in concentration and harmless, it is easily formed as disinfection by-products, including trihalomethanes and haloacetic acids when the source water containing NOM is chlorinated in the disinfection process (Zazouli et al., 2008). The fraction of NOM is humic and fulvic acids (Katsoufidou et al., 2008). Humic acid is the principal component of NOM (contains at least 70 %) (Ghous et al., 2010). Despite the use of membrane technology in NOM removal has undergone rapid advances, membrane fouling is still a major issue that has yet to be solved obstacle to the widespread of this separation process. Membrane fouling is a phenomenon where undesired substances deposit on membrane surface to form a foulant layer. The formation of foulant layer will increase the hydraulic resistance against water permeation and subsequently lead to a remarkable and severe decrease in flux (Liu et al., 2011). The rate and extent of membrane fouling are greatly influenced by operating conditions, such as the applied pressure and crossflow velocity (Seidel and Elimelech, 2002; Koo et al., 2012). Crossflow operation is applied in the external membrane system with the aim to create a high shear condition at the surface of membrane (Bian et al., 2000; Bérubé et al., 2006). High crossflow velocity that is parallel to membrane surface could substantially decrease resistance formed by the concentration polarization and cake layer (Choo and Lee, 1998; Bérubé et al., 2006). Due to this effect, permeate flux increases linearly with increasing crossflow velocity (Choi et al., 2005).

Mattaraj et al. (2010) conducted a study to investigate the effect of crossflow velocity on permeate flux of 10 mg/L NOM at low and high ionic strength suspensions (0.01 and 0.05 M NaCl) using thin film polyamide RO membrane from GE Osmonics. They found that the increase of crossflow velocity showed no significant effect on initial flux rate during the first 50 min of filtration time. However, the flux rate was markedly enhanced by the increase of crossflow velocity when the filtration time was extended. In a separate study carried out by Seidel and Elimelech (2002), they observed that crossflow velocity caused a significant impact on the reduction of flux decline rate when the initial permeate flux was sufficiently high (i.e. 36 gfd or 61.12 LMH). They concluded that, the control of proper operational parameters (initial flux and crossflow velocity) would maintain the performance of membrane and minimize the potential of membrane fouling. The paper presents a quantitative evaluation on the effect of crossflow velocity on the permeate flux and rejection of organic compound in NF and RO membrane processes. The study provides a detailed insight into the effect of crossflow velocity on the permeate flux and AHA rejection. A synthetic organic compound namely Aldrich humic acid is selected to perform these fouling tests.

2. MATERIALS AND METHODS

2.1. Filtration experimental setup

This study adopted similar filtration unit with the previously reported studies (Koo et al., 2013), but operated under a constant pressure mode. All the filtration experiments were conducted using a crossflow bench-scale membrane unit as shown in Figure 1. The bench-scale unit was equipped with feed and collection tanks, a feed pump, a crossflow membrane filtration cell (SEPA CF, GE Osmonics©, Minnetonka, MN), a flowmeter,
pressure gauges, and an electronic scale which were connected to a computer. The crossflow cell was designed in a plate and frame configuration with the thickness and width of spacer were ~ 1.45 mm and 95 mm, respectively. The dimension of the cell body is 53 mm × 216 mm × 165 mm and the effective area of membrane is 0.0155 m² with a volume hold-up of 70 ml. All the experiments were commenced by pumping the feed solution into the crossflow cell using a piston-driven diaphragm pump (Hydracell pump, USA). The pump was driven by an adjustable / variable speed drive (Vacon 10, Finland). The function of the variable speed drive is to control the feed in flowrate of the filtration unit. The tests were carried out through an identical feed suspension at the same operating conditions, except that the crossflow velocity was set as a variable. The crossflow velocity of 0.27, 0.39, and 0.6 m/s was selected to investigate their effects on the permeate flux of membranes in this study. In addition, the constant operating pressure was maintained at ±7.0 bar by controlling the Control Valve.

In the experiment test, the permeate was collected in a collection tank until a steady state pressure was achieved. The accumulative mass of permeate in the collection tank was continuously measured by an electronic balance (AND, GF-6100, Japan) at an interval time of 15 min. The feed in flowrate (Burkert, SE36, France) was measured and continuously logged in a data logger (Kobold, ZLS, Germany) installed in the control panel of the filtration unit during the filtration process. The operating temperature of the test was monitored throughout the filtration test. It was notably that only a minimal variation (within the range of 22-25°C) in the temperature was observed. The entire duration of the filtration process was run for 8 h. The time and mass of permeate from the crossflow filtration cell were recorded to calculate the permeate flux, $J$ (LMH) using Eq. (1).

$$\text{Permeate flux, } J = \frac{Q_p}{A_m}$$

Eq. (1)

where $Q_p$ is the permeate flowrate (L/h) and $A_m$ is the active area of membrane (m²). The crossflow velocity, CFV (m/s) was calculated using Eq. (2) (Shamel and Owee, 2006).

$$\text{Crossflow velocity, CFV} = \frac{Q_f}{A_c}$$

Eq. (2)

where $Q_f$ is the permeate flowrate (m³/s) and $A_c$ is the cross-sectional area of membrane (m²).

Figure 1. Schematic diagram of bench-scale NF / RO filtration setup.
2.2. Membranes characteristics

Commercial NF and RO membranes of polyethersulfone (PES) material were employed in this study. The pure water flux of NF and RO membranes were 65 and 50 LMH, respectively. All the new NF and RO membrane samples were received as large sheets and were stored dry in the dark. They were cut and soaked in deionized (DI) water overnight prior to each run of experiments to remove the unwanted preservative liquids injected by manufacturer. Each of the membranes was initially filtered with UP water prior to AHA suspension in order to confirm the existence of substantial effect of AHA suspension on the flux of membranes.

2.3. Feed solution

A commercial Aldrich humic acid (AHA) from Sigma Aldrich was selected as the model organic foulant in this experiment. Stock solution of AHA (0.2 g/L) was prepared by dissolving the powdered form AHA in 0.05 M of sodium bicarbonate solution (NaHCO\textsubscript{3}) to enhance its solubility (Adekunle et al., 2007). Foulant suspension was prepared by adding DI water to the stock solution to obtain the desired concentration. In this study, the concentration of AHA tested was 15 mg/L and the dissolved AHA suspension was pH 7. The final AHA suspension was adjusted to pH 8.5 with dilute sodium hydroxide (NaOH).

2.4. Analytical methods

The rejection parameter of AHA was characterized based on the concentration of permeate. The AHA concentrations of feed and permeate samples were determined by measuring the wavelength of UV absorbance at 254 nm using UV/Vis spectrophotometer (Perkin Elmer Lambda 35, Wellesley, USA). Solute rejection, \( R \) can be defined by Eq. (3).

\[ R\% = 1 - \frac{C_p}{C_f} \times 100\% \]  

Eq. (3)

where \( C_p \) is the concentration of permeate and \( C_f \) is the concentration of feed.

3. RESULTS

3.1. Effect of crossflow velocity on flux performance

Figure 2(a), (b) and (c) compares the permeate flux behaviours of the NF and RO membranes as a function of filtration time tested under the crossflow velocity of 0.27, 0.39, and 0.60 m/s, respectively. The permeate flux for both NF and RO membranes tested with AHA foulant increased slightly with time at the crossflow velocities of 0.39 and 0.60 m/s. When comparing the flux between NF and RO membranes, as expected, the flux of NF membrane was higher than that of RO membrane over the filtration time at all crossflow velocities applied. This is because of the NF membrane has a relatively higher permeability than the RO membrane.

Figure 3 presents the comparison of final flux for NF and RO membranes as a function of different crossflow velocities. It is clearly seen that the permeate flux increased linearly with the increased crossflow velocity because the mass transfer increased at a high crossflow velocity as discussed earlier (Madaeni and Daneshvar, 2005). However, the trend of flux increases for the NF and RO was not proportional. A higher crossflow velocity was more effective to increase flux and reduce fouling in the RO membrane than the NF membrane. The finding was supported by Choi et al. (2005) who found that the
permeate flux varied linearly with the crossflow velocity in MF and UF filtration processes. A high crossflow velocity increases the permeate flux due to the increase of solute backtransport to the bulk solution (Mattaraj et al., 2010; Koo et al., 2013). In addition, a high crossflow velocity would also decrease the flux decline and solute accumulation by sweeping away the solute from the membrane surface (Mattaraj et al., 2010; Badawy et al., 2011). Even though the permeate flux increased linearly with an increase in the surface shear force as a result of the increase in crossflow velocity, however, the permeate flux plateaued once a certain shear force level was reached (Bérubé et al., 2006). This phenomenon happened in the NF membrane. Increasing the crossflow velocity above 0.39 m/s did not result in a further increment in the permeate flux for the NF membrane. As the crossflow velocity increased from 0.27 to 0.39 m/s, the permeate flux of NF membrane increased rapidly from 23.2 to 34 LMH (flux decline ratio = −46.6 %), while the flux of the NF membrane increased marginally from 34 to 34.4 LMH (flux decline ratio = −1.2 %) at a high crossflow velocity region. The results indicated that the maximum flux of NF membrane was almost achieved when the crossflow velocity was 0.39 m/s. Liu et al. (2011) revealed that an increase in the crossflow velocity would lead to an increase in the equilibrium permeate flux for the NF and RO membranes. The shearing effect at lower crossflow velocity had given a larger effect on reducing the extent of flux decline than that at higher crossflow velocity. They added that the increase in the stabilized permeate flux at a high crossflow velocity is likely caused by the reduced concentration polarization and foulants adsorption on membrane surface. However, the rate of permeate flux increases as a function of crossflow velocity for the NF membrane was less than that of RO membrane at high crossflow velocity. The achievable permeate flux of NF membrane could not be further increased once the limiting flux had been reached.

![Figure 2](image1.png)

**Figure 2.** Comparison of permeate flux as a function of filtration time for NF and RO membranes at 0.39 m/s. Driving pressure = 7 bar; Organic compound concentration = 15 mg/L AHA. Crossflow velocity at: (a) 0.27 m/s. (b) 0.39 m/s. (c) 0.60 m/s.

![Figure 3](image2.png)

**Figure 3.** Variation of flux with crossflow velocity for NF and RO membranes. Driving pressure = 7 bar; Organic compound concentration = 15 mg/L AHA.
3.2. Effect of crossflow velocity on rejection performance

3.2.1. AHA rejection

Solute rejection is another key factor for the performance evaluation of membrane processes. Figure 4 shows the AHA rejection as a function of crossflow velocity for the NF and RO membranes. Surprisingly, the effectiveness of AHA rejection increased with the increased crossflow velocity. As the crossflow velocity increased from 0.27 to 0.39 m/s, the AHA rejection for the NF membrane increased from 81.2 to 83.8 %. Similar trend of AHA rejection with the increase of crossflow velocity was also observed for the RO membrane. The AHA rejection at the crossflow velocities of 0.27, 0.39, and 0.60 m/s for the RO membrane was 95.4, 95.6, and 97.7 %, respectively. The results were supported by Chang et al. (2009) who conducted a systematic experimental study to investigate the effect of operating parameters on the NOM rejection for a lake water in an NF filtration. The performance of NF membrane on NOM rejection was assessed by measurement of DOC. They claimed that the foulant on the membrane surface was removed more effectively at a high crossflow velocity (Chang et al., 2009). However, they reported that the effect of crossflow velocity on the DOC rejection ratio was not significant for an operating pressure of below 7.6 bar. Their results showed good comparisons with the observations obtained from the present study as the filtration system was performed at a constant driving pressure of 7 bar. Besides, Liu et al. (2011) also investigated the effect of crossflow velocity on the COD removal of textile wastewater treated by NF and RO membranes. They elucidated that the better rejections of COD for both the NF and RO membranes at a high crossflow velocity can be attributed to the reduction of concentration polarization and membrane fouling. The extent of concentration polarization and membrane fouling is associated with the loss of membrane rejection capability. It is learnt that an increase in the crossflow velocity would increase the mass transfer coefficient and subsequently minimize the effect of concentration polarization, causing higher solutes rejection by the membrane (Ismail et al., 2012). Despite the organic rejections increased with the increased crossflow velocity, the rejection performance of AHA suspension was only marginally affected by the variation of crossflow velocity. This observation was in good agreement with studies reported by Öner et al. (2011), whereby they discovered that the increase of flowrate did not affect salt, boron, and silica rejections significantly.

![Figure 4. AHA rejection (%) as a function of crossflow velocity for NF and RO membranes. Driving pressure = 7 bar; Organic compound concentration = 15 mg/L AHA.](image)
5. CONCLUSIONS

A crossflow bench-scale membrane unit was employed to study the effect of crossflow velocity on the permeate flux and AHA rejection in NF and RO membranes. The flux of NF and RO membranes increased markedly when a high crossflow velocity was applied. The extent of crossflow velocity on flux is dependent on the suspension characteristics (type, concentration, pH, etc) and initial permeation flux. Despite the organic rejections increased with the increased crossflow velocity, the rejection performance of AHA suspension was only marginally affected by the variation of crossflow velocity. Fouling phenomena have not been observed in the NF and RO membranes throughout the studied duration (i.e. 8 h). It is safe to claim that the NF and RO membranes employed in this study possess a good resistance against organic fouling. To study the fouling behaviour of these membranes, it is suggested that an AHA feed with higher concentration, an addition of calcium ions, a longer filtration duration, and a higher initial flux should be used.

REFERENCES