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RETENTION OF HUMIC ACID FROM WATER BY NANOFILTRATION MEMBRANE AND INFLUENCE OF SOLUTION CHEMISTRY ON MEMBRANE PERFORMANCE

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ABSTRACT

The objectives of this research were to investigate the rejection efficiency of salt and hydrophobic fraction of natural organic matter, to study the flux decline behavior with a spiral wound nanofiltration membrane, and also to survey the influence of water chemistry on membrane performance. Experiments were conducted using a cross flow pilot-scale membrane unit with a full circulation mode. Humic acid was used as hydrophobic organic matter and NaCl as background electrolyte. Results showed that flux reduction increased with increasing ionic strength and humic acid concentration, and with lower pH. The rejection efficiency of organic and salt decreased with the decrease in pH and increase in ionic strength, because of osmotic pressure increase, leading to permeate flux decline and decrease in salt rejection. In addition, the improved salt rejection was likely due to Donnan exclusion by humic material close to membrane surfaces. The average rejection efficiency of humic acid and salt ranged between 91.2%-95.25% and 63.6%-80%, respectively. Dissolved organic carbon concentration was less than 0.57mg/L in permeate for all experiments. With increasing organic concentration, the charge of the membrane surface has become more negative due to the adsorption of organic foulants on the membrane surface, and thus increased the electrostatic repulsion. However, the increasing surface charge had the potential to result in a larger molecular weight cut-off of a fouled membrane due to membrane swelling which can lead to lower rejection solutes. Therefore, results of this study indicated that membrane fouling may significantly affect the rejection of organic and ion solute.

Key words: Natural organic matter, humic acid, membrane fouling, nanofiltration, water treatment

INTRODUCTION

Membrane technology and the related separation systems such as reverse osmosis (RO) and nanfiltration (NF) membranes are now widely recognized as the best technologies for water treatment (Zularisam *et al*., 2006). However, fouling remains as one of the major challenges in membrane applications. Fouling of RO and NF membranes causes significant loss of productivity and added operational cost.

Natural organic matter (NOM) has been identified as one of the major foulants for these membranes (Tang *et al*., 2007). NOM is abundant in natural water resources and is derived both from natural degradation of some organic substances within the ecological systems and from human activities. Although, NOMs are considered harmless, but they have been recognized as disinfection by-products (DBPs) precursors during the chlorination process. Formation of DBPs highly depends on the composition and concentration of NOM which can be broadly divided into two fractions of hydrophobic (humic) and hydrophilic (non-humic) substances (Zazouli *et al*., 2007). Humic substances (HS) are comprised of humic and fulvic

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acids and non-humic substances (non-HS) include carbohydrates, lipids, and amino acids (Croue *et al*., 1993; Owen *et al*., 1995). Among many potential organic foulants, humic acid (HA), which is an important foreboding of trihalomethanes, has been considered to be one of the most significant foulants in the surface water. Solution chemistry has a major role in controlling the charge and configuration of HA molecules and determining between HA molecules and HA molecules–membranes interactions, and hence this membrane performance. HA molecules are mostly coiled densely at higher concentrations, lower pH, or higher ionic strength, and behave like flexible linear colloids at lower concentrations, higher pH and lower ionic strength. As a result, physical and chemical properties of HA could vary significantly at different conditions (Wang *et al*., 2005).

Membrane fouling results in several deleterious effects, including a decrease in water production because of a gradual decline in flux, an increase in applied pressure required for a constant rate of water production, a gradual membrane degradation which results in a shorter membrane life, and a decrease in the permeate quality (Belkacem *et al*., 2007). Membrane fouling is still a major obstacle for efficient operation of NF plants and a fundamental understanding of fouling mechanisms and the influence of fouling on both quantity of flux and permeate product water quality is of paramount importance. Therefore, the objectives of this study are to understand the effects of the solution chemistry such as pH, ion strength, and organic concentration on a spiral wound NF membrane performance at a pilot scale and to determine salt and organic retention.

MATERIALS AND METHODS

NF membrane characteristics

The NF membrane used in this study was designed by the manufacturer as HL2521TF (Desal Osmonics). It was made with a polyamide thin-film composite membrane in spiral wound configuration with an approximate molecular weight cut-off of 150-300 Daltons for uncharged organic molecules. The dimensions of the membrane were: outside diameter(ID):2.5in and length(L)=21in. Module performances based on factory tests were: 58L/h permeate rate, 98% sulfate magnesium rejection (as obtained in permeation test with 2000ppm $MgSO_4$ solution, 100PSI, 25°C and pH=7.5 after 24h); typical operating pressure of 200 psig and pH range in continuous operation=3–9. The effective membrane surface area was 12ft^2.

Membrane filtration experiments

Experiments were conducted using a cross-flow pilot-scale membrane unit as shown in Fig. 1. It was equipped with a feed tank, a pressure vessel containing the membrane module, an alternative circulation and pressurization pump with a security valve, two pressure gauges, a tap water heat exchanger for temperature control, three flow-meters on feed water, permeate and retentate pipes. Full circulation mode was used during the experiments and the retentate and permeate were returned to the feed tank with the volume of 35L, in order to maintain constant concentration. Each membrane filtration test was conducted at 22±1°C by using a heat exchanger.

Before the experiment, the membrane was cleaned through standard procedures to remove preservatives and rinsed with deionized water (DI) until the conductivity of permeate reached below 2μmhos/cm. The experiments were carried out with the following protocol:

1-For the first 30min the membrane was rinsed with DI water followed by measuring the pure water flux as a reference.

2-For the fouling experiments, permeate samples were taken at the start, at the end, and at several predetermined time intervals (15min) during the fouling experiment.

3-The feed concentrations were measured midway in every 15min period or in every one-hour period.

4-Samples were analyzed for conductivity, pH and TOC concentration. Retention solute of TOC and conductivity was calculated according to Eq (1) (Tchobanoglous *et al*., 2003):

$$R(\%) = \frac{C_f - C_p}{C_f} \times 100 = 1 - \frac{C_p}{C_f} \times 100 \qquad (1)$$

Where:
R (%) is the retention percent, C_f and Cp are solute concentrations in feed and permeate, respectively.

5-Permeate flux shown as J and J_0 (as Liter/m^2/ hour or LMH) was calculated by the ratio between the permeate flux (Q_P) and the membrane surface area as follows (WEF, 2006):

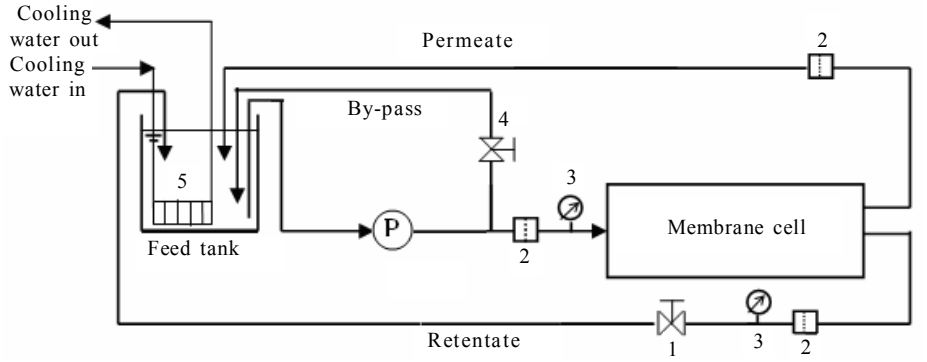
$$J_0 = \frac{Q_{p-initial}}{A} \quad \text{or} \quad J = \frac{Q_{p-end}}{A} \qquad (2)$$

Where:
J_0 is the initial permeate flux at filtration start time and J is the permeate flux at filtration time t. $Q_{p\text{-}intial}$ is the permeate flux at filtration start time and $Q_{p\text{-}end}$ is the permeate flux at filtration time t or filtration end time. It should be noted that $Q_{p\text{-}intial}$ and $Q_{p\text{-}end}$ are as liter per minute however J_0 and J are as LMH.

6-Permeate flux decline (PFD) was used in this study to describe the fouling extent of membranes. Permeate flux decline is defined as the percentage of reduced permeate flux compared to initial permeate flux based on the following equation (Xu *et al*., 2006):

$$PFD(\%) = \left(1 - \frac{J}{J_0}\right) \times 100 \qquad (3)$$

After each experiment, the membrane was rinsed with DI water for 30min and the pure water flux was measured. Chemical cleaning involved storage in acid solution (citric acid; pH=4) and base-solution (TSP; pH=9) for at least 15min, followed by rinsing with DI water for 15min. The difference between water flux before and after the chemical cleaning characterized the extent of irreversible fouling. After the experiments, the membrane was stored in DI water (Broeckmann *et al*., 2005).



1: Regulating valve, 4: By-pass valve,
2: Flow meters, 5: Heat exchanger,
3: Manometers, P: pump

Fig. 1: Schematic diagram of experimental apparatus

Feed solutions

Deionized water (DI) was used for the preparation of all stock solutions and membrane performance experiments. 0.1N NaOH and 0.1N HCl solutions were used for pH adjustment. Salt stock solutions were prepared using certified analytical grade sodium chloride (NaCl) dissolved in deionized water (DI). Humic acid (HA) (Humic acid sodium salt from Rohm and Haas Co.) was used as the index for NOM. In all filtration experiments, background electrolyte solution contained NaCl with varying conductivity because NaCl is easily found in water and wastewater. Therefore, to investigate the influence of ionic strength or conductivity on the membrane fouling process, fouling experiments were performed at three different ionic concentrations of 250,500 and 1000µmhos/cm. Also pH was changed and adjusted at 6.5, 7.5 and 8.5 by using NaOH and HCl solutions.

Analytical methods

The humic acid content of the feed, the permeate and the retentate were analyzed by measuring the UV_{254} (UV absorbance at a wavelength of 254nm) and DOC (dissolved organic carbon, mg/L). DOC measurements were performed using a Total Organic Carbon (TOC) analyzer (Shimadzu, Japan, Model: TOC-VCSH) in accordance with the Standard Method 5310B. UV absorbance at 254nm was analyzed in accordance with the Standard Method 5910B by using a Lambda 25 UV/Vis spectrophotometer. Potassium hydrogen biphthalate (KHP) was used to check the precision of the spectrophotometer. The conductivity (µmhos/cm) and pH of the feed, the permeate and the retentate were measured according to Standard Methods (APHP, 2000).

RESULTS

In Fig. 2 the fouling behavior is shown in the form of the permeate flux decline vs. time. Tables 1 and 2 show the rejection of humic acid and salt with ionic strength as well as pH. Fig. 2 clearly shows that the membrane fouling becomes more significant as the ionic strength of the feed solution increases. Also as it is shown in Tables 1 and 2, increase of the ionic strength of the feed solution slightly decreases the retention of dissolved organic carbon and conductivity.

It was observed that the permeate flux declines (PFD) were estimated about 4.3%, 5.3% and 6.7% for 250, 500 and 1000µmhos/cm ionic strength, respectively. When ionic strength is changed from 250 to 1000µmhos/cm (at pH 7.5), the rejection of humic acid and salt is decreased from 92.92% to 92.38% and 75.2% to 68.6%, respectively, which is not significant.

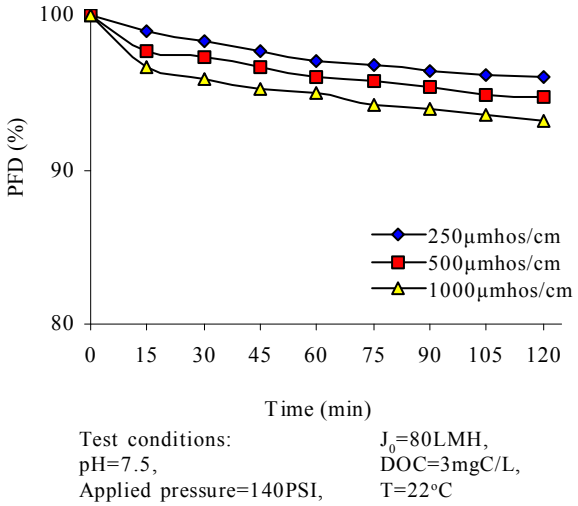


Fig. 2: Effect of conductivity on flux reduction and NF membrane fouling

Table1: Humic acid retention at varying pH and conductivity

EC (µS/cm)	pH=6.5		pH=7.5		pH=8.5	
	Concentration*	R (%)**	Concentration	R (%)	Concentration	R (%)
250	239.5	92.02	212.5	92.92	207	93.1
500	245.5	91.75	222.5	92.58	216	92.8
1000	251.5	91.62	228.5	92.38	221.5	92.62

Test conditions: Applied pressure =140PSI, 3mgC/L, T=22°C
***** Permeate concentration as µgC/L.
******Rejection percent.

Table 2: Salt retention at varying pH and conductivity

EC (µS/cm)	pH		
	6.5	7.5	8.5
250	71.2	75.2	80
500	68.6	71.6	75.2
1000	63.6	68.6	71.7

Test conditions: applied pressure=140PSI, DOC=3mgC/L, T=22°C

Fig. 3 shows the influence of solution pH on membrane fouling; also Tables 1 and 2 show the rejection of humic acid and salt retention with pH as well as ionic strength. The rejection efficiency of organic and salt slightly increased with an increase in pH. The DOC retention of all tested conditions varied from 92.01% to 93.1% was not significant. The salt retention varied from 63.6% to 80%.

It was observed that the permeate flux decline (PFD) were about 6%, 5.3% and 4.6% for pH=6.5, 7.5 and 8.5, respectively (Fig. 3). A more observed

significant decline in permeate flux was observed at pH=6.5 compared to pH=8.5.

Table 3 shows that when the concentration of the feed water was increased approximately from 3 to 12mgC/L, the DOC retention increased from 98.35% to 99.3%. Fig. 4 shows the influence of humic acid concentration on membrane fouling. It was that the permeate flux declines (PFD) were about 5.3%, 8.8% and 12% for 3, 6 and 12 mgC/L respectively. Increasing humic acid concentrations increased the rate and extent of flux reduction greatly because of the accumulation of a fouling layer on the membrane with the membrane fouling; therefore it may hinder the organic transport through the membrane.

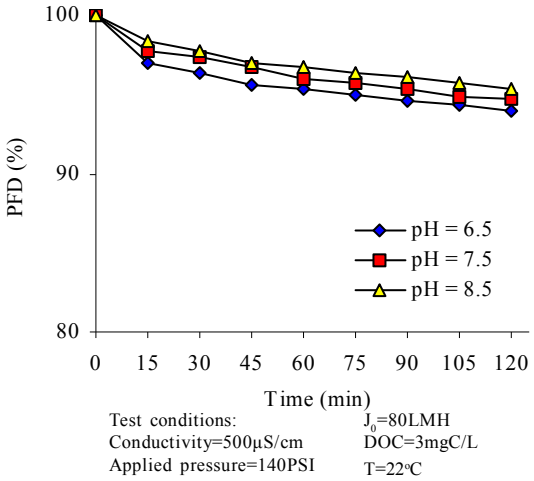


Fig. 3: Effect of pH on flux reduction and NF membrane fouling

Table 3: Humic acid and salt retention at varying humic acid concentration

Concentration* (mgC/L)	Organic matter		Conductivity	
	Concentration	R (%)	Concentration	R (%)
3	222.5	92.58	142	71.6
6	342	94.22	130	74
12	567.5	95.27	119	76.2

Test conditions: Conductivity=500(µS/cm), pH=7.5, applied pressure=140PSI, T=22°C
*Organic matter concentration in permeate as µgC/L and conductivity as µS/cm

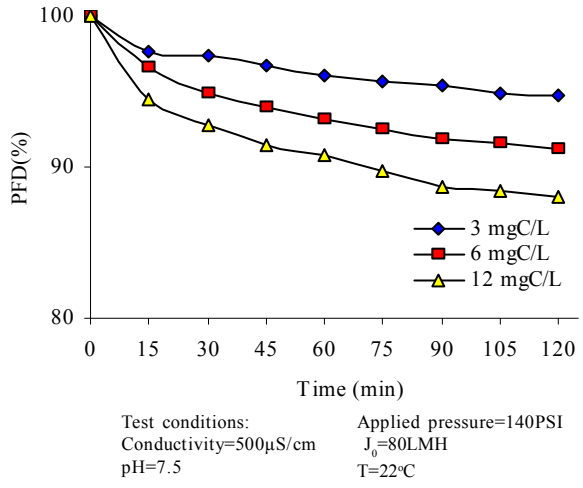


Fig. 4: Effect of humic acid concentration on flux reduction and NF membrane fouling

DISCUSSION

As it is shown in Fig. 2, the membrane fouling increased with the ionic strength of the feed solution. Also, increasing of the ionic strength of the feed solution slightly decreases the retention of dissolved organic carbon and conductivity. At higher ionic strengths, the charges of the humic acids and the membrane are reduced due to double layer compression, leading to a decrease in electrostatic repulsion among humic acid molecules and between the humic acid molecules and the membrane surface. As a result, humic acid molecules deposition and concentration polarization onto the membrane surface increases and the membrane fouling layer becomes thicker. In addition, due to reduced electrostatic repulsion at high ionic strength, humic acid molecules become more coiled and form a more compact fouling layer. The resulting fouling layer provides an additional hydraulic resistance to permeate flow through the membrane and leads to significant flux decline. In contrast, the strong electrostatic repulsion among organic molecules and between organic molecules and the membrane surface at low ionic strength, significantly prevents the humic acid molecules accumulation on the membrane surface. Similar trends of decreased flux decline with increasing ionic strength for charged NOM were observed by Lee *et al.*, 2006.

Tang *et al.*, (2007) showed that higher ionic strength had the effect to slightly increase the charge density; it also shielded the charges due to increased concentration of counter ions, leading to a net reduction in the electrostatic repulsion between humic acid molecules. Consequently, more flux reduction occurred at higher ionic strengths (Tang *et al.*, 2007).

Jarusutthirak *et al.*, (2005) investigated the NF membrane fouling due to monovalent cation and

reported that the experimental results fitted with pore blocking model (at low ionic strength of 0.01 M), possibly due to reduced charge repulsion between positively charged Na^+ and negatively charged membrane, thus affecting membrane surface and/or pores. At higher ionic strength of 0.05M NaCl, the results were followed with cake formation. This was possibly dominated by reduced charge repulsion between positively charged Na^+ and negatively charged NOM, thus resulting an increase of NOM accumulation on the membrane surface. However, an increase of ionic strength from 0.01 to 0.05M can also decrease charge repulsion between positively charged Na+ and negatively charged membrane. They observed that the rejection of conductivity decreased from 25.3% to 13.7% with increasing ionic strength from 0.01 to 0.05M, possibly due to decrease double layer thickness on membrane matrix. The rejection of dissolved organic carbon (DOC) was about 94.9–95.3% (Jarusutthirak *et al*., 2005).

Our finding was in accordance with the results of theanother study (Lee *et al*., 2005). They indicated that the reduction in electrostatic double layer repulsion by the electrolyte (NaCl) results in the formation of a thick cake layer on the membrane surface, which significantly hinders the back diffusion of accumulated salt. The marked increase in osmotic pressure at the membrane surface caused a substantial reduction in the driving force and hence severe flux decline. Much more severe flux decline was observed for runs at higher ionic strength and initial permeate flux due to accumulation of a thicker cake layer and the greater osmotic pressure buildup at the membrane surface. And also, as fouling progresses, enhanced salt concentration near the membrane surface increases. The enhanced salt concentration results in a marked flux decline and greater salt transport across the membrane, which results in reduction of salt rejection. The increase in ionic strength results in a more severe enhanced concentration polarization also results in greater deterioration of salt rejection.

As it is shown in Fig. 3, the permeate flux increased with pH. Also, the rejection efficiency of organic and salt increased slightly with an increase in pH (Tables 1 and 2).The possible explanation is that the membrane surface charge and humic charge were more negative due to deprotation functional groups under alkaline condition. Under these conditions, humic accumulation on the membrane surface decreases. This behavior is attributed to the less electrostatic repulsion among the humic acid molecules and between the humic acid molecules and the membrane surface at this pH. The transport of ionic organic contaminants was hindered as a result of improved Donnan exclusion. The increasing negative surface charge could, however, expand the molecular weight cut off (MWCO) of a fouled membrane due to membrane swelling, resulting in a lower rejection (Xu *et al*., 2006). In general, flux decline at pH=6.5-8.5 is very small because all the functional groups are already deprotonated and the membrane is negatively charged. As a result, humic accumulation on the membrane surface is not substantial. In addition, the shape of humic acid molecules are different with pH, due to increased electrostatic repulsion between negatively charged neighboring carboxyl groups, and thus form a sparser fouling layer. Similar trends of increased flux decline with decreasing pH for charged natural organic matter (NOM) molecules were observed by others (Lee *et al*., 2006; Liikanen *et al*., 2005). Yoon *et al*., (1998) reported that the negative charge of humic acid as well as the negative zeta potential of the membrane surface fouled membrane increased with pH and the deposition of humic acid on the membrane surface was expected to decrease with higher pH because of larger repulsive forces. The number of negatively charged functional groups of humic acid would be increased with pH (Yoon *et al*., 1998).

Increasing humic acid concentrations increased greatly the rate and extent of flux reduction (Fig. 4) because of the accumulation of a fouling layer on the membrane; therefore it hindered the organic transport through the membrane. The adsorption of organic foulants on the membrane surface may also increase the negative charge of the membrane surface, and thus increase the repulsion forces and consequently retention. Water molecules are small and almost without charge, and they pass through the fouled membrane more easily than organic molecules (Yoon *et al*., 1998). Tang and co-

workers reported that the rate at which humic acid molecules accumulate on a membrane surface is determined primarily by the collision frequency of humic acid molecules onto the membrane surface, which increases at higher feed concentrations, and the collision efficiency, which is defined as the ratio of the number of molecules deposited onto the membrane surface over the total number of collision events. As a result, more humic molecules are generally deposited onto a membrane when the feed concentration increases (Tang *et al*., 2007).

As it is shown in Table 3, increasing humic acid concentrations increased the conductivity rejection. Salt rejection increased from 96.4% to 97.12% when humic acid concentrations changed from 3 to 12mgC/L. Humic acid deposits on membranes can improve salt rejection by two possible mechanisms: size exclusion and Donnan exclusion. Donnan exclusion is likely the dominant mechanism in the current study, where Cl^- anions are repelled by negatively charged humic acid. Meanwhile, counter ions of Na^+ are retained to maintain solution neutrality. If size exclusion were the dominant mechanism, salt rejection improves due to the formation of much denser and less porous foulant layers (Tang *et al*., 2007). Size exclusion mechanism is weak here because it is important when divalent cation (Ca^{2+}) is present but background electrolyte is monovalent cation, (Na^+). Similar results were observed by Xu *et al*., (Xu *et al*., 2006; Liikanen *et al*., 2005) reported that an increased feed water organics concentration caused an increased retention of organic matter, most probably due to the formation of a denser dissolved organic matter (DOM) foulant layer on the membrane surface and DOM molecule aggregation to bigger, less permeable particles (Liikanen *et al*., 2005).

Therefore, the chemical composition of feed water greatly influences the membrane fouling. It is accelerated at lower pH, higher ionic strength, and in the presence of high humic concentration. Permeate salt concentration was also significantly reduced immediately upon exposing membranes to humic acid. The improved salt rejection was due to several mechanisms such as size exclusion and Donnan exclusion. The main mechanism in this was likely Donnan exclusion by humic material close to membrane surfaces. In addition, the adsorption of organic foulants on the membrane surface may also increase the negative charge of the membrane surface, and thus increase the repulsion (electrostatic) forces and consequently retention. An increased feed water organics concentration caused an increased retention of organic matter, most probably due to the formation of a denser foulant layer on the membrane surface and molecule aggregation to bigger and less permeable.

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