Desalination and Water Treatment
www.deswater.com

1 (2009) 194–200

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Combined humic substance coagulation and membrane filtration under saline conditions

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Received 3 August 2007; Accepted 20 August 2008

ABSTRACT

The effects of poly diallydimethylammonium chloride (PDADMAC) and copolymer of dimethyl aminoethyl acrylate (CoAA) coagulants on membrane performance are investigated under different conditions using ultrafiltration (UF) and nanofiltration (NF) membranes. It is evident that PDADMAC performance is better than CoAA in removing humic substances (HS) with both membranes, P005F and NF270, having equal fouling potential. Salinity results showed reduction in HS retention and increase in fouling with increasing salinity from 10,000 to 25,000 ppm NaCl using P005F UF membrane. No further reduction in retention or increase in fouling was experienced when salinity was increased to 35,000 ppm NaCl, while NF270 NF membrane experienced reduced retention and increased fouling throughout the studied salinity range. Finally, TMP did neither affect HS retention nor NF270 fouling, but increased P005F fouling.

Keywords: Membranes; Seawater; Humic substances; Polyelectrolytes

1. Introduction

Membrane technology is widely accepted as a means of producing various qualities of water. Over the past years, membrane processes have been widely adopted by different industries [1,2]. Membrane filtration such as ultrafiltration (UF) and nanofiltration (NF) are emerging as new methods of water pre-treatment prior to reverse osmosis [3–7]. Although UF and NF produce high removal of humic acids, their common drawbacks are low degree removal of low molecular weight substances such as humic substances and membrane fouling [8,9].

Fouling often associated with accumulation of substances on the membrane surface or within the membrane pore structure, worsens membrane performance and ultimately reduces membrane efficiency and shortens membrane life [10–12]. In general, the main factors which play a major role on membrane fouling are feed properties and composition, hydrodynamic condition, and membrane geometry and retention characteristics [13–16].

In the past inorganic coagulants were used to aid HS removal, but recently, organic polyelectrolytes have been used instead. Polyelectrolyte coagulation can be as effective as inorganic coagulants and it avoids precipitation of hydroxides formed by hydrolysis when inorganic coagulants are used [17,18]. The ability of a polymer to act as a flocculent depends on its ability to bond to the surface of the colloidal particles. As a result, in many cases these materials are quite specific [19].

The objectives of this study are to investigate the combined effects of polyelectrolyte coagulation and membrane filtration on HS removal at different salinity levels. Two polyelectrolytes are studied, PDADMAC and CoAA, and two membranes are used, P005F UF and NF270 NF. The role of salinity, HS concentration, polyelectrolyte type and concentration, and trans-membrane pressure (TMP) on HS retention and membrane fouling are investigated.

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2. Materials and methods

De-ionized water used in this study was obtained through demineralization using ion exchange followed by reverse osmosis. The conductivity of the water was lower than 1 µS/cm. All the chemicals used in the experiments were reagent grade. All glassware used in the experiments were rinsed with de-ionized water and dried at 70°C overnight. NaCl was purchased from Fisher scientific-UK with purity higher than 99.5%.

Membranes used during the study were the 5 kDa UF polyethersulfone (PES) and the NF270 polyamide NF. The UF membrane was provided by Nadir Filtration (Germany) and the NF membrane was supplied by FILMTEC, manufactured by Dow Chemical (USA).

High purity poly diallydimethylammonium chloride (PDADMAC) was purchased from Sigma Aldrich. The cationic PDADMAC was supplied as viscous liquid of 20% dissolved in water. It has an average MW of 200–350 kDa and 100% cationic charge density. Due to the volatility of the copolymer, the real concentration was measured by dilution with de-ionized water. The concentration was then measured by evaporating 10ml of the diluted sample at 105°C.

Copolymer of dimethyl aminoethyl acrylate (CoAA) was kindly supplied by Ciba Specialty Chemicals, UK. CoAA has a MW >2000 kDa and has a cationic charge density of 85%.

2.1. Humic substance extraction

Humic acids (HA) and fulvic acids (FA) were extracted from soil using a modified procedure originally developed by Thurman and Malcolm [28,29]. First-class soil with low fertiliser contents was purchased from Sainsbury's Homebase. 6.0 M hydrochloric acid (HCl) solution, solid anhydrous sodium hydroxide (NaOH) pellets and non-ionic polymethyl methacrylate (XAD-8) adsorption resin were all purchased from Sigma-Aldrich; 0.5 M NaOH was prepared from NaOH solid pellets and used through out the experimental work. An oven at 105°C was used to gravimetrically measure the concentration of the solutes i.e., salt, HS and other solid contaminants; and a furnace at 600°C was used for salt concentration gravimetric measurements. The purity of the extracted HA and FA are 89.5% and 74.5%, respectively. HA and FA were mixed before performing any experiment in a ratio of 1:1.

2.2. Equipment

A Shimadzu total organic carbon analyzer model TOC-5050A was used to measure the concentration of organic carbon of the solution. A user-friendly program was used in junction with the analyzer to provide an automated calibration curves and readings. The analyzer took three replicate readings provided that the coefficient of variance was less than 2%. In cases where the precision was greater than 2%, the instrument recorded a further two readings and the anomalous readings were discarded.

2.3. Method

Membrane filtration experiments were carried out in a laboratory-scale filtration cell especially designed for this work. A schematic diagram of the experimental set-up is shown in Fig. 1. Five litres of the feed were pumped using a stainless steel gear pump into the filtration cell. A rectangular shaped membrane (3 cm × 10 cm × 0.5 cm) with an effective membrane area of 30 cm^2 was employed. The operating pressure and volumetric flow rate were adjusted using the concentrate (reject) outlet valve. The pressure was varied between 1–9 bar. The experiments were carried out at ambient temperature in total recirculation mode, i.e. both the concentrate and the permeate streams are recirculated into the feed tank, so that the feed concentration is kept approximately constant.

Synthetic stock solutions of 1 g/l concentration were prepared for the tested chemicals by dissolving/diluting using de-ionized water. Due to the high viscosity of CoAA, the concentration of the stock solution used was 0.2 g/l. The stock solutions were then diluted with de-ionized water and were used within a week of preparation. Solid NaCl pellets were dissolved in the HS solution and stirred at 400 rpm for 1 h using a magnetic stirrer to obtain the desired salinity level of the tested HS solution. The desired mixture of HS and polyelectrolyte concentration was obtained by adding the appropriate amount of polyelectrolyte stock solution to the HS solution and stirrer at 400 rpm for 5 min. The pH of all solutions was regulated at ~7 before each experiment using NaOH. Prior to any filtration experiment, membrane compaction was undertaken using de-ionized water for 2 h at 9 bar using NF membranes. No membrane compaction was required for UF membranes. Pure water flux (J_0) was calculated by measuring the time taken to collect 20 ml of permeate and using the following

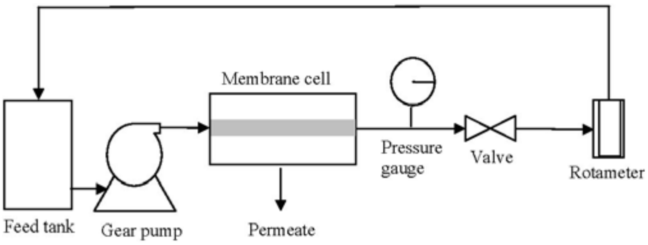

Fig. 1. Cross flow filtration model.

equation:

$$J = \frac{V}{At} \tag{1}$$

where J represents permeate flux (L/m^2.h); J_0 is pure water flux and J_v is solution permeate flux. V is the volume of permeate collected (L), A is the effective membrane area and t is the time taken to collect the permeate (h).

De-ionized water was then replaced by 5 L of the tested synthetic solution. The system was run until an approximate constant permeate flux was observed. The solution permeate flux (J_v) was measured using Eq. (1). The concentration of permeate collected was analyzed using TOC analyzer. HS retention was measured using [22]

$$R = 1 - \frac{C_p}{C_b} \tag{2}$$

where R is retention, C_p permeate concentration (mg/l) and C_b is bulk concentration (mg/l). Membrane fouling is calculated using [23]:

$$Fouling = \left(1 - \frac{J_v}{J_0}\right) \times 100 \tag{3}$$

where *fouling* is the total fouling during the period of the filtration (%).

3. Results and discussion

3.1. Humic substance retention

The influence of salinity, HS concentration, polyelectrolyte type and concentration, and TMP on HS retention was studied using P005F and NF270 membranes. The P005F membrane experienced lower retention compared to NF270 membrane as shown in Fig. 2. HS retention was 0.92 and 0.96 using P005F and NF270, respectively. NF270 higher retention is due to its lower MWCO compared to P005F membrane as investigated previously [24,25]. NF270 HS retention is also dependent on membrane surface charge and its interaction with the bulk solution. NF270 membrane surface is negatively charged, which repels the anionic charged HS.

Using the P005F membrane, HS retention decreased when salinity level increased from 10,000 ppm to 25,000 ppm NaCl, but no further increase in retention was experienced when salinity level was increased further to 35,000 ppm NaCl as shown in Fig. 2. HS retention was 0.95, 0.92 and 0.91 at salinity levels of 10,000, 25,000 and 35,000 ppm NaCl, respectively. Ionic strength has an effect on HS retention due to the increased coiling of HS molecules with increasing ionic strength. At low salinity level, HS functional groups are stretched. When the salinity level is increased, these groups curl up and aggregate causing reduction in size of colloids thus increasing HS permeability, as shown in [8,26,27]. This phenomenon is called double layer compression [28]. The increase in salinity from 25,000 to 35,000 ppm did not exert any change in HS retention due to the very high salinity of the feed; salinity is no longer an important factor. The stability of HS is a function of the attraction force and the repulsive force. The attraction force is independent of the ionic strength, whilst the repulsive force is. Repulsive force affects the stability of HS through the factors $\sum\left(n_i z_i^2\right)^{-1}$ and $e^{-\Sigma\left(n_i z_i^2\right)}$ where z_i is the valency and n_i is the number of ions of the ith species per unit volume. Due to the negative exponential factor, the increase in double-layer compression will rapidly become smaller as the ionic strength grows. Therefore, at a certain point HS colloids can be considered fully destabilized and any additional increase in ionic strength will not affect HS colloids structure [29].

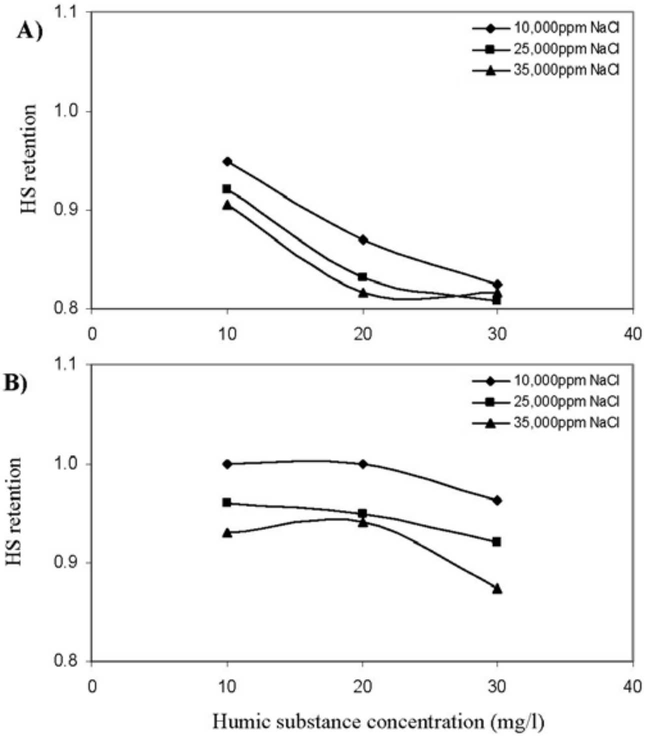

Fig. 2. Effects of membrane type, salinity and HS on HS retention. A) P005F operated at 3 bar and B) NF270 operated at 9 bar. Initial feed concentration of 2 mg/l PDADMAC.

HS retention decreased slightly when salinity level increased using NF270 membrane. HS retention was 1.0, 0.96 and 0.93 at salinity levels of 10,000, 25,000 and 35,000 ppm NaCl, respectively. NaCl cationic species affect the NF270 membrane surface as well as the HS structure due to its negatively charged surface. NaCl cationic species affect the surface of NF membranes as well as the HS structure. Braghetta et al. [30] provided a comprehensive explanation of the effects of salinity on NF membrane surface. The negatively charged NF270 membrane contains an electric double layer at its surface which repels anionic HS, thus increasing HS retention. Braghetta et al. [30] showed figures for the combined effect of steric hindrance, solution chemistry and the chemical properties of the membrane surface on HS retention. An increase in ionic strength will reduce the area of electric double layer (grey area) and increase the area available for the transport of negatively charged species (white area) as shown in the figures in Braghetta et al. [30]. Therefore, although the increase in salinity from 25,000 to 35,000 ppm NaCl did not affect the colloidal structure of HS as experienced in UF membrane experiments, it reduced the membrane area available for the transport of HS through NF270 membrane.

HS retention decreased with HS concentration. HS retention using P005F was 0.92, 0.83 and 0.81 at HS concentration of 10, 20 and 30 mg/l, respectively. As HS concentration increases, the number of HS species settling at the surface of membrane will increase. This settling will enhance concentration polarization at the surface of the membrane and reduce HS retention.

Fig. 3 shows the effect of polyelectrolyte type and concentration on HS retention. HS retention using PDADMAC was higher than CoAA. HS retention using P005F was 0.92 and 0.88 using PDADMAC and CoAA, respectively. HS retention increased with polyelectrolyte concentration. HS retention using P005F was 0.72, 0.75, 0.82 and 0.92 at PDADMAC concentration of 0, 0.1, 1 and 2mg/l, respectively. Polyelectrolytes strengthen the linkage between colloidal HS, which enlarge the size of the colloids, thus increasing their retention using the tested membranes. Furthermore, the polyelectrolytes' molecular weights are very high (>250 kDa) and HS particles might be adsorbed onto the polyelectrolyte flocs forming polymer–floc complexes, leading to higher HS retention [17,31]. Coagulation performance exhibited by the various types of polyelectrolytes is influenced by the charge density of the polyelectrolyte rather than the molecular weight. PDADMAC produces higher retention of HS because PDADMAC has charge density of 100% compared to 85% charge density of CoAA. Increasing polyelectrolyte concentration will provide more cationic species to interact with the HS, thus increasing HS neutralization and HS retention.

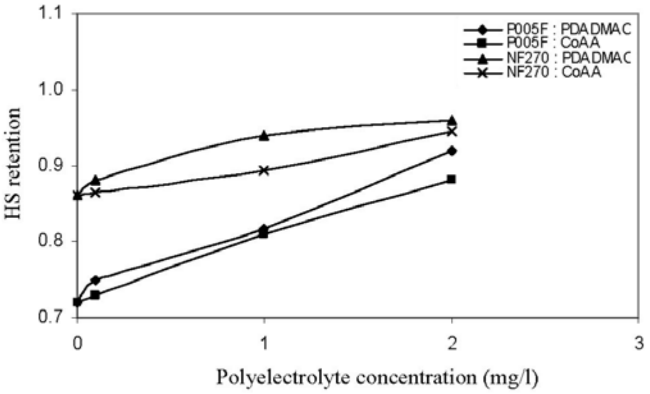

Fig. 3. Effects of polyelectrolyte type and concentration on HS retention; P005F and NF270 membranes operated at 3 and 9 bar, respectively. Initial feed concentration of 25,000 ppm NaCl and 10 mg/l HS.

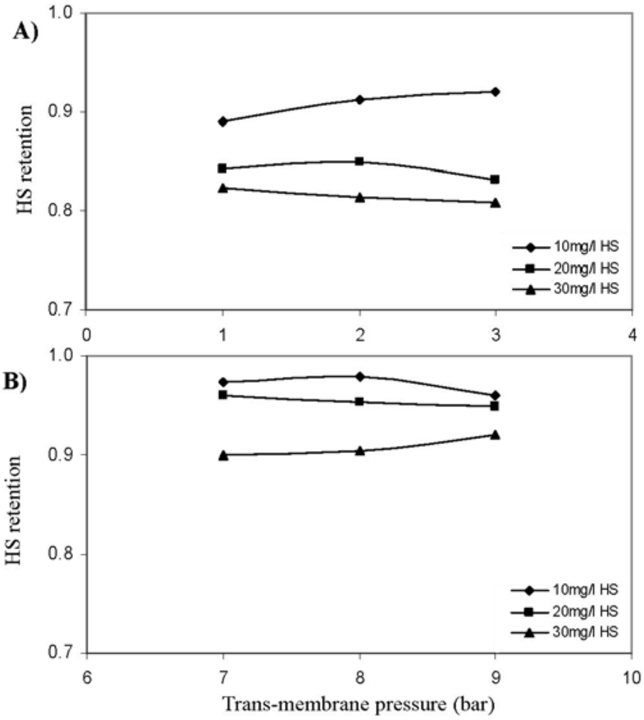

Fig. 4. Effects of trans-membrane pressure on HS retention. A) P005F membrane and B) NF270 membrane. Initial feed concentration of 25,000 mg/l NaCl and 2 mg/l PDADMAC.

No change in HS retention was experienced when TMP was increased as shown in Fig. 4. HS retention using NF270 was 0.97, 0.98 and 0.96 at TMP of 7, 8 and 9 bar, respectively. Two competing phenomena determine the separation behaviour of HS with respect to TMP: concentration polarization and dilution effect. Concentration polarization increases with TMP causing reduction in retention, while the dilution effect counteracts the concentration polarization effect. The dilution effect increases with TMP by increasing the permeate water flux through the membrane, while the ion flux remains

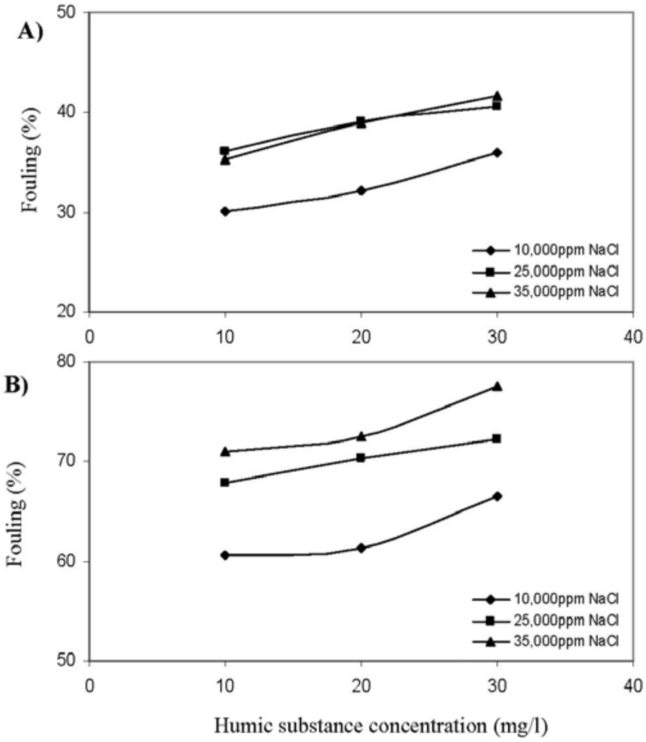

Fig. 5. Effects of membrane type, salinity and HS on membrane fouling. A) P005F operated at 3 bar and B) NF270 operated at 9 bar. Initial feed concentration of 2 mg/l PDADMAC.

virtually unchanged resulting in lower solute concentration at permeate.

3.2. Membrane fouling

The influence of salinity, HS concentration, polyelectrolyte type and concentration, and TMP on membrane fouling was studied using P005F and NF270 membranes. Fig. 5 shows the effect of membrane type and salinity level on membrane fouling. P005F membrane experienced lower total membrane fouling compared to the NF270 membrane. Fouling was 36.0 and 67.9% using P005F and NF270 membranes. Increasing salinity level from 10,000 ppm NaCl to 25,000 ppm NaCl increased P005F membrane fouling, but no further increase in fouling was experienced when salinity was increased to 35,000 ppm NaCl. P005F fouling was 30.1, 36.0 and 35.2% at salinity levels of 10,000, 25,000 and 35,000 ppm NaCl, respectively. Increasing the ionic strength compresses the diffuse layer of HS colloids. Double layer compression reduces the HS colloidal charge and the electrostatic repulsion between HS colloidal macromolecules. The reduction in HS interchain repulsion will coil up HS colloids forming as a result a more densely packed deposition of HS at the surface of the membrane and formation of a compact fouling layer.

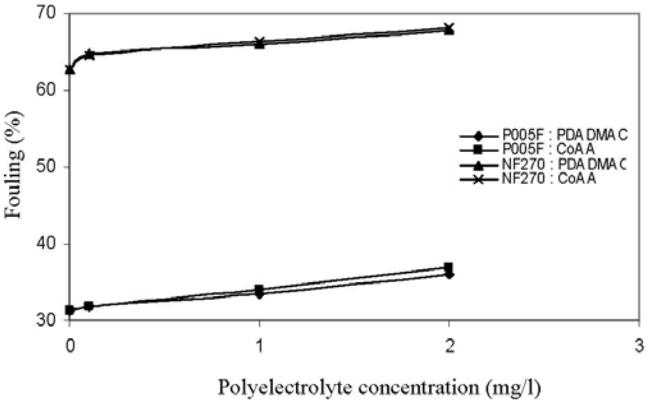

Fig. 6. Effects of polyelectrolyte type and concentration on membrane fouling. P005F and NF270 membranes operated at 3 and 9 bar, respectively. Initial feed concentration of 25,000 ppm NaCl and 10 mg/l HS.

The increase in salinity from 25,000 to 35,000 ppm did not exert any change in HS colloids; due to the very high salinity of feed, salinity is no longer an important factor as explained in Section 3.1. NF270 membrane fouling increased with salinity. NF270 was 60.7, 67.9 and 70.9% at salinity levels of 10,000, 25,000 and 35,000 ppm NaCl, respectively. Salinity affects the NF membrane surface as well as the HS structure. Braghetta et al. [30] showed the combined effect of solution chemistry and the chemical properties of the membrane surface on membrane fouling. An increase in ionic strength will reduce the area available (bounded by solid lines) for solvent transport of the NF membrane thus increasing fouling.

Fig. 5 shows the effect of HS concentration on membrane fouling. Membrane fouling increased with HS concentration. P005F fouling was 36.0, 39.2 and 40.6% at HS concentration of 10, 20 and 30mg/l, respectively. As HS concentration increases, the number of HS molecules settling at the surface of membrane will increase. This settling will enhance concentration polarization at the surface of the membrane and increase membrane fouling.

Fig. 6 shows the effect of polyelectrolyte type and concentration on membrane fouling. No difference in fouling was experienced using PDADMAC and CoAA coagulants. NF270 fouling was 67.9 and 68.2% using PDADMAC and CoAA, respectively. Membrane fouling increased with increasing polyelectrolyte concentration. NF270 fouling was 62.8, 64.7, 66.0 and 67.9% at PDADMAC concentration of 0.0, 0.1, 1.0 and 2.0 mg/l, respectively. The increase in fouling with increase in polyelectrolyte concentration is due to the increase in polyelectrolyte and colloids settling at the surface of membrane. An increase in polyelectrolyte concentration will increase the amount of polyelectrolyte molecules settling at the surface of the membrane inducing concentration. The addition of polyelectrolyte also changes the

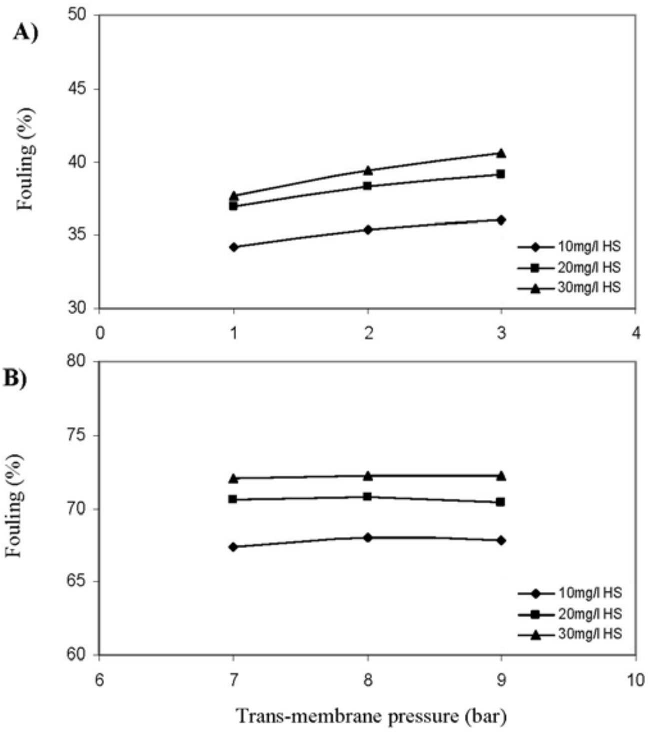

Fig. 7. Effects of trans-membrane pressure on membrane fouling. A) P005F membrane and B) NF270 membrane. Initial feed concentration of 25,000 mg/l NaCl and 2 mg/l PDADMAC.

structure of the HS molecules enabling them to foul the membrane more extensively.

Fig. 7 shows the effect of TMP on membrane fouling. P005F fouling increased with TMP, while NF270 fouling was independent of TMP. P005F fouling was 34.2, 35.4 and 36.0% at TMP of 1, 2 and 3 bar, respectively, and NF270 fouling was 67.4, 68.0 and 67.9% at TMP of 7, 8 and 9 bar, respectively. These effects may be due to the compressibility of the fouling layer formed at the surface of the membrane. At P005F studied range of TMP (1–3 bar), concentration polarization layer was compressed when TMP increases. The compression of the concentration polarization layer reduces the permeate flux, thus increasing membrane fouling. Concentration polarization at NF270 membrane surface was incompressible at the tested TMP range, 7–9 bar.

4. Conclusions

The NF270 NF membrane has higher HS retention due to size exclusion and charge repulsion, where this is not experienced using the P005F UF membrane. NF270 also experienced higher fouling potential mainly due to the high salinity of the feed. NF270 performance was reduced throughout the studied salinity range, while no change in performance was experienced using P005F when salinity is increased from 25,000 to 35,000 ppm NaCl. These results indicate that the main cause of performance reduction using P005F is due to the effect of salinity on HS structure rather than the membrane surface.

HS retention is higher using PDADMAC compared to CoAA because PDADMAC has a higher charge density. Both membranes experienced equal membrane fouling, indicating the superiority of PDADMAC at the studied conditions. In addition, TMP does not affect either HS retention or NF270 fouling, but increases P005F fouling. This is because of the opposing effects of concentration polarization and dilution effect on membrane retention.

Acknowledgment

The authors would like to thank the Middle East Desalination Research Center (MEDRC) for funding this work (project number 03-AS-02).

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