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Effect of shear rate on the performance of nanofiltration membrane for water desalination

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Abstract

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Asymmetric nanofiltration membranes were fabricated from a ternary dope composition consisting of cellulose acetate (CA), formamide and acetone using a simple dry/wet phase inversion process. In order to fabricate a high performance nanofiltration membrane, the effects of rheological factor of dope solutions, that is shear rate on the performance of nanofiltration membranes for water desalination has been studied. The membranes performances that are based on percentage of rejection of sodium chloride (NaCl) and fluxes with different concentrations of sodium chloride are reported. Generally, the percentage of rejection and fluxes were found to increase with increasing of shear rate until a critical level of shear rate is achieved. The experimental results showed that the fluxes were increased and percentage of rejection is decreased with sodium chloride concentrations. An optimum percentage of rejection and fluxes obtained were about 56.76% and 7.44×10^{-4} m/s, respectively. The optimum shear rate was found to be at 304 s^{-1}. It was also found that membranes with shear rate below 152s^{-1} are not suitable to be used as a nanofiltration membrane due to their low mechanical strength.

Key words : asymmetric membrane, nanofiltration, water desalination, shear rate, cellulose acetate, fluxes and percentage of rejection

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Nanofiltration (NF) membranes have become the most important recent advance in membranes technology due to their increasing demand in separation process on a world-wide basis and because of their advantages, such as low operation pressure, high flux, high retention of multivalent anion salt and organic molecule above 300 Dalton, and relatively low operation and maintenance cost (Lu *et al*, 2002).

Development of integrally skinned asymmetric membranes by Loeb and Sourirajan in 1960's was a major breakthrough in membranes technology (Ismail and Yean, 2002; Idris *et al*, 2002; Ismail and Shilton, 1998). Integrally skinned asymmetric membranes can be prepared through the phase inversion method, where a multi-component casting solution is immersed in a coagulant bath. An asymmetric membrane having a very thin dense skin layer can be prepared by a dry/wet phase inversion process. The skin layer of this asymmetric membrane becomes defect-free by introduction an evaporation step (Pinnau and Koros, 1991). Since the dense skin layer is formed by a phase inversion process which occurs by bringing an initially thermodynamically stable polymer solution to unstable state during the coagulation step, the complicated mass transfer and solvent exchange during the demixing generally yield defective skin layers (Chung *et al*, 2000). The controlling of the membrane surface morphology is very important to the performance. In 1998, Albecht applied the atomic force microscope (AFM) in the observation of surface layer for the first time. It opened a new door to the study on the membrane morphology. Bowen and Mukhtar (1996) analyzed the pore size and its distribution in RO, UF, and NF membranes using AFM. Hirose *et al*. (1996) found that the water flux increased as the roughness of the membrane increased, when they were observing the surface of RO membrane.

Previously research in membrane formation has focused on the phase inversion process parameters, which generally influenced the general morphology of the membranes, such the skin layer thickness and surface porosity. This parameter eventually is the determining factor of membrane separation performance. In addition to phase inversion, it has also been recognized that molecular orientation will affect membrane rejection rate and its can be brought by altering the rheological conditions during fabrication. Shear during casting and spinning has been shown to affect the flux rate of cellulose acetate membranes and this has been attributed to molecular orien-tation in the active layer (Ismail and Yean, 2002; Idris *et al*, 2002a; Idris *et al*, 2002b; Ismail *et al*, 1997). In recent years, scientists have gradually recognized that the rheological conditions also play an important role on the membrane performance. The effect of shear-induced orientation has been observed in the separation performance of ultrafiltration (UF) and gas separation membranes (Chung *et al*, 2000).

Molecular orientation in membranes can now be directly measured by spectroscopic techniques. Plane polarized infrared spectroscopy has been used recently to confirm the presence of shear rate induced molecular orientation in reverse osmosis (RO) and gas separation membranes. For cellulose acetate flat sheet and hollow fiber membranes, increased shear were reported to elevate membrane rejection rate beyond the intrinsic value of the polymer (Idris and Ismail, 2002; Ismail and Shilton, 1998). Phase inversion usually involves casting a shear-thinning and viscoelastic solution during which shear is applied prior to a rapid coagulation. Shear-thinning properties of polymer solution often suggest a progressive alignment of polymer molecules under shear in the flow direction. As a result, shear-induced molecular orientation induces favorable effects on the membrane properties (Ismail and Yean, 2002; Ismail and Shilton, 1988; Ismail *et al*, 1997).

During casting a shear thinning and viscoelastic solution, polymer molecules are maintained in an oriented (partially) conformation by castline deformation. After casting, polymer molecules would relax to some preferred state. However, they recover only a portion of their total deformation. The as-cast membrane is then put through forced-convective evaporation. Dry phase separation progresses instantaneously and limits conformational and configurational rearrangement especially in the nascent skin region. Polymeric material has no chance of relaxing and therefore shear-induced molecular orientation will be frozen into the nascent skin layer of membrane. As a result, the nascent skin layer with sufficiently rigid structures forms a well-defined skin layer with enhanced molecular orientation.

Nanofiltration has been widely used in the pharmaceutical industry, drinking water treatment and the environment protection (Bowen and Welfoot, 2002). Other major applications of the NF include the removal of salts in water treatment and the fractionation of salts and small molecules in a number of industries (Bowen and Mukhtar, 1996). Recently, NF membranes have been widely used in the partial or full water desalination and inorganics removals from sea and brackish water (Bremere *et al*, 2001). Desalination technology is finding new outlets in supplying water for a huge demand of fresh water consumption. The separation process is based on the difference in size and charge of the solutes. The use of desalination is increasingly seen as a means of additional water treatment to meet municipal domestic needs of urban populations (Bremere *et al*, 2001).

The flux rate of the NF membrane decreases with an increase in shear rate but the separation performance for a particular solute increases with increasing shear. This is because the pore size of the skin may decrease with increasing shear rate and due to the smaller pore size of the final membranes result in better rejection for a solute solution and higher resistance for water permeation or probably due to increased polymer molecules orientation in the membrane active layer. Permeation and selectivity of membrane are found to increase with increasing shear; some selectivity even surpass the generally recognized instrinsic selectivity (Ismail and Yean, 2002; Idris *et al*, 2002b).

Therefore, this study was carried out to investigate the effect of casting shear rate on asymmetric cellulose acetate NF membrane structures and the separation performances for water desalination. The NaCl solutions with different concentrations were prepared to measure the membrane's performances based on the percentage rejection and flux rate. Flat membranes were cast at different shear rates using our newly developed pneumatically controlled casting system. This is done in an attempt to induce greater shear thus greater molecular orientation, which would in turn significantly alter the separation characteristic of the membranes. The combined effect of phase inversion parameters and rheological conditions during membrane fabrication is a unique approach in membrane research. The performance of the NF membrane was characterized and its dense and subporous layer structure imaged by SEM. At last, the relationship between membrane structure and effect of molecular orientation on the performance of the NF membrane was explored.

Experimental

Materials

Cellulose acetate (CA) with 39.8% acetyl content made by Aldrich Chemical Co. Inc. was used as a membrane material. Acetone and formamide, purchased from Merck, Darmstadt, Germany, were used as a solvent and non-solvent, respectively, whereas tap water were used as coagulation medium. Sodium chloride (NaCl) of analytical purity grade was supplied by Merck, Darmstadt, Germany.

Membrane preparation

Cellulose acetate was dissolved at about 56 ^{o}C in a multicomponent solvent. The casting solution consisted of 23.5% CA, 9.5% formamide and 67.0% acetone. The polymer solution was put into an ultrasonic bath for about 3 hours to remove the bubbles and then was kept at room temperature for 24 hours. The asymmetric NF membranes were fabricated by dry/wet casting technique using our pneumatically-controlled casting machine. The membranes were cast onto a glass plate at ambient temperature with a casting knife notch of 200 µm. The thickness of the fabricated membrane is about 200 µm. The membranes were cast at various casting speed and hence various shear rates (152 s^{-1} to 507 s^{-1}). An inert nitrogen gas stream was flushed across the as-cast membrane surface for about 30s to induce forced-convective evaporation prior to immersion into an aqueous bath, where it remained for 1 day.

Membrane performance measurement

The membrane permeation tests were performed with a permeation cell as shown schematically in Figure 1. Circular membrane discs were cut and mounted in a stainless steel, cylindrical membrane test cell by a porous support and tightened by a rubber *O*-ring. Effective permeation area of each membrane was 13.2 cm^2. Prior to testing, the pure water flux was measured to ensure that the membranes used were stable. Feed pressure was controlled at about 7 bar while the permeate side was opened to the atmosphere. Experiments were carried out at ambient temperature (27°C). The flux rate and solute rejection were measured using a different concentrations of NaCl solution. Permeate was collected in the cylinder and the conductivity was measured using conductivity meter, model LF 330. Each set of data was determined as an average of three replicates.

Flux rate and percentage of rejection

For the NF process, the membrane productivity is expressed as the permeate flux through the membrane. For the pure water and the NaCl solutions, the flux rate of the solutions (J) containing small molecules such as salts rejected by the membrane, is a function of the difference between volume permeation rate (V/t), m^3/s and the membrane area (A), m^2 and the unit for flux is (m^3/s).

$$\text{Flux, J} = \frac{\text{Volume permeation rate, } V/t}{\text{Membrane area, A}}$$

The selectivity of a membrane for a given solute is usually expressed by the percentage of rejection, which is defined by the concentration of solute in the permeate phase, C_p, relative to the concentration of the solute in feed solution, C_f.

$$\text{Percentage of rejection, } R(\%) = \left[1 - \frac{Cp}{Cf}\right] \bullet 100\%$$

The rejection of the solutes depends on the size, shapes and charge (linear or spherical, flexible or rigid and positive or negative) configuration of the solutes relative to the pore sizes of the membrane. It can also be influenced by chemical properties of the solution and by the interactions between the membrane and solute such as adsorption, concentration polarization, fouling, and ion exclusion effects (Alborzfar *et al*, 1998). For ionic species, the average rejection for a NF membrane depends both on the total concentrations of ions present in the solution, and on the ratio of divalent to monovalent ions. They can

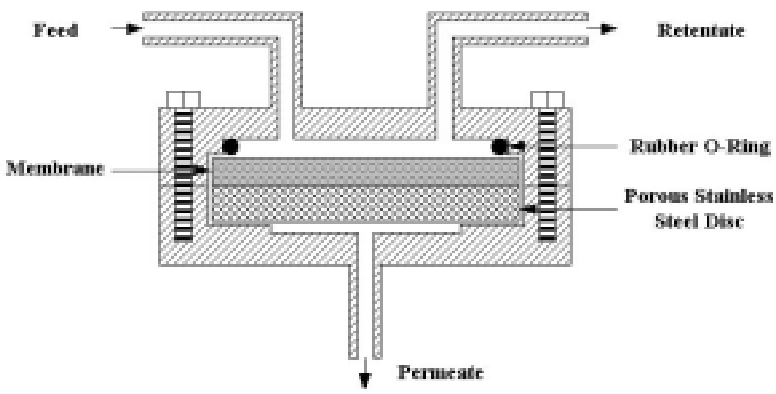

Figure 1. Permeation cell

be identified into the sieving (steric-hindrance) effect and the Donnan (electrostatic) effect from the viewpoint of membranes separation mechanism (Bowen and Mukhtar, 1996).

Scanning electron microscopy (SEM)

The cross-sections of the prepared membranes were inspected with scanning electron microscope (SEM) using a Philips SEMEDAX; XL40; PW6822/10 scanning microscope with potentials of 20.0kV in achieving magnification ranging from 10x to 10000x. For this purpose, the samples of the membranes were fractured cryogenically in liquid nitrogen. After sputtering the parts with gold, they were transferred into the microscope and the working voltage was 20.0kV.

ATR - FTIR spectroscopy

Plane polarized IR radiation is a good probe of molecular orientation, because of the preferred orientation of specific functional groups can be determined. This technique can reveal anisotropy on the molecular level within the membrane sample. Pronounced infrared dichroism (the difference in absorption between parallel and perpendicular polarized light). The IR spectra were recorded on a Nicolet Magna-IR 560 Fourier transform infrared spectrometer. The samples of NF membranes were mounted at the sample position with the outer skin surface facing the infrared beam and were rotated according to the shear direction (either vertical or horizontal). Thus, linear dichroism spectra were obtained by straightforward subtraction of perpendicular-polarized spectrum from parallel-polarized spectrum.

Results and Discussion

Effect of shear rate on the membrane performance

Before permeation experiment was conducted with NaCl solutions, the pure water flux of the membranes was first measured in order to confirm the stability of the NF membranes used. Based on the experimental results, the pure water fluxes of the four membranes at different shear rates were about 7.28×10^{-4} m/s, 7.66×10^{-4} m/s, 7.41×10^{-4} m/s and 8.02×10^{-4} m/s, respectively under the conditions of 27°C temperature and of about 7 bar applied pressure. The results showed that the pure water fluxes were increased with increasing of shear rate until an optimum shear was achieved. According to the experimental data shown in Table 1 and Table 2, the flux and percentage of rejection were increased with the increase of shear rates. It is also found that the critical shear rate was determined to be around 304 s^{-1} and membranes cast with shear rate below 152 s^{-1} were not suitable to be used as a NF membrane due to their low mechanical strength. Critical shear is a optimum shear rate that can induce a certain degree of molecular orientation to yield membrane morphology with optimum separation performance (Idris *et al*, 2002a).

Table 1. Fluxes for NF membranes at various shear rate using NaCl solutions at different concentrations

Concentration of NaCl, mg/l / Shear Rates, s^{-1}	Fluxes, J x 10^{-4} (m/s)				
	1.00	5.00	25.00	125.00	500.00
152.00	8.01 ± 0.0015	6.85 ± 0.0091	6.77± 0.0012	6.61 ± 0.0011	5.82 ± 0.0033
217.14	7.43 ± 0.0008	6.10 ± 0.0082	7.82 ± 0.0019	6.17 ± 0.0012	7.34 ± 0.0042
304.00	7.37 ± 0.0041	6.72 ± 0.0071	6.98 ± 0.0002	7.23 ± 0.0048	7.44 ± 0.0018
506.67	8.12 ± 0.0035	7.11 ± 0.0008	7.88 ± 0.0003	6.73 ± 0.0051	7.25 ± 0.0041

Table 2. Percentage of rejection for NF membranes at various shear rate using NaCl solutions at different concentrations

Concentration of NaCl, mg/l / Shear Rates, s^{-1}	Percentage of rejection, R (%)				
	1.00	**5.00**	**25.00**	**125.00**	**500.00**
152.00	48.21 ± 0.0023	49.26 ± 0.0017	50.33 ± 0.0041	52.11 ± 0.0049	52.72 ± 0.0023
217.14	51.17 ± 0.0026	55.42 ± 0.0043	57.20 ± 0.0068	52.40 ± 0.0036	53.48 ± 0.0012
304.00	53.28 ± 0.0035	57.11 ± 0.0018	58.97 ± 0.0011	55.14 ± 0.0033	56.76 ± 0.0038
506.67	54.95 ± 0.0042	52.22 ± 0.0008	54.14 ± 0.0044	53.33 ± 0.0004	53.10 ± 0.0001

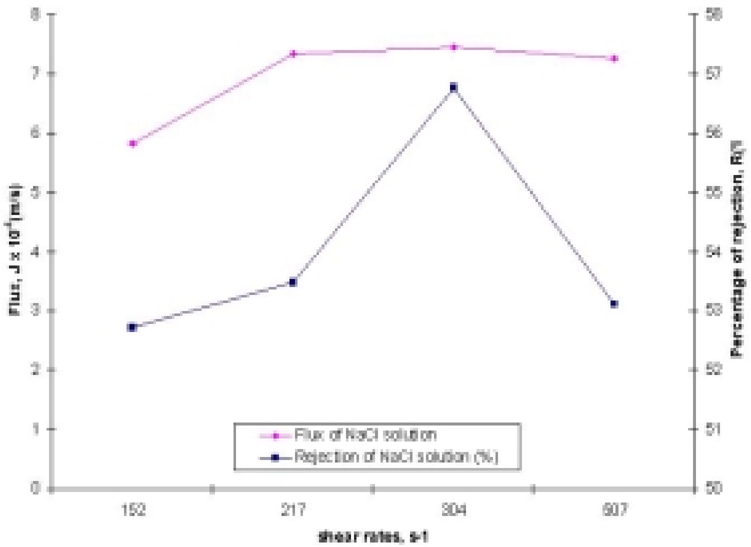

Figure 2. Flux and percentage of rejection of NaCl solutions (500 mg/l) versus shear rates

Since the solution used in this study was shear-thinning, when shear rate reached beyond the critical point, a severe decrease in solution viscosity occurred presumably due to chain entanglement losses in solution. In this case, membrane might undergo an early demixing and precipitation to result in a porous and highly oriented skin layer (Sharpe *et al*, 1999; Idris *et al*, 2002b). Furthermore, casting membrane at an extremely high shear rate (over the critical shear rate) pulled molecular chain or phase-separated domains apart and began to create slight imperfections (defects) in the skin layer (Sharpe *et al*, 1999). As shown in Figure 2, the highest shear rate (507 s^{-1}) caused an abrupt deterioration in flux and percentage of rejection of NaCl solutions.

Figures 3-6 show the IR spectra for NF membranes at four different shear rates. The spectra were plotted as absorbance against wave number, where all four membranes exhibit dichroism in the infrared spectra. However, the extent of the IR dichroism was very much pronounced in the membranes cast at higher shear rates. The difference in absorption of diagnostic peaks of the cellulose acetate membranes (absorption in parallel polarization minus the ab-

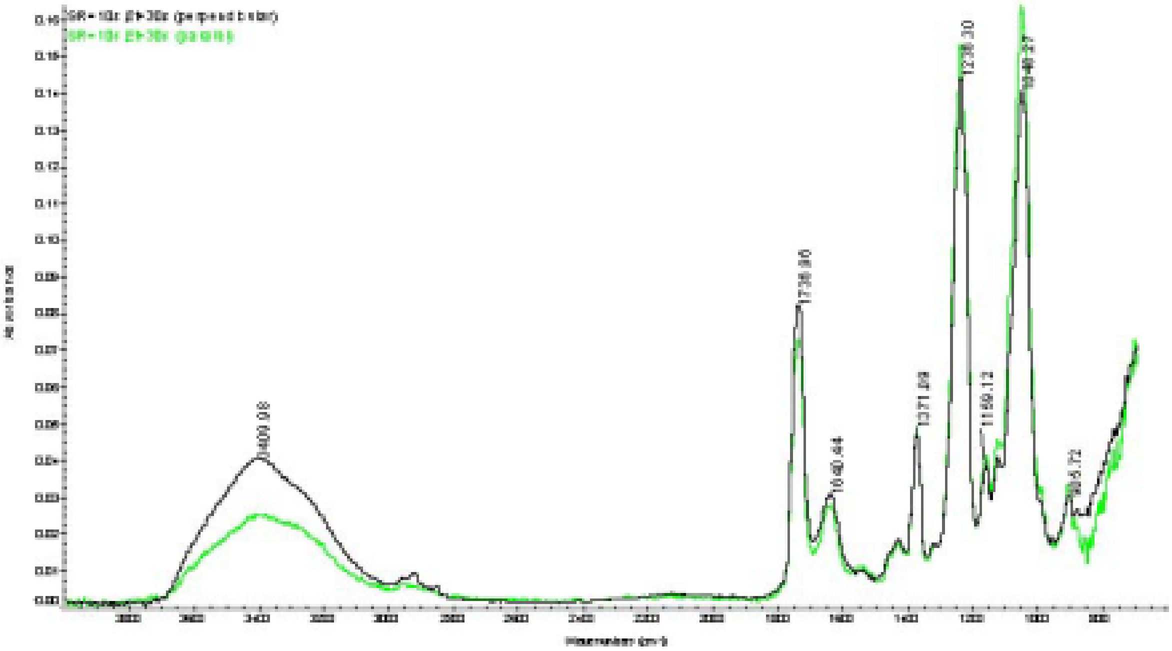

Figure 3. Polarized reflection IR spectra of the NF membranes at shear rates of 152.00s^{-1}. The plane of polarization of the IR beam was parallel (lighter line) and perpendicular (darker line) to the shear direction

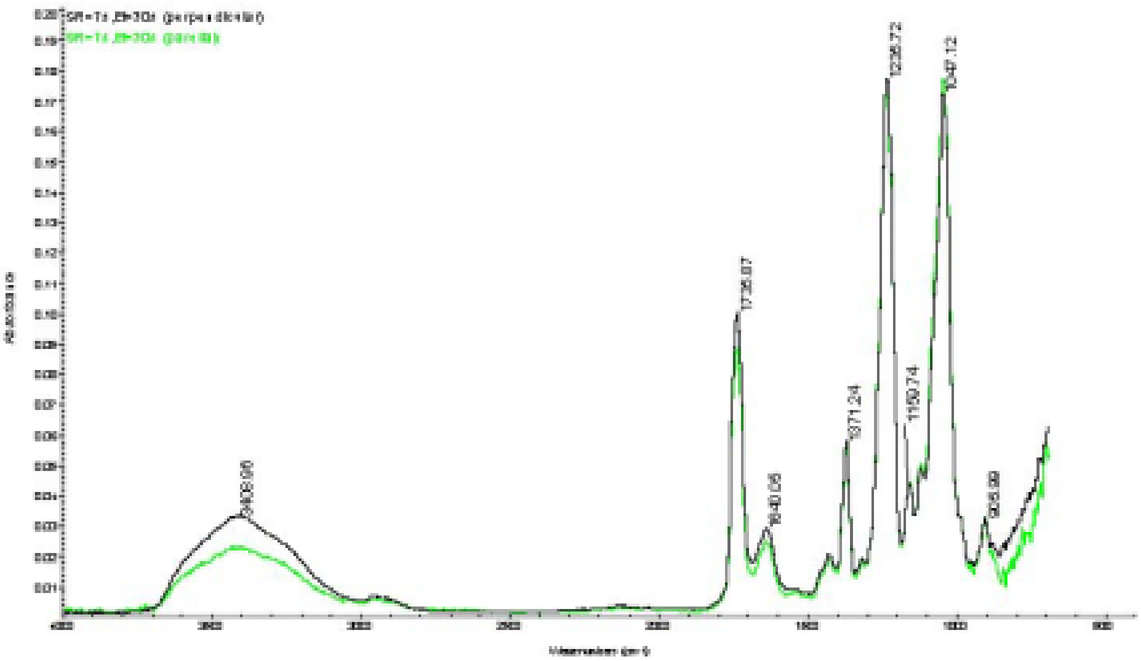

Figure 4. Polarized reflection IR spectra of the NF membranes at shear rates of 217.14s^{-1}. The plane of polarization of the IR beam was parallel (lighter line) and perpendicular (darker line) to the shear direction

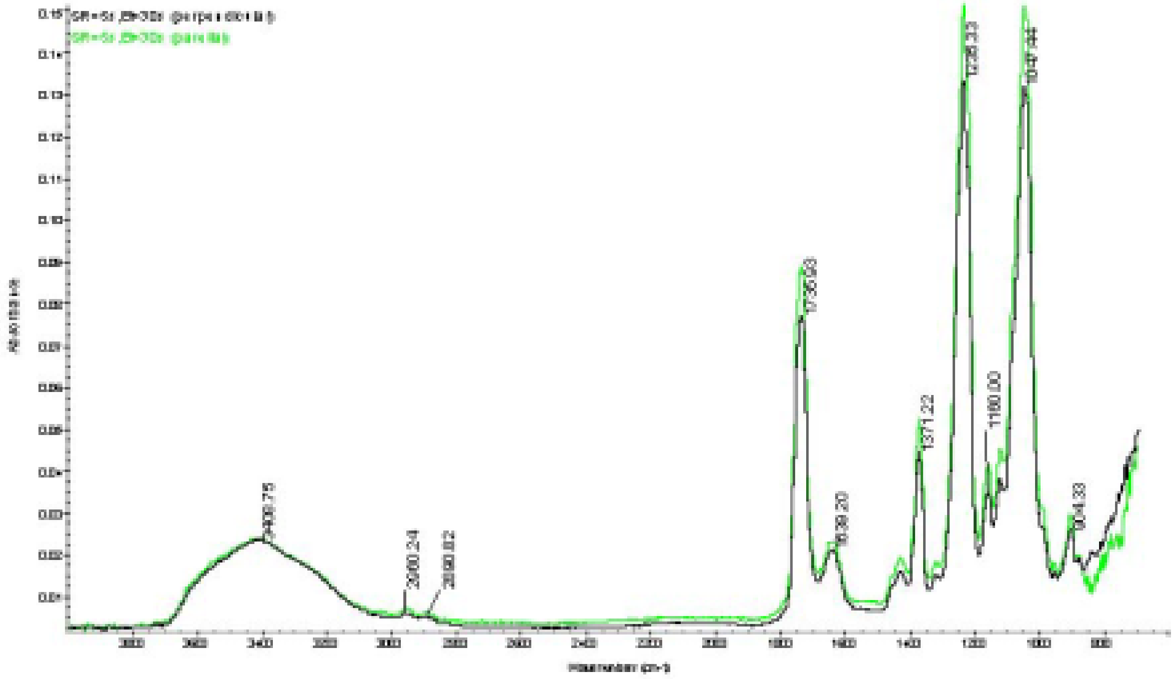

Figure 5. Polarized reflection IR spectra of the NF membranes at shear rates of 304.00s^{-1}. The plane of polarization of the IR beam was parallel (lighter line) and perpendicular (darker line) to the shear direction

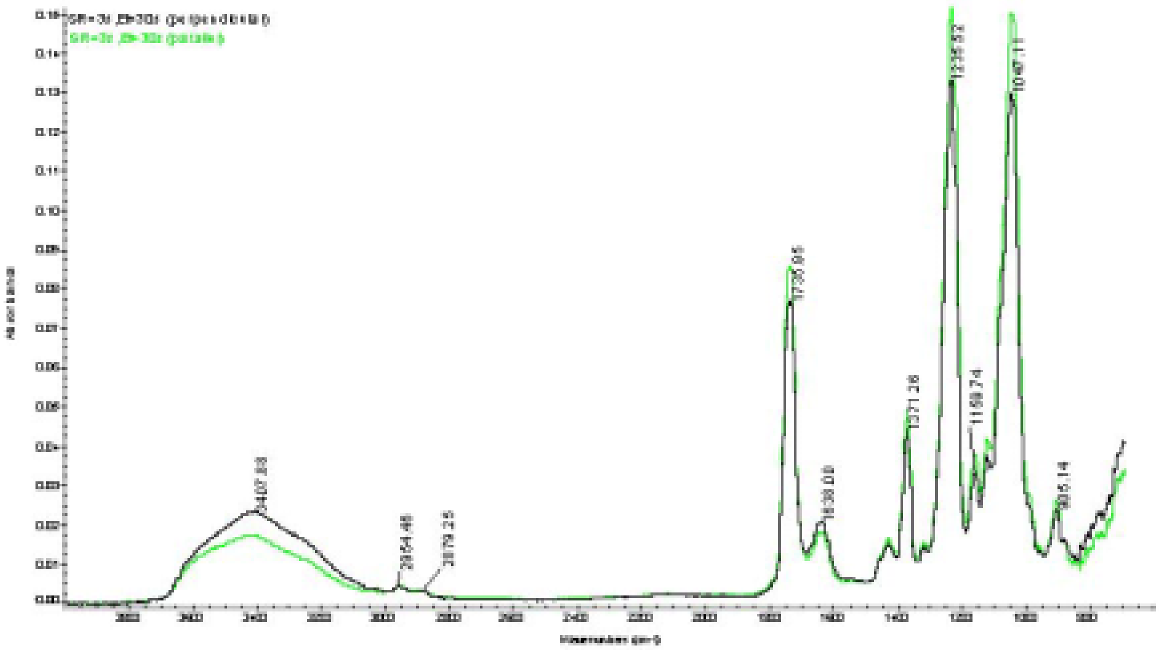

Figure 6. Polarized reflection IR spectra of the NF membranes at shear rates of 506.67s^{-1}. The plane of polarization of the IR beam was parallel (lighter line) and perpendicular (darker line) to the shear directio

sorption in the perpendicular direction) for high shear membranes is larger and more pronounced compared to the low shear membranes suggesting higher concentration of the acetate groups in the parallel direction as compared to the perpendicular direction thus implying greater molecular orientation. The IR spectra of cellulose acetate are dominated by absorption peaks characteristic of the C=O (carbonyl functional group) at 1741 cm^{-1}, the CH_3 (methyl group) at 1369, vibration of acetate group at 1228 cm^{-1} and by the C-O-C ether band at 1041 cm^{-1}. Thus, the absorbance of the acetate functional groups can be used to gauge the degree of molecular orientation of the membranes at difference shear rates.

Amongst the four difference membranes characterized, the membranes cast at shear rates of 304 s^{-1} showed the largest difference in spectrum (absorption in parallel polarization minus absorption in perpendicular polarization) suggesting that there is a maximum molecular orientation occurring at shear rates of 304 s^{-1}. Also at this particular shear rate, the rejection rate of the membranes is the best, indicating that higher molecular orientation enhanced separation performance. The relative difference in IR absorptions exhibited by the membranes cast at shear rates of 507 s^{-1} is clearly much larger than that by membranes at lower shear rates of 217 s^{-1} and 152 s^{-1}, although lesser compared to that by membranes cast at a shear rate of 304 s^{-1}. Further increase of shear rates beyond 304 s^{-1} does not seem to cause further molecular orientation to take place suggesting that there is a maximum molecular orientation induced at optimum shear rate.

The observed direction of linear dichroism for most of the functional groups accords fully with the expectation that shear will tend to align the polymer back-bone in the shear direction. However, the results also indicate that increase in the molecular orientation is highest at an opti-

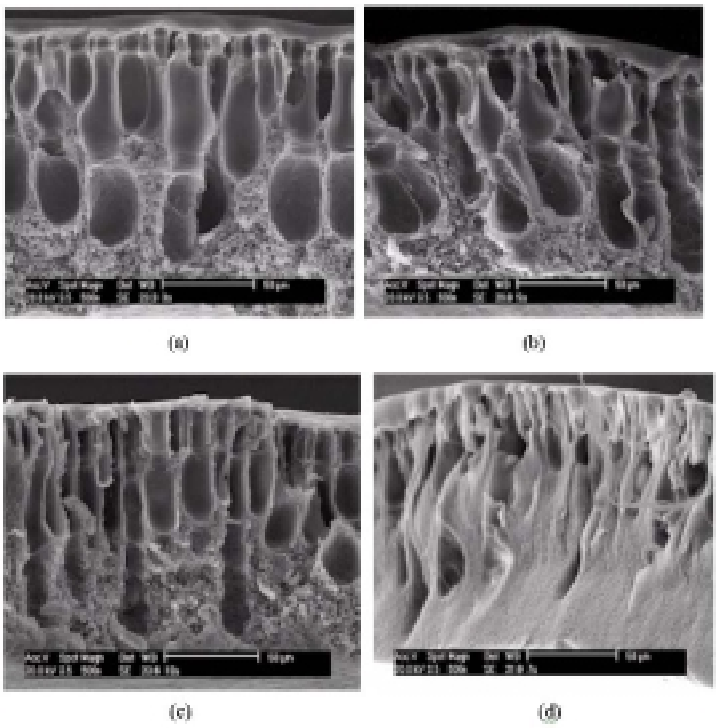

Figure 7. SEM of cross-section of NF membranes at different shear rates; (a) 152 s^{-1}, (b) 217 s^{-1}, (c) 304 s^{-1}, (d) 507 s^{-1}

mal shear rate. Further increase in shear rate does not seem to further increase molecular orientation.

Effect of shear on membrane morphology

The electron micrographs cross-section of the membranes is shown in Figure 7. As illustrated, the NF membranes developed in this study comprised a dense skin layer with large finger-like porous substructure. As shear rate increases, there is a transformation from thick skin to thin skin. A relatively thick transition layer was observed in the membrane at lowest shear rate (152 s^{-1}) and it also seems that the increasing shear rate will be cause a reduction of membrane thickness and a porous substructure. In addition, it also causes an increase in fluxes and decrease in rejection rate. However, beyond the critical shear rate, the surface pores became detrimental to the rejection rates.

Conclusion

The results showed that increasing of shear rate would increase the permeation flux and percentage rejection of sodium chloride solutions significantly. These effects were found to influence the structure of the active skin layer of asymmetric membranes. An increased of shear rate will result in a finger-like porous substructure and also cause a reduction in the skin active layer thickness. The spectroscopy analysis provided evidence to suggest that increased molecular orientation occurs in high shear rate. However, a critical shear rate exists beyond which molecular orientation will no longer be further increased. The results clearly suggested that there is an optimum shear rate that can induce a certain degree of molecular orientation to yield membrane morphology with an optimum separation performance. In this study, the NF membrane with pure water flux (8.02×10^{-4} m/s), permeate flux rate ($7.44 \times 10^{-4} \pm 0.0018$ m/s) and a moderate percentage of rejection (56.76%) using NaCl solution with -500mg/l concentration, suitable for a water desalination process, has been fabricated.

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