Characteristic of co-polyamide nanofiltration membrane: Effect of reaction time

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Abstract

Modified poly(piperazinamide) polyamide nanofiltration membranes were fabricated under different reaction time. The membranes were characterized for its pore size and effective thickness/porosity using Donnan Steric Pore Flow Model. It was found that the pore size and crosslinking extent was different from what normally observed in poly(piperazinamide) membrane. Pore size was reduced initially due to the crosslinking process but become larger at longer reaction time because of the weaker pores wall. On the other hand, the effective thickness/porosity grows exponentially with polymerization time. The effect of reaction time on pore size is not as significant as effective thickness/porosity. Within 2 minutes of polymerization time, the effective thickness of the barrier layer would vary about 150%.

Keywords: Nanofiltration, reaction time, pore size, effective thickness/porosity

1. Introduction

Nanofiltration (NF) can be considered as a relatively new type of pressure driven membrane compared to reverse osmosis and ultrafiltration. Higher flux and lower operating pressure of nanofiltration make the membrane become feasible to be applied in both water and wastewater treatment process. Nowadays, nanofiltration has been used widely in drinking water industry\(^1\) and wastewater treatment for removal of contaminants such as pesticides\(^2\), arsenic\(^3\), soil leachate\(^4\) and dyes\(^5\). Recently, nanofiltration membranes were also studied for the application in food\(^6\) and bio-process\(^7\) purposes.

By definition, the pore size of NF membranes is around 1nm. Since the pores are so small, the electrostatic interactions between the membrane material and ions in solution are likely to play a significant role on the electrolyte transport through the membrane pores\(^8\). Therefore, for ionic solutes, the interactions between the solutes and the membrane cannot be governed by steric hindrance alone. Electrolyte transport mechanisms through nanofiltration membranes should be investigated in terms of convection, diffusion and electromigration.

According to the Donnan Steric Pore Flow Model, the membranes were assumed to consist of a bundle of identical straight cylindrical pores. The neutral solute transports through the membrane effective layer is controlled by the pore size \(r_p\) and effective thickness/porosity \((\Delta x/A_k)\). By understanding membrane fabrication condition like reactant concentration and reaction time, membrane with specific characteristic \((r_p, \Delta x/A_k)\) could be tailor-made.
Interfacial polymerization (IP) technique is one of the techniques used in preparing composite nanofiltration membranes. The membranes produced are high in water permeation flux and salt rejection. There are several advantages in making membrane using the IP process. The IP film which forms the selectively permeable barrier layer can be made quite thin to less than 0.1µm\(^9\). The thin film composite (TFC) membranes made by the IP process also offers good selectivity and high permeability of water. Besides, IP technique allows the properties of the permselective barrier layer to be optimized independently from the supporting layer.

It was found that the critical parameters for thin film coating are reaction time, relative humidity and coating temperature. These parameters play an important role in determining the structure of the interfacially polymerized surface film and subsequently the membrane performance\(^{10,11}\). Up to now several studies have tried to relate the membrane performance to the reaction time. However few studies have been carried out to really look into the effect of reaction time on pore size and effective thickness/porosity. This relationship is very important in order to explore the behaviour of flux and rejection in nanofiltration membrane. The objective of this paper therefore is to study the effect of reaction time on the membranes characteristics like pore size and effective thickness/porosity using Donnan Steric Pore Flow Model.

2. Theory

2.1. Model assumptions

In order to determine the pore size and effective thickness/porosity Donnan Steric Pore Flow Model (DSPM) was used\(^{12,13}\). Below are the assumptions applied to the derivation of DSPM model:

- The membrane consists of a bundle of identical straight cylindrical pores of radius \(r_p\) and length \(\Delta x\)
- A very diluted system was used which enable the coupling effect between the component in the solution to be neglected
- For porous membranes, the fluxes, concentrations, potentials and velocity were all defined in terms of radially averaged quantities.

2.2. Fundamental equations of DSPM

The solute velocity was assumed fully developed inside the pore and has the parabolic profile of the Hagen-Poiseuille type. \(K_{id}\) and \(K_{ic}\) are related to the hydrodynamic coefficients as

\[
K_{id}=K^{-1}(\lambda,0)=1.0-2.30 \lambda+1.154 \lambda^2+0.224 \lambda^3 \quad (1)
\]

\[
K_{ic}=(2- \Phi)G(\lambda,0)=1.0+0.054 \lambda-0.988 \lambda^2+0.441 \lambda^3 \quad (2)
\]

For neutral solute (glucose), the solute flux through the membrane could be expressed as:

\[
j_i = -D_p \frac{dc_i}{dx} + K_{ik} c_i J_v \quad (3)
\]
For purely steric interactions between the solute and the pore wall, $\Phi$ is the steric terms relate the finite size of the solute and pore size.

$$\Phi = (1-\lambda)^2$$  \hspace{1cm} (4)

Where $\lambda$ is a ratio of solute radius, $r_s$ (m) to pore size, $r_p$ (m). In terms of real rejection, Eq.(3) becomes,

$$R_{real} = 1 - \frac{C_{i,p}}{C_{i,m}} = 1 - \frac{K_{i,c} \Phi}{1 - \exp(-Pe_m)[1 - \Phi K_{i,c}]}$$  \hspace{1cm} (5)

Where $C_{i,m}$ and $C_{i,p}$ were concentration on the feed side of membrane (mol m$^{-3}$) and concentration in permeate (mol m$^{-3}$) respectively. The peclet number, $Pe_m$ was defined as

$$Pe_m = \frac{K_{i,c} J_v \Delta x}{K_{i,d} D_{i,\infty} A_k}$$  \hspace{1cm} (6)

where $D_{i,\infty}$ was the bulk diffusivity (m$^2$s$^{-1}$), $J_v$ was the volume flux (based on membrane area)(m.s$^{-1}$) and $\Delta x$ was the effective thickness,(m) and $A_k$ was porosity of the membrane.

The Hagen-Poiseuille equation gives the relationship between the pure water flux and the applied pressure across the membrane$^{14}$.

$$J_w = \frac{r_s^2 \Delta P}{8 \mu (\Delta x / A_k)}$$  \hspace{1cm} (7)

where $J_w$ was the water flux (m.s$^{-1}$), $\Delta P$ was the applied transmembrane pressure (kPa) and $\mu$ was viscosity of the solution (kPa.s)

To find the film layer concentration, the concentration polarization equation was employed. For a stirred cell configuration, the observed rejection was related to the real rejection by volume flux, $J_v$ and mass transfer coefficient, $k$ as follow$^{15}$;

$$\ln \left( \frac{1 - R_{obs}}{R_{obs}} \right) = \ln \left( \frac{1 - R_{real}}{R_{real}} \right) + \frac{J_v}{k}$$  \hspace{1cm} (7)

$$k = k' \omega^{0.567}$$  \hspace{1cm} (8)

where,
\[ k' = 0.23 \left( \frac{r^2}{v} \right)^{0.567} \left( \frac{v}{D_m} \right)^{0.33} \frac{D_m}{r} \]  

where \( k' \), \( \omega \), \( r \) and \( v \) were mass transfer coefficient (m s\(^{-1}\)), stirring speed (s\(^{-1}\)), stirrer radius (m) and kinematic viscosity (m\(^2\)s\(^{-1}\))

3. Experimental

3.1. Material

The polysulfone Udel P-1700 (Mn : 17,000) is a product of Union Carbide Corporation. Piperazine, 3,5-diaminobenzoic acid, n-hexane, Sodium chloride and glucose were supplied by Merck Company. N-methylpyrrolidone and trimesoyl chloride were purchased from Fluka and polyvinylpyrrolidone from Sigma-aldrich Co. The tightly woven polyester, style 0715 Dacron Fabric was supplied by Texlon Corporation (USA).

3.2. Preparation of polysulfone support layer

The polysulfone support was prepared by dissolving 15% polysulfone (Udel P-1700) in N-methylpyrrolidone with 18% polyvinylpyrrolidone as pore-former. The solution was casted onto a tightly woven polyester fabric with a thickness of 150µm. Then the membrane was immersed into a water bath and kept in the water bath for 24 hour until most of the solvent and water soluble polymer was removed\(^{16} \).

3.3. Fabrication of thin film composite membranes

The support layer which was taped on a glass plate was immediately dipped into an aqueous diamine solution containing 2w/w% piperazine (PIP) and 0.1w/w% 3,5-diaminobenzoic acid (BA) for 5 minutes at ambient temperature. The solution was casted onto a tightly woven polyester fabric with a thickness of 150µm. Then the membrane was immersed into a water bath and kept in the water bath for 24 hour until most of the solvent and water soluble polymer was removed\(^{16} \).

3.4. Membrane permeation characterization

Membrane permeation test was carried out using the Amicon 8200 stirred cell at five different pressures: 150kPa, 250kPa, 350kPa, 400kPa and 450kPa. The membrane was cut to a diameter of 5.5cm (effective area of 28.27cm\(^2\)) and then mounted at the bottom of the stirred cell. For each operating pressure, fresh solution was used as a feed. Bulk feed concentration was calculated based on the average of initial and final feed concentration. Nitrogen gas was used to pressurize the water flux through the membrane. The solution was stirred at the speed of 350 rpm to reduce concentration polarization. The feed solutions are pure water, 0.001M NaCl, 0.01M NaCl, 0.1M NaCl solution and 300ppm glucose solution. The NaCl permeate concentrations were measured using conductivity meter (Hanna Instruments, Italy,
Model: HI8633) while glucose permeate concentration was analyzed using spectrophotometer (Thermo Spectronic, USA, Model: GENESYS 20) at 485nm.

Each membrane was subjected for pressure pre-treatment at 500kPa for 1 hour before the permeation experiments. The flux was equilibrated for the passage of first 20ml permeates and the following 10 ml permeate was collected for concentration analysis.

4. Results and discussion

The effect of polymerization time on $r_p$ and $\Delta x/A_k$ were shown in Fig. 1 and Fig. 2 respectively. Fig. 1 showed that below 60s of reaction time, the effect of polymerization time on pore size was not significance. However, there was a slightly drop in pore size from 5s to 15s. The pore size tends to grow at reaction time beyond 75s.

 Initially, as reaction time increase (<15s), the polymer layer tends to be crosslinked to produce a tighter membrane with smaller pore size. At longer reaction time (>75s), an adverse trend was observed. This phenomenon can be explained by looking at the slower reactivity of 3,5-diaminobenzoic acid compared to piperazine. The electron-drawing carboxylic group in BA makes the diamine functional group less nucleophilic, therefore reducing its reactivity. At longer reaction time, the content of BA in the polyamide skin layer increased. Higher content of BA leads to a higher ratio of hydrophilic group in the membrane\textsuperscript{17}. Consequently, exceeding water uptake produced the pores with weaker pore wall. The adjacent pores wall would coalesce together to produce an average bigger pore size. This explained why at higher polymerization time, poorer rejection was obtained. In overall, polymerization time is not an important parameter to determine the pore size. The pore size in the study range (5s to 120s) differ about 12% only with an average of 0.5nm.

\[ y = 6E-15x^2 - 4E-13x + 5E-10 \]

\[ R^2 = 0.9542 \]

FIGURE 1 : Effect of Polymerization Time on the Membrane Pore Size
On the other hand, the effect of polymerization time on the membrane thickness was more significance. If the porosity of the membrane was assumed to be unity, then, within this polymerization time, the effective thickness of the barrier layer would vary about 150% as shown in Figure 2.

From Figure 2, it was noted that the effective layer growth exponentially with polymerization time. The rate of layer formation was high below 15s and started to level-off beyond 75s polymerization time. This might be due to the reaction became diffusion control at thicker skin layer and film growth becomes self-limiting owing to the inability of the two reactants to interpenetrate after sufficient densification has occurred toward the organic side of the membrane\textsuperscript{18}. It was also postulated that the reducing $\Delta x/A_k$ was caused by the increasing porosity. As shown in Figure 1, the pore size turn out to be bigger after 60s of reaction time which contributed to a more porous membrane.

The growth of the film could be expressed in the exponential terms as below (assume unity porosity):

$$\Delta x = 5.18 \times 10^{-7} \ln(t) + 1.25 \times 10^{-7} \quad (10)$$

Where $\Delta x$ is the effective membrane thickness (m) and (t) is the polymerization time (s).

The interfacial polymerised (IP) film which forms the selectively permeable layer can be made quite thin ($0.1<\mu$m)\textsuperscript{18}. However, in this system, to produce a skin layer about 0.1µm, the reaction time calculated from Eq. 10 would be 0.95s. A parameter that seems difficult to be controlled solely by reaction time because of the high film growth rate. Therefore, other parameters like reactant concentration should be investigated.
5. Conclusion

The effect of polymerization time on the pore size is not significant as compared to its effect on effective thickness/porosity. The pore size was reduced initially because of crosslinking process between the reactants but at longer polymerization time, the pores tends to coalesce to produce a bigger pore size. On the other hand, the effective thickness/porosity growth exponentially with polymerization time. The effect is crucial with approximately 150% of increment in $\Delta x/A_k$ within 2 minutes of reaction time. The growth of the film could be expressed in the exponential terms as $\Delta x = 5.18 \times 10^{-7} \ln (t) + 1.25 \times 10^{-7}$ if an unity porosity was assumed.

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