ABSTRACT

PREPARATION OF DIFFERENT POLYAMIDE NANOFILTRATION MEMBRANES BY INTERFACIAL POLYMERIZATION AND THE EFFECT OF POST-POLYMERIZATION TREATMENT ON SEPARATION PERFORMANCE

by
Yu Qin

Interfacial polymerization (IP) is a powerful technique for fabrication of thin film composite (TFC) membranes. In this study, polyamide nanofiltration (NF) composite membranes ware prepared by interfacial polymerization of polyethylenimine (PEI) or m-phenylene diamine (MPD) with isophthaloyl dichloride (IPD) on the surface of a porous polyethersulfone (PES) support. Concentrations of monomer reactants for this reaction were decided by equivalent weight ratio. A standard IP procedure was applied to successfully coat PES flat films. After preparation, three different post-polymerization treatments were employed and one optimal treatment was proven after membrane testing.

The TFC flat film membranes were characterized by nanofiltration of brilliant blue R (MW 826) and safranin O (MW 351) dyes in water. For testing the performance of new TFC membranes, transmembrane pressures ranging from 69 kPa to 413 kPa were used to detect solvent permeation flux and solute rejection at different pressures. The solvent permeation flux and the solute rejections were time dependent for an extended initial period; the membranes had to be compacted at a higher pressure to achieve nearly steady-state results. Furthermore, the collected data from the optimized nanofiltration membrane showed stable and supreme performance.

Differently from PEI that is a polymer, m-phenylene diamine (MPD) could also react with IPD to form TFC NF film by acting as monomer. By mixing MPD and PEI in

different ratios in the aqueous phase and then reacting the new aqueous solution with the organic phase containing IPD, new TFC NF membranes were prepared. The performances of these membranes having different MPD/PEI ratios were investigated by solute rejection and solvent flux determined.

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CHAPTER 1

INTRODUCTION

1.1 General

1.1.1 Nanofiltration

Nanofiltration (NF) has recently gained significant attention because of its advantages such as relatively low operating pressure, high fluxes and low operating and maintenance costs (Lu, 2002). The average pore diameter of most NF membranes is around 1-2 nm (Raman et al., 1994). NF is used to achieve a separation between sugars, other organic molecules and multivalent salts on one hand and monovalent salts and water on the other. NF is in between ultrafiltration (UF) and reverse osmosis (RO) (Figure 1.1), with an operating pressure lower than RO but higher than UF.

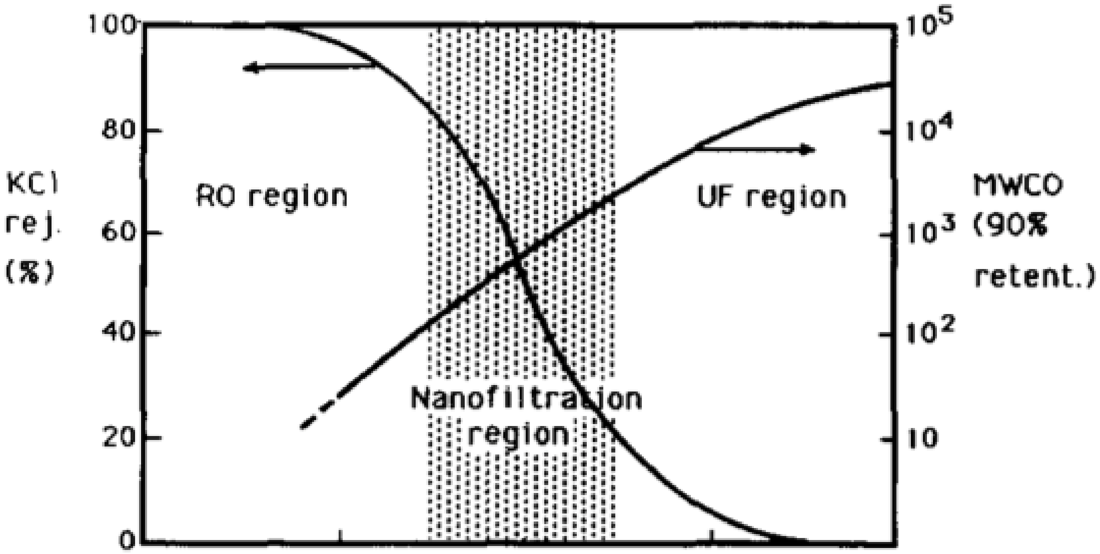

Figure 1.1 Diagram of the region of nanofiltration membrane performance relative to reverse osmosis and ultrafiltration membranes (Peterson, 1993).

Nanofiltration membranes are generally fabricated by the method used to making composite membranes. A typical composite membrane as commercially produced today is shown schematically in Figure 1.2. “A base layer of a woven or a nonwoven fabric is overcoated with a layer of an anisotropic microporous polymer. The surface of the microporous support is coated with an ultrathin veneer of a polymeric composition, which provides the controlling properties as to semipermeability” (Peterson, 1993).

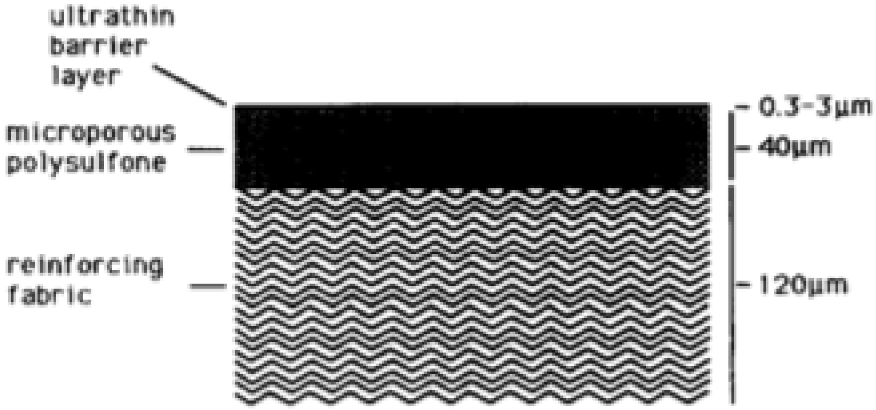

Figure 1.2 Schematic diagram of a thin film composite membrane (Peterson, 1993).

In a thin film composite membrane, each individual layer can be optimized for its particular function, i.e. the thin barrier layer can be optimized for the desired combination of solvent flux and solute rejection, while the porous support layer can be optimized for maximized for maximum strength and compression resistance combined with minimum resistance to permeate flow. Preparing thin film composite (TFC) membranes via interfacial polymerization (IP) is the most effective method as these membranes provide high fluxes over nanofiltration membranes fabricated by other methods (Lu, 2002).

1.1.2 Interfacial Polymerization and Polyamide TFC Membranes

Interfacial polymerization (IP) method for making membrane has been developed by Cadotte (Cadotte, 1978), and it is now the most important route to RO and NF membranes. In TFC by IP, reactive monomers are dissolved in two immiscible phases and the polymerization of the reactive monomers takes place on the surface of the porous support membrane. The benefit of TFC by IP is that the membrane properties can be controlled by optimizing the characteristics of the selective layer and support. Meanwhile the selective layer can be optimized for solute rejection and solvent flux by controlling the coating conditions and characteristics of the reactive monomers (Kosaraju and Sirkar, 2008). The selective layer is formed in situ by polycondensation or polyaddition of reactive (bis- and trisfunctional) monomers or prepolymers on the surface of a porous support (Figure 1.3). Post-treatment such as heating is often applied in order to obtain a fully cross-linked structure of the selective barrier (Lau, 2011). Washing can help to clean surface impurities and optimize the modification of membrane, usually followed by drying overnight at room temperature (25°C).

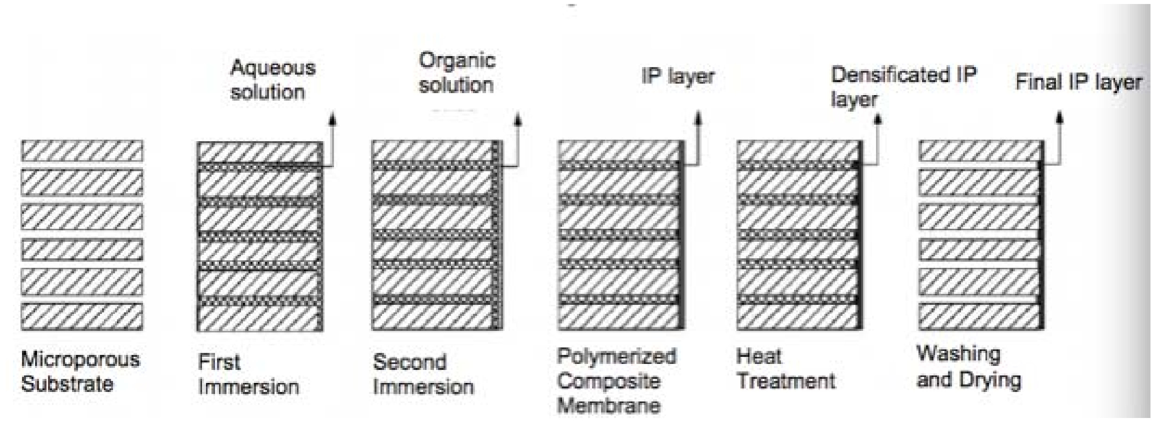

Figure 1.3 Schematic diagrams of the preparation process of TFC membrane by conventional IP technique (Lau, 2011).

Today, thin film composite (TFC) membranes prepared by coating a very thin layer of aromatic polyamide (PA) onto microporous membrane are well accepted for water and wastewater treatment processes. “To prepare polyamide TFC membranes, the monomers are a polyfunctional amine and an acid chloride, dissolved in immiscible solvents, one of which, the aqueous amine solution, initially is used to impregnates the support. An ultrathin film (skin), well under half a micron thick, is quickly formed at the interface and remains attached to the support” (Lau, 2011). It is commonly believed that the reaction takes place at the organic side of the interface due to the negligible solubility of acid chlorides in water and the fairly good solubility of amines in organic solvents. The thickness of the polymer layer (e.g., cross-linked polyamide) is limited by its barrier properties for further diffusion of reactants into the reaction zone.

In the past decades, many attempts have been reported to enhance properties of composite membrane through variation of many parameters involved in membrane preparation process. Of these, researches focused on the effects of reactive monomer type, concentration of reactant, reaction time and additive added during IP process are of particular interest among membrane community (Lau, 2011).

The support membranes generally used in IP-based processes for membrane making are polysulfone (PS), polyethersulfone (PES) or polypropylene (PP) ultrafiltration membranes. Since polypropylene and polysulfone are hydrophobic, they have to be hydrophilized first to fabricate TFC. Applying PES will avoid hydrophilization process since PES is hydrophilic. Hydrophilic solvent-stable ultrafiltration (UF) membranes have a distinct advantage compared to hydrophobic ones: they can be also used easily with aqueous solutions (for a hydrophobic pore of diameter

10nm, the water bubble point pressure is 2.9×10^7 Pa). The monomeric system chosen for IP in this study was polyethyleneimine (PEI) in aqueous phase and isophthaloyl dichloride (IPD) in organic phase. For monomers such as diamine and diacyl chloride, polyamide is the reaction product forming a selective layer of the membrane (Figure 1.4). The nature of the solvents and the monomers as well as the monomer concentrations and reaction time define the porosity, pore size and thickness of the selective layer (Korikov et al., 2006)

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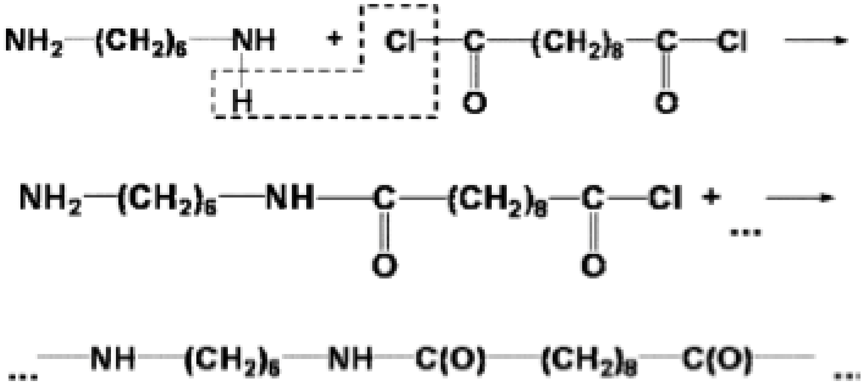

Figure 1.4 Polyamide formation by reaction between diamine and diacyl chloride (Korikov et al., 2006).

A major advantage of IP over preparation of membranes by casting from solution, phase inversion and plasma polymerization is the combination of the thin selective layer formed, its high quality and its solvent resistance (Korikov et al., 2006). Often, correctly chosen support, monomers and conditions can repeatedly provide defect-free membranes.

The composition and morphology of the interfacially formed polymer film will be dependent on several variables, including:

a. Concentrations of reactants;

b. Partition coefficients of the reactants;

c. Reactivity ratio where blends of reactants are employed;

d. Solubility of nascent polymer in the solvent phase as it is formed;

e. The overall kinetics and diffusion rates of reactants;

f. Presence of by-products (such as hydrogen chloride in the case of reaction of amine with an acyl chloride);

g. Hydrolysis or other potentially competitive side reactions;

h. Crosslinking reaction; and

i. Post-reactions or treatments of the resulting interfacial films.

The first five of these factors must be considered to adequately explain membrane formation behavior and subsequent properties. The latter four factors should also be considered for their effect on the membrane's performance and properties (Petersen, 1993).

1.2 Scope of Thesis

This thesis has three distinct parts:

-The preparation of polyamide NF membrane using PEI-IPD system.

-Post-treatment of new membranes under different conditions followed by testing the performance and selecting the best conditions.

-Preparation of polyamide NF membranes using other monomer systems, such as MPD-IPD and MPD/PEI-IPD and then compare their performances.

1.2.1 Polyethersulfone (PES) Support Membrane

Polyethersulfone (PES) membrane is a hydrophilic membrane made from pure polyethersulfone polymer. PES membrane filters are designed to remove particulates during general filtration. Their low protein and drug binding characteristics also make polyethersulfone (PES) membrane disc filters ideally suited for use in life science applications. The uniformity and high sensitivity of PES membrane help to maximize performance of fabricated TFC NF membranes.

Compared with ultrafiltration membranes, microfiltration membranes as a support can increase the solvent flux of TFC membranes. Microporous PES membrane used in this study is constructed from a high-temperature polyethersulfone polymer that is acid and base resistant. The strength and durability of the PES membrane filters are especially advantageous during procedures that require aggressive handling or automated equipment.

For PES used in this study, it is unnecessary to carry out any additional steps because of its hydrophilic property. It was directly used after proper cutting to appropriate size.

1.2.2 Polyethyleneimines (PEIs)

Two types of PEIs are known: linear PEIs and branched PEIs. Linear polyethyleneimines (PEIs) contain all secondary amines, in contrast to branched PEIs, which contain primary, secondary and tertiary amino groups. The linear PEIs are solids at room temperature; The branched PEIs are available over a range of molecular weights $1.7x10^4$-$5.3x10^6$ g/mol (Park, 1996).

The PEI used was branched, essentially globular polymer made by a ring-opening polymerization of aziridine, which has a substantial degree of branching and a ratio of primary: secondary: tertiary amines as 3:4:3 (Figure 1.5). PEI acts as a multifuncational amine and has been widely applied to prepare RO and NF membranes. At a temperature of 110°C, internal crosslinking of PEIs takes place via ammonia elimination from adjacent amino groups (Kosaraju and Sirkar, 2007). That is the reason why this study used 110°C to do post-polymerization treatment.

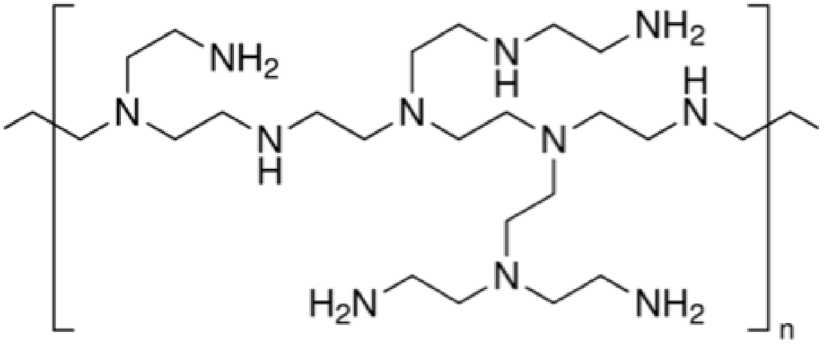

Figure 1.5 Chemical structure of branched PEI.

1.2.3 Isophthaloyl Dichloride (IPD)

IPD is slightly soluble in water, always chosen with PEI to act as the monomeric system for interfacial polymerization. Its structure is shown in Figure 1.6.

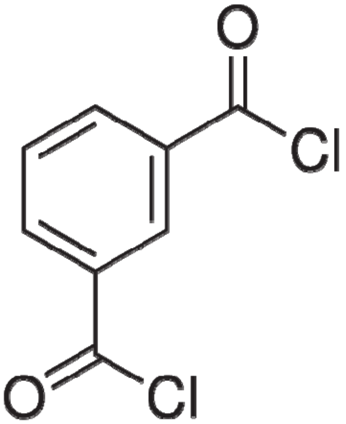

Figure 1.6: Chemical structure of IPD.

1.2.4 m-Phenylene Diamine (MPD)

MPD is used as a key component in the manufacture of engineering polymers, aramid fibers, epoxy resins, wire enamel coatings and polyurea elastomers. MPD is also used for removing aldehyde impurities in chemical processing, as an accelerator for adhesive resins, and as a component in dyes for leather and textiles.

MPD is offered in flake and cast solid forms. MPD used in this experiment consisted of flakes. MPD flakes are beige to off-white in color. The cast form is a tan crystalline solid, and molten MPD is a clear liquid. All forms tend to darken in storage. MPD is soluble in water, alcohol, and most organic solvents. MPD chemical structure is shown as Figure 1.7.

For interfacial polymerization, MPD is widely used with trimesoyl chloride (TMC) to form TFC RO membranes. In this study, MPD was reacted with isophthaloyl dichloride (IPD) to prepare TFC NF membranes to compare with the ones made from PEI and IPD. Furthermore, it was mixed with PEI, and then reacted with IPD to prepare some novel membranes.

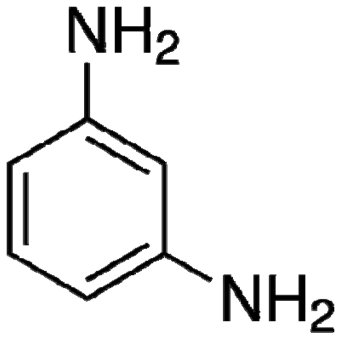

Figure 1.7 Chemical Structure of MPD.

1.2.5 Reaction Mechanisms for PEI-IPD and MPD-IPD

The chemical reaction of PEI and IPD is shown in Figure 1.8.

The chemical reaction of MPD and IPD is shown in Figure 1.9.

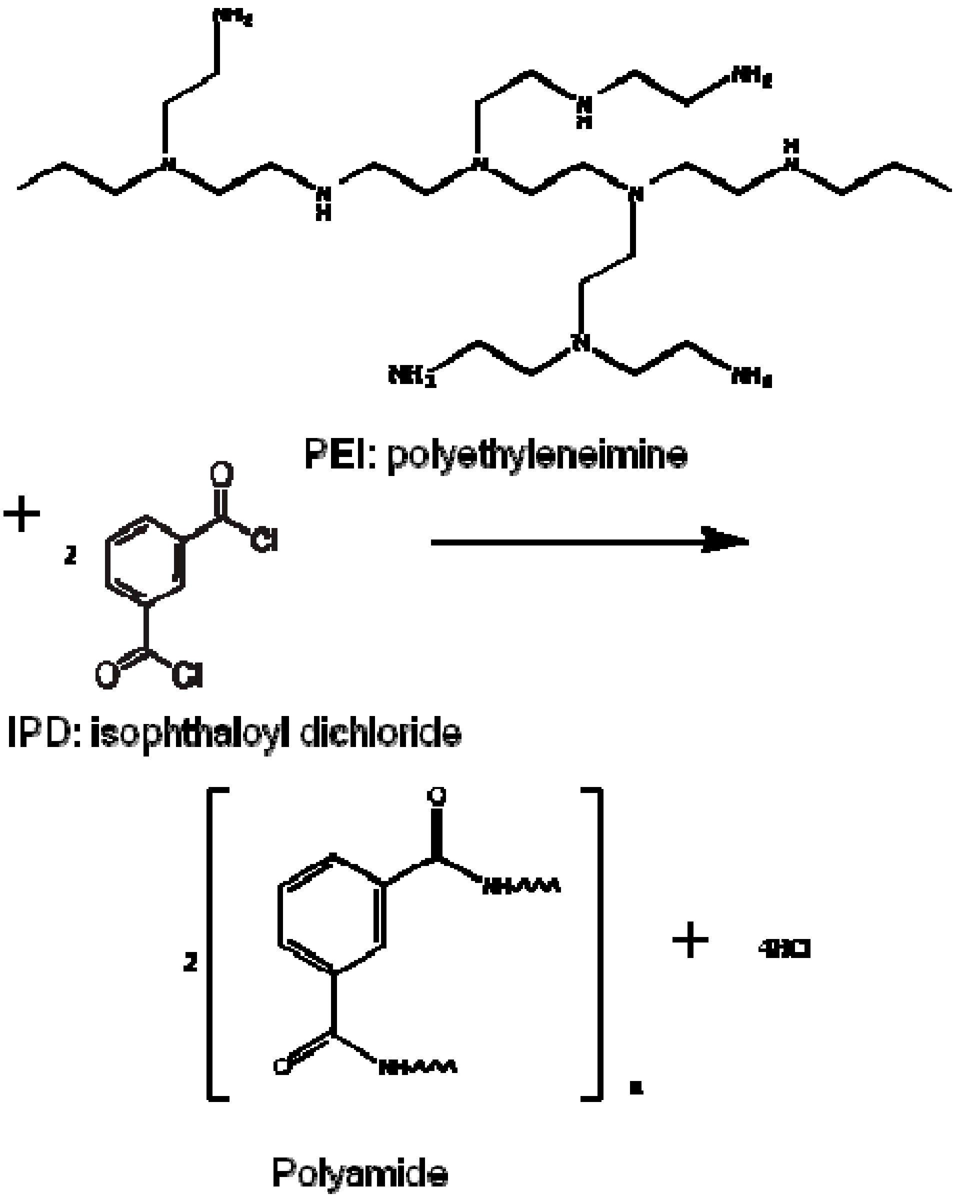

Figure 1.8 Chemistry of polyamide TFC NF membrane by PEI and IPD.

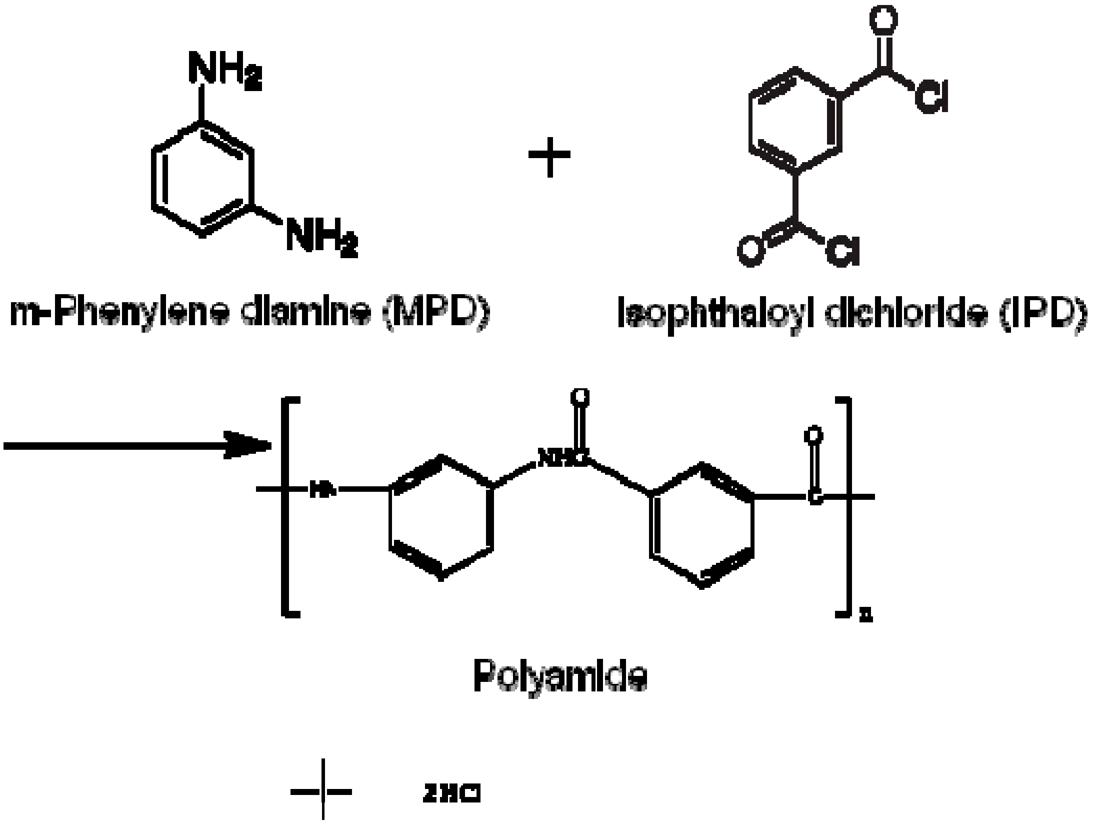

Figure 1.9 Chemistry of polyamide TFC NF membrane by MPD and IPD.

CHAPTER 2

CALCULATION CONSIDERATIONS

2.1 Reactant Concentration Calculation

2.1.1 Equivalent Weight

Equivalent weight has the dimensions and units of mass, unlike atomic weight, which is dimensionless. Equivalent weights were originally determined by experiment, but (insofar as they are still used) are now derived from molar masses. Additionally, the equivalent weight of a compound can be calculated by dividing the molecular weight by the number of positive or negative electrical charges that results from aqueous dissolution of the compound.

For PEI, the primary amine (-NH_2) was reacted to form the amide linkage. The molecular weight of one individual unit of PEI is 473 and each unit contains 4 amine functional groups. So the equivalent weight for PEI is 118.25g (473/4). The same method is used to get the equivalent weight of IPD as101.50g (203/2) and MPD is 59.0g (108/2). Further the ratio of PEI: IPD should be around 2.33:2 and MPD: IPD was about 1.12:2.

2.2 Equations Employed for Rejection and Flux Calculations

The dye rejection of the membrane is calculated by following equation:

$$R_j(\%) = (1 - \frac{C_i}{C_0}) \times 100 \tag{2.1}$$

Here R_j is the dye rejection, C_i (g/L) is the permeate concentration and C_0 (g/L) is the feed concentration. Samples were collected at every half hour. The dye concentration was measured by a UV spectrophotometer. A calibration has been done to measure the concentration for future testing results.

The solvent flux (J) of each membrane sample was determined by measuring the obtained permeate during a predetermined time using a measuring cylinder to read and the following equation:

$$J = \frac{V}{S \bullet \Delta t} \qquad (2.2)$$

Here V (ml) is the volume of the obtained permeates during a predetermined NF operation time Δt (min) and S is the membrane area.

2.2 Modified Calculation Method for Solute Rejection

To avoid the impact of permeated volume on the remaining dye solution, this study began to consider adapting the following method to calculate the solute rejection that used a new feed volume after each permeation to calculate a more precise feed concentration, to obtain the rejection. The calculation method is as follows:

$$V_{01} = V_0 - V_1$$
$$C_{01} = \frac{C_0 \bullet V_0 - C_1 \bullet V_1}{V_{01}}$$
$$V_{02} = V_{01} - V_2$$
$$C_{02} = \frac{C_{01} \bullet V_{01} - C_2 \bullet V_2}{V_{02}}$$
$$\vdots$$
$$\vdots$$
$$V_{0n} = V_{0(n-1)} - V_n$$
$$C_{on} = \frac{C_{0(n-1)} \bullet V_{0(n-1)} - C_n \bullet V_n}{V_{0n}} \qquad (2.3)$$

In Equation 2.3, V_0 is the volume of feed solution before the experiment started, V_{01} is the volume of feed solution after the first permeation, V_{02} is the volume of feed solution after the second permeation, and V_{0n} is the volume of feed solution after nth permeation, V_n is the volume of permeate solution after nth permeation. C_0 is the original concentration of feed solution, C_{01} is the concentration of the feed solution after the first permeation, and C_{0n} is the concentration of the feed solution after n-time permeation, C_n is the volume of permeate solution after nth permeation. V_1 is the volume of the first permeation having a solute concentration of C_1; Similarly V_2 is the volume of the second permeate having a solute concentration of C_2.

In the case above, the dye solute rejection was calculated by Equation 2.4.

$$R_{jn}(100\%) = (1 - \frac{C_n}{C_{0n}}) \times 100 \qquad (2.4)$$

Here R_{jn} is the dye rejection for nth permeation, C_n (g/L) is the permeate concentration and C_{0n} (g/L) is the feed concentration after nth permeation.

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals

The following chemicals were used: xylene (Certified ACS), methanol (Histological Grade), safranin O (dye content 86%) (Fisher Scientific, Fair Lawn, NJ); brilliant blue R (dye content 60%), Poly(ethyleneimine) Solution (50% w/v in water), Isophthalogy dichloride (>99%), m-Phenylene diamine (MPD) (flakes, 99+%), Acetone (Histological grade, 99.5+%) (Sigma-Aldrich, St. Louis, MO); High purity Nitrogen (Welco CGI, Newark NJ); Deionized water (17.8 MΩ cm) used for all experiments was obtained from Barnstead system with Module ORGANICfree (Barnstead, Dubuque, Iowa).

3.2 Membranes

The support microfiltration membranes utilized in this study were manufactured by Sterlitech Company, Kent, WA. These were 200 × 200mm with 0.03 micron pore diameter. Polyethersulfone (PES) membrane is hydrophilic.

3.3 Instruments

UV Visible Spectrophotometer (Model Cary 50Bio, Varian, Walnut Creek, CA)

3.4 Experimental Setup

A schematic of the laboratory setup utilized for the experiments is shown in Figure 3.1. Separation tests were performed in a pressure cell (model 56414 SEPA® ST: Osmonics, Minnetonka, MN). A schematic of the cell is shown in Figure 3.2. The cell consisted of a 300 cm^3, 316 stainless steel cylindrical body provided with high pressure-resistant couplings (up to 1000 psig), placed on a variable-speed stirring plate. A flat, round-cut membrane having a diameter of 5 cm and an effective (exposed or active) membrane area of 12.56 cm^2 was placed on top of a porous stainless steel support disk. A 0.16 cm (1/16″) thick, 20 μm porous support disk was provided by the manufacturer along with the pressure cell. The hold-up volume underneath the porous support was 1 cm^3. Stirring was provided by means of a teflon-coated magnetic stir bar mechanism supported on a rim in the internal wall of the cell body. The permeate tube consisted of a 22 cm long, 0.32 cm (1/8″) diameter, plastic, removable tube, to facilitate permeate collection. The original, 8 cm long, 0.32 cm (1/8″) diameter, stainless steel tube was welded to the permeate orifice at the tapered base of the cell and was replaced with a Swagelok® 1/8″ female pipe connector for a safer operation and easier cleaning. A 1/4″ diameter inlet tube was provided at the top the cell. The pressure cell was placed on a variable-speed stirring plate (Whu et al., 2000).

Feed solution pressurization was provided by compressed nitrogen (extra dry) and a single stage stainless steel pressure regulator (Matheson Gas Products, East Rutherford, NJ) was controlled the pressure. A pressure gauge, attached to the inlet line, allowed convenient readings of the system pressure. Valves, ball valves, a back pressure regulator (range 345-4826 kPa, from Matheson, E. Rutherford, NJ) were checked before usage.

The setup was also provided with connections to a tank, which was used to provide a large volume of feed solution (up to 2000 ml) to maintain steady performance for a longer period.

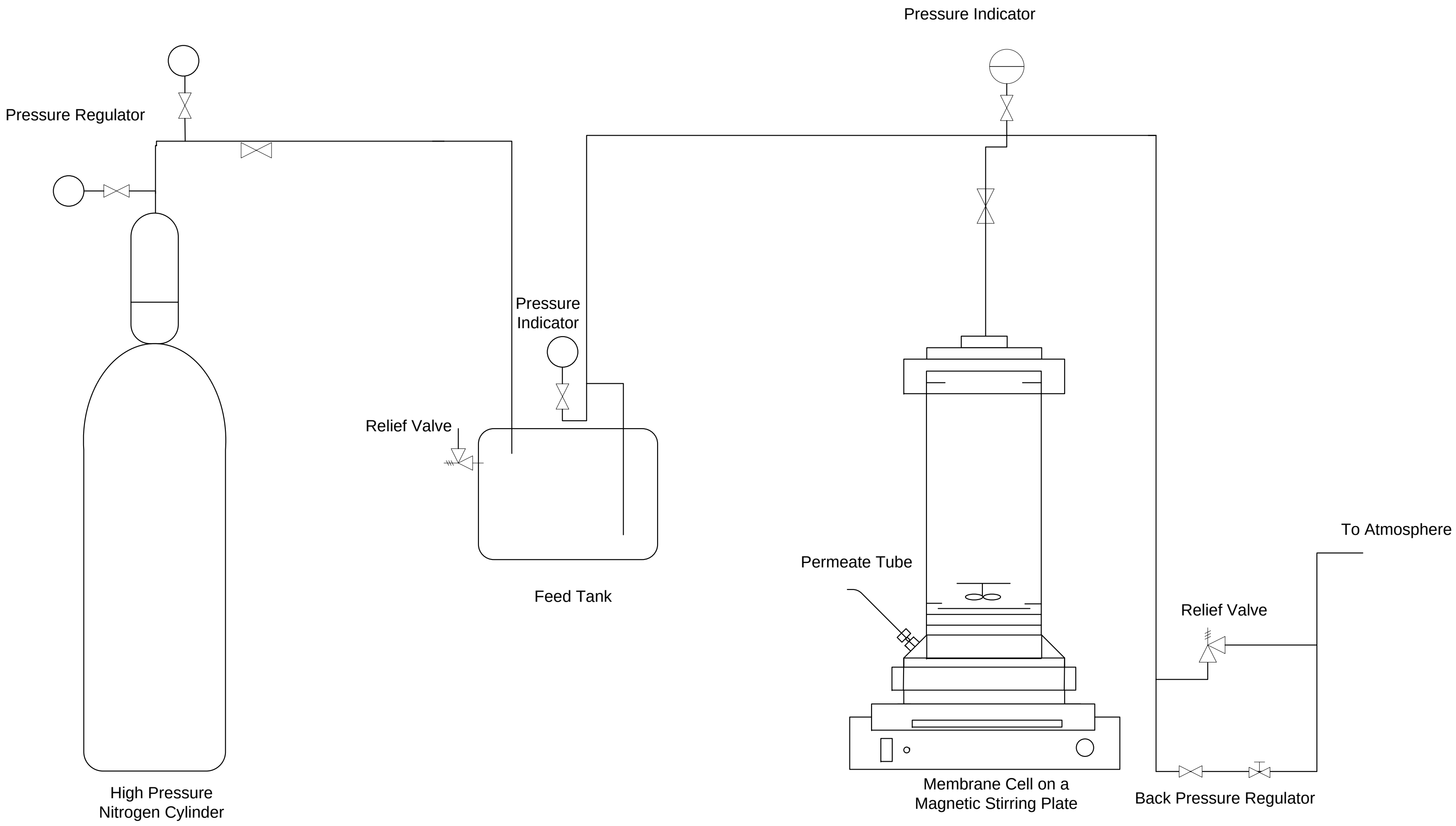

Figure 3.1 Schematic diagram of the laboratory setup.

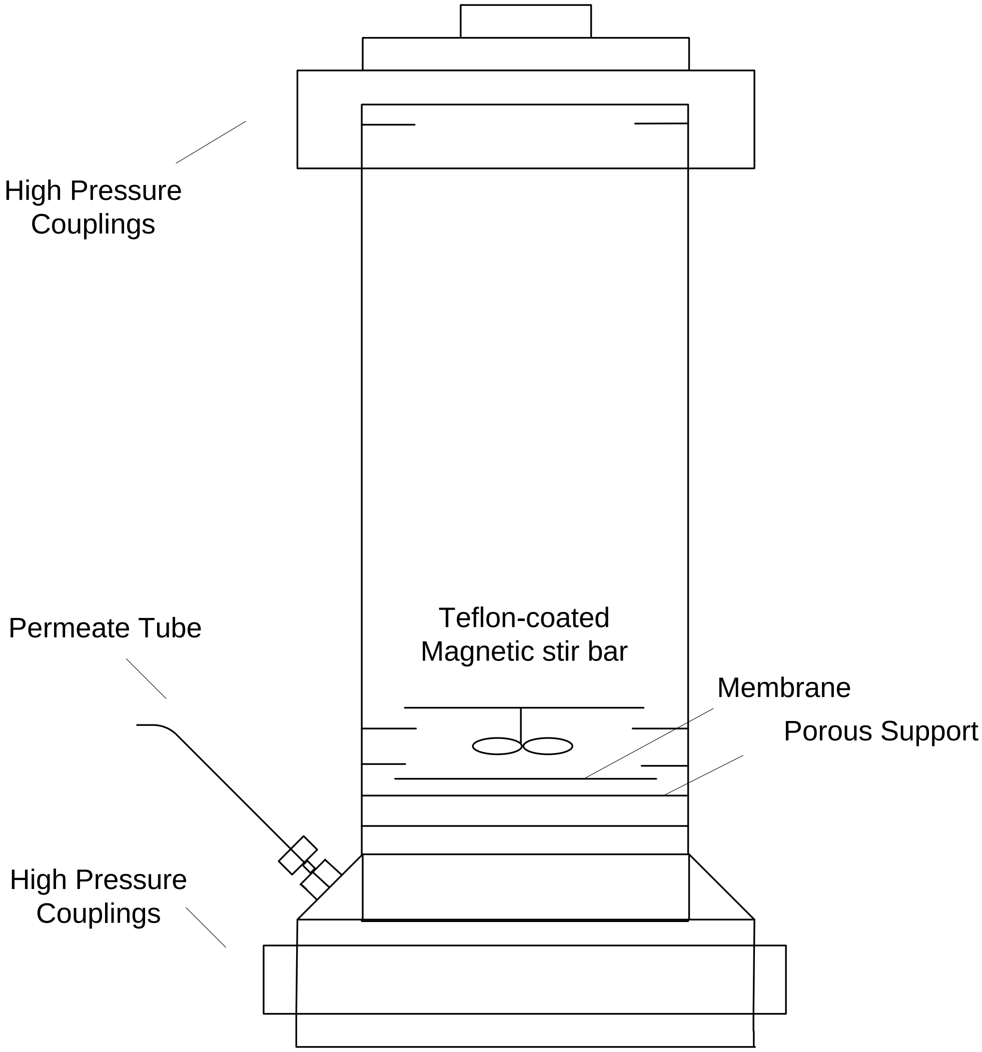

Figure 3.2 Schematic diagram of the pressure cell.

3.4 Experimental Procedure

3.4.1 Preparation of PEI-IPD TFC NF Membrane

3.4.1.1 Support Membrane Preparation. As the first step, a circular piece of PES membrane was cut from the sheet according to the exact size of testing cell with diameter 5cm. Two reactant solutions were prepared respectively per the following Table 3.1 for membrane type M1. Concentrations were calculated by equivalent weight shown in Chapter 2.

Table 3.1 Solution Concentrations (M1)

Solution	Concentration (%w/w)
Polyethyleneimine (PEI) in Water	2.33
Isophthaloyl dichloride (IPD) in Xylene	2.0

3.4.1.2 Interfacial Polymerization. A flat PES membrane was soaked in an aqueous solution of PEI having a concentration of 2.33 wt% for 60 min (30 min in one glass container of PEI solution and 30 min in another one). Subsequently, the treated membrane was drained, placed and secured on a cylindrical PTFE roller support and fixed by two O rings, further reacted with a xylene solution of IPD having a concentration of 2.0 wt%. The reaction time was approximately 20 seconds. The resulting TFC membrane was drained and ready to be post-treated.

3.4.1.3 Post-polymerization Treatment for TFC NF Membrane. The most common post-treatment is heat treatment. The membranes were put in an oven at 110°C for 8 minutes. The newly TFC prepared membranes were treated in three different ways shown in Table 3.2 to select the optimum treatment. Note, M1A membrane was put into 110°C oven as soon as it was made. M1B membrane was left at room temperature (25°C) for 1 hour and then was shifted into 110°C oven for eight minutes. After being kept for 12-hour long at room temperature (25°C), the M1C membrane was put into oven at 110 °C for an eight minute heat-treatment.

Table 3.2 Different post-treatment times and temperatures for TFC NF membrane

PEI-IPD membrane	Treatment time for keeping at room temperature (25°C) (hr)	Treatment time at 110°C oven (min)
M1A	0	8
M1B	1	8
M1C	12	8

3.4.1.4 Membrane Washing. The post-treated membranes were kept in clean glass containers and kept at room temperature overnight (>12 hr) and then washed. The washing system was made up of three parts as shown Figure 3.3: deionized water, methanol and xylene, each part had the same volume. Water and xylene were immiscible so that application of methanol here could help to dissolve both organic and inorganic impurities for its miscibility to both water and xylene.

Membranes were soaked into water for first, using a forceps to rinse, then moved the membranes to immers it into methanol by forceps, followed by xylene rinsing. After that, membranes were clipped back to methanol and then to water. The key step here was avoiding the direct washing process between water and xylene without the intermediate methanol-washing step. The sequence for a completely washing process run as: water-methanol-xylene-methanol-water. Repeat this process for 7-8 times, approximately 2 minutes for each time. Once washing work was done, the membrane was kept at room temperature overnight to dry it completely.

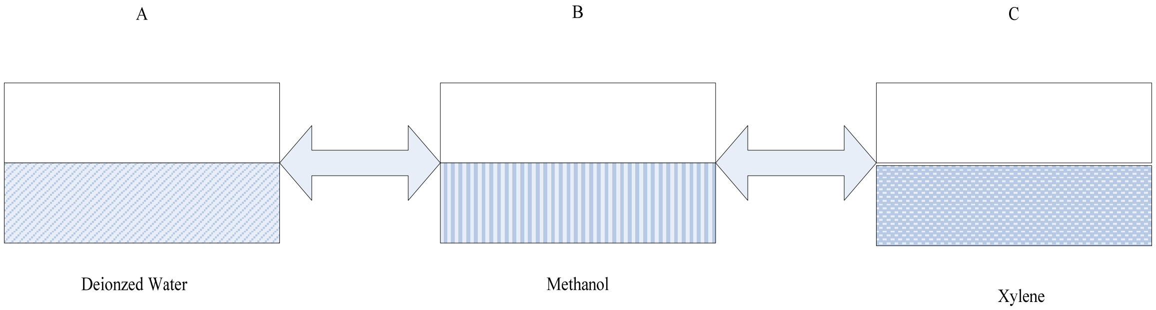

Figure 3.3 Process of washing modified TFC NF membranes.

3.4.2 Membrane Performance Evaluation

The performance tests of TFC NF membranes were conducted in a cell (Figures 3.1 and 3.2), using a dye solution (0.05% w/v) of Brilliant Blue R (MW 826) in distilled water at different constant pressures (through 69 kPa to 413.7 kPa) and room temperature (25°C). Two or three membranes for each type of TFC NF membranes were used for testing. For one membrane after detecting through testing cell, it was recovered by washing in 10% methanol in water for reusing. Circular membrane samples (11.34 cm^2) were placed in cell with the active layer facing the incoming feed. The feed solution was pressurized to the prescribed pressure and permeate samples were collected in a measuring cylinder per designated time. Further, safranin O (MW 351) in water (0.05% w/v) was used too.

3.4.2.1 Solute Rejection and Solvent Flux. The flux and the solute rejection were determined respectively by measuring the volumetric permeate flow directly ($ml/cm^2 \bullet sec$) and brilliant blue R UV absorbance at 590 nm (A); the calibration curve for UV absorbance-concentration is shown in Figure 3.4.

The equation to indicate the relationship between UV absorbance and concentration was clearly shown as:

$$C = 0.0019A - 0.0001 \tag{3.1}$$

Here C (g/L) is the concentration of dye solution (Brilliant Blue R) in deionized water and A (A) is the UV absorbance of dye solute at 590 nm wavelength.

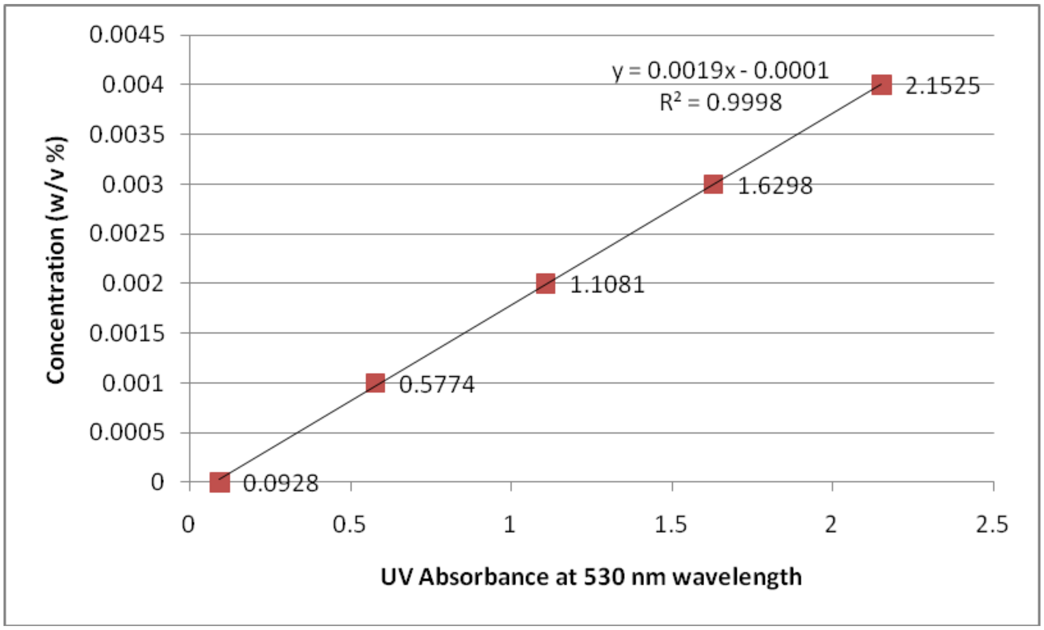

Figure 3.4: Brilliant blue R UV absorbance-concentration curve at 590 nm wavelength.

3.4.3 Preparation of MPD-IPD TFC NF Membrane

3.4.3.1 Preparation of M2 Membrane. To compare the difference between a monomer and a polymer in the aqueous phase on the aspect of forming a thin film composite, m-phenylene diamine (MPD) was applied to prepare a novel TFC instead of PEI. MPD is usually applied for IP with trimesoyl chloride (TMC) to prepare RO TFC films. This is an attempt to put MPD together with IPD to react them to prepare a novel TFC film. According to equivalent weight, the concentration ratio between MPD and IPD should be 0.56:1 to create the best match. The solution was prepared as shown in Table 3.3; M2 membrane was prepared by the same IP, post-treatment, washing processes, and then was dried and remained at room temperature for future use.

Table 3.3 Solution concentrations (M2)

Solution	Concentration (%w/w)
m-Phenylene diamine (MPD) in water	1.12
Isophthaloyl dichloride (IPD) in xylene	2

3.4.3.2 Preparation of M3 membrane. Considering the impact from the monomer concentration, this research included one more experiment to prepare another membrane by increasing the concentration of IPD from 2 to 3%w/w (MPD concentration was increased by the same ratio from 1.12 to 1.68%w/w). All data were prepared following Table 3.4.

Table 3.4 Solution concentration (M3)

Solution	Concentration (%w/w)
m-Phenylene diamine (MPD) in water	1.68
Isophthaloyl dichloride (IPD) in xylene	3

3.4.4 Preparation of MPD-PEI-IPD TFC Film.

Since PEI and MPD have different mechanisms of IP with IPD, it is useful to investigate novel membranes that are attained by mixing PEI and MPD to react with IPD at the same time and condition. This experiment involved 4 different membranes by applying different concentration ratios of MPD: PEI to study the impact from concentration ratio. These four compositions for four types of membranes are shown in Table 3.5.

Table 3.5 Four types of MPD-PEI-IPD TFC membranes

MPD-PEI-IPD TFC Membranes	Ratio of MPD: PEI	Concentration of MPD in water (w/w %)	Concentration of PEI in water (w/w %)
M4A	25%: 75%	0.28	0.575
M4B	50%: 50%	0.56	1.15
M4C	75%: 25%	0.84	1.725
M4D	100%: 100%	1.12	2.33

Four membranes were prepared by following the same process for IP, post-treatment and washing. They were kept at room temperature (25°C) for performance testing. Detailed concentrations for three reactants are provided in Tables 3.6-3.9. Before all NF experiments were examined at 206.9 kPa, each membrane was placed in the filtration cell and pressurized at 344.7 kPa for at least 2 hours using deionized water, to obtain a stable performance for future experiments.

Table 3.6 Solution concentrations (M4A)

Solution	Concentration (%w/w)
m-Phenylene diamine (MPD) in water	0.28
Polyethyleneimine (PEI) in water	1.673
Isophthaloyl dichloride (IPD) in xylene	2

Table 3.7 Solution concentrations (M4B)

Solution	Concentration (%w/w)
m-Phenylene diamine (MPD)in water	0.56
Polyethyleneimine (PEI) in water	1.165
Isophthaloyl dichloride (IPD) in xylene	2

Table 3.8 Solution concentrations (M4C)

Solution	Concentration (%w/w)
m-Phenylene diamine (MPD)in water	0.84
Polyethyleneimine (PEI) in water	0.56
Isophthaloyl dichloride (IPD) in xylene	2

Table 3.9 Solution concentrations (M4D)

Solution	Concentration (%w/w)
m-Phenylene diamine (MPD)in water	1.16
Polyethyleneimine (PEI) in water	2.33
Isophthaloyl dichloride (IPD) in xylene	2

3.4.5 Membrane Performance Evaluation for MPD-IPD TFC Film And MPD-PEI-IPD TFC Membranes

After all the novel membranes were prepared, they were put into the same testing system as Figures 1.1 and 1.2. Samples were collected to determine by the UV absorbance for the solute rejection through the calibrated UV absorbance-concentration curve (Figure 3.5). The calibration curve was developed again because systematical error happened in the UV Visible Spectrophotometer after the earthquake on August 23rd, 2011. The membranes made after that date were evaluated using the new calibration curve (Figure 3.5) for brilliant blue R; and calibration curve for safranin O (Figure 3.6). Meanwhile the solvent flux were calculated by measuring the permeate volume out a period of time.

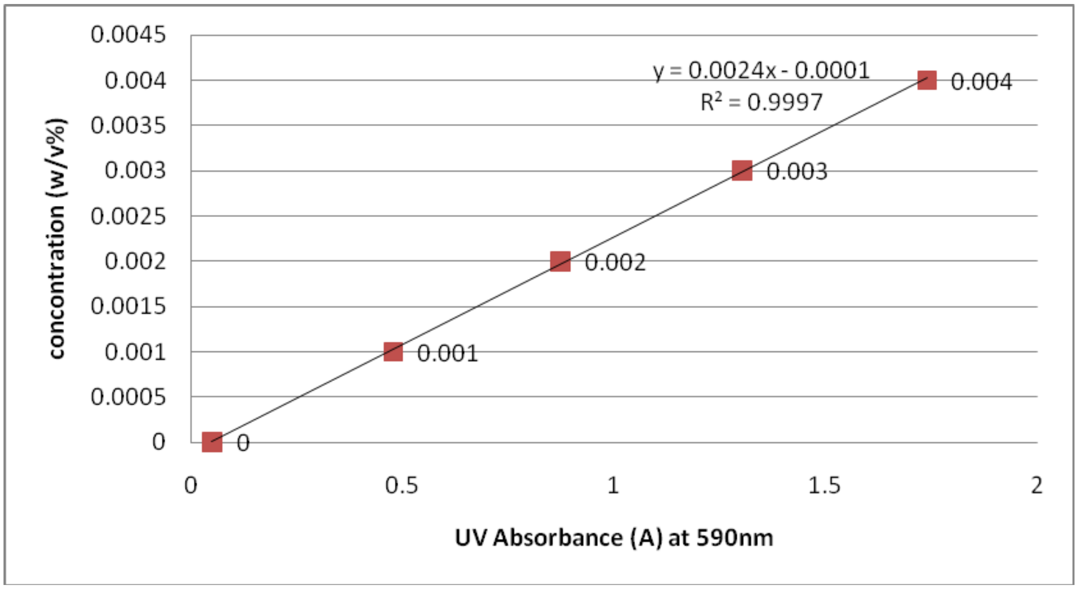

Figure 3.5 Brilliant blue R UV absorbance-concentration curve at 590 nm wavelength.

Through the Figure 3.5, the equation to indicate the relationship between UV absorbance and concentration was clearly shown as:

$$C = 0.0024A - 0.0001 \tag{3.2}$$

Here C (g/L) is the concentration of dye solution (Brilliant Blue R) in deionized water and A (A) is the UV absorbance of dye solute at 590 nm wavelength.

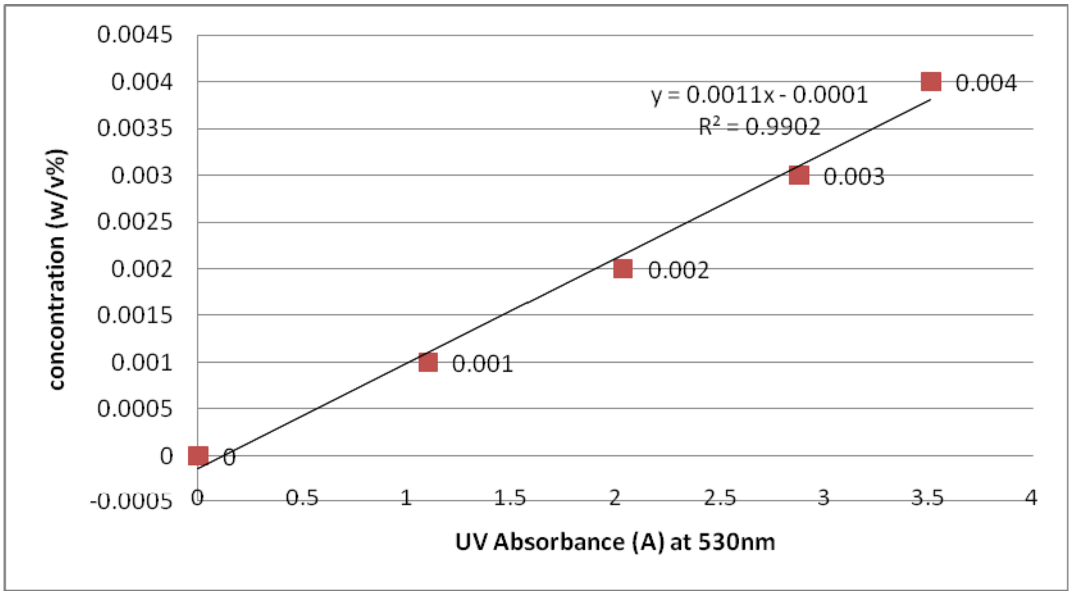

Figure 3.6 Safranin O UV absorbance-concentration curve at 530 nm wavelength.

In order to detect the performance of newly prepared membranes in different dye solution, safarin O (0.005% w/v) in water was used to get solute rejection and solvent flux as well. The solute rejections were calculated according to the UV absorbance-concentration curve shown as Figure 3.6.

$$C = 0.0011A - 0.0001 \tag{3.3}$$

In which C (g/L) is the concentration of dye solution (Safranin O) in deionized water and A (A) is the UV absorbance of dye solute at 530 nm wavelength.

CHAPTER 4

RESULTS AND DISCUSSION

The membrane modification results from three post-polymerization treatments and TFC NF membrane performances from three composite monomer systems (PEI-IPD, MPD-IPD, PEI/MPD-IPD) are presented and discussed in this chapter. For every type of membrane used for detecting, two pieces of membrane were made and tested to get the average data that was used to show the experimental results.

4.1 Post-polymerization Treatment Selection

Three membranes interfacially polymerized under the same conditions (reactant concentrations, IP time) were post-treated following Table 3.2.

4.1.1 Solute Rejection and Solvent Flux of M1A, M1B and M1C Membranes

Solution rejection and flux from M1A, M1B and M1C were indicated and compared as follows. In Tables 4.1-4.3, solvent flux and solute rejection at different pressures were shown for 3 types of membranes.

Table 4.1 Solute rejection and water flux over 68.95-413.7 kPa for M1A membrane

Pressure (kPa)	Solute rejection (100%)	Water flux (Gal/day•ft^2)
68.95	88.65	97.54
137.9	50.35	139.95
206.8	40.99	181.52
275.8	39.04	187.48
344.7	45.59	205.93
413.7	35.08	209.08

Table 4.2 Solute rejection and water flux over 68.95-413.7 kPa for M1B membrane

Pressure (kPa)	Solute rejection (100%)	Water flux (Gal/day•ft^2)
68.95	95.05	19.46
137.9	87.37	28.78
206.8	82.93	45.09
275.8	78.44	48.62
344.7	79.27	53.06
413.7	78.23	57.34

Table 4.3 Solute rejection and water flux over 68.95-413.7 kPa for M1C membrane

Pressure (kPa)	Solute Rejection (100%)	Water flux (Gal/day•ft^2)
68.95	92.54	9.14
137.9	77.81	20.36
206.8	71.68	27.02
275.8	45.55	36.18
344.7	46.12	41.14
413.7	44.98	41.81

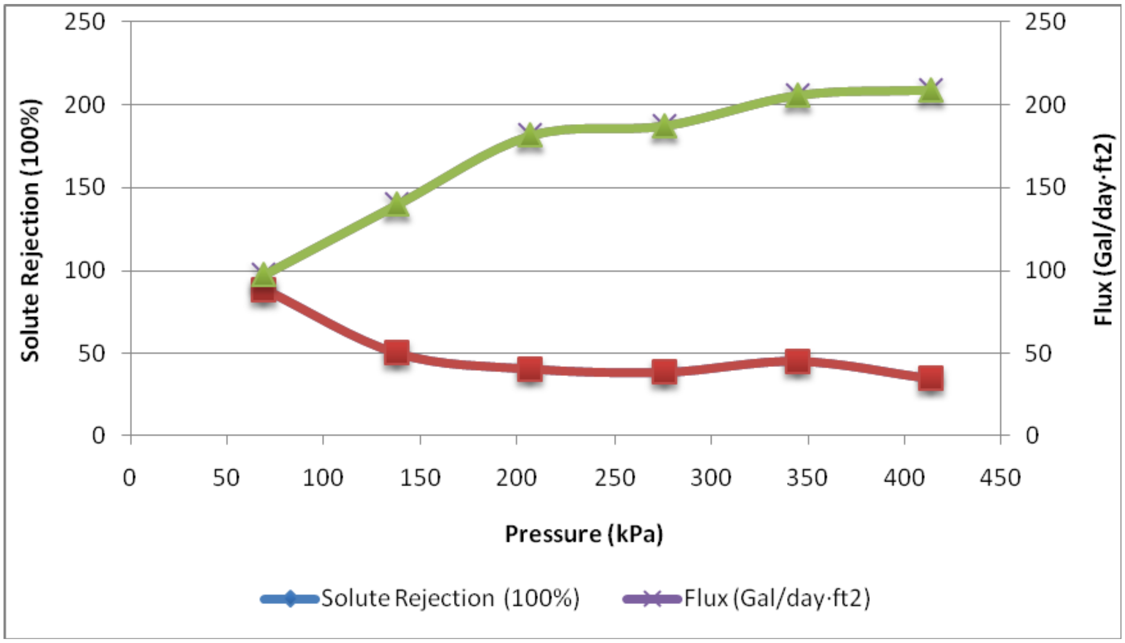

Figure 4.1 Solute rejection and water flux over 68.95-413.7 kPa for M1A membrane.

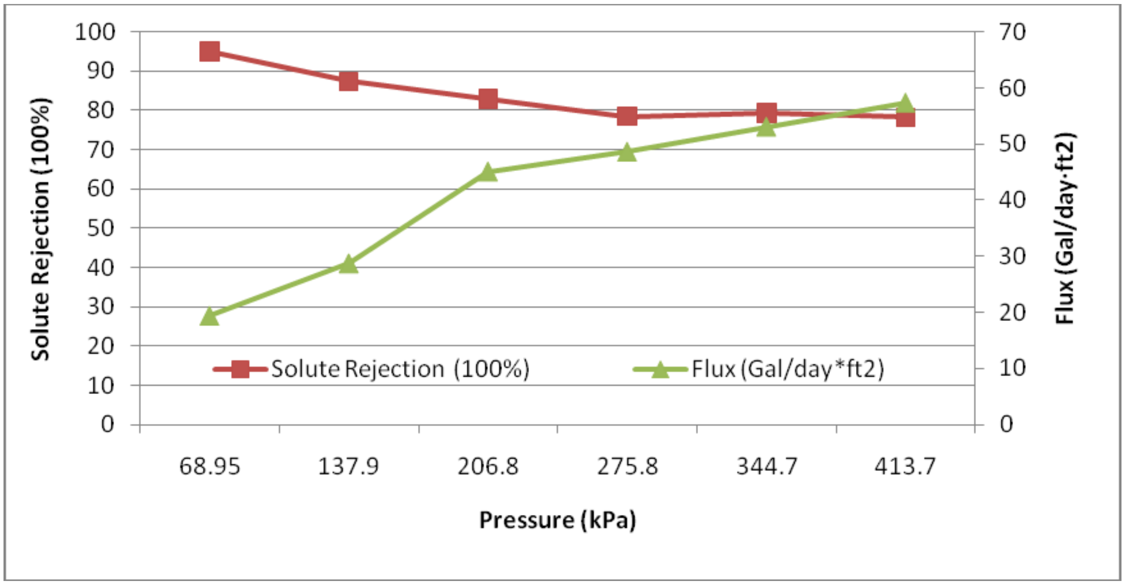

Figure 4.2 Solute rejection and water flux over 68.95-413.7 kPa for M1B membrane.

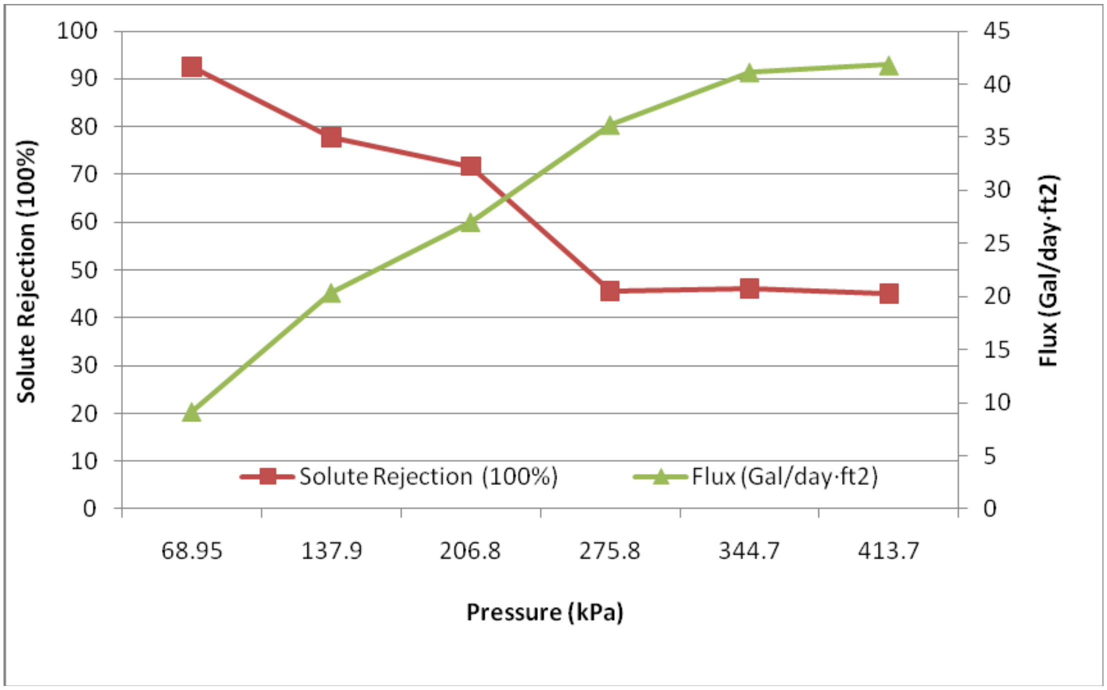

Figure 4.3 Solute rejection and water flux over 68.95-413.7 kPa for M1C membrane.

4.1.2 Comparison of Membranes M1A, M1B and M1C

From a comparison of solute rejection as well as flux data (Figures 4.4 and 4.5), M1B post-treated via one-hour gap between IP and 110°C heat treatment had relatively better performances in terms of higher solute rejection and a higher flux than M1C.

4.1.2.1 Solute Rejections from M1A, M1B and M1C. Obviously M1B performed the best in solute rejection when compared to those from the other two. Solute rejection of M1B was around 90% and relatively stable with respect to pressure (Figure 4.4). Therefore one-hour gap between IP and 110°C heat treatment is beneficial to improve the solute rejection performance. Too short or too long a time gap resulted in poorer membrane performance.

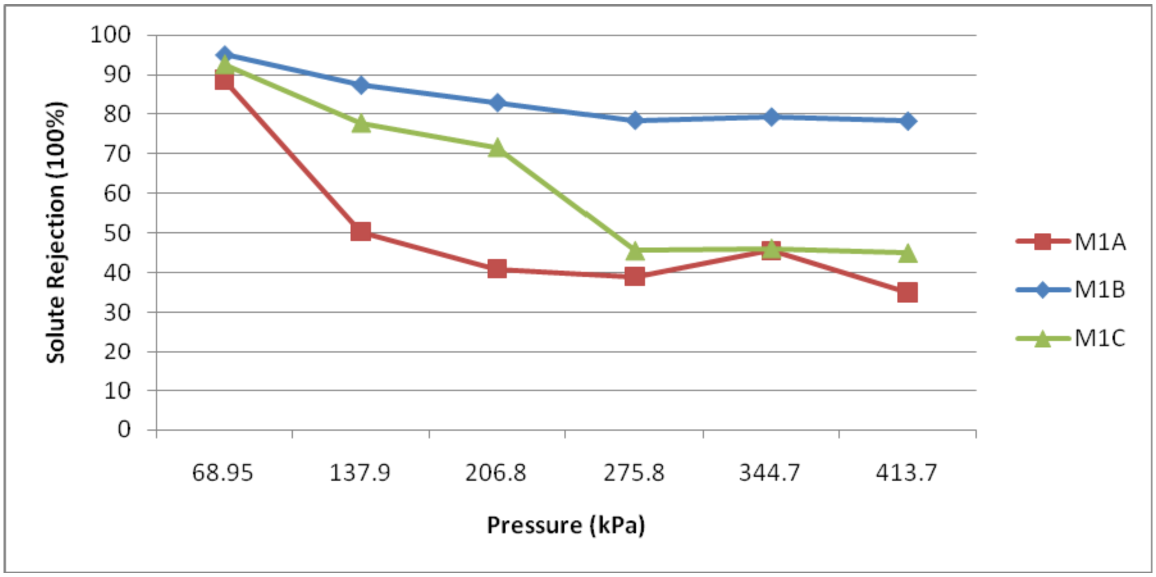

Figure 4.4 Solution rejections of membranes M1A, M1B and M1C over 68.95-413.7 kPa.

4.1.2.2 Solvent flux from M1A, M1B and M1C. M1A yielded a very high solvent flux. Among M1B and M1C, M1B showed a relatively higher solvent flux.

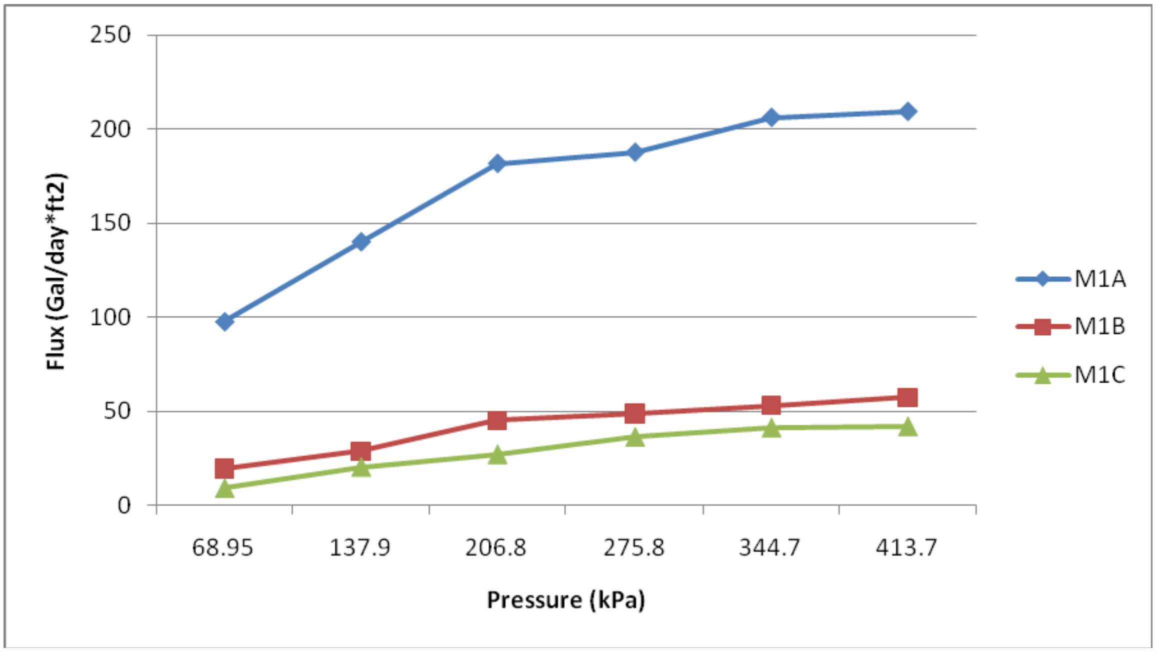

Figure 4.5 Solvent flux values for M1A, M1B and M1C membranes over 68.95-413.7 kPa.

4.2 Performance of Membranes

In this part, for M1 membrane, both brilliant blue R and safranin O were employed to illustrate the different solute rejection and solvent flux. The performance of M2 was compared with that of M1 to investigate the difference between polymeric and monomeric amines. Further, the behavior of M2 was compared with that of M3 to indicate the impact of the concentration of monomers. In addition, four types of M4 membranes made by different ratios of MPD-PEI were compared, the performance of M4B was compared to that of M1 to present the impact of adding MPD in the IP reacting system.

4.2.1 Solute rejection and solvent flux of M1 membrane for both brilliant blue R and safranin O

According to the results from Section 4.1.1, post-treatment procedure of one-hour gap between IP and high temperature treatment (110°C) would be the best way to get a TFC NF membrane with better performance (relatively higher solute rejection and good water flux). All membranes made later follow the same post-treatment to optimize their performances. An improved calculation method mentioned in Chapter 2 was adopted here (Table 4.4b); Table 4.4a does not take into account a change in the feed solute concentration with time.

4.2.2.1 Performance of brilliant blue R solution.

Table 4.4a Solute rejection and solvent flux as a function of time at 206.8 kPa for M1 membrane via brilliant blue R

Time difference (min)	Solute rejection (100%)	Flux (Gal/day*ft^2)
30	98.19	74.80
60	97.96	65.45
90	97.39	63.58
120	96.07	48.62
150	95.89	50.49
180	95.63	48.62
210	94.34	42.07
240	92.54	39.27
270	90.99	37.40

Following the new calculating method, new data came out in Table 4.4b.

Table 4.4b New solute rejection and solvent flux via equations (2. 2) (2. 3) and (3. 2) at 206.8 kPa (M1) by brilliant blue R

Time difference (min)	New Feed Solution Concentration	Solute Rejection (100%)	Flux (Gal/day*ft^2)
30	0.00548	98.02	74.80
30	0.00553	97.98	65.45
30	0.00558	97.44	63.58
30	0.00563	96.17	48.62
30	0.00567	96.03	50.49
30	0.00570	95.80	48.62
30	0.00574	94.59	42.07
30	0.00577	92.92	39.27
30	0.00580	91.49	37.40

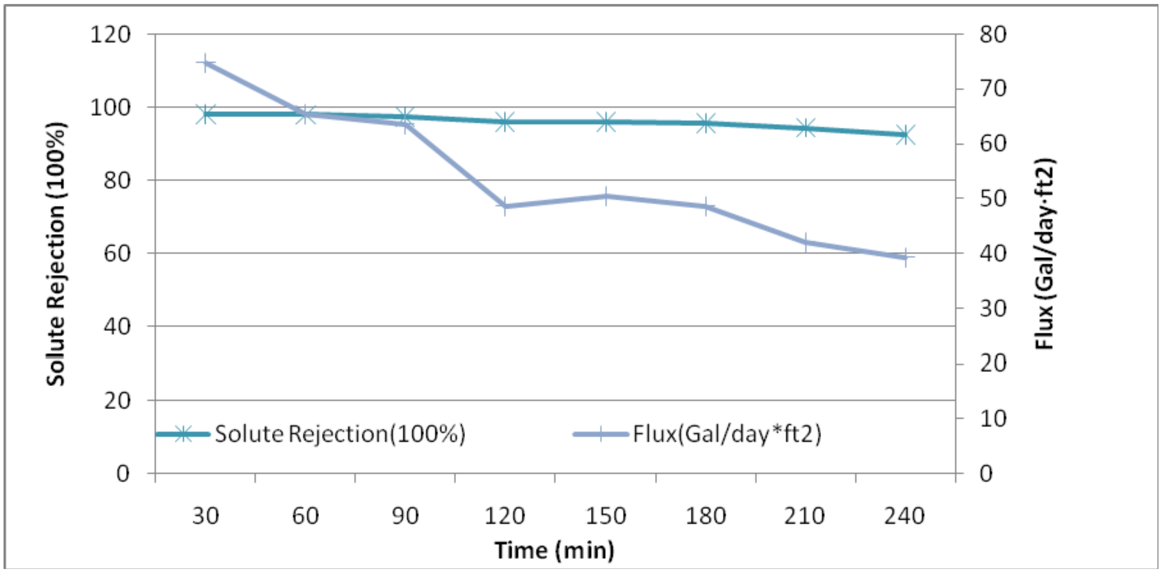

Figure 4.6 Solute rejection and solvent flux of M1 membrane as a function of time (brilliant blue R).

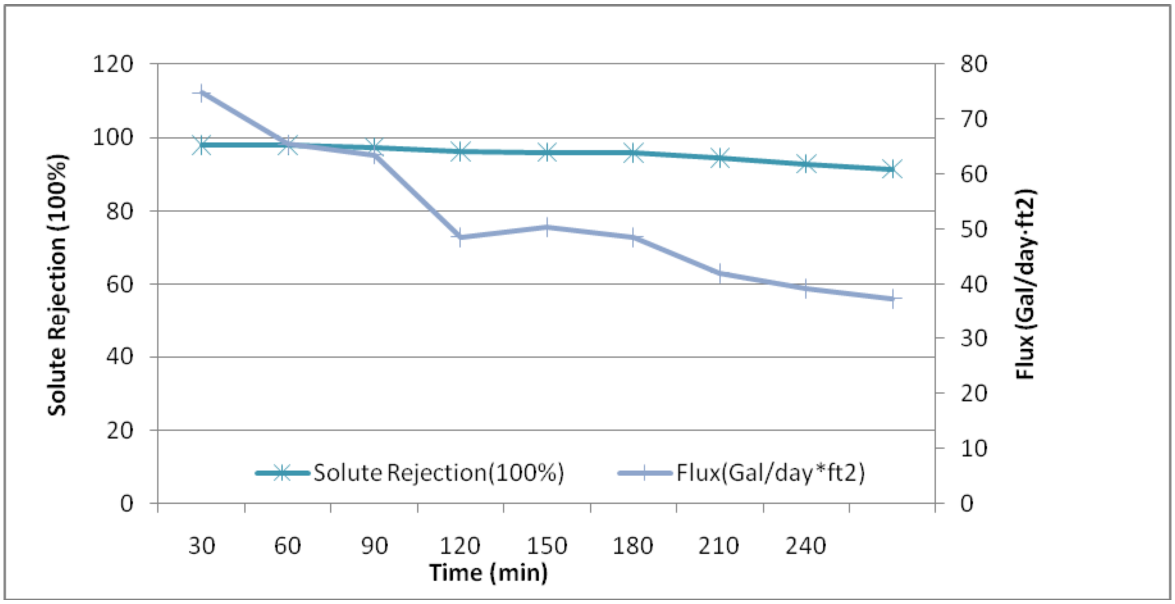

Figure 4.7 New solute rejection and flux of M1 as a function of time (brilliant blue R).

By considering the impact from the changing feed concentration of solution concentration in the remaining feed volume after every permeation, a slightly higher concentration of feed solution was supposed to replace the previous one as that the actual rejection (Figure 4.7) would be higher than the one which ignored this impact (Figure 4.6). The difference has been illustrated in Figure 4.8.

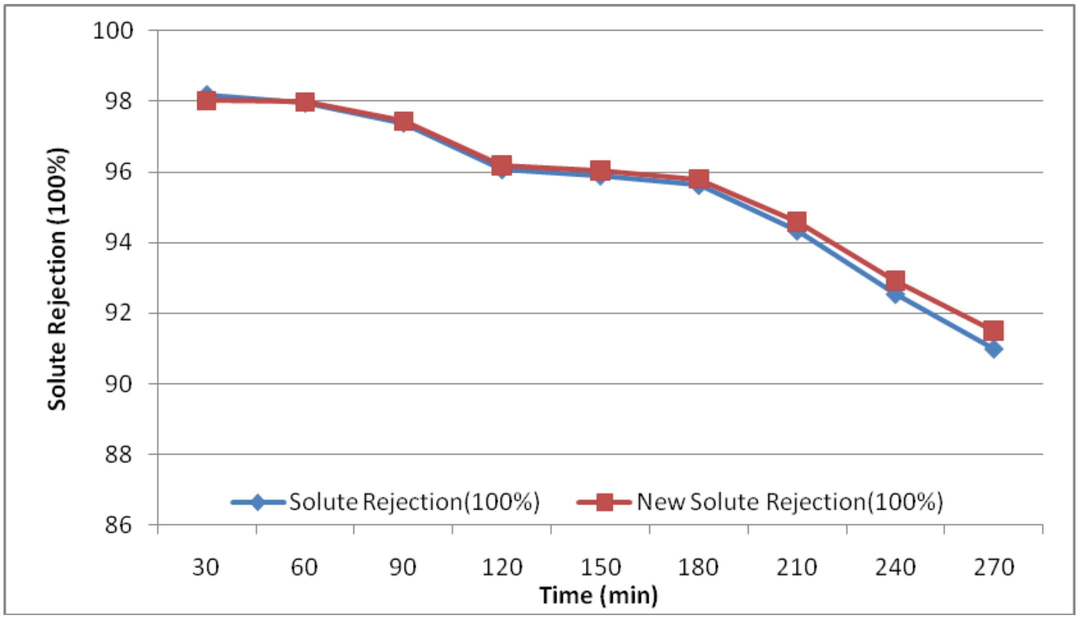

Figure 4.8 Original and new solute rejections of M1 as a function of time (brilliant blue R).

4.2.2.2 Performance for safranin O.

Table 4.5 Solute rejection and solvent flux as a function of time at 206.8 kPa for M1 membrane for safranin O

Time difference (min)	Solute Rejection (100%)	Flux (Gal/day*ft^2)
30	20.13	2056.89
60	18.74	1252.83
90	16.82	1260.31
120	16.00	850.80
150	14.95	719.91
180	14.57	635.77
210	15.11	579.67
240	15.32	523.57
270	15.56	476.82
300	15.35	430.08
330	16.37	476.82
360	14.55	430.08

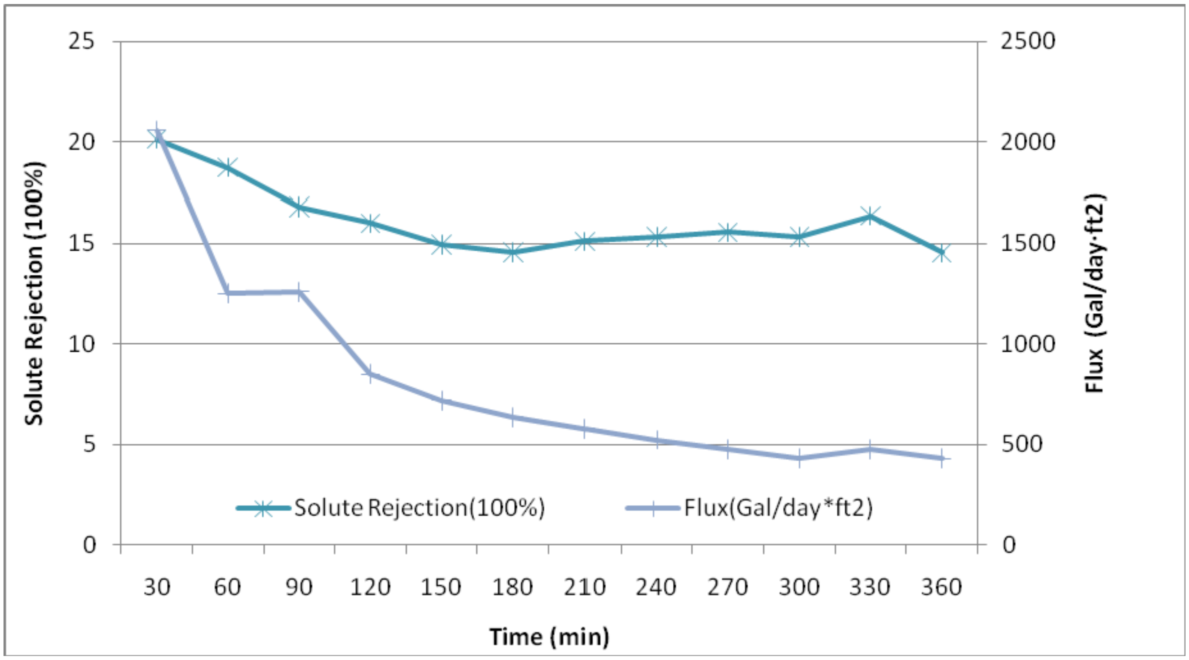

Figure 4.9 Solute rejection and solvent flux as a function of time at 206.8 kPa for M1 membrane for safranin O.

Solute rejection detected by brilliant blue R showed a much higher rejection (91%-99%) than safranin O which was rejected only around 15%-20% (Figures 4.9-4.11). From the tremendous difference for flux of brilliant blue R and safranin O, it showed the M1 membrane reused for safranin O testing had developed some defects: it was useless. For the same membrane, it should present similar solvent flux to same solvent (water in this study) no matter which dye was dissolved in that.

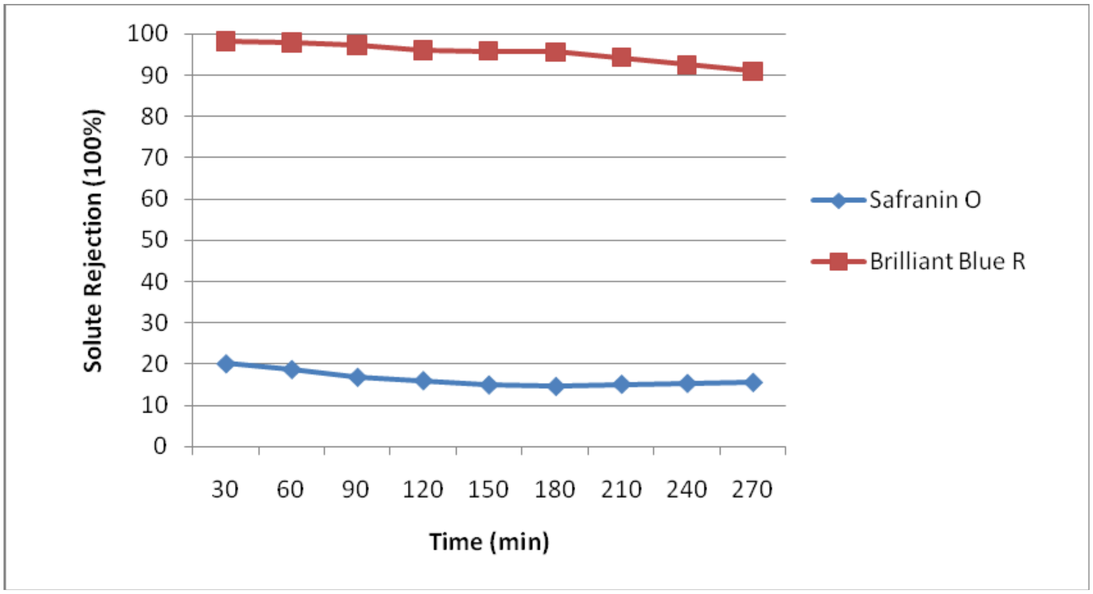

Figure 4.10 Solute rejections from safranin O and brilliant blue R (M1 membrane).

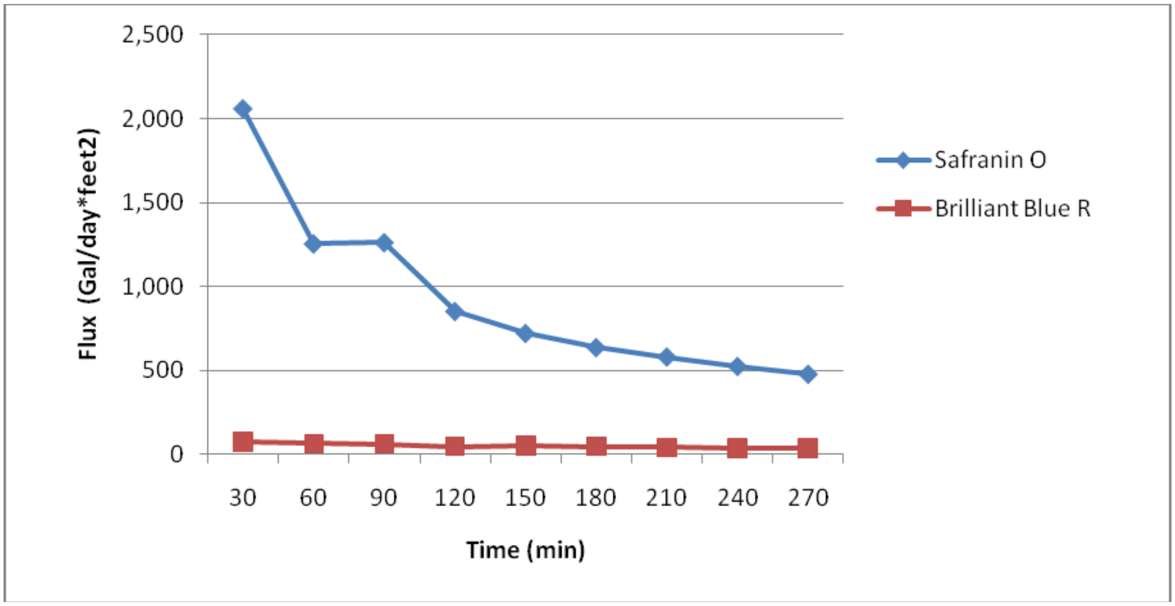

Figure 4.11 Solvent flux from safranin O and brilliant blue R (M1 membrane).

4.2.3 Solute Rejection and Solvent Flux of M2 Membrane

The performance of MPD-IPD TFC NF membranes made from Table 3.2 was determined and results are shown in Table 4.6 and Figure 4.11.

Table 4.6 Solute rejection and flux as a function of time at 206.8 kPa for M2 membrane

Time (min)	Solute rejection (100%)	Flux (Gal/day•ft^2)
30	90.62	439.43
60	90.87	331.91
90	92.06	310.40
120	93.21	289.83
150	86.48	261.79
180	87.39	210.36
210	88.83	205.69
240	90.16	206.62
270	90.16	186.99

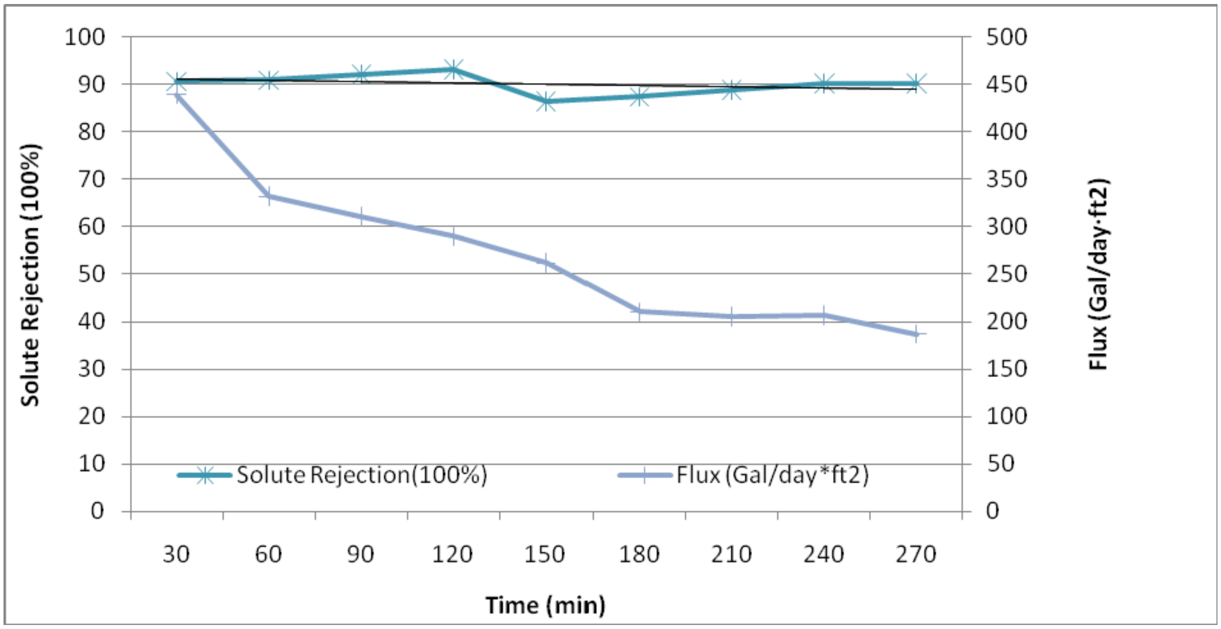

Figure 4.12 Solute rejection and flux as a function of time at 206.8 kPa for M2 membrane.

M2 and M1 showed different performances for both solute rejection and solvent Flux (Figures 4.11 and 4.12). M1 had a higher solute rejection but lower Flux than M2, which indicates that the TFC formed in the aqueous phase by PEI (polymer) and IPD can provide better performance than the one in the organic phase by MPD (monomer) and IPD. M4 membrane made up with mixture of PEI and MPD was an attempt to get both high solute rejection and flux.

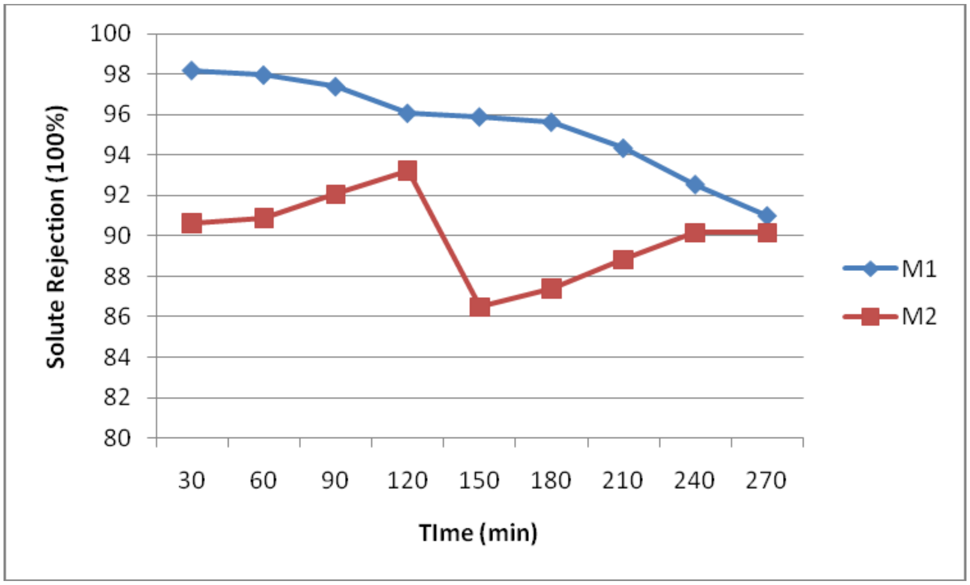

Figure 4.13 Solute rejections of M1 and M2 as a function of time at 206.8 kPa for brilliant blue R.

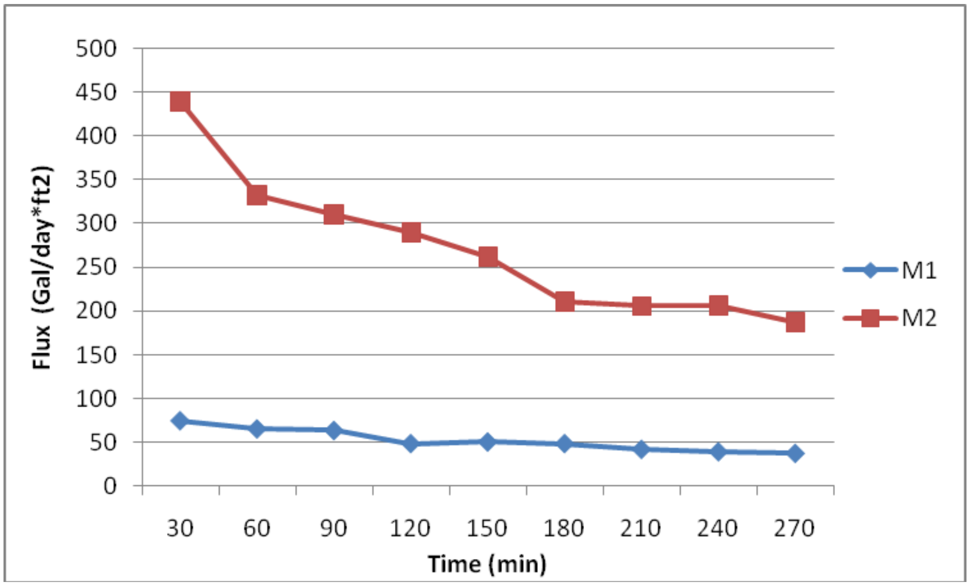

Figure 4.14 Flux of M1 and M2 as a function of time at 206.8 kPa for brilliant blue R.

4.2.3 Solute Rejection and Solvent Flux of M3

M3 membrane was prepared using a higher concentration of both IPD and MPD (Table 3.3).

Table 4.5 Solute rejection and flux as a function of time at 206.8 kPa for M3 membrane

Time (min)	Solute Rejection (100%)	Flux (Gal/day*ft^2)
30	75.13	455.32
60	74.37	327.23
90	78.16	274.88
120	80.34	244.96
150	82.28	229.06
180	84.21	225.32
210	86.97	210.36
240	88.16	205.69
270	88.92	201.95

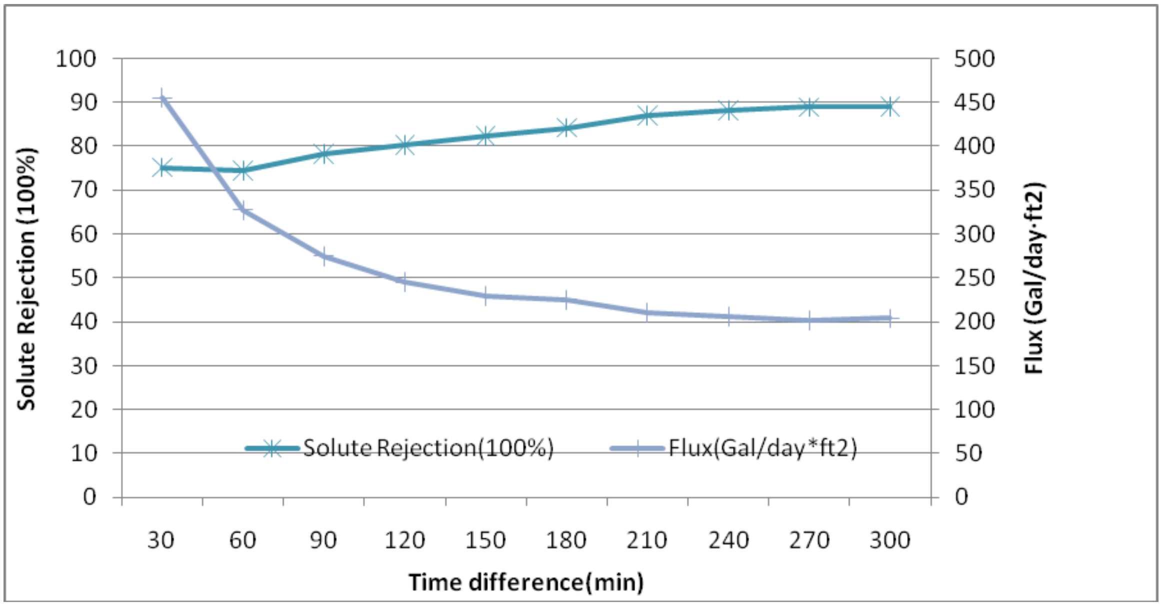

Figure 4.15 Solute rejection and flux as a function of time at 206.8 kPa for M3 membrane for brilliant blue R.

Compared to M2, M3 provided a lower solute rejection and similar high Flux (Figures 4.14 and 4.15). In that case, this study supplied a concentration of IPD as 2.0% w/w and used the corresponding amine concentration.

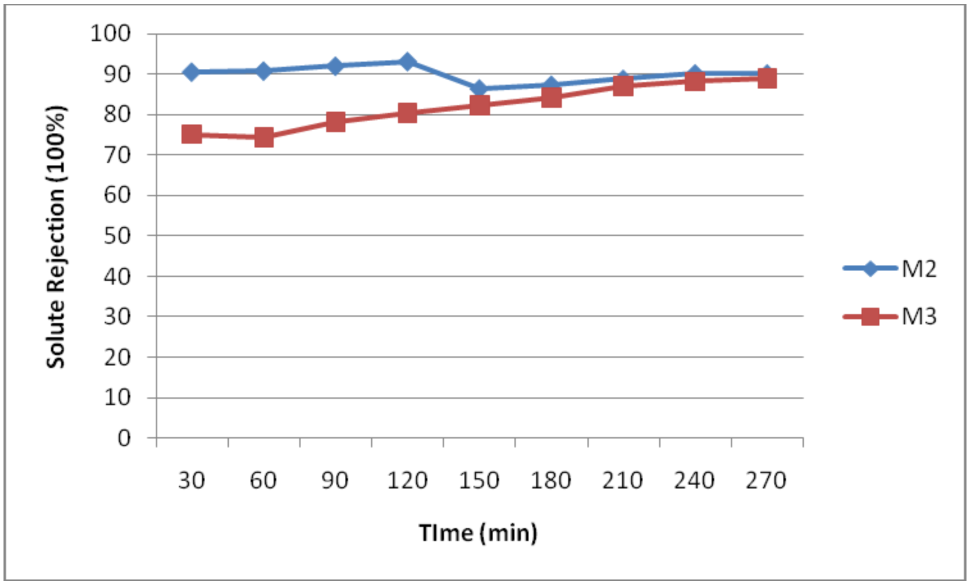

Figure 4.16 Solute rejections of M2 and M3 as a function of time at 206.8 kPa for brilliant blue R.

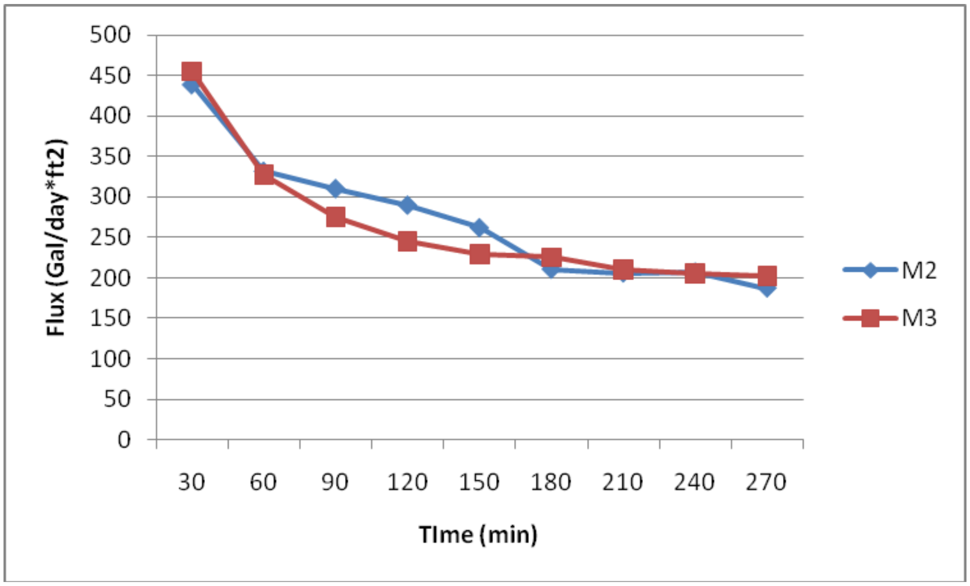

Figure 4.17 Flux of M2 and M3 as a function of time at 206.8 kPa for brilliant blue R.

4.2.4 Solute Rejection and Solvent Flux of M4A, M4B, M4C, M4D Membranes. All data were collected for solute rejection and solvent flux of M4A, M4B, M4C and M4D membranes and are shown in Tables 4.6-4.9. Figures 4.18-4.21 illustrates the solute rejection and solvent flux of all four membranes.

Table 4.6 Solute rejection and flux as a function of time at 206.8 kPa for M4A membrane

Time (min)	Solute Rejection (100%)	Flux (Gal/day*ft^2)
30	99.70	107.52
60	99.72	86.02
90	99.67	81.34
120	99.44	74.80
150	99.53	65.45
180	99.39	60.77
210	99.34	61.71
240	99.32	59.84

Table 4.7 Solute rejection and flux as a function of time at 206.8 kPa for M4B membrane

Time (min)	Solute Rejection (100%)	Flux (Gal/day*ft^2)
30	99.03	138.37
60	99.24	102.84
90	99.70	93.49
120	99.75	91.63
150	99.69	84.15
180	99.71	83.21
210	99.87	84.15

Table 4.8 Solute rejection and flux as a function of time at 206.8 kPa for M4C membrane

Time (min)	Solute Rejection (100%)	Flux (Gal/day*ft^2)
30	99.63	98.17
60	99.87	83.21
90	99.73	74.80
120	99.71	72.93
150	99.57	70.12
180	99.72	67.32
210	99.71	68.25
240	99.66	67.78

Table 4.9 Solute rejection and flux as a function of time at 206.8 kPa for M4D membrane

Time (min)	Solute Rejection (100%)	Flux (Gal/day*ft^2)
30	99.91	98.17
60	99.75	83.21
90	99.28	71.99
120	98.89	62.64
150	98.35	48.62
180	96.16	49.55

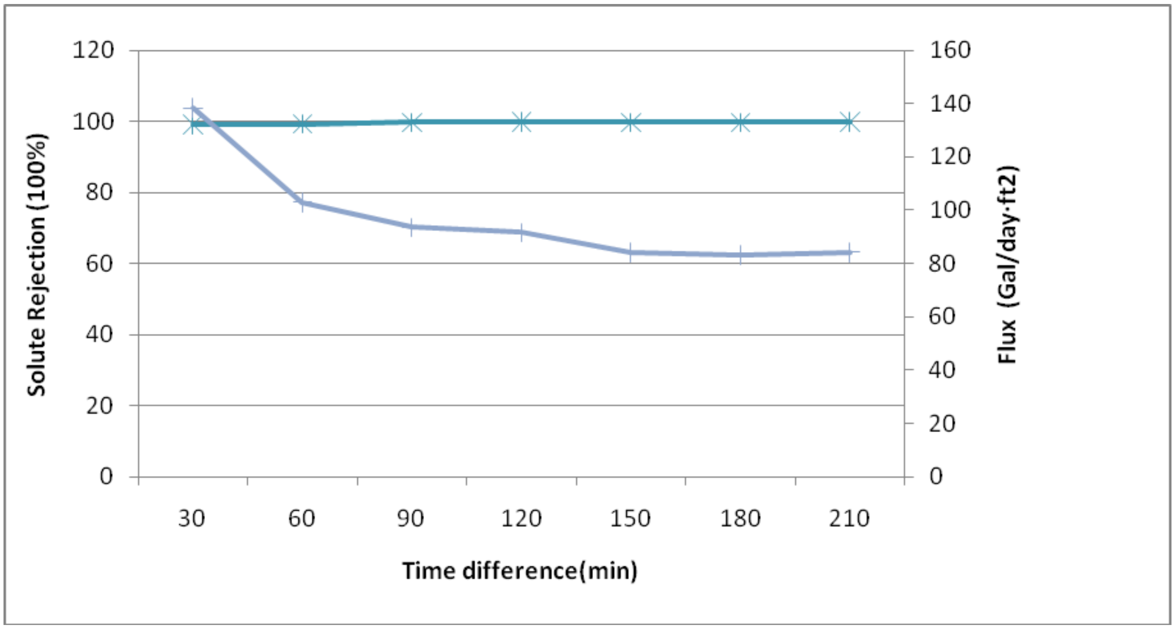

Figure 4.18 Solute rejection and flux as a function of time at 206.8 kPa for M4A membrane for brilliant blue R.

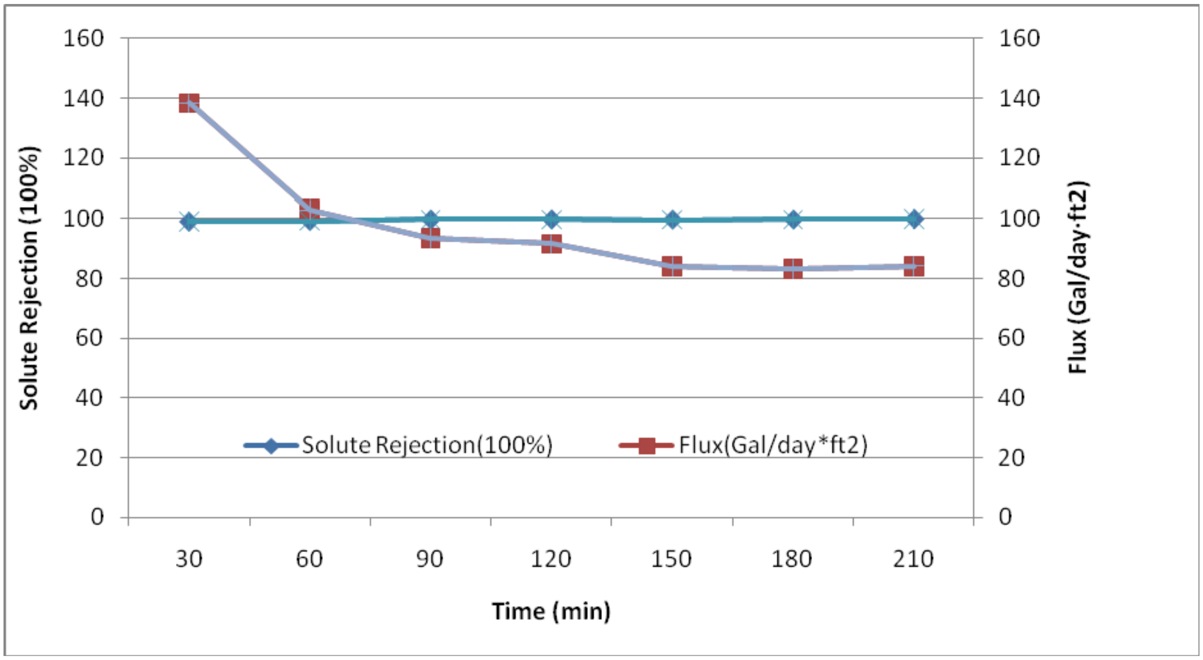

Figure 4.19 Solute rejection and flux as a function of time at 206.8 kPa for M4B membrane for brilliant blue R.

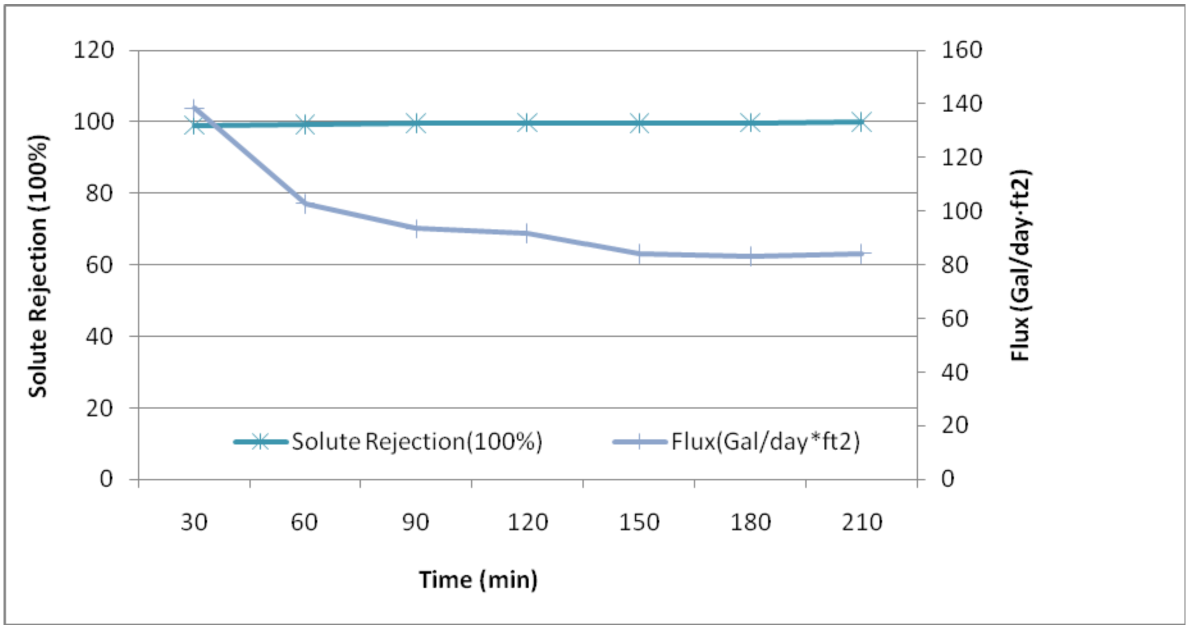

Figure 4.20 Solute rejection and flux as a function of time at 206.8 kPa for M4C membrane for brilliant blue R.

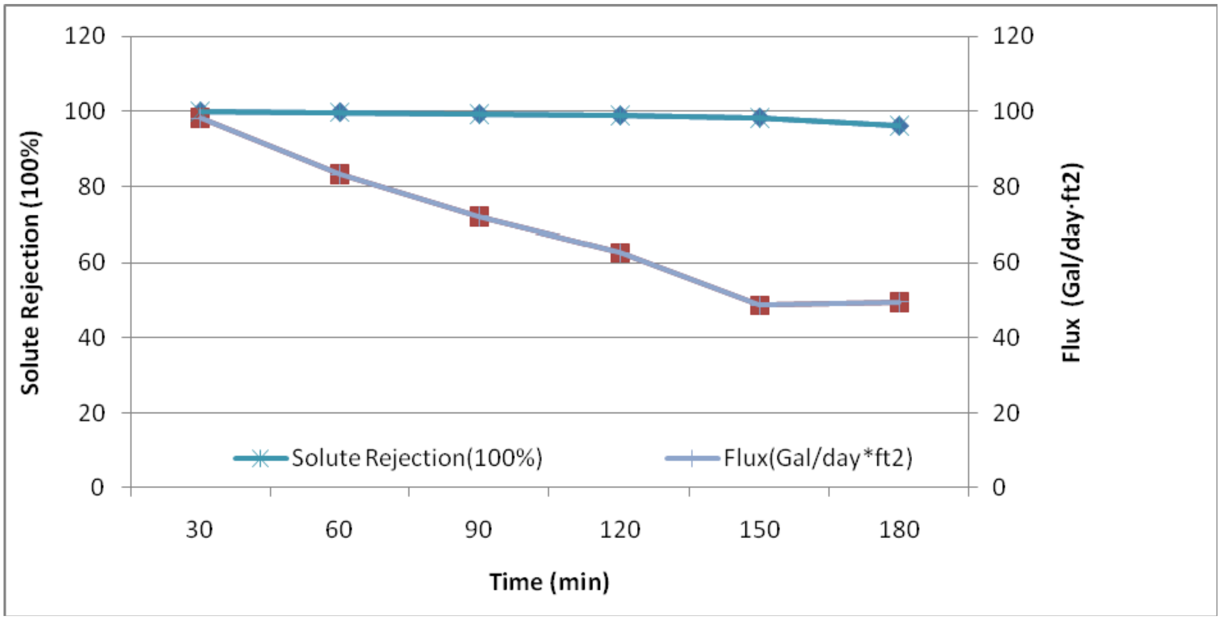

Figure 4.21 Solute rejection and flux as a function of time at 206.8 kPa for M4D membrane for brilliant blue R.

By comparing performances of these four membranes (Figure 4.22 and 4.23), M4B showed a higher solvent flux, similar high solute rejections similar to those from the other three membranes.

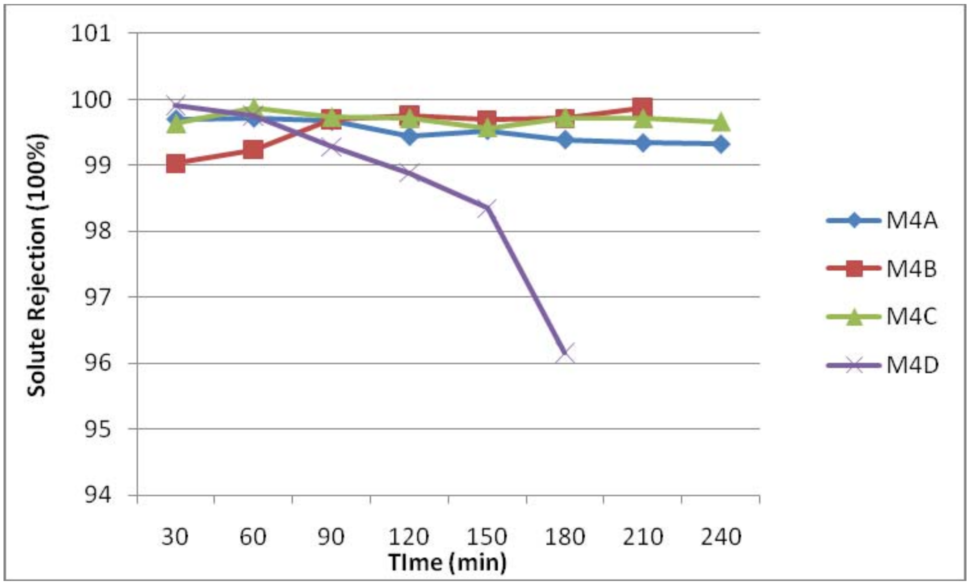

Figure 4.22 Solute rejections of M4A, M4B, M4C and M4D as a function of time at 206.8 kPa for brilliant blue R.

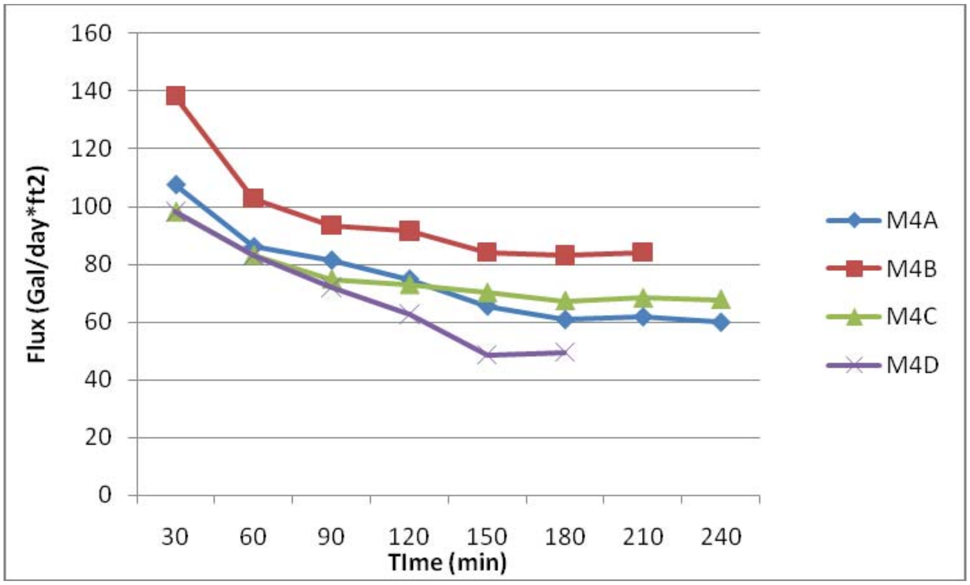

Figure 4.23 Flux of M4A, M4B, M4C and M4D as a function of time at 206.8 kPa for brilliant blue R.

By comparing M4B and M1, we found M4B can provide a much higher (>99%) solute rejection as well as higher Flux than M1 (Figures 4.24 and 4.25). That would be novel modification for TFC NF membrane and the notion of mixing polymeric and monomeric amines was proven as feasible.

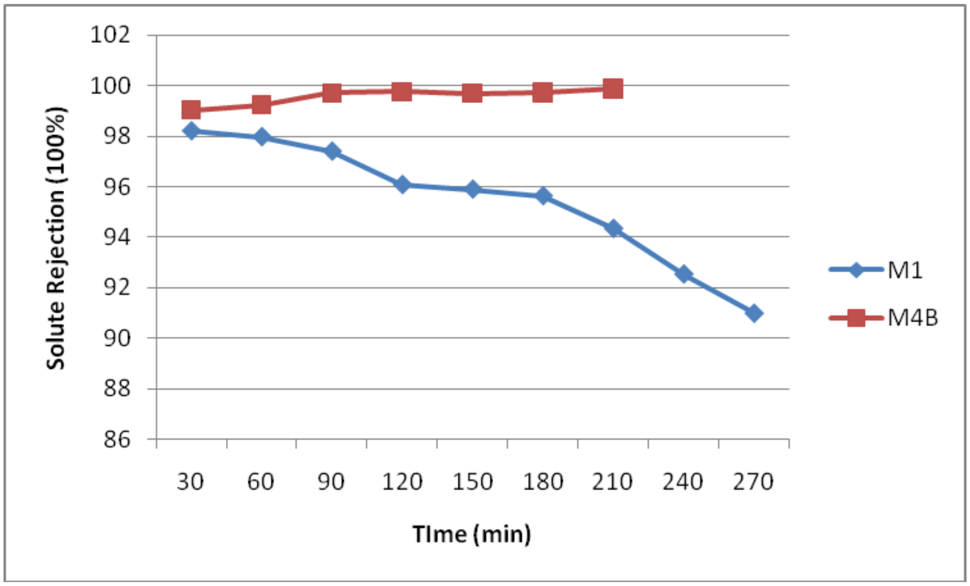

Figure 4.24 Solute rejections of M1 and M4B as a function of time at 206.8 kPa for brilliant blue R.

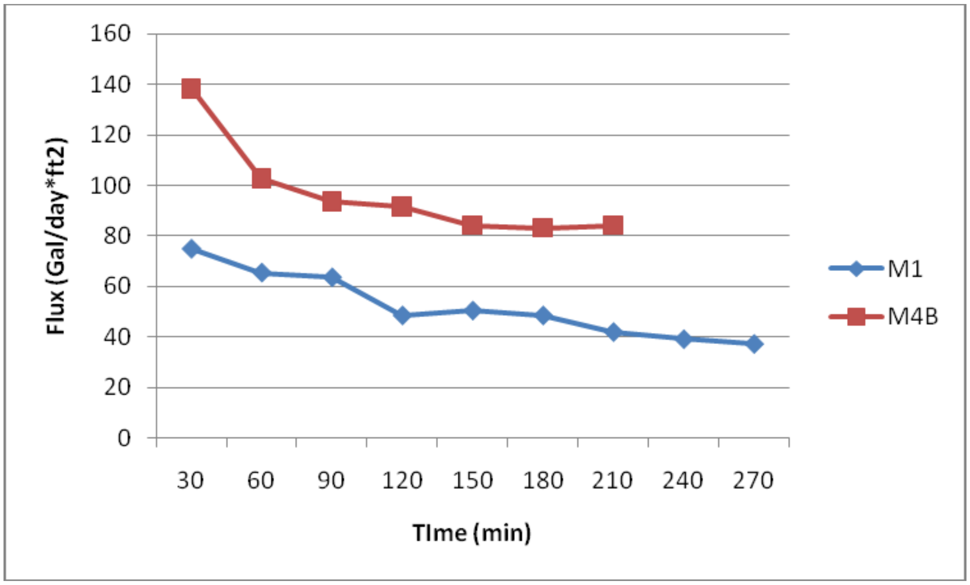

Figure 4.25 Flux of M1 and M4B as a function of time at 206.8 kPa for brilliant blue R.

4.3 Discussion

By conventional investigation, a strong body of evidence has been developed in the field of interfacial polyamide synthesis to indicate that polymer formation takes place in the organic phase. Thus, the diamine diffuses across the water-solvent interface and reacts with the dicloride in the organic phase. e.g. MPD-IPD monomeric system. A smooth polymer film initially forms at the interface. Further polymer formation takes place on the organic solvent side of the deposited film. This latter surface becomes increasingly rough as polymer formation proceeds. The polymer film is normally porous, allowing for the transport of amine reactant and the acid byproducts across the interfacial region (Cadotte, 1981).

However, in the case of polyethylenimine (PEI), the reaction of this polyamide with isophthaloyl dichloride (IPD) at the interface should result in the instantaneous formation of a barrier layer through which further polyamine, because of its high molecular weight, cannot penetrate. Thus, after the initial formation of a continuous film, further reaction must take place not in the organic phase but in the aqueous phase. Because of the low solubility of isophthaloyl dichloride in the aqueous phase, a thin skin develops which only slowly increases in cross-section thereafter. A graded structure is also developed, ranging from complete acylation on the organic solvent side to the barest insolubilization on the aqueous face(Cadotte, 1981).

Actually a layer of unreacted polyethylenimine becomes entrapped between the interfacial polyamide deposit and the microporous reacted polyethylenimine is both dried and insolubilized. The insolubilization takes place mainly by the splitting out of ammonia via post treatment, but also involves oxidation and generation of ketonic groups (Cadotte, 1974; Rozelle, 1977).

The final result is a three-layer structure that consists of a microporous substrate, an intermediate layer of insolubilized polyethylenimine, and a surface barrier layer of dense polyamide material. The intermediate layer serves as transition zone between the polyethursulfone substrate and the polyamide barrier layer, providing additional support to this extremely thin barrier surface. The final composite thus withstands 100 atmospheres pressure without difficulty (Cadotte, 1981).

In contrast to this three-layer structure from PEI-IPD reaction, the TFC membrane from MPD-IPD does not form an intermediate zone between the barrier layer and the polyethursulfone surface, that can explain the poorer performances of membranes from MPD-IPD than that from PEI-IPD. SEM is usually used to investigate the surface properties of TFC membranes.

The combination of MPD and PEI to form the new system with IPD was supposed to form a novel TFC NF membrane which has two layers: one is formed by MPD and IPD in organic phase and one is formed by PEI and IPD in aqueous phase. From experiments in this study, the new method can prepare a membrane with very high solute rejection for brilliant blue R (>99%) and high water flux. It showed better performance than each of the two traditional systems (MPD-IPD and PEI-IPD).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 Conclusions

Thin-film composite nanofiltration membranes can be readily prepared by interfacial polymerization techniques. The performances of newly prepared polyamide TFC NF membranes depend on series of factors, e.g. monomeric or polymeric IP system, monomer concentrations, post-polymerization treatment conditions, etc.

From this study, one optimal post-polymerization treatment was proven that one-hour gap between IP and 110°C high temperature treatment would be the best treatment compared to no time gap and more than 12 hours gap. By following the optimal post-treatment, a list of TFC NF membranes were made. By forming thin film composite in aqueous phase, polymeric system (PEI-IPD) was proven to provide better performances (high solvent flux and high solute rejection) than monomeric system (MPD-IPD), which forms TFC in organic phase. Both brilliant blue R and Safranin O were used as dye solutions with water to detect the performances of newly prepared membranes. Brilliant blue R was continuously used in this study for its proper molecular weight for nanofiltration membrane testing. Meanwhile, an improved calculation method was adopted here and results presented eliminated the impact of changing feed solution volume and concentration.

A key attempt in this study is to combine both polymeric and monomeric systems to react with dichloride during IP process. The performance from MPD-PEI-IPD membrane was apparently better than that of either MPD-IPD or PEI-IPD membrane. It provided a very high solute rejection up to 99.9% and relatively high water flux (80-140)

Gal/day*ft^2). Two thin layers were supposed to be interfacially polymerized in aqueous and organic phase respectively that is why the solute rejection increased.

5.2 Future Work

By now, “the research activities on the improvements of TFC membranes can be generally divided into three main areas, i.e. (1) top active layer improvements by using newly developed monomer and/or innovative nano-scale particles such as titanium oxide and carbon nanotubes, (2) development of thermally and chemically stable supporting membranes, and (3) modification on the conventional IP technique” (Lau, 2011). Based on this study, using the novel IP monomeric/polymeric diamine – dichloride system was proven to be feasible and optimal so far. However, we still need to pursue additional avenues, e.g. the investigation of the membrane structure and surface properties by Scanning electron microscope (SEM) would help to understand the results of reactions in either aqueous or organic phase.

Moreover, additional investigation of different ratio of MPD/PEI could be meaningful to get the best way to combine monomeric and polymeric diamines in aqueous solution which leads to one MPD-PEI-IPD TFC NF membrane with the best performance. Especially the ratios close to 50%: 50% (MPD : IPD) may lead to even new better results for membrane performance.

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