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Effects of interfacial polymerization conditions on performance of polyamide reverse osmosis membranes and optimization of polymerization conditions by statistical methodology

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ABSTRACT

Effect of fabrication parameters on the performance of polyamide reverse osmosis membrane was systematically investigated and the design of experiment (DOE) method was used as a tool for assessing the degree of contribution of individual parameters on the resultant membrane performance; this was in order to determine the optimized combination of the various parameters. The parametric studies for fabrication included reaction time, temperature of monomer containing solutions, type of organic solvents and monomer concentration. Reaction time controlled the amount of *m*-phenylenediamine (MPD) diffusing into organic solvents, and the temperature of MPD solution determined the hydrolysis rate of trimesoyl chloride (TMC) taking place exclusively in aqueous phase. Seven organic solvents were investigated to generate various diffusion rate of MPD monomers into the organic solvents, and the thin-film composite (TFC) membranes prepared from higher diffusion rate of MPD into organic solvents showed dense and thinner polyamide layers. Concentration of TMC in organic phase and MPD in aqueous phase showed the effects on the amount of TMC available on the reaction zone and the degree of MPD diffusing across the interface, respectively. Optimum combination of MPD, TMC and aqueous additive concentrations was established with the DOE method for TFC polyamide reverse osmosis (RO) membrane. The reliability of optimum settings for RO membrane preparation condition was verified by confirmation experiments. This study showed that various combinations of monomer concentration for fabrication of RO membranes with tailor-made performance could be provided from DOE and response surface methodology analysis.

Keywords: Polyamide; Reverse osmosis membrane; Interfacial polymerization; Design of experiment

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1. Introduction

Reverse osmosis (RO) is a demineralization process adopting permselective membrane to separate the dissolved solids from aqueous solution. RO membrane process has been regarded as the most economically feasible separation technology for the both desalination of seawater and purification of surface water contaminated with pesticides, heavy metals and other emerging micropollutants. Furthermore, RO process can also be used for recycling wastewater and reclaiming highly valuable resources from the various industrial waste streams along with food and beverage processing. In this regard, one of the most successfully commercialized RO membranes is the polyamide-based membrane, and is prepared by interfacial polymerization between diamine in aqueous solution and acyl halide in organic solvent. The polyamide RO membrane

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usually is comprised of three structural components: polyester nonwoven fabric, polysulfone support and polyamide thin film layer. The polyester nonwoven fabric occupies almost the entire thickness of the polyamide thin-film composite (TFC) RO membrane and provides the membrane with the required mechanical strength to sustain high operating pressures. The highly porous polysulfone support layer also provides the required mechanical strength as a support of the active layer and the top thin polyamide layer, at approximately 0.1–0.2 μm thickness, acts as a permselective barrier which determines the entire TFC RO membrane performance with regard to permeate flux and salt rejection [1–19]. Composite membranes have advantages over single-material-based asymmetric membranes, because the upmost permselective polyamide layer is prepared in situ interfacial polymerization method. Therefore, the chemical characteristics and structural features of the top selective layer and the bottom substrate can be independently optimized to attain maximized performance of the entire composite membrane. Up until now, numerous attempts have been devoted to enhance the properties of composite membrane through varying the parameters involved in membrane preparation process, including kinetics of the polymerization reaction, diffusion coefficient of monomers, reaction time, curing time and structural characteristics of support layer. The research for optimization of TFC RO membranes can be generally divided into three main categories of: (1) polyamide layer modifications by adopting newly developed monomers or inclusion of innovative nanoparticles, (2) functionalized TFC membranes with enhanced fouling resistance, chemical stability and chlorine tolerance and (3) modification of the conventional interfacial polymerization processes for specialized membrane performance [20–25].

Few studies have been conducted including both interfacial polymerization condition and corresponding optimization study adopting a statistical experiment design method. The objective of this study was to evaluate the feasibility of statistical experiment design method in predicting the resultant membrane performance and setting up the monomer concentration for specified polyamide RO membrane performance. The research reported here intended to discuss the effect of interfacial polymerization reaction conditions on the performance of polyamide RO membranes. In the first part of the research, parametric studies including modifying reaction time, temperature of the monomer containing solution, types of organic solvents used and monomer concentration were performed. In addition, an aqueous additive for interfacial polymerization was not adopted in parametric studies to verify the effect of considering factors on membrane performance more exclusively. In the second part of the study, optimum combination of *m*-phenylenediamine (MPD), trimesoyl chloride (TMC) and aqueous additive concentration was established with design of experiment (DOE) method for TFC polyamide RO membrane [26,27]. Both permeate flux and salt removal rate of the RO membranes prepared from preliminary parametric studies were relatively lower than the minimum target value. Therefore, aqueous additive was introduced in the DOE study to obtain acceptable membrane performance. In this study, structured experimental design based on the DOE method was utilized in order to achieve tailor-made performance of TFC RO membrane. The predicted membrane performance, including various concentration combinations of interfacial polymerization reactants, was expressed as a contour shape. The reliability of settings established by the DOE method was verified through confirmation experiments to evaluate the consistency of the predictions [28–31].

2. Materials and methods

2.1. Chemicals and reagents

Polysulfone support was prepared by phase inversion method using polysulfone beads with molecular weight of 35,000 Da (Solvay Advanced Polymers, L.L.C., USA) and *N,N*-dimethylformamide (DMF; Acros Organics, USA). Chemicals used in polyamide skin layer formation included MPD (Sigma-Aldrich, USA) and di(ethylene glycol) monomethyl ether (DEGME; Daejung, Korea) dissolved in deionized water and TMC (Sigma-Aldrich, USA) in seven different types of organic solvents. The variance of organic solvents was selected in order to generate wide variations of MPD solubility and diffusivity into the organic phase. *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, cyclohexane were obtained from Fisher Scientific (USA), and isoparaffin (Isol-C) were purchased from SK Chemical Inc. (Korea).

2.2. Preparation of microporous polysulfone support and thin-film composite RO membranes

The polysulfone support was prepared by dissolving 18 wt% of polysulfone in DMF aprotic solvent. The polymer solution was stirred with a heating magnetic stirrer until the polysulfone polymer beads were completely dissolved. The polymer solution was then cast on nonwoven polyester fabrics with a thickness of 100 μm using a comma knife. Polysulfone support casting was conducted in a constant temperature and humidity chamber which maintained a temperature of 24°C–26°C and relative humidity of 50%–60%. The cast polymer film was then immersed into coagulation water bath for at least 24 h until residual solvent and water-soluble low molecular weight polymer were thoroughly removed. In particular, all of the polysulfone support membranes used in this study were prepared continuously at the same time by utilizing a lab-scale casting machine in order to minimize the experimental error due to the change of the support membrane characteristics. Then, the polysulfone support layer on the polyester fabric was dipped into an aqueous solution, which contained MPD monomer and additive for a predetermined time. The MPD solution-soaked polysulfone support was squeezed by soft rubber roller to extract excessive aqueous MPD solution from the support membrane surface. The membrane was then immersed into water immiscible organic solution containing TMC for predetermined time, which led to polyamide thin film layer formation on the surface of the polysulfone support. After interfacial polymerization reaction, the membrane was dried in air at ambient conditions for 1.5 min and stored in deionized water until use.

2.3. Characterization of amine monomer and organic solvent

The diffusion of MPD monomer into organic solvents was relatively evaluated with the slope of MPD absorbance in seven different types of organic solvents as a function of time. A 100 mL of pure organic solvent was added in a beaker filled with 2 wt% MPD solution in distilled water. After addition of organic solvent into aqueous MPD solution, the organic solvent was recirculated from the beaker to UV–Vis spectrometer (HP8453, Hewlett Packard, USA) by sipper system (equipped with a peristaltic pump). The absorbance of MPD diffusing from bottom aqueous solution into upper organic solvent was monitored with absorbance at 290 nm wave number according to elapsed time (Fig. 1). This gave an understanding about the relative diffusion rates of MPD in seven types of organic solvents. Surface tension (gas phase/liquid phase) of each organic solvent was measured using a tensiometer (K100, Kruss, DE), equipped with Wilhelmy plate.

2.4. Membrane performance evaluation and characterization

The performance of the polyamide membrane prepared by various formation conditions was investigated with a laboratory crossflow filtration system (Fig. 2). Rectangular membrane samples with nominal dimensions of 7 cm ´ 4 cm were placed in flat sheet membrane test cells. Feed solution, 2,000 ppm NaCl solution that had a temperature of 25°C and pH 7, was pumped out of feed tank and pressurized at 1.5 MPa by a high-pressure pump. Membrane performance was evaluated by measuring two representative parameters: permeate flux and salt rejection. Flux is described as the total volume of permeate water pass through the membrane per unit area and given time. The flux unit was gallon/ft^2/d (gfd). Salt rejection is the difference of salt concentration between feed and permeate. Salt rejection value is a dimensionless parameter expressed as a percentage of permeate solution, and varies from 100% (complete rejection of the solute) to 0% (complete passage of solute through the membranes). The water flux was evaluated by measuring the weight of permeate water directly, and solute rejection was measured by conductivity (Conductivity162A, Orion Research Inc., USA) of feed and permeate. The membrane performance data shown in the figures are an average of six membrane coupons prepared under the same formation condition. Attenuated total reflection-fourier transform infrared (spectroscopy) (Nicolet 6700, Thermo Scientific, Waltham, MA, USA) spectrometer was used to evaluate the ratio of amide peak intensity (1,540 cm^{-1}) to aromatic ring band intensity (1,588 cm^{-1}). The prepared membrane with varying organic solvent types were thoroughly rinsed after polymerization reaction and then dried in a drying oven for 2 d at 50°C. The prepared membrane samples were then placed on the ATR Ge crystal at an incident angle of 45° and pressed. N_2 gas was used to purge the spectrometer to prevent any interference of moisture and atmospheric CO_2. X-ray photoelectron spectroscopy (XPS; Sigma Probe, Thermo VG Scientific Ltd., UK) was adopted to estimate the atomic percent and ratios of carbon, oxygen and nitrogen of the membranes prepared from different organic solvent types [8,9].

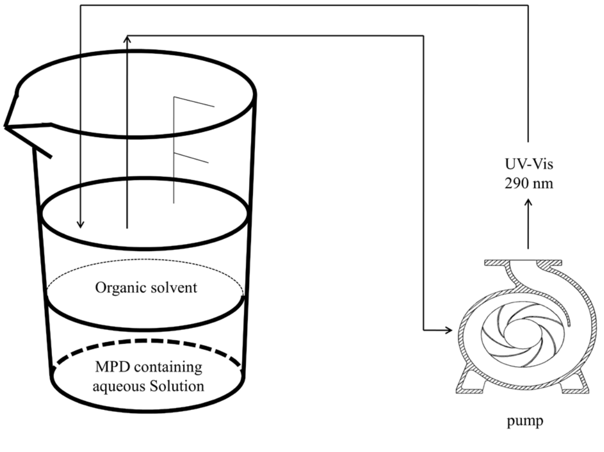


Fig. 1. Scheme of measuring diffusivity of MPD in organic solvents with interfacial polymerization at 2 wt% MPD in aqueous solution.

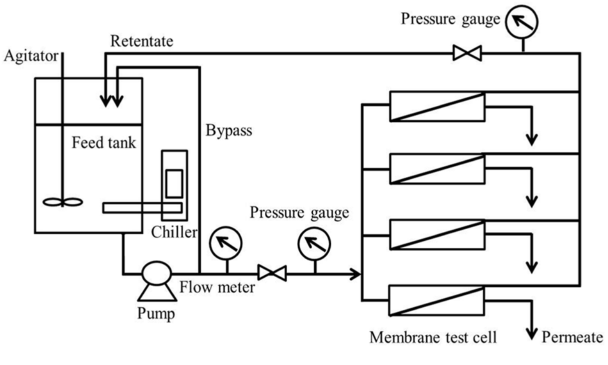


Fig. 2. Schematic of flat sheet reverse osmosis crossflow filtration system.

3. Results and discussion

3.1. Effect of preparation conditions on the performance of TFC polyamide RO membrane

TFC polyamide RO membranes were prepared in situ on the porous polysulfone substrate by an interfacial polymerization reaction between the MPD in deionized water and the TMC in organic solvent. Membrane performance is, in general, governed by the chemical property and physical characteristics of the active layer. Chemical nature is an intrinsic characteristic of the selective thin polymer layer; otherwise, the physical characteristics are determined by preparation conditions during the skin layer formation. When two immiscible monomer solutions (MPD in water and TMC in organic solvent) are in contact with each other, both monomers moves toward the liquid–liquid interface to partition across the interface and react with each other to form a polymer at the interface. However, the interfacial polymerization has been reported to occur dominantly in the organic phase because solubility of the TMC monomer in water is relatively low compared with the counterpart case [1–5,13–15]. Thus, when preparing the polyamide active skin layer, considerably larger amount of MPD compared with that of TMC was used to promote the MPD diffusion into the organic phase [32]. In this study, 2 wt% MPD in aqueous solution and 0.1 wt% TMC in organic solvent were selected for the preparation of TFC RO membrane to estimate the effect of other factors including reaction temperature, reaction time and organic solvent type on membrane performance.

3.1.1. Effect of reaction time on membrane performance

TFC membranes were prepared with 2 wt% MPD in aqueous solution and 0.1 wt% TMC in Isol-C organic solution at various interfacial reaction times, and the influence of polymerization reaction time on the resultant membrane performance is shown in Fig. 3. With increasing reaction time from 30 to 180 s, water flux of the membranes monotonically decreased from 27 to 23 gfd. On the other hand, the salt rejection quickly increased from 91% to 98% within 60 s and then nearly leveled off at 99%. The diffusion of MPD monomer into organic phase is known to be governing factor in interfacial polymerization reaction. At an initial stage of reaction (30 s), the amount of MPD which diffused through the water–organic interface was limited to form a thin and lose polyamide layer, causing high permeation of water and salts. Increasing reaction time to 60 s had more MPD diffuse to crosslink with TMC and subsequently made the polyamide active layer crosslinked and thicker, resulting in declined permeate flux and increased salt rejection rate. However, when the reaction time further increased to a certain value, the crosslinked and thick layer prevented the diffusion of diamine monomer through the interface, and thus, polymerization reaction became very slow [33,34]. In this study, 90 s was selected as an optimal condition for reaction time as it exhibited proper permeate flux with relatively high salt rejection.

3.1.2. Effect of reaction temperature of aqueous and organic solution

The temperature of aqueous or organic solution was varied at the interfacial reaction, and their effects on the resultant membrane performance were evaluated. Fig. 4 shows permeate water flux and salt removal rate of the TFC membranes fabricated at various temperatures for both monomer containing solutions. When estimating the effect of each solution temperature, the counterpart solution temperature was fixed at 25°C. Interfacial polymerization reaction time was maintained as 90 s, and the other preparation parameters were the same as in section 3.1.1. When MPD aqueous solution temperature increased from 5°C to 25°C, there was slight decline of salt rejection. However, further increasing temperature to 35°C dropped the salt rejection from 98% to 94%. Raising the solution temperature might not only increase polymer forming reaction but also accelerate the hydrolysis reaction. The hydrolysis of TMC due to the increased temperature of MPD aqueous solution led to less crosslinking and formed a relatively loose polyamide film, consequently, both permeate water flux and salt passage increased. It is well known that the TMC hydrolysis is induced by water, and it can be accelerated in the presence of hydroxyl ion [11]. The hydrolysis of the acyl chloride of TMC to acetate occurs when the TMC contacts with water (H_2O). The activity of H_2O and equilibrium constant for the reaction in which liquid H_2O dissociate to H^+ and OH^- increase significantly with increasing temperature (0.293×10^{-14} at 10°C, but 1.008×10^{-14} at 25°C) [35]. Furthermore, the temperature increase of aqueous solution causes the enhanced diffusion of H_2O to organic TMC solution, causing more hydrolysis of the acyl chloride. In Fig. 4(a), both water flux and salt passage increased monotonically with increasing temperature of aqueous solution, which imply the less crosslinking of resultant polyamide films. On the other hand, the temperature of TMC organic solution caused less effect on the rejection of the resulting membranes because acid chloride hydrolysis occurs exclusively in the aqueous phase. With increasing temperature of the TMC solution, density/surface tension/viscosity of organic solvent decreased, promoting MPD diffusion into organic phase [15]. Higher MPD diffusivity is

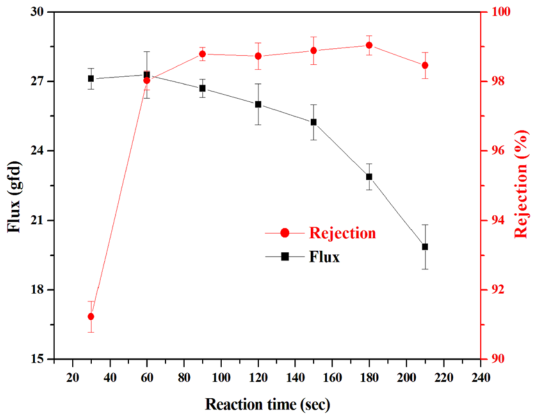
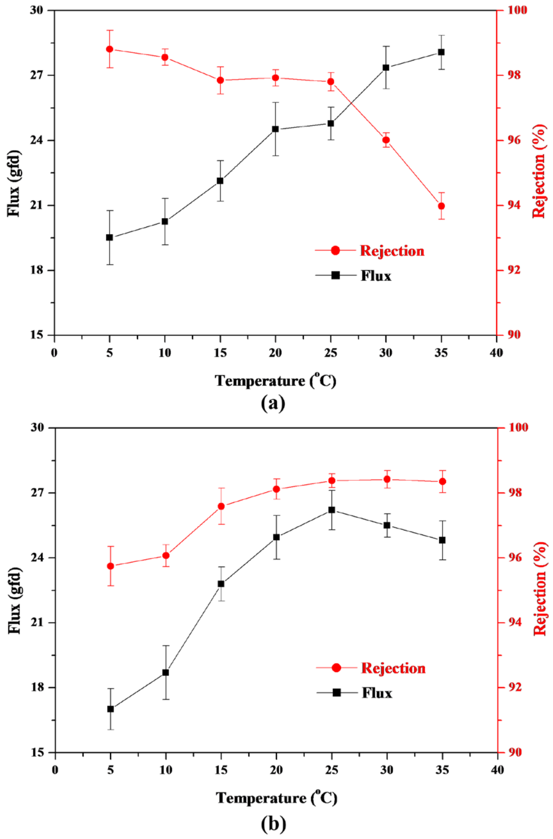


Fig. 3. Effect of interfacial reaction time on membrane performance.



(a)

(b)

Fig. 4. Effect of: (a) MPD and (b) TMC solution temperature on membrane performance.

known to produce more crosslinked and thinner polyamide active films [29,30]. At low temperatures below 25°C, relatively loose and thicker polyamide films formed with deteriorated membrane performance accompanied by lower water flux and high salt passage. Further increase of TMC solution temperature up to 35°C caused slight flux reduction with almost maintained salt rejection. Similar to organic solvent type test results, organic solvent temperature will affect MPD diffusion into organic phase. As the organic solvent temperature increases, the surface tension will decrease, and as a result, the diffusion of MPD will continue to increase. Up to 25°C, MPD diffusion increase leads to an appropriate ratio of amine and acyl halide in the reaction zone to form a thinner and more dense polyamide structure which exhibits both higher water flux and salt rejection. However, further diffusion increases the thickness of the polyamide layer which might cause marginal flux decline above 25°C TMC solution temperature. Excessive polyamide crosslinking at high TMC solution temperature probably prevented water passage through the membrane and the subsequent decline of flux with constant salt rejection. Considering the reasonable salt removal rate and permeate water flux, 25°C was chosen as the optimum value for both solutions.

3.1.3. Effect of organic solvent type

The choice of organic solvent is one of the most influencing parameters in the interfacial polymerization process, since the organic solvent immiscible with aqueous solution phase can affect the diffusion of the reacting monomers and consequently establish the physical properties of the resultant polyamide active skin layer [11,36]. Kim et al. [37] demonstrated that using Isol-C as an organic solvent produced RO membrane with smaller pore size and improved rejection. Additionally, Ghosh et al. [36] also showed that high flux membranes with superior salt rejection were obtained by selecting organic solvents with high surface tension and lower viscosity. Seven organic solvents were investigated to generate various diffusion rate of MPD monomers into the organic solvents. Relative diffusion of MPD into organic solvents was evaluated using absorbance change per unit time (Fig. 5). The performance of the membranes prepared by using various solvents is shown in Table 1. Diffusion of MPD into various organic solvents decreased in the following order: *n*-hexane > *n*-heptane > Isol-C ≅ *n*-octane > *n*-nonane ≅ *n*-decane > cyclohexane. Water flux of the prepared membrane was ascertained from highest to lowest in accordance with following gradations: Isol-C > *n*-octane ≅ *n*-hexane ≅ *n*-heptane > *n*-nonane > *n*-decane > cyc1ohexane, whereas salt rejection decreased in order of *n*-hexane > *n*-heptane > Isol-C ≅ *n*-octane > *n*-nonane ≅ *n*-decane ≅ cyc1ohexane. Diffusion and salt rejections showed good correlation with each other. The ratio of amide peak intensity (1,540 cm^{-1}) to aromatic ring band intensity (1,588 cm^{-1}) in the FTIR analysis is shown in Table 1, indicating that the TFC membranes prepared from higher diffusion of MPD to organic solvents caused thinner polyamide active layers. The higher MPD diffusion led to the formation of more dense (more crosslinked) and thinner polyamide film layer at the polymerization which could exhibit both higher rejection rate and permeate water flux. Furthermore, it is interesting to note that the diffusion of MPD to organic solvent was inversely proportional to the surface tension of the organic solvents. More intensive investigation on the crosslinking density of the polyamide layer prepared by adopting various types of organic solvent was also carried

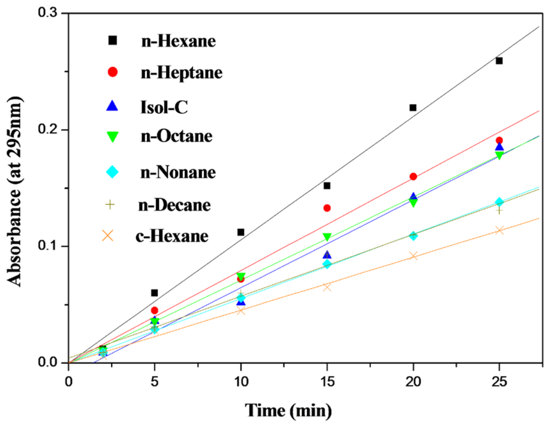


Fig. 5. Diffusivity of MPD into organic solvents with interfacial to 2 wt% MPD aqueous solution.

Table 1
Effect of MPD diffusion on the performance of RO membrane (MPD = 2.0 wt%, TMC = 0.1 wt%, aqueous phase and organic phase temperature = 25°C)

Organic solvent	Absorbance change rate caused by the diffusion of MPD into organic solvents (min^{-1})	Surface tension of organic solvent (mN/m)	IR absorbance ratio of TFC RO membrane (1,540 cm^{-1}/1,586 cm^{-1})	Performance[a]	
				Flux (gfd)	Rejection (%)
n-Hexane	0.0106	17.23	0.78	29.3	98.5
n-Heptane	0.0079	19.28	0.78	29.8	98.3
Isol-C	0.0075	18.44	0.87	32.3	98.0
n-Octane	0.0071	21.49	0.88	30.8	98.0
n-Nonane	0.0055	21.8	1.09	23.1	97.5
n-Decane	0.0053	22.75	1.19	20.6	97.2
Cyclohexane	0.0045	24.51	2.10	16.8	97.9

[a] 0.2 wt% NaCl aqueous solution at 1.5 MPa, 25°C and pH 7.0.

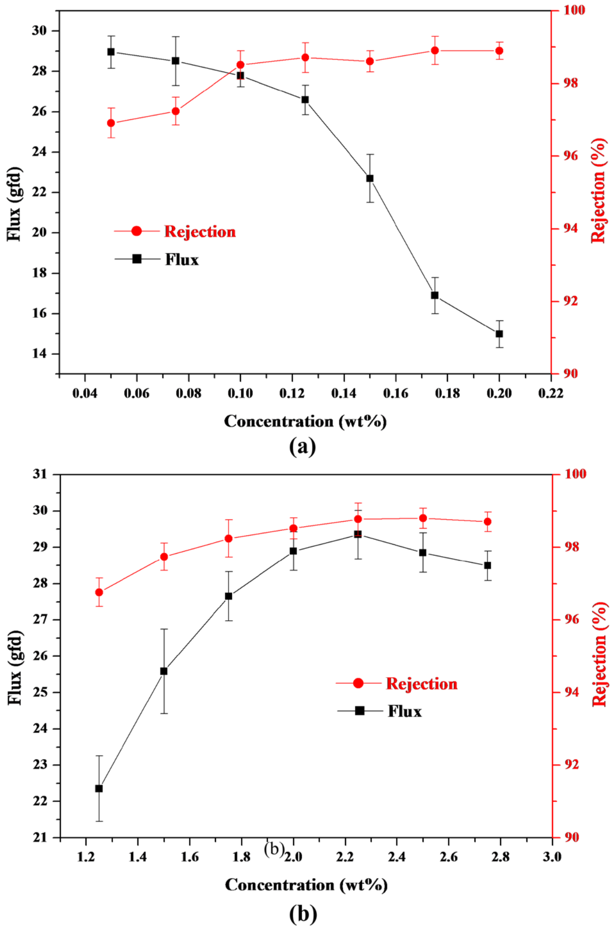
out by using XPS. The elemental compositions and oxygen to nitrogen (O/N) ratios of four RO membranes are shown in Table 2. Based on the chemical structure of polyamide layer prepared from MPD and TMC, the theoretical O/N ratio of fully crosslinked polyamide is 1.0, and the O/N ratio becomes to 2.0 for totally linear polyamide with no crosslinking [8,9]. As can be seen in Table 2, the crosslinking density expressed as O/N ratio increased along with the decrease of organic solvent surface tension, and this trend was also comparable with the relation between MPD diffusivity and FTIR absorbance ratio described in Table 1.

3.1.4. Effect of monomer concentration

Concentration of reactants for the preparation of TFC polyamide RO membrane is one of major preparation conditions which determine the resultant membrane's properties [3–5,7,38]. In this section, the influence of concentration variation of the MPD and TMC was estimated, and the optimum ratio of two reacting monomers was determined based on the performance of the fabricated membranes. Fig. 6(a) exhibits the performance of the RO membranes prepared using various concentrations of TMC and fixed 2.0 wt% MPD concentration, with all the other variables kept constant. With increasing the concentration of TMC from 0.05 to 0.2 wt%, the salt removal rate increased from 97% to 98.8% but the flux decreased from 29 to 15 gfd. When limited amount of TMC monomer was available at the interfacial reaction zone, the prepared active layer became loose and thin, indicating high flux and low salt rejection. With increasing TMC concentration, the active polyamide layer became denser and thicker, resulting in low permeate flux and high salt rejection. Fig. 6(b) describes the membrane performance prepared by adopting various concentrations of MPD monomer with fixed TMC concentration of 0.1 wt%. Both salt removal rate and permeate water flux increased with increasing MPD concentration from 1.25 to 2.25 wt%, and then the salt rejection remained almost constant but the permeate water flux gradually declined. It seems that the controlled diffusion of MPD monomers into organic phase was the primary reason for the performance trend as was the case shown for changes in TMC solution temperature on performance (Fig. 4(b)). Higher concentration of MPD might enhance the amount of MPD diffusing into organic solvent, showing a similar effect to the enhanced diffusion at the high TMC solution temperature. At lower MPD concentration, less dense (lower degree of crosslinking) and bulky polyamide film formed which could hinder water passage and promote salt passage. Further increment of MPD monomer concentration up to about 2.25 wt% enabled the formation of more dense and compact polyamide film during the reaction. The change from bulky polyamide to relatively compact structure could provide less of the flow hindrance effect (water flux was enhanced and salt passage was decreased). However, further increase of MPD concentration beyond 2.25 wt% deteriorated the water flux due to the excessive polymer crosslinking followed by decline of water flux with constant salt rejection. The reason of different membrane performance alteration trend between the MPD concentration and that of TMC is known to result from the fact that the diffusion of TMC is limited up to the interface between two immiscible solvents, due to its extremely low solubility in aqueous phase. On the other hand, MPD contains almost unrestricted diffusivity into the organic phase until reaching the partition equilibrium, although the MPD concentration in equilibrium is still below the TMC concentration in the bulk phase [11,39]. From the above results, we can confirm that the highest performance of the TFC membrane can be obtained at an MPD to TMC ratio about 20–22.

Table 2
Elemental compositions and relative ratios of the RO membranes prepared with varying the types of organic solvents

Sample	XPS surface elemental analysis			Relative ratio
	C (%)	O (%)	N (%)	O/N
n-Hexane	75.2	13.4	11.4	1.18
Isol-C	75.5	13.5	11.0	1.22
n-Nonane	75.3	13.8	10.9	1.27
Cyclohexane	74.3	14.9	10.8	1.38
Fully crosslinked	75.0	12.5	12.5	1.0
Fully linear	71.4	19.1	9.5	2.0



(a)

(b)

Fig. 6. Effect of: (a) TMC and (b) MPD concentrations on membrane performance.

3.2. Optimization of the TFC membrane preparation using DOE methodology

The DOE method was used as a tool to assess the degree of contribution of individual factors to the resultant membrane performance, and to determine the optimized combination of several factors. In this study, three variables and controllable factors were considered in preparation of the polyamide RO membrane. Concentrations of MPD, TMC and DEGME as additive made up the three factors. DEGME, a surfactant, was used as an additive for polyamide RO membrane preparation [40,41]. The additive was introduced in DOE study to generate more rough surface structure and thus provide enhanced membrane performance because of the marginally deficient performance of membranes prepared without additives at the preliminary parametric studies. The designs utilized standard arrays and the three factors were set as five experimental levels to estimate the effects on membrane performance. In total, 20 cases of experimental fabrication conditions were tested with varying the MPD, TMC and DEGME concentrations. Performance of polyamide membranes prepared from the 20 experimental conditions is listed in Table 3. Reliability of this DOE study was evaluated by the analysis of variance (ANOVA), and the membrane performance from experiments with the MPD, TMC and DEGME variables and their optimum combination was determined by response surface methodology (RSM).

3.2.1. Analysis of variance and determination of the optimum membrane preparation condition by RSM

The quantitative estimation of the influence of each factor was conducted by the ANOVA (Table 4). *p* Value is the portion of the total variance observed in the experiments ascribed by individual influencing factors and expressed as function of the sum of squares for each significant item

Table 4
Analysis of variance (ANOVA) table for predicting the performance of the membrane with varying monomer concentration compositions

Source	DF	SS	MS	*F*	*p*
Analysis of variance for flux					
Regression	9	319.043	35.449	8.26	0.001
Linear	3	229.829	76.610	17.85	0.000
Square	3	72.501	24.167	5.63	0.016
Analysis of variance for rejection					
Regression	9	0.601	0.068	7.52	0.002
Linear	3	0.422	0.141	15.81	0.000
Square	3	0.135	0.049	5.05	0.022

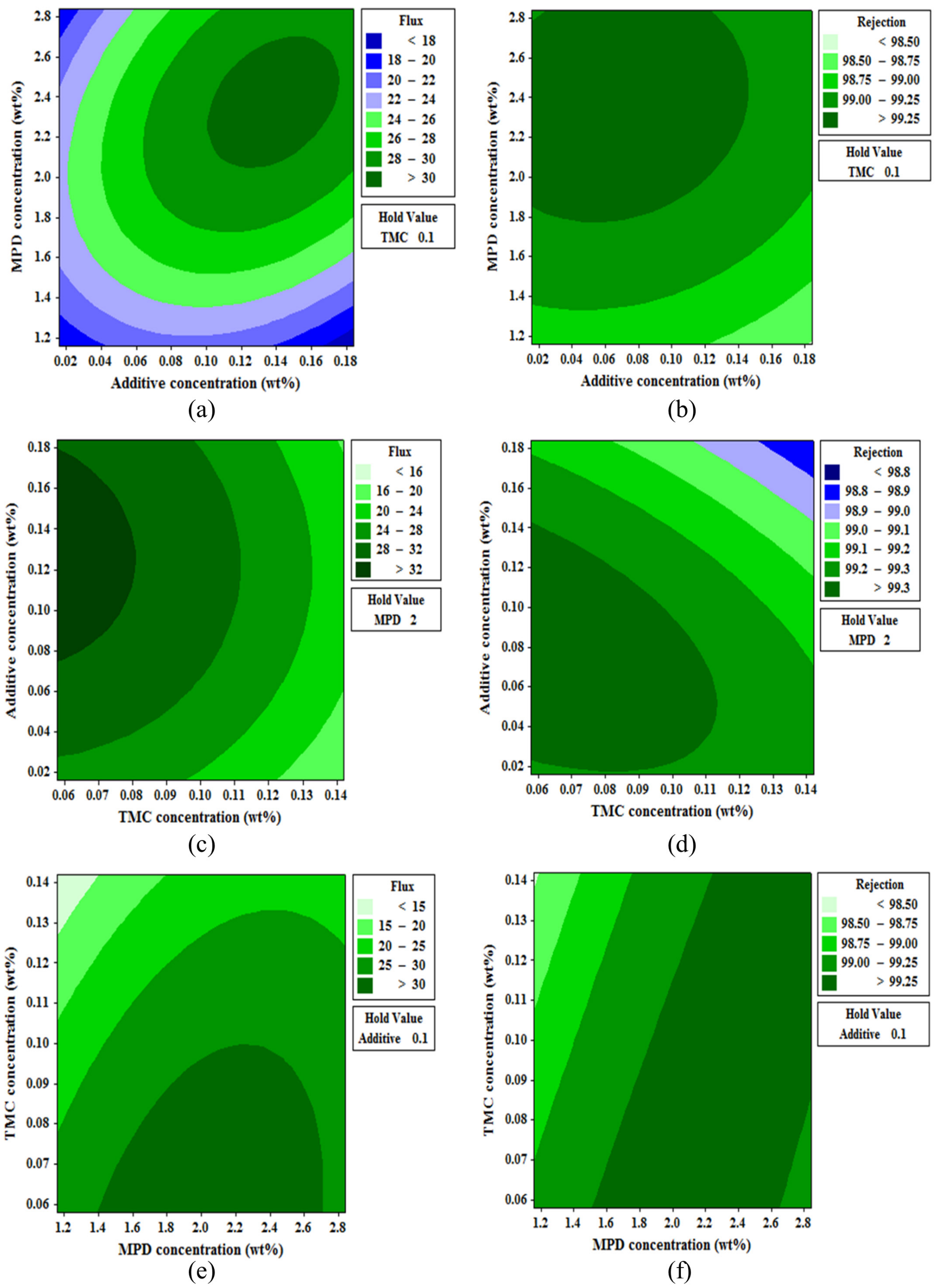
Note: DF – Degrees of freedom; SS – Sum of square; and MS – Mean square.

Table 3
Optimal design arrangements and responses for the resultant membrane performance

Experiment number	Factors			Response[a]	
	MPD (wt%)	DEGME (wt%)	TMC (wt%)	Flux (gfd)	Rejection (%)
N1	1.500	0.050	0.075	26.1	99.26
N2	2.500	0.050	0.075	28.8	99.40
N3	1.500	0.150	0.075	28.1	99.19
N4	2.500	0.150	0.075	32.1	99.20
N5	1.500	0.050	0.125	18.0	99.10
N6	2.500	0.050	0.125	21.2	99.31
N7	1.500	0.150	0.125	16.3	98.72
N8	2.500	0.150	0.125	27.1	99.20
N9	1.159	0.100	0.100	23.9	98.67
N10	2.841	0.100	0.100	27.0	99.33
N11	2.000	0.016	0.100	24.3	99.21
N12	2.000	0.184	0.100	29.1	99.02
N13	2.000	0.100	0.058	32.7	99.26
N14	2.000	0.100	0.142	24.4	99.16
N15	2.000	0.100	0.100	28.5	99.31
N16	2.000	0.100	0.100	29.4	99.31
N17	2.000	0.100	0.100	29.4	99.24
N18	2.000	0.100	0.100	29.8	99.27
N19	2.000	0.100	0.100	31.4	99.34
N20	2.000	0.100	0.100	28.0	99.30

[a] 0.2 wt% NaCl aqueous solution at 1.5 MPa, 25°C and pH 7 (reaction time = 90 s, aqueous and organic phase temperature = 25°C, organic solvent = Isol-C).

[42,43]. The ANOVA test procedure produces an *F* ratio, which is used to calculate the *p* value. The *F* ratio (also called variance ratio) is the ratio of the variability between groups compared with the variability within the groups. If this ratio is large, then the *p* value is small which can produce a statistically significant result. Based on the test results, $p < 0.05$ was for both flux and rejection regression models. It means that the attained experimental results and optimized combinations for permeate water flux and the salt removal rate were both statistically significant with a 95% confidence level within the variation range considered [30]. When the multiple input variables affect the experimental result in combination with other variables, RSM can be used as a statistical method to determine the optimal combination of input variables. In this study, minimum 30 gfd and beyond 99.2% at predetermined operation condition were established as target values for flux and rejection, respectively. Fig. 7 includes contour shape graphs to predict the membrane performance



(a) (b) (c) (d) (e) (f)

Fig. 7. Contour plot of flux and rejection with varying concentrations of (a) and (b) MPD and additive (fixation factor = TMC 0.1 wt%), (c) and (d) TMC and additive (fixation factor = MPD 2 wt%), (e) and (f) TMC and MPD (fixation factor = additive 0.1 wt%).

variation of the resultant membrane with increasing concentration of two factors. Meanwhile, concentration of the other third factor was fixed as median value of DOE experiment. When TMC concentration was fixed at 0.1 wt%, both MPD and additive concentration increment enhanced the permeate flux; however, further increment of MPD and additive concentration rather reduced the permeate flux (Fig. 7(a)). Rejection constantly increased with the MPD concentration increments. On the other hand, rejection variation was not sensitive to the additive concentration, and slight decline of the rejection was predicted along the concentration increment (Fig. 7(b)). Figs. 7(c) and (d) are the prediction results when MPD was fixed at 2%. The continuous flow rate decrease was predicted as the gradual increase of TMC concentration. On the contrary, water flux was enhanced as the additive concentration increment. However, excessive increase of additive concentration lowered the flux, and this trend became more evident, especially at lower TMC concentrations. Both TMC and additive had optimal concentrations for enhanced salt rejection, and further increment of concentrations deteriorated the rejection of the resultant membrane. The last parameter was the fixation of additive concentration at 0.1 wt%. As shown in Figs. 7(e) and (f), slightly reduced flux and rejection was anticipated upon increasing the TMC concentration. Contrary to TMC, MPD concentration augment enhanced the flux and rejection, but an MPD concentration beyond a certain range rather lowered the flux and rejection. In addition, membranes in Fig. 6 prepared from solely MPD and TMC were evaluated for the effect of additive during interfacial polymerization. When comparing membrane performance trends for the membranes with no additive, as seen in Figs. 6(a) and (b), similar flow rate trends were seen for both TMC and MPD concentration changes (Fig. 7(e)). In the case of rejection, more enhanced and less sensitive variation trend was predicted in DOE study cases. The rejection variance of parametric study (Figs. 6(a) and (b)) within the DOE study concentration range was 97.24%–98.71% in the TMC case and 96.76%–98.80% in the MPD case, respectively. However, according to Fig. 7(f), at least 98.75% removal rate was predicted for both TMC and MPD variation cases. Furthermore, the removal rate fluctuations along the TMC and MPD concentrations regarded as the gap between maximum and minimum rejection value were also predicted to be relieved by introducing the additive during interfacial polymerization.

3.2.2. Confirmation experiment

Based on the RSM analysis, the optimum concentration combination of the three factors to achieve target membrane performance of 30 gfd and 99.20% at given test condition was determined to be MPD 2.250 wt%, TMC 0.097 wt% and DEGME 0.143 wt%. Since the optimized setting was not one of the experimental runs already conducted during the DOE step, this prediction must be verified by performing an additional experiment. This confirming test is essential and is part of the DOE method as it can provide supporting evidence for the prediction studies [44]. The confirmation test results to verify the optimum setting are shown in Table 5. The predicted membrane performance at optimum monomer concentration composition was 30.88 gfd flux and 99.25% salt rejection. These results were very close to the values from the confirmation experiments data, which were 30.69 gfd flux and 99.23% salt rejection and were the average values of six membrane coupons prepared by analogous monomer concentration compositions. To further validate the consistency of confirmation experiments, one sample *t*-test statistical test was conducted on the experimental results. This statistical test evaluates the mean difference between the experimental results and the predicted values. Generally, with a null hypothesis of one sample *t*-test, there would be no significant difference between predicted values and mean value of experimental results. If *p* value is higher than 0.05, the null hypothesis should not be dismissed, and it can be concluded that there was no significant difference between predicted values and mean value of experimental results. From the

Table 5
Optimum settings from RSM analysis and confirmation experiment results

Factor	Value (wt%)	Prediction		Experimental results	
		Flux (gfd)	Rejection (%)	Flux (gfd)	Rejection (%)
MPD	2.250	30.88	99.25	30.69 (*p* 0.556[a])	99.23 (*p* 0.631[a])
TMC	0.097				
DEGME	0.143				

	Experimental results[b]	
	Flux (gfd)	Rejection (%)
Coupon 1	29.33	99.05
Coupon 2	30.91	99.27
Coupon 3	30.71	99.37
Coupon 4	30.48	99.28
Coupon 5	31.44	99.15
Coupon 6	31.25	99.24

[a] Estimated from one sample *t*-test analysis on the experimental results.

[b] Operation condition: 0.2 wt% NaCl aqueous solution at 1.5 MPa, 25°C and pH 7 (reaction time = 90 s, aqueous and organic phase temperature = 25°C, organic solvent = Isol-C).

confirmed p value, the prediction model in this DOE study was sufficient to describe the dependence of the responses on the variable factors.

4. Conclusions

TFC polyamide RO membranes were fabricated under various preparation conditions and the effects of these preparation conditions on membrane performance were systematically discussed. With increasing reaction time, water flux monotonically decreased; however, the salt rejection first increased from 91% to 98.8% and then almost leveled off. Controlling the temperature of MPD solution was more important than that of the organic phase, because of the accelerated hydrolysis of TMC in the aqueous phase. If higher MPD diffusivity is achieved by adopting a lower surface tension organic solvent, the resultant RO membrane could exhibit higher permeate water flux and lower salt passage. With increasing concentration of TMC, both the salt passage and permeate water flux decreased. In the case of membrane prepared by using increasing concentrations of MPD monomer, both permeate water flux and salt removal rate increased simultaneously; however, there was a limit to this increase as additional increments of MPD concentration reduced water flux with constant salt rejection. With the DOE method, optimum concentration combination of MPD, TMC and additive was established for the TFC polyamide RO membrane manufacture. The optimal interfacial polymerization conditions obtained in this study for the polyamide RO membranes were as follows: MPD 2.250 wt%, TMC 0.097 wt%, DEGME 0.143 wt%, reaction time of 90 s, aqueous solution temperature of 25°C and organic solution temperature of 25°C. The reliability of the optimum settings for RO membrane preparation condition was verified by confirmation experiments. In summary, various combinations of monomer concentration for RO membranes manufacture for a tailor-made performance can be provided by DOE and RSM analysis.

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References

[1] W. Byrne, Reverse Osmosis, 2nd. ed., Tall Oaks Publishing Inc., Littleton, CO, 1995.

[2] J. Kucera, Reverse Osmosis, John Wiley & Sons, Hoboken, MA, 2010.

[3] J.E. Cadotte, R.S. King, R.J. Majerle, R.J. Petersen, Interfacial synthesis in the preparation of reverse osmosis membranes, J. Macromol. Sci., A, 15 (1981) 727–755.

[4] R.E. Kesting, Synthetic Polymeric Membranes, McGraw-Hill Book Company, New York, St. Louis, San Francisco, 1971.

[5] M. Mulder, Basic Principles of Membrane Technology, 2nd ed., Kluwer Academic Publishers, Dordrecht, 1996.

[6] A.K. Ghosh, E.M.V. Hoek, Impacts of support membrane structure and chemistry on polyamide–polysulfone interfacial composite membranes, J. Membr. Sci., 336 (2009) 140–148.

[7] I.J. Roh, Influence of rupture strength of interfacially polymerized thin-film structure on the performance of polyamide composite membranes, J. Membr. Sci., 198 (2002) 63–74.

[8] Y.-N. Kwon, S. Hong, H. Choi, T. Tak, Surface modification of a polyamide reverse osmosis membrane for chlorine resistance improvement, J. Membr. Sci., 415–416 (2012) 192–198.

[9] Y.-N. Kwon, J.O. Leckie, Hypochlorite degradation of crosslinked polyamide membranes, J. Membr. Sci., 283 (2006) 21–26.

[10] Y.-N. Kwon, J.O. Leckie, Hypochlorite degradation of crosslinked polyamide membranes: II. Changes in hydrogen bonding behavior and performance, J. Membr. Sci., 282 (2006) 456–464.

[11] P.W. Morgan, Condensation Polymers: By Interfacial and Solution Methods, John Wiley & Sons, New York, 1965.

[12] J.-E. Gu, B.-M. Jun, Y.-N. Kwon, Effect of chlorination condition and permeability of chlorine species on the chlorination of a polyamide membrane, Water Res., 46 (2012) 5389–5400.

[13] S. Hong, I.-C. Kim, T. Tak, Y.-N. Kwon, Interfacially synthesized chlorine-resistant polyimide thin film composite (TFC) reverse osmosis (RO) membranes, Desalination, 309 (2013) 18–26.

[14] Y.-N. Kwon, R. Joksimovic, I.-C. Kim, J.O. Leckie, Effect of bromide on the chlorination of a polyamide membrane, Desalination, 280 (2011) 80–86.

[15] Y.-N. Kwon, K. Shih, C. Tang, J.O. Leckie, Adsorption of perfluorinated compounds on thin-film composite polyamide membranes, J. Appl. Polym. Sci., 124 (2012) 1042–1049.

[16] T.P.N. Nguyen, B.-M. Jun, J.H. Lee, Y.-N. Kwon, Comparison of integrally asymmetric and thin film composite structures for a desirable fashion of forward osmosis membranes, J. Membr. Sci., 495 (2015) 457–470.

[17] T.P.N. Nguyen, E.-T. Yun, I.-C. Kim, Y.-N. Kwon, Preparation of cellulose triacetate/cellulose acetate (CTA/CA)-based membranes for forward osmosis, J. Membr. Sci., 433 (2013) 49–59.

[18] H. Choi, J. Park, T. Tak, Y.-N. Kwon, Surface modification of seawater reverse osmosis (SWRO) membrane using methyl methacrylate-hydroxy poly(oxyethylene) methacrylate (MMA-HPOEM) comb-polymer and its performance, Desalination, 291 (2012) 1–7.

[19] Y.-N. Kwon, M.-J. Kim, Y.T. Lee, Application of a FO/MD-combined system for the desalination of saline solution, Desal. Wat. Treat., 57 (2016) 14347–14354.

[20] Y. Song, P. Sun, L.L. Henry, B. Sun, Mechanisms of structure and performance controlled thin film composite membrane formation via interfacial polymerization process, J. Membr. Sci., 251 (2005) 67–79.

[21] B.-H. Jeong, E.M.V. Hoek, Y. Yan, A. Subramani, X. Huang, G. Hurwitz, A.K. Ghosh, A. Jawor, Interfacial polymerization of thin film nanocomposites: a new concept for reverse osmosis membranes, J. Membr. Sci., 294 (2007) 1–7.

[22] J. Xu, Z. Wang, J. Wang, S. Wang, Positively charged aromatic polyamide reverse osmosis membrane with high anti-fouling property prepared by polyethylenimine grafting, Desalination, 365 (2015) 398–406.

[23] J. Yu, G.-A. Shin, B.S. Oh, J.-I. Kye, J. Yoon, N-chlorosuccinimide as a novel agent for biofouling control in the polyamide reverse osmosis membrane process, Desalination, 357 (2015) 1–7.

[24] M. Kim, M. Kim, B. Park, S. Kim, Changes in characteristics of polyamide reverse osmosis membrane due to chlorine attack, Desal. Wat. Treat., 54 (2015) 923–928.

[25] E. Alayemieka, S. Lee, Modification of polyamide membrane surface with chlorine dioxide solutions of differing pH, Desal. Wat. Treat., 45 (2012) 84–90.

[26] R.K. Roy, A Primer on the Taguchi Method, Van Norstrand Reinhold, New York, 1990.

[27] T. Khamplod, S. Loykulnant, C. Kongkaew, P. Sureeyatanapas, P. Prapainainar, Electron beam radiation grafting of styrene on natural rubber using Taguchi's design, Polymer, 79 (2015) 135–145.

[28] J.P. Chen, S.L. Kim, Y.P. Ting, Optimization of membrane physical and chemical cleaning by a statistically designed approach, J. Membr. Sci., 219 (2003) 27–45.

[29] C. Cojocaru, G. Zakrzewska-Trznadel, Response surface modeling and optimization of copper removal from aqua solutions using polymer assisted ultrafiltration, J. Membr. Sci., 298 (2007) 56–70.

[30] V. García, J. Landaburu-Aguirre, E. Pongrácz, P. Perämäki, R.L. Keiski, Dehydration of water/dichloromethane/n-butanol

mixtures by pervaporation; optimisation and modelling by response surface methodology, J. Membr. Sci., 338 (2009) 111–118.

[31] M. Khayet, C. Cojocaru, M. Essalhi, Artificial neural network modeling and response surface methodology of desalination by reverse osmosis, J. Membr. Sci., 368 (2011) 202–214.

[32] A. Ahmad, B. Ooi, Properties–performance of thin film composites membrane: study on trimesoyl chloride content and polymerization time, J. Membr. Sci., 255 (2005) 67–77.

[33] A. Prakash Rao, N.V. Desai, R. Rangarajan, Interfacially synthesized thin film composite RO membranes for seawater desalination, J. Membr. Sci., 124 (1997) 263–272.

[34] Y. Liu, R. Wang, T.-S. Chung, Chemical cross-linking modification of polyimide membranes for gas separation, J. Membr. Sci., 189 (2001) 231–239.

[35] V.L. Snoeyink, D. Jenkins, Water Chemistry, John Wiley & Sons, Hoboken, NJ, USA, 1980.

[36] A.K. Ghosh, B.-H. Jeong, X. Huang, E.M.V. Hoek, Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties, J. Membr. Sci., 311 (2008) 34–45.

[37] I.-C. Kim, J. Jegal, K.-H. Lee, Effect of aqueous and organic solutions on the performance of polyamide thin-film-composite nanofiltration membranes, J. Polym. Sci., Part B: Polym. Phys., 40 (2002) 2151–2163.

[38] I.J. Roh, A.R. Greenberg, V.P. Khare, Synthesis and characterization of interfacially polymerized polyamide thin films, Desalination, 191 (2006) 279–290.

[39] W. Xie, G.M. Geise, B.D. Freeman, H.-S. Lee, G. Byun, J.E. McGrath, Polyamide interfacial composite membranes prepared from *m*-phenylene diamine, trimesoyl chloride and a new disulfonated diamine, J. Membr. Sci., 403–404 (2012) 152–161.

[40] M. Hirose, H. Ito, Y. Kamiyama, Effect of skin layer surface structures on the flux behaviour of RO membranes, J. Membr. Sci., 121 (1996) 209–215.

[41] T. Kamada, T. Ohara, T. Shintani, T. Tsuru, Controlled surface morphology of polyamide membranes via the addition of co-solvent for improved permeate flux, J. Membr. Sci., 467 (2014) 303–312.

[42] A. Idris, A.F. Ismail, M.Y. Noordin, S.J. Shilton, Optimization of cellulose acetate hollow fiber reverse osmosis membrane production using Taguchi method, J. Membr. Sci., 205 (2002) 223–237.

[43] S. Pourjafar, M. Jahanshahi, A. Rahimpour, Optimization of TiO_2 modified poly(vinyl alcohol) thin film composite nanofiltration membranes using Taguchi method, Desalination, 315 (2013) 107–114.

[44] M.S. Phadke, Quality Engineering Using Robust Design, Prentice-Hall, Englewood Cliffs, New Jersey, 1989.