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Optimization of preparation conditions of polyamide thin film composite membrane for organic solvent nanofiltration

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Abstract−Separation performance of polyamide composite membranes is affected by several parameters during formation of thin upper layer via interfacial polymerization. We investigated the effect of various polyamide synthesis conditions on the performance of organic solvent resistant polyamide composite membranes through the model equations designed by 2-level fractional factorial design. The dewaxing solvent recovery was selected as separation process. Five factors were changed in two level includin; TMC concentration (0.05-0.1%), MPD concentration (1-2%), support immersion time in organic solution (2-4 min), support immersion time in aqueous solution (1-2 min), and curing temperature (70-80 °C). The resultant equations showed 93.48% and 94.82% of the variability (R^2_{adj}) in data used to fit oil rejection and permeate flux models, respectively. The analysis of variance revealed that both models were high significant. It was also observed that TMC concentration, MPD concentration and immersion time in TMC have more pronounced effect on the oil rejection and permeate flux than other factors and interactions. Optimal polyamide preparation conditions were obtained using multiple response method for 94% oil rejection as target value. According to the results, the best value of permeate flux (8.86 $l/(m^2\cdot h)$) was found at TMC concentration of 0.1%, MPD concentration of 1.94%, immersion time in TMC of 3.88 min, immersion time in MPD of 1.95 min and curing temperature of 71.96 °C with desirability factor of 1.

Keywords: Organic Solvent Nanofiltration, Thin Film Composite Membrane, Factorial Design, Polyamide, Interfacial Polymerization, ANOVA

INTRODUCTION

Thin film composite (TFC) membranes prepared via interfacial polymerization (IP) have been used in membrane processes, such as reverse osmosis (RO) and nanofiltration (NF) [1,2]. Most of the commercial TFC membranes consist of upper ultra thin polyamide layer coated over porous support layer by interfacial polymerization of an aromatic polyamine in an aqueous phase and one or more polyacyl halides in an organic phase [3]. Among polyamide composite membranes, the one fabricated by IP of m-phenylenediamine (MPD) as diamine monomer and trimesoyl chloride (TMC) as acid chloride monomer shows the most successful performance for separation processes, especially in aqueous systems [4-7].

Although polyamide composite membranes are generally used in water and wastewater treatment, they have been found suitable for non-aqueous separation processes. There are a few studies which focus on the performance of polyamide thin film composite membranes in organic solvent separation [8-10].

Both support layer and ultrathin selective layer should be controlled and optimized to tailor superior TFC membrane performance. Among all polymers used for the fabrication of support layer, polysulfone and polyethersulfone have been more considered by researchers. Although PSf support membrane has widely been applied as support film of commercial TFC membranes, it has low chemical stability in harsh environment such as high or low pH medium, high temperature processes and organic solvent separation [4]. Therefore, other candidates such as PAN (polyacrylonitrile), PP (polypropylene), PI(polyimide), PEI (polyetherimide) introduced in literature to overcome these limitations [8-13]. In addition to chemical stability, surface chemistry (hydrophilicity) and morphology of support layer have an influential effect on permeability and selectivity of membrane [4]. To assess the relation between pore size distribution of PSf support membrane and polyamide layer properties, Singh et al. [14] found that PSf substrate with the pore size about 0.07 μm has higher salt rejection in comparison with one including larger pore size (0.15 μm). Furthermore, Gosh and Hoek [15] prepared PSf support membrane with wide range of hydrophilicity and pore structure, and presented conceptual models to give a comprehensive understanding of the impact of support on polyamide layer structure. In this case, TFC membrane with different permeability and selectivity through water treatment can be fabricated.

Apart from the support layer, separation performance of polyamide composite membranes can also be affected by several parameters during thin film polyamide formation, such as monomer concentration, reaction time, solubility and diffusivity of diamine monomer in organic solvent, and heat curing. Earlier, the dependency of polyamide composite performance on the abovementioned parameters was considered in literature by the one-factor-at-a-time experiment method which focuses on aqueous separations [5,7,16-20]. In this case, only one parameter is changed at a time and large number

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of experiments must be performed when multiple parameters are involved. Statistical experimental design, known as factorial design, was recommended in literature to reduce the number of trials and to prevent drowsy and time-consuming experiments. Factorial design can determine the effect of each parameter as well as the combination of factors on individual response. By factorial design, it is possible to present a model which demonstrates the effect of each parameter on a defined process. Besides, insignificant parameters and parameter interaction can be distinguished in this technique [21, 22]. Although factorial design is widely applied in various areas of separation processes such as adsorption [23,24], nanocomposite synthesis [25] and membrane preparation and membrane separation processes [26-29], there is no report about the combination effect of polyamide preparation parameters on the performance of resultant TFC membrane. In addition, no attempts have been made to investigate the impact of polyamide preparation factors on the performance of solvent-resistant thin film composite membranes up to now.

In the present work, the performance of solvent resistant polyamide composite membrane for separation of dewaxing solvents from lube oil was investigated. Permeate flux and oil rejection were determined in various polyamide synthetic conditions including concentration of monomers, support immersion time in organic solution and aqueous solution and curing temperature. Two-level fractional factorial design was introduced to reduce experimental trials. Models were obtained to indicate the relation between significant factors and factor interaction by oil rejection and permeate flux as responses.

MATERIALS AND METHODS

1. Materials

Trimesoyl chloride (TMC, purity 98%) and m-phenylenediamine (MPD, purity 99%) as reactive monomers were supplied by Sigma-Aldrich. Fumed silica nanoparticles (Aerosil 380) with 14 nm average particle size were provided by Degussa. Aminopropyldiethoxym-

Table 1. Fractional factorial design results for dewaxing solvent recovery by polyamide composite membrane

Run	TMC concentration (a)	MPD concentration (b)	Immersion time in TMC solution (c)	Immersion time in MPD solution (d)	Curing temperature (e)	Permeate flux ($l/(m^2\cdot h)$)	Rejection (%)
1	0.10	1.00	2.00	1.00	70.00	15.2047	82.7692
2	0.05	2.00	2.00	1.00	70.00	15.7982	85.2143
3	0.05	2.00	4.00	1.00	80.00	9.84795	87.7049
4	0.10	1.00	2.00	1.00	70.00	17.4678	85.7709
5	0.05	2.00	4.00	2.00	70.00	16.3411	84
6	0.10	1.00	4.00	2.00	70.00	13.4881	85.2381
7	0.10	1.00	4.00	2.00	70.00	12.143	87.8261
8	0.05	1.00	2.00	1.00	80.00	16.5583	82.3125
9	0.10	2.00	2.00	1.00	80.00	13.0351	88.1757
10	0.05	2.00	4.00	2.00	70.00	16.041	86.851
11	0.10	2.00	2.00	2.00	70.00	14.6529	78.75
12	0.05	2.00	2.00	1.00	70.00	12.4584	80.3151
13	0.05	1.00	4.00	2.00	80.00	12.2807	85.7585
14	0.10	2.00	4.00	2.00	80.00	5.30595	98.0392
15	0.10	2.00	4.00	1.00	70.00	9.4561	94.3391
16	0.10	1.00	2.00	2.00	80.00	15.5945	81.5678
17	0.05	2.00	2.00	2.00	80.00	18.5924	79.7474
18	0.05	1.00	2.00	2.00	70.00	19.9573	68.6313
19	0.10	1.00	4.00	1.00	80.00	16.5119	89.1213
20	0.10	1.00	2.00	2.00	80.00	13.1631	83.6364
21	0.05	1.00	4.00	2.00	80.00	13.2709	87.21
22	0.05	1.00	4.00	1.00	70.00	17.0117	73.8043
23	0.05	1.00	2.00	2.00	70.00	21.2501	69.26
24	0.10	2.00	4.00	1.00	70.00	8.75076	93
25	0.05	1.00	2.00	1.00	80.00	17.2888	83.2534
26	0.10	1.00	4.00	1.00	80.00	17.2849	85.2941
27	0.10	2.00	4.00	2.00	80.00	6.7071	97.2831
28	0.05	1.00	4.00	1.00	70.00	17.4035	75.2119
29	0.10	2.00	2.00	1.00	80.00	12.1004	87.2039
30	0.05	2.00	2.00	2.00	80.00	18.6781	80.21
31	0.1	2.00	2.00	2.00	70.00	15.2105	81.23
32	0.05	2.00	4.00	1.00	80.00	9.2103	85.2101

ethylsilane (APDEMS, Sigma-Aldrich) was used to functionalize silica nanoparticles according to the procedure presented by Li et al. [30]. Polyetherimide (PEI, Sigma-Aldrich), N-Methyl-2-Pyrrolidone (NMP, Merck) and amino-functionalized silica were used to prepare support membrane. n-Hexane with analytical grade was supplied by Merck.

2. Polyamide Composite Membrane Preparation

Polyetherimide (20 wt%) support membrane embedded with optimal amount of amino-functionalized silica was fabricated by immersion precipitation method according to procedure presented in our previous study [31]. Briefly, amino-functionalized nanoparticles at loading of 5% (based on the weight ratio of SiO_2 to PEI) were added to NMP, stirred for 2 h and then sonicated for 60 min. PEI was gradually added to the above mixtures and stirred for 24 h. The resultant solutions were cast on non-woven polyester using adjustable casting bar (Neurtek2281205) with a thickness of 250 µm and then allowed to be in atmosphere for 15 s. The formed films were immersed in a water coagulation bath for one day, then air-dried over night to remove residual solvent and water.

To prepare polyamide composite membrane, certain amount of MPD and TMC was dissolved in deionized water and n-Hexane, respectively. The nanocomposite support was immersed in TMC solution for a period of time and kept under a hood to evaporate excess solution on the surface. Then support was immersed in MPD solution for a certain time to form the polymeric network. To stabilize polyamide thin film, the resultant membrane was kept in an oven for 4 min and finally rinsed with deionized water.

3. 2^k Factorial Design

2^k factorial design was employed to investigate the impact of polyamide synthetic conditions on the performance of TFC membrane. In 2^k full factorial design, each factor is set at two levels and $r2^k$ run is essential to perform experimental design analysis where r and k are the number of replicate and factors [21]. Five factors were selected, including TMC concentration (A), MPD concentration (B), immersion time in TMC solution (C), immersion time in MPD solution (D) and curing temperature (E). With respect to the number of factors (k=5), for two replicates, 64 tests should be performed. To avoid wasting time, half-fraction design with the resolution of V was chosen. In this case, every main effect is aliased with a four factor interaction and two factor interactions are aliased with three factor interactions. This results in 32 tests. The standard array for five factors and 32 experiments is shown in Table 1.

4. Polyamide Composite Membrane Performance

Polyamide composite membrane performance was evaluated through separation of dewaxing solvent from lube oil. A cross-flow system was used for OSN experiments (Fig. 1). All experiments were carried out at 15 bar and ambient temperature in two repeats. The 316L stainless steel cell has an effective membrane area of 8.56 cm^2. The feed consisted of 20 wt% lube oil (viscosity index:83), 40 wt% MEK and 40 wt% toluene, which were kindly supplied by Pars Oil Company (Iran). Feed flow rate was adjusted at 550 *l*/h. The permeate flux, J ($l/(m^2\ h)$) was calculated using Eq. (1):

$$J = \frac{V}{A.t} \tag{1}$$

where V (*l*) is the volume of permeate after 1 h, A (m^2) is the effective membrane surface area and t (h) is the permeate collection time. After steady state flux was achieved, samples were collected to determine oil concentration in permeate by gravimetric analysis. The oil rejection was calculated by Eq. (2):

$$\text{Oil rejection } (\%) = \left(1 - \left(\frac{\%\text{ oil in permeate}}{\%\text{ oil in feed}}\right)\right) \times 100 \tag{2}$$

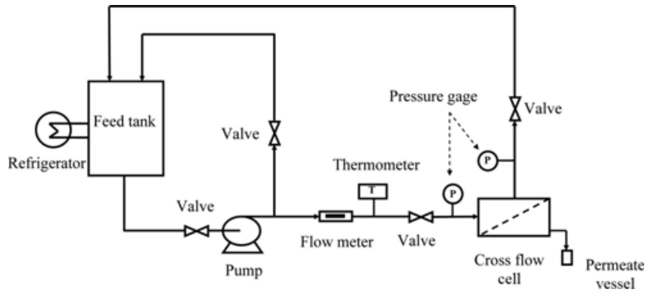

Fig. 1. Scheme of nanofiltration setup.

RESULTS AND DISCUSSION

1. Response Analysis Using Half Normal Plot

The half normal plot demonstrates the absolute value of standardized effects of factors and interactions. The standardized effect of a factor is the difference between the average response over high level of factor and the average response over the low level of the factor. The half normal plot is an easy graphical way to assess which factors have a significant effect to be included in the model. The insignificant factors and interactions sit on the straight line, which indicates near zero effect level. Fig. 2 and Fig. 3 show the half normal plot of effects on the oil rejection and permeate flux responses, respectively. According to Fig. 2, BD, CE, AB, and AD interactions, which lie along the red line, are unimportant and can be used for the formation of the error mean square. Besides, Fig. 3 demonstrates that the immersion time in MPD solution (D), the interaction of TMC concentration and immersion time in TMC (AC) and MPD con-

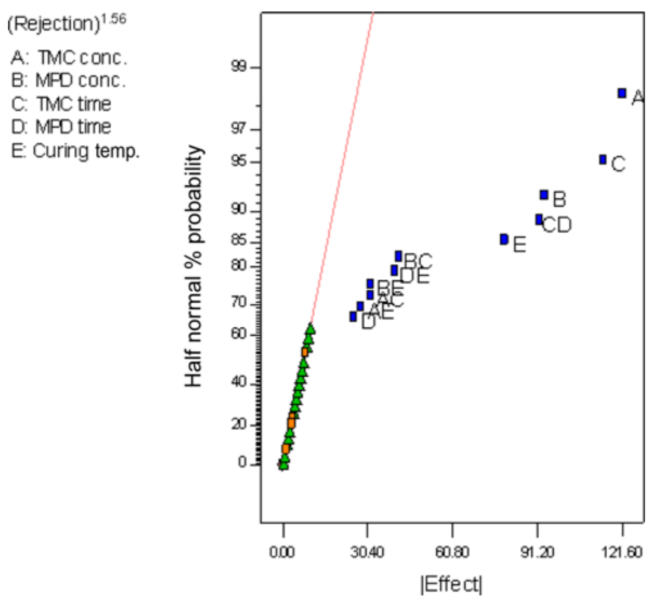

Fig. 2. Half-normal plot of oil rejection.

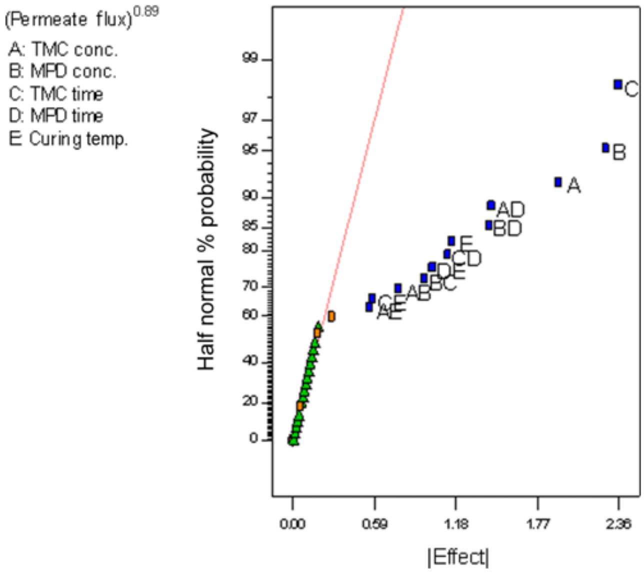

Fig. 3. Half-normal plot of permeate flux.

centration-curing temperature interaction (BE) should be eliminated from the permeate flux prediction model. Regarding the above findings, it is possible to offer a regression model for aforementioned responses.

2. Regression Model

We used multiple linear regression to present the predicting model of oil rejection and permeate flux for dewaxing solvent recovery through OSN process. The resultant models in terms of coded factors are shown in Eqs. (3) and (4):

$$(\text{Permeate Flux})^{0.89}=10.64-0.96\,A-1.13\,B-1.18\,C-0.58\,E-0.38\,A.B-0.72\,A.D+0.28\,A.E-0.48\,B.C+0.71\,B.D-0.56\,C.D-0.29\,C.E-0.51\,D.E \quad (3)$$

$$(\text{Rejection})^{1.56}=1010.52+6080\,A+46.91\,B+57.46\,C-12.74\,D+39.70\,E+15.71\,A.C-14.03\,A.E+20.78\,B.C-15.76\,B.E+45.95\,C.D+20.11\,D.E \quad (4)$$

Table 2. Coefficients of multiple determinations for permeate flux and oil rejection models

Model	R^2 %	Adjusted R^2 (R^2_{adj}) %	Predicted R^2 (R^2_{pred}) %
Permeate flux	96	93.48	88.67
Oil rejection	96.66	94.82	91.44

Table 2 illustrates the coefficients of multiple determinations for above equations. Although both equations have high R^2 value, one cannot say that the presented models are good ones due to dependency of R^2 value on the number of factors, regardless of their importance. In contrast to R^2, adjusted R^2 will often decrease when insignificant terms are added to the model. So it is preferred to apply adjusted R^2 for determination of regression model usefulness [21]. When R^2 and R^2_{adj} differ noticeably, this means the presence of insignificant terms in the model. As can be seen, for the rejection fit model R^2 and R^2_{adj} are very close together. This indicates that all factors and interactions incorporated in model are significant. The permeate flux fit model also has relatively close R^2 (96%) and R^2_{adj} (93.48%) values.

Another coefficient which can be applied to assess the adequacy of model in predicting ability of model is predicted R^2. According to predicted R^2 value, the models show the 88.67% and 91.44% variability in predicting new observations of rejection and flux, whereas 93.48% and 94.82% of the variability (R^2_{adj}) were observed in data used to fit model. The results show that for both models, R^2_{adj} and R^2_{pred} are in reasonable agreement. Temporarily, the calculated coefficients of multiple determination show that both models can predict the performance of prepared TFC membrane for separation of dewaxing solvent from lube oil.

3. Analysis of Variance (ANOVA)

The validity of fitted models was tested with analysis of vari-

Table 3. Analysis of variance for permeate flux

Source	Sum of squares	df	Mean square	F-value	P-value	% Contribution
Model	193.56	12	16.13	38.04	<0.0001	
A	29.47	1	29.47	69.51	<0.0001	14.62
B	41.00	1	41.00	96.71	<0.0001	20.34
C	44.39	1	44.39	104.69	<0.0001	22.02
E	10.59	1	10.59	24.99	<0.0001	5.25
AB	4.70	1	4.70	11.09	0.0035	2.33
AD	16.56	1	16.56	39.06	<0.0001	8.21
AE	2.48	1	2.48	5.84	0.0259	1.23
BC	7.29	1	7.29	17.19	0.0005	3.61
BD	16.13	1	16.13	38.04	<0.0001	8
CD	10.07	1	10.07	23.76	0.0001	5
CE	2.69	1	2.69	6.34	0.0209	1.33
DE	8.19	1	8.19	19.31	0.0003	4.06
Residual	8.06	19	0.42			
Lack of fit	0.91	3	0.30	0.68	0.5763	0
Pure error	7.14	16	0.45			
Total	201.61	31				

Table 4. Analysis of variance for oil rejection

Source	Sum of square	df	Mean square	F-value	P-value	% Contribution
Model	4.665E+005	11	42407.79	52.57	<0.0001	
A	1.183E+005	1	1.183E+005	146.64	<0.0001	24.51
B	70418.70	1	70418.70	87.29	<0.0001	14.59
C	1.057E+005	1	1.057E+005	130.98	<0.0001	21.89
D	5195.25	1	5195.25	6.44	0.0196	1.08
E	50423.58	1	50423.58	62.50	<0.0001	10.45
AC	7897.25	1	7897.25	9.79	0.0053	1.64
AE	6299.80	1	6299.80	7.81	0.0112	1.31
BC	13821.23	1	13821.23	17.13	0.0005	2.86
BE	7949.96	1	7949.96	9.85	0.0052	1.65
CD	67572.29	1	67572.29	83.76	<0.0001	14
DE	12942.23	1	12942.23	16.04	0.0007	2.68
Residual	16134.91	20	806.75			
Lack of fit	728.14	4	182.03	0.19	0.9406	0
Pure error	15406.77	16	962.92			
Total	4.826E+005	31				

ance (ANOVA). This can be accomplished by sum of squares (SS) and F-value determination. As the F-value increases the significance of the corresponding factor also increases. The P-value is used as the level of significance leading to the rejection of the null hypothesis. In fact, each factor and interaction has significant effect when the measured P-value is less than individual probability level (<0.05). Tables 3 and 4 present the analysis of variance on the permeate flux and oil rejection for polyamide composite membrane. The model F-values of 38.04 and 52.57 imply the models are significant for determination of permeate flux and rejection, respectively. Besides, the results from Table 3 demonstrate that A, B, C, E, AB, AD, AE, BC, BD, CD, CE, DE are significant model terms. In the case of oil rejection, A, B, C, D, E, AC, AE, BC, BE, CD, DE are significant model terms, regarding to P-value <0.05 (Table 4). Additionally, the importance of each factor and two factor interaction can also be evaluated by contribution percent presented in Tables 3 and 4. From Table 3, immersion time in TMC solution, MPD concentration and TMC concentration with the contribution of 22.02, 20.34 and 14.62% are the most significant parameters affecting permeate flux. In the case of oil rejection, TMC concentration, immersion time in TMC and MPD concentration with the contribution of 24.51, 21.89 and 14.59% are more effective than other parameters in the

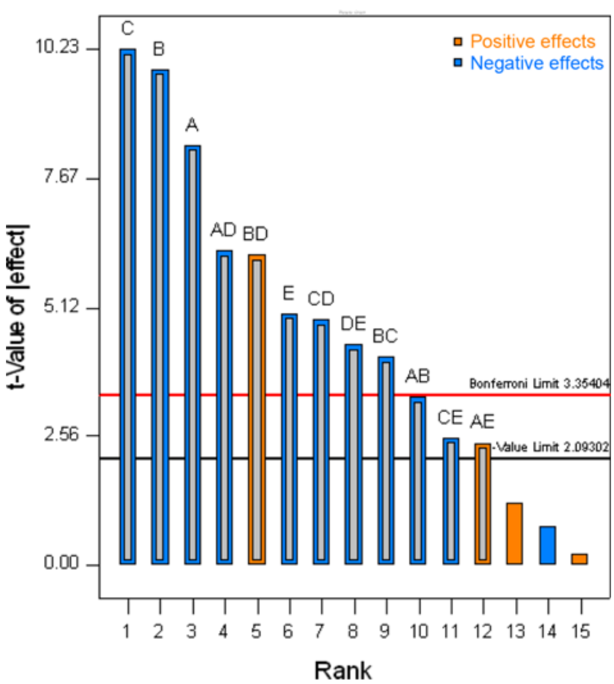

Fig. 4. Pareto chart of statistical effects on the permeate flux of polyamide composite membrane.

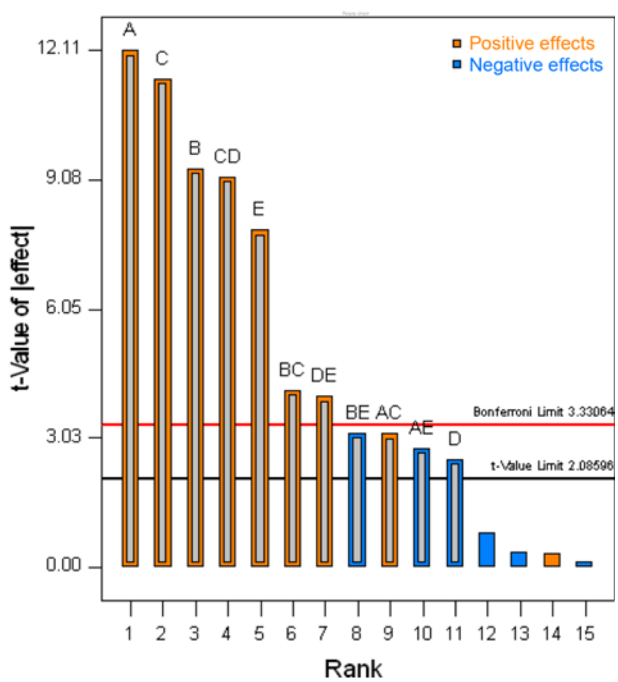

Fig. 5. Pareto chart of statistical effects on the oil rejection of polyamide composite membrane.

oil rejection respose. This result indicates that the increase of oil rejection of prepared membrane was mainly due to the change of monomer concentration in organic phase, while the permeate flux was more affected by monomer concentration in aqueous phase rather than in organic phase.

Based on the results, immersion time of support in MPD solution has low contribution (1.08%) on the rejection and no contribution on the permeate flux. This can be attributed to the MPD concentration range. Immersion time in MPD is reaction time, which affects the thickness of polyamide layer and subsequently oil rejection and permeate flux. When the thickness of the polyamide layer exceeds a certain amount, it obstructs the MPD diffusion into the organic phase. This leads to stopping the growing of the top layer thickness and then the separation performance of composite membrane becomes almost constant [16]. Thus, it can be concluded that the reaction time was not the dominant factor for polymerization in some range.

Beside the factors and interactions, the significancy of lack of fit should be checked. Lack of fit is defined as the sums of squares for the interactions that were removed from the model. The F-values of lack of fit for both models indicate that lack of fit is not significant. Thus, one can conclude that the specified models predicting permeate flux and oil rejection are adequate.

4. Student t Test

Pareto charts were also presented to graphically summarize and demonstrate the significance of main effects and interactions (Fig. 4 and Fig. 5). Student t-test was performed to provide Pareto charts for each group of response data. The t values of all main effects and interactions were studied by two limit lines, namely the Bonferroni limit line and t limit line. The t value of factor above the Bonferroni line is assigned as high significant factor and the ones with t value between Bonferroni line and t limit line are probably signifi-

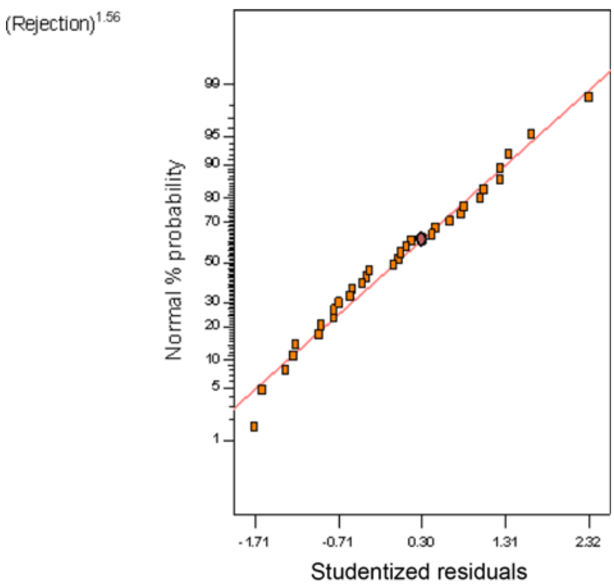

Fig. 6. Normal probability plot of residual values for oil rejection.

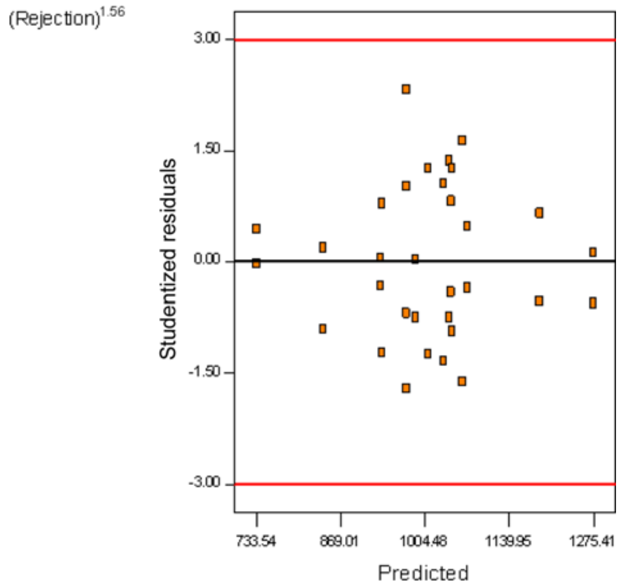

Fig. 8. Residual versus predicted plot for oil rejection.

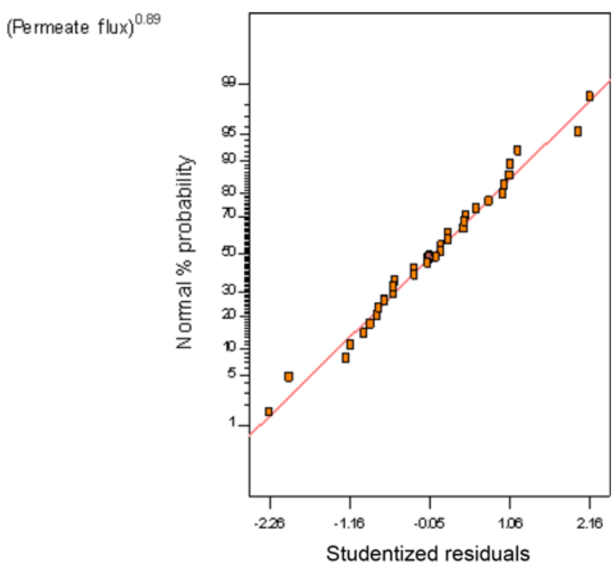

Fig. 7. Normal probability plot of residual values for permeate flux.

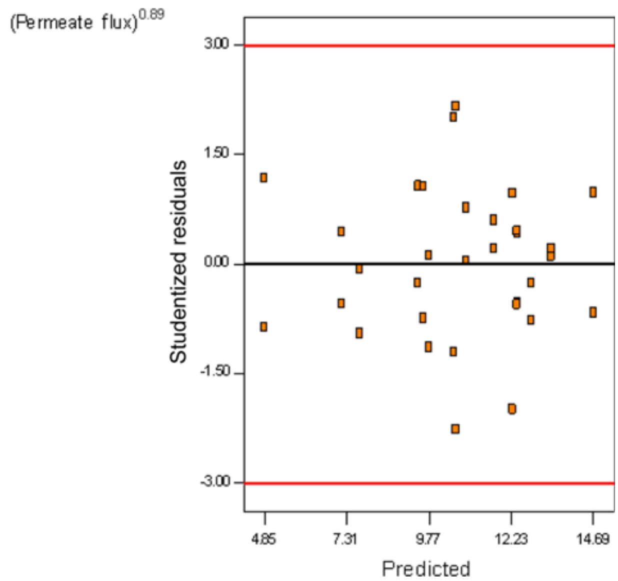

Fig. 9. Residual versus predicted plot for permeate flux.

cant. The t value of effect below the t limit line is certainly insignificant. For permeate flux data, as can be seen in Fig. 4, main effects and interactions which participate in permeate flux formula have t value above t limit line. Similarly, t-value of all factors and interactions in presented oil rejection model was higher than 2.0859 (t value limit) (Fig. 5). It can be said that Pareto charts confirmed pervious findings on the importance of studied factors and their interactions.

Besides, the color of the columns delineates whether the effect of factors or interactions is positive (orange) or negative (blue). As can be seen in Fig. 4 and Fig. 5, all significant main factors have negative effect on permeate flux and positive effect on oil rejection due to trade off between two response. Similar trend was observed when monomer concentration and curing temperature were changed to prepare TFC membrane for aqueous and organic systems [5,8,16].

5. Residual Analysis

Hypothesis testing, which is used in analysis of variance, requires that the error in the model be normally and independently distributed. Thus, preparation of residual plots is necessary to check the adequacy of models. The normal probability plots of the residuals from oil rejection and permeate flux are shown in Figs. 6 and 7. The figures reveal normality of errors for results. Figs. 8 and 9 present the studentized residual versus predicted plot for oil rejection and permeate flux, respectively. The figures show no individual pattern in the variability and residuals are normally distributed. Thus, it can be supposed that applied transformations for both responses are adequate. The aforementioned finding was also approved by the Box-Cox plot. Also, the standardized residuals lie in the interval −3 to 3 and no outliers are observed.

6. Two Factors Interactions

The mutual interactions between five main factors on the oil rejection and permeate flux were studied (Fig. 10 to Fig. 13). All plots interpret two factor interactions when other factors are fixed at the average of high level and low level values. No parallelism is observed in the lines of the interaction plots for each response parameter. This means that the effect of one factor depends on the level of the other, so all interactions included in the two models are effective. As can

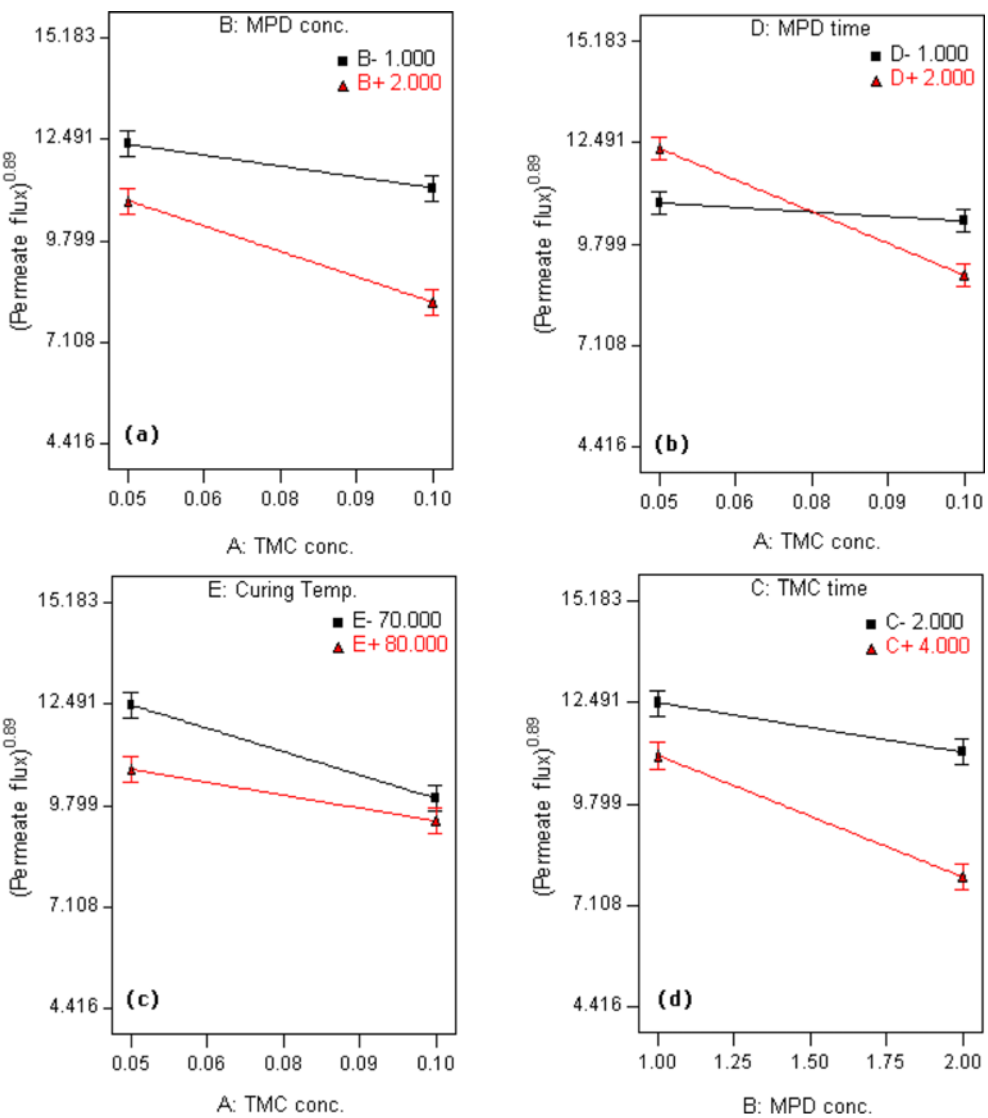

Fig. 10. Two factor interaction plots for permeate flux: (a) TMC concentration-MPD concentration, (b) TMC concentration- immersion time in MPD, (c) TMC concentration-curing temperature, (d) MPD concentration-immersion time in TMC.

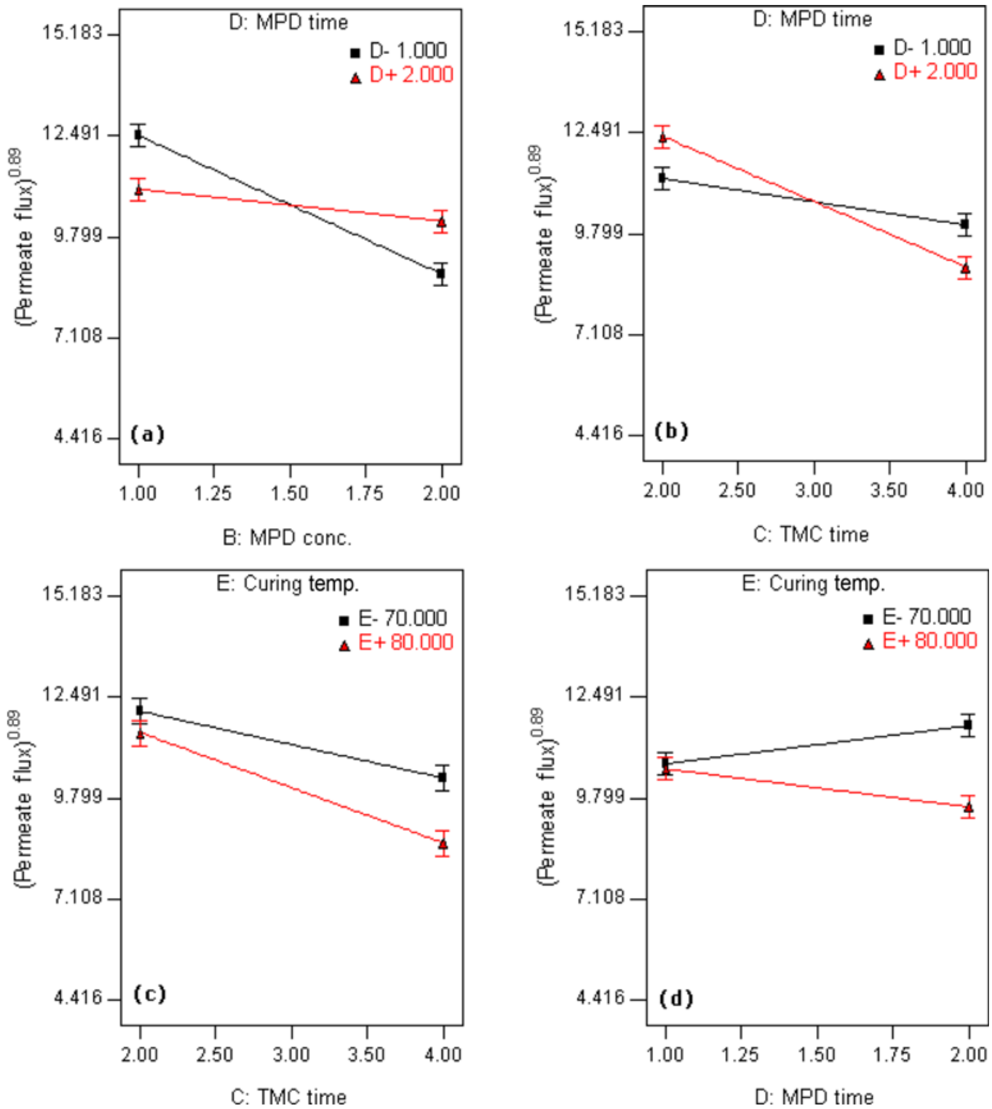

Fig. 11. Two factor interaction plots for permeate flux: (a) MPD concentration- immersion time in MPD, (b) immersion time in TMC-immersion time in MPD, (c) immersion time in TMC-curing temperature, (d) immersion time in MPD-curing temperature.

be seen in Fig. 10 and Fig. 11, the TMC concentration-immersion time in MPD, MPD concentration-immersion time in MPD and immersion time in TMC-immersion time in MPD interactions (AD, BD and CD) have more effect on the permeate flux value. In the case of AD interaction factor, when the immersion time in MPD is fixed at 1 min, altering the TMC concentration from 0.05% to 0.1% decreases the permeate flux slightly. While by increasing the immersion time in MPD, the impact of TMC concentration becomes more severe. Similar trend was observed for the immersion time in TMC-immersion time in MPD interaction (CD). In contrast for BD, when the immersion time in MPD increased from 1 min to 2 min, the impact of MPD concentration on the permeate flux declined.

For the interaction of immersion time in MPD and curing temperature (DE), an interesting trend was observed. At low level of curing temperature (70 °C), increasing immersion time in MPD from 1 to 2 min increased the permeate flux. Whereas, at low level of curing temperature (80 °C), increasing the immersion time in MPD shows slight reduction in the permeate flux. Other two factor interactions including BC AB, CE, and AE display less effectiveness on the permeate flux response.

Fig. 11 and Fig. 12 illustrate the two factor interaction in oil rejection of polyamide thin film composite membrane. As can be seen, the immersion time in TMC-immersion time in MPD is the most significant two factor interaction for oil rejection response. In this case, when the time of support immersion in MPD is fixed at 1 min, increasing TMC immersion time shows no considerable effect on the rejection. It can be said that immersion of support in MPD solution for 1 min is not sufficient to form selective polyamide thin layer on the support layer. But for 2 min immersion in MPD, the oil rejection increased by increment of immersion time in TMC. The TMC concentration-immersion time in MPD and MPD concentration-immersion time in MPD interactions shows the least effectiveness in the rejection. This may be attributed to the strong effect of monomer concentration versus immersion time in MPD.

7. Optimal Design

Multiple response method was applied to find optimal polyamide

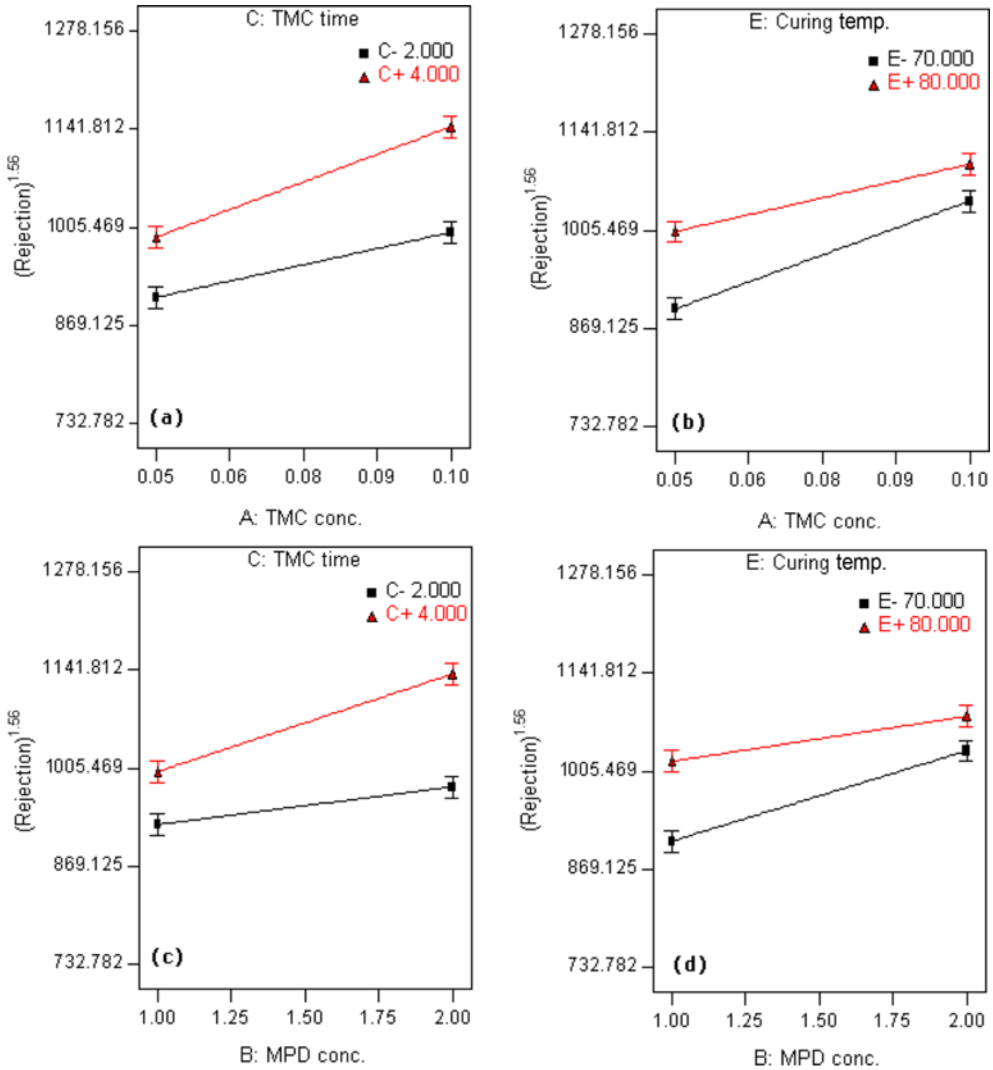

Fig. 12. Two factor interaction plots for oil rejection: (a) TMC concentration- immersion time in TMC, (b) TMC concentration-curing temperature, (c) MPD concentration- immersion time in TMC, (d) MPD concentration- curing temperature.

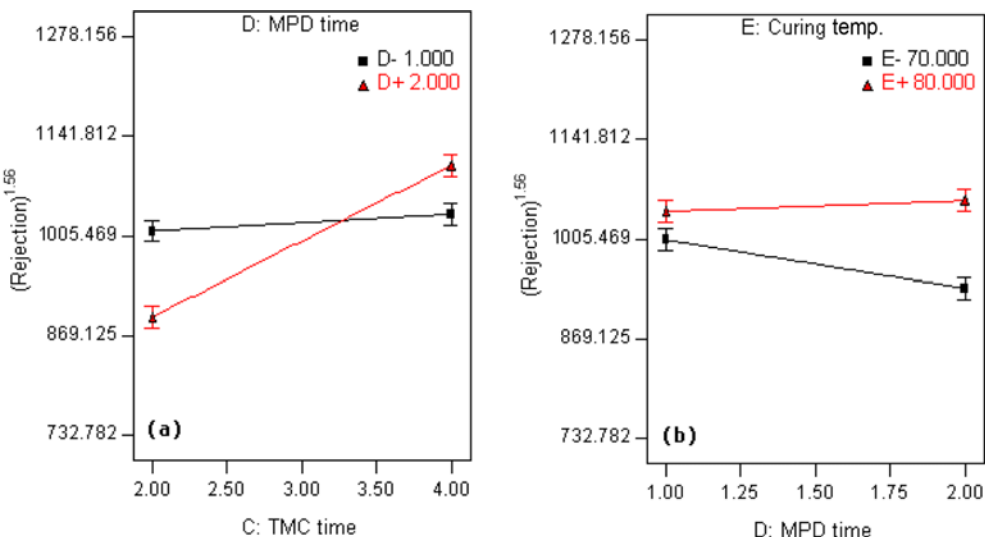

Fig. 13. Two factor interaction plots for oil rejection: (a) immersion time in TMC- immersion time in MPD, (b) immersion time in MPD-curing temperature.

Table 5. Optimal condition for preparation of polyamide composite membrane

	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
Constraints						
TMC concentration	is in range	0.05	0.1	1	1	3
MPD concentration	is in range	1	2	1	1	3
Immersion time in TMC	is in range	2	4	1	1	3
Immersion time in MPD	is in range	1	2	1	1	3
Curing temperature	is in range	70	80	1	1	3
Case 1:						
$(\text{Permeate flux})^{0.89}$	Maximize	4.4161	15.1828	1	1	3
$(\text{Rejection})^{1.56}$	Maximize	732.782	1278.16	1	1	3
Case 2:						
$(\text{Permeate flux})^{0.89}$	is in range	4.4161	15.1828	1	1	3
$(\text{Rejection})^{1.56}$	is target=1196.96	732.782	1278.16	1	1	3

Solution	TMC conc.	MPD conc.	Immersion time in TMC	Immersion time in MPD	Curing temp.	Permeate flux	Rejection	Desirability
Case 1	0.10	1.00	2.06	1.00	78	17.97	86.19	0.68
Case 2	0.1	1.94	3.88	1.95	71.96	8.86	93.94	1

preparation conditions. According to the literature, there is trade-off between permeability/permeate flux and rejection of TFC membranes [32]. In this case, maximum permeate flux of membrane denotes lowest solute rejection. Thus, it is necessary to optimize membrane performance by considering both permeate flux and rejection. In this study optimal design was carried out by using two different objectives. Table 5 shows numerical optimization result for two cases, including the optimal level for each factor. In the first optimization process, both permeate flux and oil rejection were set to maximum, where all factors were set to within the range. In this case, permeate flux of 17.97 ($l/(m^2$ h)) and oil rejection of 86.19% with desirability factor of o.68 were obtained. In second case, oil rejection was set to a target value (94%) and permeate flux was set within the range. The target value of oil rejection was selected according to the results reported by Kong et al. [33] during separation of lube oil from dewaxing solvents at 15 bar. Likewise to case 1, the constraints used were low level and high level of each factor. According to the results, the best value of permeate flux (8.86 $l/(m^2$ h)) was found at TMC concentration of 0.1%, MPD concentration of 1.94%, immersion time in TMC of 3.88 min, immersion time in MPD of 1.95 min and curing temperature of 71.96 °C with desirability factor of 1. To validate presented models, most similar operating conditions to optimal predicted conditions were applied to prepare TFC membrane in our recent study [31]. The prepared TFC membrane showed the oil rejection of 94.72±1.31% and permeation flux of about 10.4±0.54 l/m^2 h. As can be seen, the results are close to what is predicted by the models.

CONCLUSIONS

The polyamide composite membrane was prepared by coating of polyamide layer on the PEI/SiO_2 nanocomposite support via interfacial polymerization. The performance of prepared membranes in various polyamide preparation conditions was investigated through the separation of dewaxing solvents from lube oil filtrates. Two-level half fraction factorial design was employed to reduce the number of time consuming experiments. The statistical analysis helped to find the prediction models for oil rejection and permeate flux for selected OSN process. The results showed that a linear regression model can predict permeate flux with adjusted R-squared of 93.48% after transformation of response data. It was also observed that oil rejection data require transformation to present satisfactory predicting model. In this case, the oil rejection model was achieved with the adjusted R-squared of 94.82%. Also, TMC concentration, MPD concentration and immersion time in TMC have more contribution to the oil rejection and permeate flux. Two factor interaction plots showed that the TMC concentration-immersion time in MPD and MPD concentration-immersion time in MPD were the most significant interaction factors in permeate flux model. In the case of oil rejection response, immersion time in TMC-immersion time in MPD interaction was the most significant two factor interaction. Using multiple response method, optimal polyamide preparation conditions were obtained with specific desirability.

REFERENCES

1. R. J. Petersen, *J. Membr. Sci.*, **83**, 81 (1993).
2. S. P. Nunes and K. V. Peinemann, *Membrane Technology in the Chemical Industry*, Wiley-VCH, Weinheim (2001).
3. T. Matsuura, *Desalination*, **134**, 47 (2001).
4. W. J. Lau, A. F. Ismail, N. Misdan and M. A. Kassim, *Desalination*, **287**, 190 (2012).
5. A. K. Ghosh, B. H. Jeong, X. Huang and E. M. V. Hoek, *J. Membr. Sci.*, **311**, 34 (2008).
6. L. F. Greenlee, D. F. Lawler, B. D. Freeman, B. Marrot and P. Moulin, *Water Res.*, **43**, 2317 (2009).
7. C. Kong, T. Shintani, T. Kamada, V. Freger and T. Tsuru, *J. Membr. Sci.*, **384**, 10 (2011).
8. P. B. Kosaraju and K. K. Sirkar, *J. Membr. Sci.*, **321**, 155 (2008).
9. M. F. J. Solomon, Y. Bhole and A. G. Livingston, *J. Membr. Sci.*,

423, 371 (2012).
10. M. F. J. Solomon, P. Gorgojo, M. Munoz-Ibanez and A. G. Livingston, *J. Membr. Sci.*, In press (2013).
11. M. Dalwani, N. E. Benes, G. Bargeman, D. Stamatialis and M. Wessling, *J. Membr. Sci.*, **372**, 228 (2011).
12. I. C. Kim, J. Jegal and K. H. Lee, *J. Polym. Sci. Pol. Phys.*, **40**, 2151 (2002).
13. N. W. Oh, J. Jegal and K. H. Lee, *J. Appl. Polym. Sci.*, **80**, 2729 (2001).
14. P. S. Singh, S. V. Joshi, J. J. Trivedi, C. V. Devmurari, A. P. Rao and P. K. Ghosh, *J. Membr. Sci.*, **278**, 19 (2006).
15. A. K. Ghoshf and E. M. V. Hoek, *J. Membr. Sci.*, **336**, 140 (2009).
16. S. H. Chen, D. J. Chang, R. M. Liou, C. S. Hsu and S. S. Lin, *J. Appl. Polym. Sci.*, **83,** 1112 (2002).
17. A. Prakash Rao, S. V. Joshi, J. J. Trivedi, C. V. Devmurari and V. J. Shah, *J. Membr. Sci.*, **211**, 13 (2003).
18. C. Y. Tang, Y. N. Kwon and J. O. Leckie, *Desalination*, **242**, 168 (2009).
19. V. Freger, *Langmuir*, **19**, 4791 (2003).
20. V. Freger, *Langmuir*, **21**, 1884 (2005).
21. D. C. Montgomery, *Design and analysis of experiments*, John Wiley, New York (1997).
22. G. E. P. Box, W. G. Hunter and J. S. Hunter, *Statistics for experimenters—an introduction to design, data analysis and model building*, John Wiley & Sons, New York (1978).
23. A. Rathinam, J. R. Rao and B. U. Nair, *J. Taiwan Inst. Chem. Eng.*, **42**, 952 (2011).
24. R. Gottipati and S. Mishra, *Chem. Eng. J.*, **160**, 99 (2010).
25. A. Mirmohseni and S. Zavareh, *J. Polym. Res.*, **17**, 191 (2010).
26. M. Takht Ravanchi, T. Kaghazchi, A. Kargari and M. Soleimani *J. Taiwan Inst. Chem. Eng.*, **40**, 511 (2009).
27. E. Shokri and R. Yegani, *J. Memb. Sep. Technol.*, **1**, 43 (2012).
28. S. A. Abdul-Wahab and J. Abdo, *Appl. Therm. Eng.*, **27**, 413 (2007).
29. M. Amirilargani, M. Sadrzadeh and T. Mohammadi, *J. Polym. Res.*, **17**, 363 (2010).
30. Y. Li, H. M. Guan, T. S. Chung and S. Kulprathipanj, *J. Membr. Sci.*, **275**, 17 (2006).
31. M. Namvar-Mahboub and M. Pakizeh, *Sep. Puri. Technol.*, **119**, 35 (2013).
32. C. Y. Tang, Y. N. Kwon and J. O. Leckie, *Desalination*, **242**, 168 (2009).
33. Y. Kong, D. Q. Shi, H. W. Yu, Y. F. Wang, J. R. Yang and Y. Y. Zhang, *Desalination*, **191**, 254 (2006).