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RESEARCH ARTICLE

The effect of preparation parameters on performance of polyvinyl alcohol thin-film composite membrane: Experimental study, modeling, and optimization

Fatemeh Medhat Bojnourd | **Majid Pakizeh**

Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, PO Box 9177948974, Mashhad, Iran

Correspondence
Majid Pakizeh, Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, PO Box 9177948974, Mashhad, Iran.
Email: pakizeh@um.ac.ir

To systematically investigate the influence of preparation conditions on pure water permeability (PWP) and solute removal performance of polyvinyl alcohol (PVA) thin-film composite (TFC) membrane, fractional factorial design was applied. The considered conditions were related to 3 steps of the TFC preparation, including support membrane preparation, PVA coating, and cross-linking. The results showed that among the selected factors, polysulfone concentration (polymer of the support membrane), heat curing time (related to cross-linking condition), and their interaction have the most significant effects on the both permeability and salt rejection. The effects of significant factors interaction on permeability and solute rejection of PVA TFC membrane were discussed. Finally, optimum preparation conditions were calculated by numerical optimization to achieve maximum permeability and solute removal, simultaneously. The prepared membrane at optimum conditions showed PWP of 1.74 L/m^{2}hbar and 96.19% Na_2SO_4 rejection. It was realized that the prediction of mathematical models at optimum conditions was reliable with absolute average relative error 7.43% and 1.18% for PWP and rejection, respectively.

KEYWORDS

fractional factorial design, optimization, polyvinyl alcohol, preparation condition, thin-film composite membrane

1 | INTRODUCTION

Accessibility to high-quality water is an important issue around the world at the present time. Population growth along with development of cities and industries in the past few years have caused many environmental problems such as water shortage and contamination. Hence, wastewater treatment has been proposed as one of the best solutions to overcome water scarcity around the globe.[1] Nanofiltration (NF), a pressure-driven membrane separation, is an effective process in water purification, water softening, and waste water treatment because of its several advantages such as efficient removal of multivalent ions and organic molecules and lower operating pressure compared with reverse osmosis membranes.[2-6] Nanofiltration membranes are fabricated in 2 types of (i)Loeb-Sourirajan membrane or (ii) thin-film composite (TFC) membranes. Anisotropic morphology of the Loeb-Sourirajan membranes is formed through the phase inversion process. Thin-film composite membranes are fabricated by the formation of a thin barrier layer on the surface of a porous substrate membrane via dip-coating or interfacial polymerization method. Generally, separation properties and permeation rates of this type of membranes are higher.[5] Polyamide composite NF membranes, prepared via interfacial polymerization, are commercially used with high retention of multivalent ions and water passage. But polyamide layer has low chemical stability and chlorine tolerance that caused restriction on their application.[7] To develop TFC membranes with high stability in strong chemical conditions and low fouling, polyvinyl alcohol (PVA) can be used for the upper layer because PVA has high hydrophilicity; exceptional chemical, thermal, and mechanical stability; and good commercial availability.[8,9] Polyvinyl alcohol TFC membrane is fabricated by coating of PVA layer on a support membrane and cross-linking of the formed layer. By this method, a selective layer is created for NF membranes with high resistance to chemicals and fouling. But this type of TFC membranes suffers from relatively low permeability or selectivity in comparison with polyamide membranes.[8-12] Hence, several efforts have been done to enhance the performance of these membranes by various methods including addition of nanomaterials to PVA layer or improving fabrication methods.[5,8,9] There are also several studies that investigated the effects of various parameters in preparation of PVA TFC membranes by the dip-coating and surface cross-linking method to achieve higher permeate flux and solute rejection.[6,10,13,14] Gohil and Ray[6] studied the variation effects of some preparation parameters including concentration of polysulfone (as the support membrane), PVA and maleic acid (as the cross-linking agent), and cure time on the membrane flux and rejection of inorganic salts. This survey was done based on one-factor-at-a-time (OFAT) method in which one parameter was varied while the others were kept constant. Eventually, the optimum membrane preparation conditions were selected based on higher performance for each parameter. Lang et al[13] also studied the effects of PVA and cross-linking agent concentrations and cross-linking time and temperature on salt rejection and water permeability of PVA TFC membrane, using OFAT method. Based on this study, some preparation conditions were considered to fabricate two series of modified membranes with priority of high separation or high product rate.[10] From these studies, it can be seen that PVA TFC membrane preparation parameters were intricately influenced the performance of membrane process with varying extent of impacts. On the other hand, needed time and material for experimental runs were high; as a result, the applied OFAT method was effortful. Furthermore, it also discarded the effect of interactions between parameters; as a result, prediction of optimum condition was inefficient in some cases.[15-17]

For obtaining the efficient optimal preparation conditions, it is essential to construct a mathematical model by considering both permeability and selectivity of PVA TFC membranes simultaneously.[18] The best route to assess the effects of preparation conditions and achieve the optimum value of impressive parameters is a systematic approach like statistical design of experiments. Among the experimental design methods, factorial design was applied as an effective procedure to determine the dominant factors.[19,20] For polyamide TFC membranes, several studies have been done by using the statistical strategies such as fractional factorial design (FFD) to analyze the effects of different factors and their interactions on the membrane performance.[17] However, to the best of our knowledge, the application of FFD method to investigate the main preparation factors of PVA TFC membrane has not been investigated yet. Hence, the purpose of this study is to elucidate the effects of the preparation factors on performance of PVA TFC membrane by using statistical experimental design and finding the best fabrication condition. The applied approach permitted consideration of more effective parameters (including support membrane preparation, PVA coating, and cross-linking conditions) in comparison with previous studies by performing reasonable numbers of experimental runs. In addition, interactions between important parameters are statistically investigated. Considering these interactions, optimum preparation conditions are calculated and the optimized membrane is experimentally prepared and tested. Preparation of the optimum membrane with higher performance could be a preliminary step to overcome low selectivity/permeability performance of the PVA TFC membranes in comparison with polyamide TFC membranes.

2 | MATERIALS AND METHODS

2.1 | Materials

Polysulfone (PSf;Ultrason-6010) was supplied by BASF (Germany) as a polymer for preparation of the support membrane. Dimethyl formamide as solvent and sulfuric acid (98%) as catalyst were supplied by Merck Company. Polyvinyl alcohol (86-88% hydrolysis, Mw 130,000 g/mol) and glutaraldehyde (GA) (50% solution) as cross-linking agent were purchased from Sigma-Aldrich. Inorganic salt Na_2SO_4 of analytical grade, used as the model solutes to determine the salt rejection characteristics of the resultant TFC membranes, was purchased from Merck Company. Deionized (DI) water was used to prepare the aqueous solutions and to soak and rinse the membrane samples during experiments.

2.2 | Preparation of polyvinyl alcohol thin-film composite membrane

The asymmetric support membranes were prepared by a phase inversion technique. Specific concentration of PSf solution (15-17 wt%) was prepared in dimethyl formamide under constant stirring with dissolution period of 15 hours. The solution was kept at room temperature over night for the removal of air bubbles. Afterward, the homogeneous solution was cast on nonwoven polyester fabric that adjoined to a clean glass plate, using adjustable casting bar (Neurtek2281205) with a predetermined thickness (150-200 μm). The glass plate with the cast solution was kept for 10 seconds in the ambient condition. After that, the support was immersed into a distilled water bath for 1 day to ensure an adequate solvent/nonsolvent exchange. Then, PSf ultrafiltration support membrane was taken out from the bath, rinsed with DI water, and surface dried by intense nitrogen gas stream for few seconds just before coating process.

Certain amount of PVA powder was dissolved in DI water at 90°C by using stirring for about 8 hours to make the desired concentration (1-2 wt%) PVA aqueous solution. Next, PVA solution was cooled to room temperature, and the porous PSf support membrane was immersed in coating aqueous solution for specific period of time (3-5 min). Excess solution was removed, and the membrane was dried at ambient temperature (25 ± 2°C) for 20 minutes to ensure achieving uniform dry surface. Thereafter, the membrane was immersed in aqueous solution of GA with specified concentration (3-5 wt%) as cross linker and 0.5 wt% H_2SO_4 as catalyst for a certain time (10-30 s). The prepared membrane was finally heat cured during the specific period of time (3-5 min) and temperature (80-100°C). The resultant TFC membrane was washed thoroughly with DI water and stored wetly for 1 day until it was tested. The schematic illustration of the applied procedure to fabricate PSf support and PVA selective barrier layer of TFC membranes is presented in Figure 1.

2.3 | Membrane testing experiment

Membrane separation performance by considering pure water permeability (PWP) and solute rejection was measured through cross-flow permeation test. All the permeation tests were performed under the

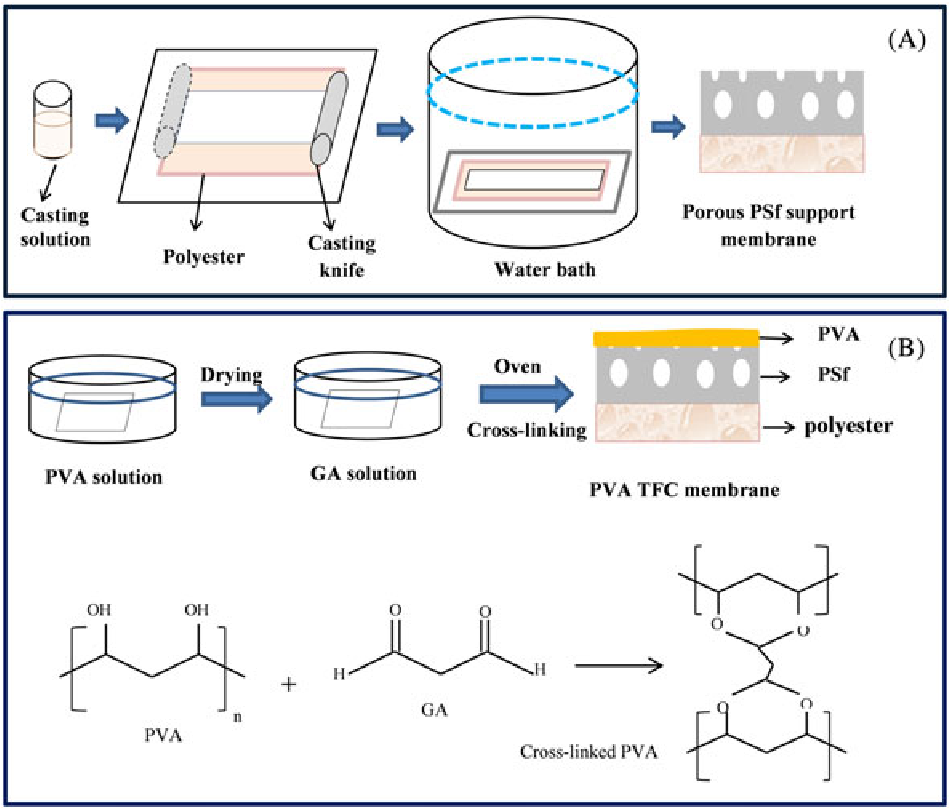

FIGURE 1 Schematic illustration of the 2-stage strategy to fabricate thin-film composite (TFC) membranes: A, Phase inversion process to fabricate polysulfone (PSf) supporting interlayer; B, coating and cross-linking polyvinyl alcohol (PVA) to synthesize the selective barrier layer including schematic of the cross-linking reaction [Colour figure can be viewed at wileyonlinelibrary.com]

circulation model at the constant temperature of 25 ± 1°C and pressure of 8 bar. A cross-flow filtration apparatus (Figure S1) was applied with circular filtration cell having an effective membrane area of 0.00138 m^2. The circular TFC membrane sheets were assembled in the filtration cell and compacted at 8 bar with DI water for at least 3 hours for stable PWP before each test.

Pure water permeability (L/m^2hbar) was calculated by using the following equation:

$$\mathrm{PWP} = \frac{V}{At\Delta p} \tag{1}$$

where V is the permeate volume (l), A is the membrane area (m^2), t is the permeation time (h), and ΔP is the pressure difference across the membrane.

The solute rejection (R) was calculated according to:

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100 \tag{2}$$

C_P and C_F are the solute concentration in permeate and feed streams, respectively. The salt concentration was obtained through conductivity measurements of the aqueous solution by using an electrical conductivity meter of Extech EC-400 (USA).

2.4 | Membrane characterization

The morphology of the surface and cross section of PSf support and PVA TFC membranes were observed with scanning electron microscopy (SEM; LED 1450 VP microscope, Germany) and field emission

TABLE 1 Factors and levels for 2^{8-4}_{IV} fractional factorial design (FFD)

Factors	Symbol	Unit	Real Values of Coded Levels −1	0	1	Values in Previous Studies
Polysulfone (PSf) concentration	A	wt%	15	16	17	13-19
Casting thickness	B	μm	150	175	200	100-200
Polyvinyl alcohol (PVA) solution concentration	C	wt%	1	1.5	2	0.5-2 (liquid separation)
Coating time	D	min	3	4	5	3-30
Glutaraldehyde (GA) solution concentration	E	wt%	3	4	5	1-5
Contact with GA time	F	s	10	20	30	1 s-30 min
Temperature of heat curing	G	°C	80	90	100	65-110
Time of heat curing	H	min	3	4	5	2-30

SEM (TESCAN, Czech Republic). For cross-sectional observation, the membrane was fractured after immersing in liquid nitrogen. The sample was coated with a thin layer of gold for electrical conductivity in a sputtering system.

2.5 | Experimental design and statistical procedure

In complicated systems, the experimental results are affected by more than 1 variable. But the study of all of them sometimes is not realistic. Thus, finding of main factors is applicable in many sciences. Factorial experimental design is 1 of the most efficient procedures for determining dominant variables for complex systems.[21] To comprehensive analysis of multivariable system, full factorial design is the perfect procedure. But the numbers of required experimental runs would be very large when the number of factors is large, and this is a serious issue. Because the number of needed runs will be (2^k) when the numbers of factors are equal to (*k*). An FFD, applying fraction of the needed number of experimental runs for full factorial design, can be used instead and achieved enough information about the main effects. Fractional factorial design is planned based on the insignificancy of the higher order interactions and is used efficient number of required runs to elucidate main effects and lower order interactions.[22] In addition, to obtain better explanation about the twisted plane response of factorial design, 3 runs are usually done at the centers of each factor value.[17,23]

In this study, the effects of 8 independent preparation factors on divalent salt separation and pure water permeation performance of PVA TFC membrane were investigated, applying 1/16 fraction of two-level 2^8 factorial design (2^{8-4}). The independent factors with the coded and actual values in the design are presented in Table 1. For

TABLE 2 Aliased terms structure for 2^{8-4}_{IV} fractional factorial design (FFD)

Main Effects
[A] = A + BCE + BDH + BFG + CDG + CFH + DEF + EGH
[B] = B + ACE + ADH + AFG + CDF + CGH + DEG + EFH
[C] = C + ABE + ADG + AFH + BDF + BGH + DEH + EFG
[D] = D + ABH + ACG + AEF + BCF + BEG + CEH + FGH
[E] = E + ABC + ADF + AGH + BDG + BFH + CDH + CFG
[F] = F + ABG + ACH + ADE + BCD + BEH + CEG + DGH
[G] = G + ABF + ACD + AEH + BCH + BDE + CEF + DFH
[H] = H + ABD + ACF + AEG + BCG + BEF + CDE + DFG

TABLE 3 Design layout and experimental results of 2^{8-4}_{IV} fractional factorial design (FFD)

Factors (Input Variables)										Responses (Output Variables)	
std	Run	A	B	C	D	E	F	G	H	PWP (L/m²hbar)	*R* (%)
11	1	−	+	−	+	+	−	+	−	2.78	77.41
5	2	−	−	+	−	+	+	+	−	3.27	75.23
8	3	+	+	+	−	+	−	−	−	1.54	90.12
6	4	+	−	+	−	−	+	−	+	0.52	93.75
3	5	−	+	−	−	+	+	−	+	0.53	85.85
2	6	+	−	−	−	+	−	+	+	1.69	96.13
4	7	+	−	−	−	−	+	+	−	1.198	95.86
9	8	−	−	−	+	−	+	+	+	1.76	97.81
16	9	+	+	+	+	+	+	+	+	0.42	97.43
7	10	−	+	+	−	−	−	+	+	0.76	95.62
13	11	−	−	+	+	+	−	−	+	0.51	87.80
18	12	0	0	0	0	0	0	0	0	0.86	97.19
17	13	0	0	0	0	0	0	0	0	1.3	95.128
10	14	+	−	−	+	+	+	−	−	2.71	88.65
15	15	−	+	+	+	−	+	−	−	2.22	70.6
14	16	+	−	+	+	−	−	+	−	0.66	95.98
1	17	−	−	−	−	−	−	−	−	5.73	71.89
12	18	+	+	−	+	−	−	−	+	0.64	95.24
19	19	0	0	0	0	0	0	0	0	1.26	96.36

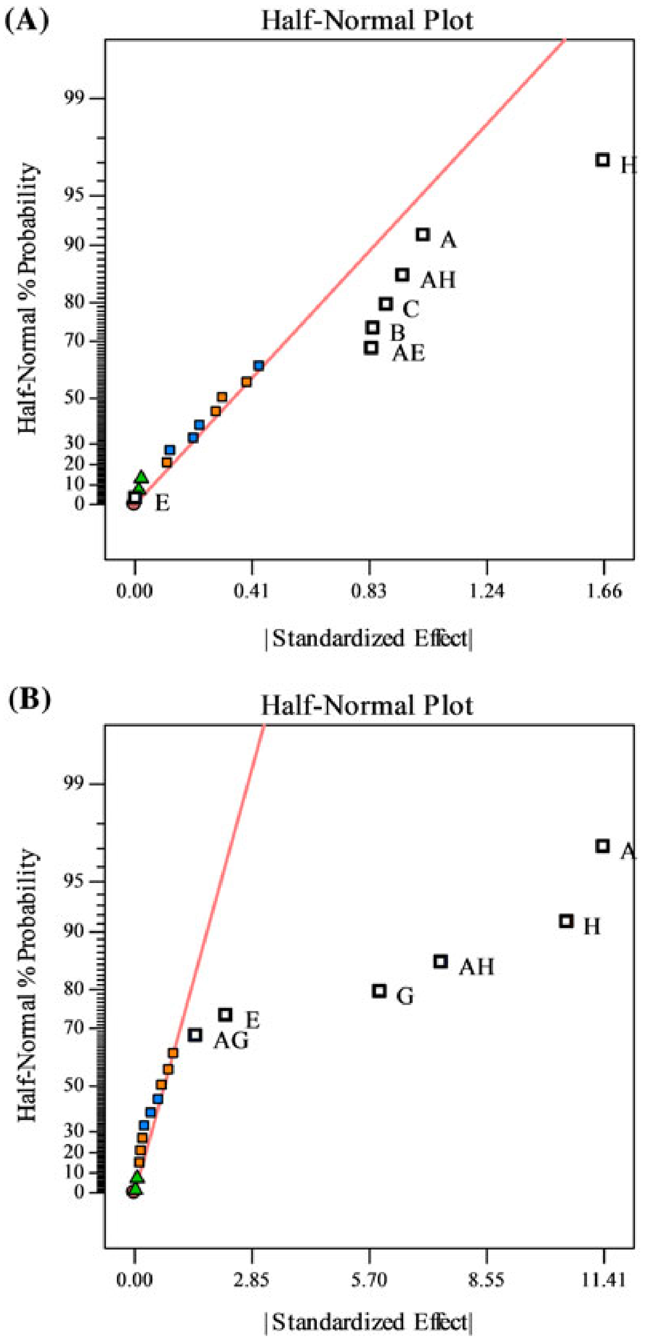

FIGURE 2 A half-normal probability plot of polyvinyl alcohol (PVA) thin-film composite (TFC) membrane filtration system, (A) pure water permeability (PWP) and (B) rejection (*R*) [Colour figure can be viewed at wileyonlinelibrary.com]

statistical analysis and constructing a mathematical model, the actual values of the independent variables (X_i) were coded by means of the following equation:

$$x_i = \frac{X_i - {\left(X_{i,\text{high}} + X_{i,\text{low}}\right)}/{2}}{{\left(X_{i,\text{high}} - X_{i,\text{low}}\right)}/{2}} \tag{3}$$

where x_i is the dimensionless coded value of X_i. $X_{i,\text{low}}$ and $X_{i,\text{high}}$ are the values of X_i at low and high values, respectively. The model will be written in the following general equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j \neq i}^{k} \beta_{ij} x_i x_j \tag{4}$$

by using multiple regressions and the least squares methods.

Actual values of each factor at 2 levels (high, +1, and low, −1, levels) were selected based on previous studies and few primary experiments. The coded level 0 (center points), which is the middle of the high and low values for each factor, is performed 3 times. Replicate runs that perform in the center of the factors are not affected by the usual effect estimates in the design and are applied to assess the analysis repeatability and to approximate the experimental error.[16]

Based on the effect hierarchy, principle lower-order effects are more important than higher order ones. Thus, by applying this principle, main effects and 2 factor interactions (2FIs) of them are considered as impressive ones and the higher-order interactions are neglected.[24] Table 2 shows the aliases structure of the $2^{8\text{-}4}_{\text{IV}}$ design. The defining relation is I=ABCE=ABDH=ABFG=ACDG=ACFH=ADEF=AEGH=BCDF=BCGH=BDEG = BEFH = CDEH = CEFG = DFGH = ABCDEFGH. Accordingly, this is called a resolution IV design because the smallest number of letters in any word in the defining relation is 4. As can be seen in Table 2, in the selected design, all of the main factors are free of 2FI's effects. Design Expert version 8.0.7.1 statistical software (Stat-Ease Inc) was used for the statistical analysis of the results and finding the optimum values of predicted responses and the related input values.

3 | RESULTS AND DISCUSSION

The data of fractional factorial experimental design $2^{8\text{-}4}_{\text{IV}}$ that were obtained from filtration laboratory test can be observed in Table 3. In the first step of factorial design model analysis, the significant factors must be selected statistically. The half-normal probability plot can be used to choose significant effects. A plot of the ordered values of a sample versus the expected ordered values from the true population

TABLE 4 ANOVA for selected factorial model (response: PWP (L/m^{2}hbar))

Source of Variation	Sum of Squares	*df*	Mean Square	*F* Value	*P* Value	
Model	27.68	7	3.95	14.22	.0002	Significant
Curvature	0.75	1	0.75	2.68	.1324	Not significant
Residual	2.78	10	0.28			
Lack of fit	2.66	8	0.33	5.62	.1597	Not significant
Pure error	0.12	2	0.059			
Cor total	31.21	18				
			R^2	0.9087		
			Adjusted R^2	0.8448		
			Adequate precision	12.191		

TABLE 5 ANOVA for selected factorial model (response: *R* (%))

Source of Variation	Sum of Squares	*df*	Mean Square	*F* Value	*P* Value	
Model	1352.32	6	225.39	194.37	<.0001	Significant
Curvature	152.49	1	152.49	131.51	<.0001	Significant
Residual	12.76	11	1.16			
Lack of fit	10.60	9	1.18	1.09	.5648	Not significant
Pure error	2.15	2	1.08			
Cor total	1517.57	18				
			R^2	0.9907		
			Adjusted R^2	0.9856		
			Adequate precision	36.523		

will be approximately a straight line. Thus, if the effects represent a sample from a normal population, we would expect to see them form an approximate straight line on a normal probability plot of the effects. In this regard, the half-normal probability plot follows the same principle as the full normal probability plot, except the sign of the effect is ignored in plotting. Thus, the outliers show up on the right side of the graph. Figure 2A and B was used to select the important factors with the farthermost to the line and put them in the model and refit the line to the remaining nonselected group of points for PWP and rejection, respectively. Selection was continued until most of the nonselected data fall on a relatively straight line. The significant factors were placed inclined from the straight line and could be recognized visually.

As a result, the order of significant factors for PWP and rejection (*R*) was *H* > *A* > *AH* > *C* > *B* > *AE* and *A* > *H* > *AH* > *G* > *E* > *AG*, respectively. Although for PWP, cross-linking concentration (*E*) main effect was not significant; these terms were added to the model to make the model hierarchical. In other words, parent (lower order) terms are added to complete the family of any higher-order terms.[16] The statistical analysis results revealed that among the studied factors, the factors *A* (PSf concentration) and *H* (heat curing time) are the most significant terms for both responses. Polysulfone concentration could have considerable impact on the structure and properties of support layer and the resulting TFC membrane.[6] In addition, most of the reported studies on PVA cross-linking reaction focused on heat curing as an important phase for stabilizing the PVA selective layer.[13,14] Thus, these 2 parameters and their interaction seem to have important effect on separation properties of PVA TFC membrane. Polysulfone casting thickness (*B*) and PVA concentration (*C*) are also significant terms with respect to PWP. Both of these factors affect the layers thickness as an impressive factor on the resistance against the flow of water.[8,13] Cross-linking agent concentration (*E*) and heat curing temperature (*G*) are significant factors for salt rejection property of PVA TFC membrane. Previous studies showed that these two factors have significant influence on cross-linking extent of the PVA layer.[6,9,13] Because the resistance against the flow of solute is contributed primarily by the cross-linked PVA layer, the significance of terms *E* and *G* for rejection response is justified.[13]

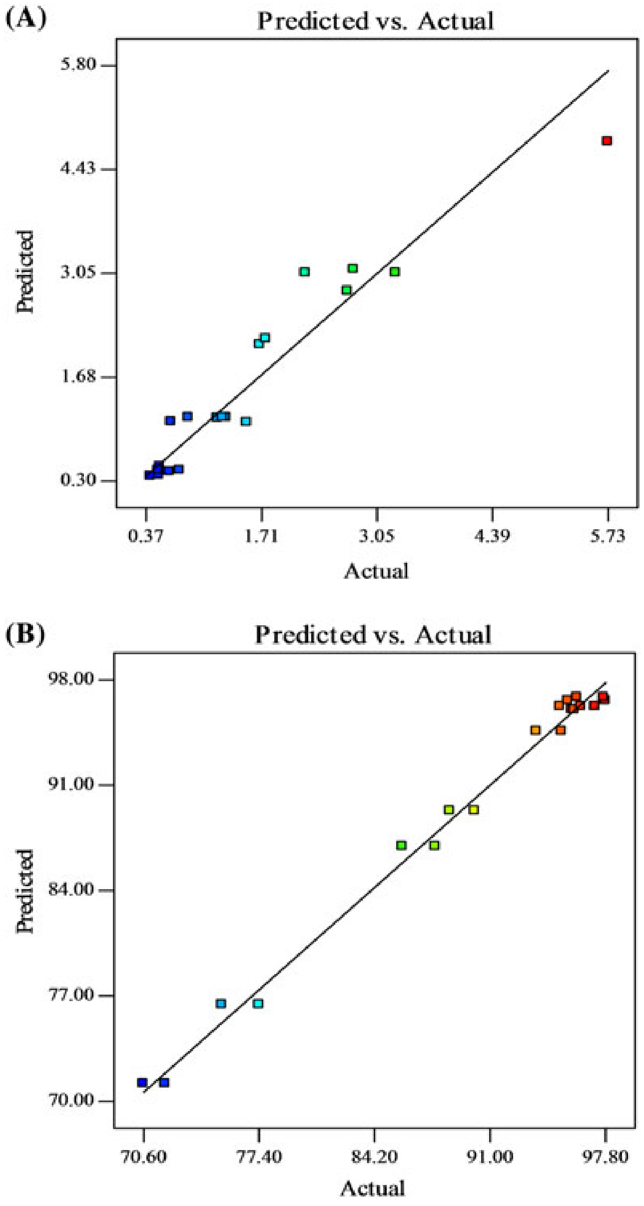

FIGURE 3 Correlation between experimental and predicted values of (A) pure water permeability (PWP) and (B) rejection (*R*) [Colour figure can be viewed at wileyonlinelibrary.com]

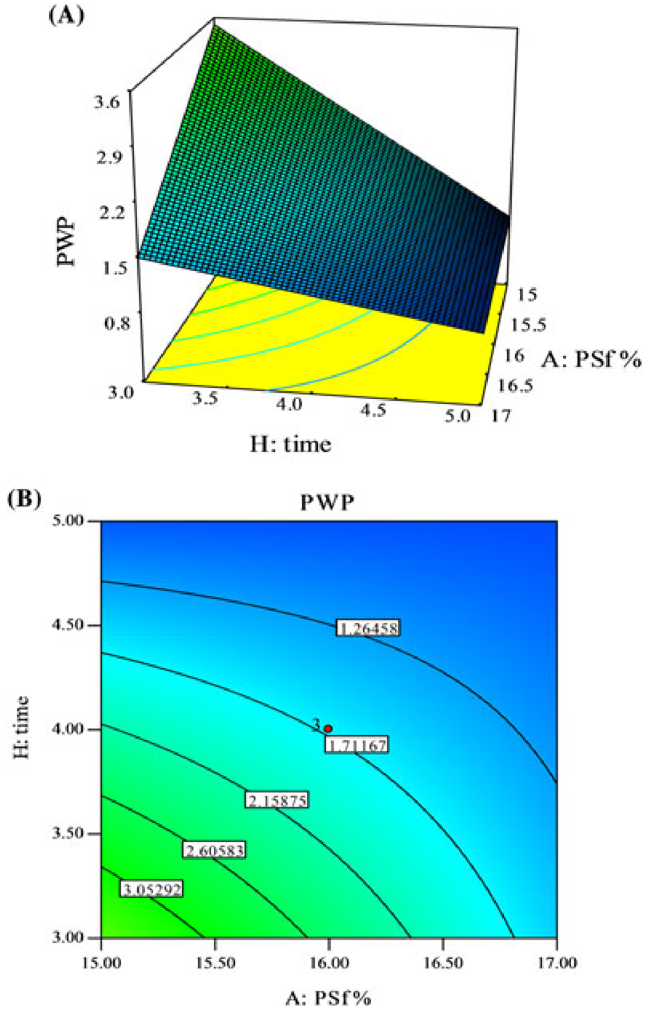

FIGURE 4 (A) 3D and (B) contour plots of the effect of polysulfone (PSf) concentration and heat curing time on pure water permeability (PWP) [Colour figure can be viewed at wileyonlinelibrary.com]

3.1 | Analysis of variance analysis

The significance of regression model, each term in the regression model, the lack of fit (LOF) and curvature were checked by means of ANOVA table.[16,25] The ANOVA for the PWP and rejection are given in Tables 4 and 5. The models *F* values implied that the two models were statistically significant. Based on models *P* values, there were only a 0.02% and 0.01% chance that "model *F* values" these large could occur due to noise for PWP and rejection, respectively. Variation of the data points, gathering from experimental runs, about the proposed model is measured in the LOF. The *P* values of 0.1597 and 0.5648 showed that the variations for both responses were not important relating to the pure error. The nonsignificant LOFs of two models also implied that the omitted factors were unessential terms.[25] The curvature *P* value <.0001 showed that there was a significant curvature for rejection response. The significant curvature showed a near-optimal space in the design region, because there was a large difference between the average of the center points and the average of the factorial points.[17]

Determination coefficient (R^2), one of the most important parameters in ANOVA table, indicates variation extent around the mean. The proposed models for PWP and rejection had R^2 values of 0.90 and 0.99, respectively. Completely close to 1 value shows good fitted models for expressing variability in both responses. When a new variable is added to the model, R^2 always increases even if the added variable is statistically nonsignificant. The adjusted coefficient of determination (adjusted R^2) is applied to this weakness resolving. The adjusted R^2 basically plateaus when insignificant terms are added to the model. According to Tables 4 and 5, R^2 (0.90 and 0.99) and adjusted R^2 (0.84and 0.98) values for both models are close to each other adequately, stating nonimpressive terms were not existed in two models. To compare the range of the predicted values at the experimental points by the average prediction error, adequate precision is used. Ratios greater than 4 indicate adequate model discrimination. The model adequate precision values of 12.19 and 36.52 implied that the models would have good performance in predictions.

Finally, the regression empirical models with the significant main effects and 2FIs, for PWP and rejection (*R*) responses of PVA TFC membrane based on coded variables, are presented as Equations 5 and 6.

$$\mathrm{PWP} = 1.68 - 0.51A - 0.42B - 0.45C - 0.00237E - 0.83H + 0.42AE + 0.48AH \tag{5}$$

$$R = 88.46 + 5.68A - 1.13E + 2.97G + 5.24H - 0.77AG - 3.75AH \tag{6}$$

Figure 3A and B shows the presence of conformity between the data acquired from the experimental runs and the predictions obtained by using the models for both PWP and *R* responses, respectively. The points should arrange randomly around the 45° line that places in the middle of the data over the whole range of the data. Figure 3 indicates that two models calculate responses in the design space close to experimental data and PWP and rejection (*R*) predictions by the FFD models would be accurate.

3.2 | Residual analysis and examining model adequacy

Assessing the studentized residuals is applied to check two assumptions of factorial FFDs: (1) normality of the errors and (2) equality of variances. For FFD in all randomized experimental runs of the design, reserving the factors at a fixed level must be observed as another checking.[22] Table 3 showed that PWP and rejection responses were obtained by performing the experiments in randomized run order at

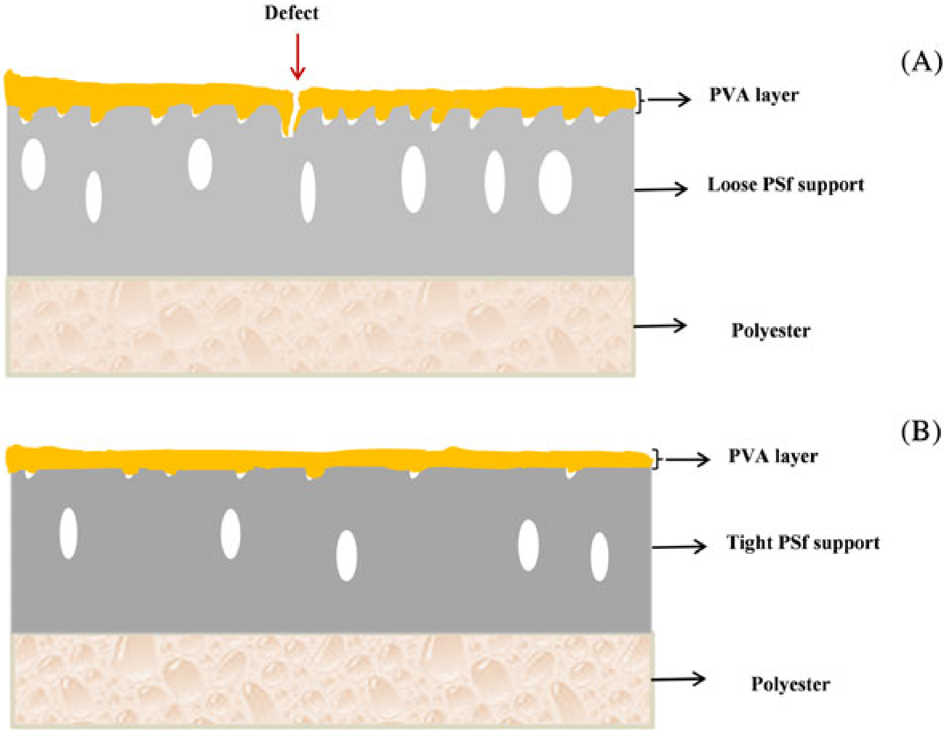

FIGURE 5 The effect of (A) loose and (B) tight support membrane on polyvinyl alcohol (PVA) top layer [Colour figure can be viewed at wileyonlinelibrary.com]

the fixed factor levels. The normal probability plot of the studentized residuals graph represents that the residuals followed a normal distribution in relatively a straight line. However, some scatters around the line may also be observed in normal data. Actually, certain patterns like the "S-shaped" pattern curve are not satisfied and transformation of the response may lead to a more accurate analysis. As shown in Figure S2, the residuals show that normal error distribution and response transformation were not necessary.

Constant variance assumption is assessed by some figures, which show the residuals versus existing variables including order of the tests, factors, and prediction values calculated by the models, for each run or factor level. The studentized residuals versus the prediction values of two responses are shown in Figure S3. It is seen that the points are scattered randomly and specific trends like positive and negative sequences of residuals are not graphically observed. The figures of the studentized residuals versus different variables such as the order of the experimental runs and factors for PWP and rejection were drawn (plots not shown). The assumption of constant variance is verified with no recognizable structure in all proposed plots.

3.3 | Effect of selected significant factors on pure water permeability and rejection of polyvinyl alcohol thin-film composite membrane

The relatively low permeate flux and rejection of the PVA TFC membranes is the most important challenges for them to achieve commercial success.[8,9] To realize the effect of important preparation condition on the performance of PVA TFC membrane, the interaction of the critical variables was studied by considering the regression model and changing values of two selected variables simultaneously, while the other variables values were in the midpoint. The statistical analysis results revealed that for both responses, factor *A* (PSf concentration) and factor *H* (heat curing time) are the most important factors. On the other hand, their interaction is also important. Thus, assessing their simultaneous effect on membrane performance would be notable. Figure 4A and B shows the 3D surface and contour plots of PWP versus binary interactions of PSf concentration (*A*) and heat curing time (*H*). As shown in this figure, increase in PSf concentration resulted in a decrease in the PWP because the pore size and general porosity of the substrate decrease with increasing polymer concentration. Thus, the water permeability of the TFC membrane decreased.[26,27] Increasing heat curing time at both low and high levels of PSf concentrations (15 and 17%) was also led to PWP decrement because more PVA layers could be cross-linked by time, although this decrement was more considerable when the polymer concentration of porous support was at low level (15%). It revealed the interaction between these two variables presented by the term of *AH* in Equation 5. Surface porosity of PSf membranes increases by decreasing the polymer concentration due to reduced local concentration of PSf in participation bath at the polymer and nonsolvent interface.[28] The loose support membrane with large surface pores that is formed at low PSf concentration is an inappropriate substrate to form dense and continuous PVA barrier layer.[6,27] More PVA could penetrate to the substrate layer because of larger pore size on the support top layer. As a result, defective and thick PVA layer is formed on the surface and pores of the substrate. Figure 5 schematically shows the effect of loose and tight support on the quality of formed PVA layer. To cross-linking of PVA chains is done to achieve PVA film stability and salt selectivity.[8,9] By increasing the heat curing time, the cross-linking reaction is fulfilled on the upper surface layers and continued for PVA chains at the lower layers and in the pores of the substrate. Thus, the thickness of dense layer (cross-linked PVA) would be larger at low PSf concentration and higher heat curing time. In addition, more cross-linking could eliminate some pores and defects, leading to higher flux reduction. Zargar et al also found the same result in investigating the effect of PSf concentration of support membrane on permeability of polyamide TFC membrane.[27]

The 3D surface and contour plots, as shown in Figure 6, present the effects of factors *A* (PSf concentration) and *H* (heat curing time) on salt rejection, while the other factors are constant. According to this figure, salt rejection increases by increasing the PSf concentration and heat curing time. The observed trend is predictable because increase in PSf concentration results in densification of support

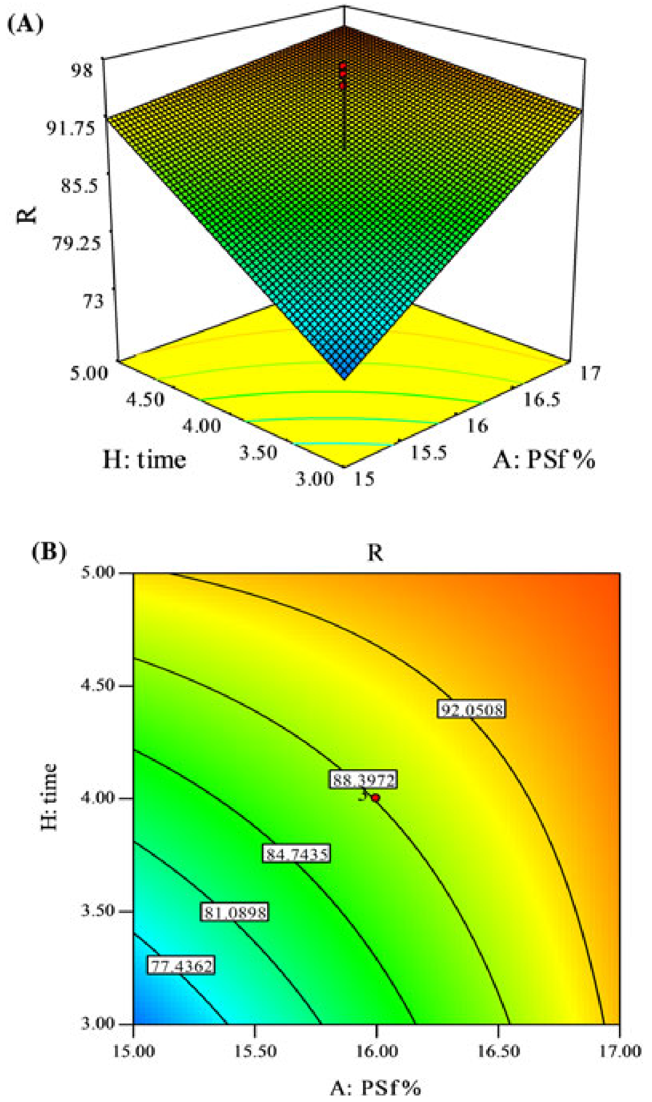

FIGURE 6 (A) 3D and (B) contour plots of the effect of polysulfone (PSf) concentration and heat curing time on salt rejection (*R*) [Colour figure can be viewed at wileyonlinelibrary.com]

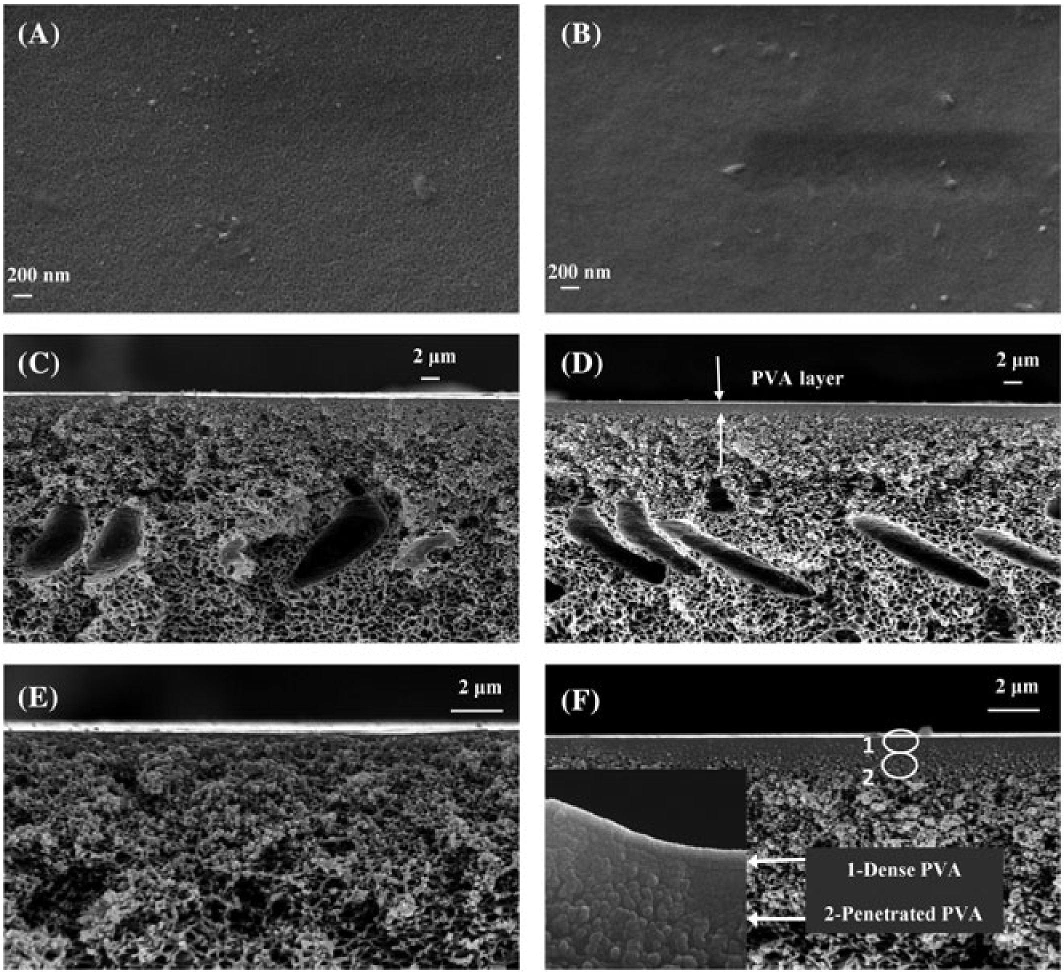

FIGURE 7 Surface of (A) polysulfone (PSf) and (B) polyvinyl alcohol (PVA) thin-film composite (TFC) membranes, (C and E) cross section of polysulfone (PSf), and (D and F) PVA TFC membranes

membrane structure with tight pore morphology.[6] Entrapment of PVA in tight PSf support will give a comparatively more uniform and uninterrupted PVA layer leading to high rejection. In addition, by increasing the heat curing time, more cross-linking is occurred by reaction of unreacted carboxyl and hydroxyl groups and PVA network is formed perfectly on the membrane surface. As a result, salt separation increases. On the other hand, at low PSf concentration, increasing heat curing time enhances PVA distension and cross-linking leads to somewhat elimination of pores and defects, and rejection increment is larger. However, salt rejection at low PSf concentration and high heat curing time is less than rejection at high PSf concentration and low heat curing time.

3.4 | Optimization of polyvinyl alcohol thin-film composite membrane preparation conditions

To determine the optimum levels of significant factors, optimization of both PWP and rejection was accomplished by a multiple response method called desirability (*D*) function. The goal of optimization was to maximize both two responses, and all factors were limited to their coded range. Finally, the optimal experimental conditions are applied, and the models accuracy was evaluated by the absolute average relative error (AARE). The AARE is calculated as follows:

$$\mathrm{AARE} = \frac{1}{N}\sum_{i=1}^{N}\left(\left|\frac{X_{\exp,i}-X_{\mathrm{pred},i}}{X_{\exp,i}}\right|\right) \tag{7}$$

The optimal conditions determined by software via numerical optimization are as follows: *A* = 15.62 wt%, *B* = 150 μm, *C* = 1 wt%, *D* = 4 minutes, *E* = 3 wt%, *F* = 20 seconds, *G* = 100°C, and *H* = 5 minutes with highest desirability (0.787) among 30 optimum points. The values for two responses are PWP = 1.89 L/m^{2}hbar and Rej = 97.37%. For validation, 3 filtration tests were carried out by the membranes, which

TABLE 6 Maximum responses and results of 3 new tests under optimal conditions for validation of the models

	Pure Water Permeability (PWP)	Rejection
Optimal responses	1.89	97.37
Three replicate	1.68	96.36
	1.83	95.13
	1.73	97.09
Average (experimental)	1.74	96.19
Absolute average relative error, AARE%	7.43	1.18

TABLE 7 Results of the some studies on preparation conditions of polyvinyl alcohol (PVA) thin-film composite (TFC) membrane

Research	Research Summary	Permeability (L/m^{2}hbar)	Rejection (Na_2SO_4)
Lang et al[10,13]	Studied the effects of PVA and cross-linking agent concentration and heat curing time and temperature by one-factor-at-a-time (OFAT) method and prepared 2 modified membrane based on priority given to higher product rate	4.27 2.8	77.3%* 87%*
Gohil et al[6]	Studied the effects of variation of different parameters like concentration of polysulfone (PSf), PVA, cross-linking agent, and cure time by OFAT method and evaluated the optimum membrane composition	1.16	90%**
This study	Studied the effects of 8 preparation parameters by systematic statistical method fractional factorial design (FFD) and obtained optimum preparation condition through numerical optimization	1.74	96.19%*

*2000 ppm feed solution concentration.

**Feed solution concentration was not mentioned.

were prepared under optimal conditions. Furthermore, the prepared optimum membrane was characterized by SEM and field emission SEM. Figure 7 presents the surface and cross-sectional micrographs of porous support and PVA TFC membranes. As can be seen, existing surface pores of the PSf (Figure 7A) were covered by PVA coated layer in which no pores were observed (Figure 7B). Figure 7D shows the good attachment of PVA layer on the surface of PSf support (Figure 7C). Figure 7F shows 2 closer views of the PVA layer on the top of the substrate (Figure 7E). From this figure, the two regions of PVA layer could be observed: (1) the dense and uniform PVA layer on the topmost of the whole membrane and (2) penetrated PVA to the surface of PSf membrane that confirms our past illustration about the formation of the PVA layer.

The PWP and rejection predicted data reported in Table 6 reveal that the prediction of two models is in good agreement with experimental data values.

Table 7 presented the results of the past researches that were carried out to obtain better performance of PVA TFC membranes by studying the coating and surface cross-linking preparation conditions. It seems systematic FFD procedure with assessing effective factors and their interactions simultaneously resulted in achieving better performance of PVA TFC membrane in both terms of permeability and solute removal at optimum preparation condition in comparison with the OFAT method. It is noteworthy that the numbers of experimental runs by FFD method were not large compared with the studies using OFAT method, even though the numbers of considered factors were quit large.

4 | CONCLUSIONS

The permeability and salt removal performance of PVA TFC membrane was investigated by considering preparation conditions including PSf concentration, substrate thickness, PVA concentration, coating time, GA concentration, contact with GA time, heat curing time, and temperature as independent variables. To find the main effects and obtaining optimum conditions, the FFD of experiment was performed by using Design Expert statistical software to model PWP and rejection of salt solution responses. The results showed that PSf concentration and heat curing time and their interaction are the most significant factors for both responses. It was suggested that the morphology of the support membrane is an impressive factor to achieve high permeability and solute removal by PVA TFC membrane. In addition, increase in heat curing time could eliminate the formed defect of the PVA layer on loose support membrane. Optimum preparation conditions were also found by numerical optimization based on highest desirability. It has been realized that the prediction of mathematical models at optimum conditions is reliable with good accuracy (AARE 7.43% and 1.18% for PWP and rejection, respectively). Finally, the better maximum permeate and rejection performance of PVA TFC membrane were obtained simultaneously based on optimum preparation conditions in comparison with performance of other studies using OFAT method.

ORCID

Fatemeh Medhat Bojnourd http://orcid.org/0000-0003-3067-7461

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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