A predictive model for tuning additives for the fabrication of porous polymeric membranes

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Keywords: porous membranes, PVDF, ultrafiltration, response surface methodology

Abstract
In order to study the influence of the preparation conditions on the performance of the polyvinylidene fluoride (PVDF) flat membranes, which were prepared via phase inversion method, a set of experiments based on response surface methodology (RSM) of central composite design (CCD) for three variables with five levels was performed. N,N-dimethyleacetamide (DMAc) and polyvinylpyrrolidone (PVP) were employed as solvent and pore former additive, respectively. PVDF and PVP conditions in the casting solution as well as the ethanol content in the coagulation bath were set as main manufacturing variables. Interactions of the preparation variables besides their quadratic main effects and on the desired responses namely; pure water flux, mean pore size, tensile strength, morphology and the porosity of the prepared membranes were investigated. The predicted and experimental results were found to be in good agreement (R2 values of 0.97, 0.95, 0.91 and 0.81 for pure water flux, mean pore size, tensile strength and porosity respectively, were obtained). The applicability of the CCD based RSM for the performance modeling of PVDF flat sheet membranes has been successfully evaluated.

Nomenclature

\[ J_w \] Permeation flux (LMH)
\[ Q \] The volumetric flow rate (L/hr)
\[ \Delta P \] The transmembrane pressure (bar)
\[ A \] The effective membrane area (m²)
\[ R \] The rejection for BSA protein solute (%)
\[ C_f \] Solute concentration in the feed solution (ppm)
\[ C_p \] Solute concentration in the permeate (ppm)
\[ \beta_{i_0}, \beta_{i_1}, \beta_{i_2}, \beta_{i_3} \] Regression coefficients
\[ \alpha \] Stokes radius (cm)
\[ d_p \] Pore size (nm)
\[ \delta \] Solute separation (%)
\[ M \] Molecular weight (g/mol)
\[ \mu_p \] Geometric mean pore size of the membrane (nm)
\[ \sigma_p \] Geometric standard deviation of pore size
\[ w_4 \] Weight of the wet membrane (g)
\[ w_2 \] Weight of the dry membrane (g)
\[ D_k \] Water density (g/cm³)
\[ D_p \] Polymer density (g/cm³)
\[ X \] Coded values
\[ X_i \] Corresponding actual value
\[ X_0 \] Actual value in the center of the domain
\[ \Delta X \] Increment of \( X_i \) corresponding to a variation of 1 unit of \( x \)
\[ R^2 \] Predicted statistic coefficient
1. Introduction

Immersion precipitation phase inversion process is a common method for preparation of ultrafiltration asymmetric membranes which can be used in various wastewater industries [1]. Despite phase inversion wide application in commercial membranes fabrication, many process aspects are still ambiguous, which makes the analysis of the process complicated due to a variety of mutual interactions between raw materials in the casting or coagulation solutions.

Generally, there are two types of dominating correlated factors which control the formation of phase inversion membrane during the solidification of casting solution namely: thermodynamics and kinetics. The phase equilibrium between components of the system the former is related to and the latter is related to the mutual diffusivities between them. In practice, the filtration efficiency of ultrafiltration membranes strongly depends on the membrane pore size distribution, which shall be adjusted exactly aiming [2] to achieve a desired membrane morphology and performance [3]. This can be done effecting by controlling two factors: composition of the dope solution and the coagulation bath [4].

Polyvinylpyrrolidone (PVP), which is known as a nontoxic, water soluble polymer and a demixing accelerator during phase inversion process or a permeate flux enhancer is a common agent, as an additive, to adjust pore size of the polymeric membranes and their pore size distribution. PVP addition enhances membrane permeability, improve its hydrophilicity and reduce fouling [5–10]. Considering its high molecular weight and non-solvent characteristics in a stable binary solution, it is very important to have some information regarding the way PVP causes thermodynamic and rheological variation [11–13]. A significant increase of the effective porosity of Polyvinilidene fluoride (PVDF) hollow fiber membrane, with improved membrane structure and excellent mechanical properties, as a result of PVP addition was observed by Simonea et al [7]. Similar results were obtained by Fontananova et al [5]. Wang et al studied the effect of PVP as an additive with different molecular weights and concentrations on the morphology and performance of hollow fiber membrane in detail [11]. They concluded that high water flux and acceptable solute retention were obtained using low molecular weight PVP (Mw: 10,000) in the casting solution, while with higher molecular weight PVP (Mw: 360,000) the opposite results were reported. In other words, while low molecular weight PVP tends to create small pores and easily leaches out of the membrane, most of the high molecular weight PVP remains in the membrane matrix and may block the path of the interconnected voids.

Coagulation medium is one of the key elements in controlling the rate of liquid–liquid demixing and crystallization. Common coagulants that have been studied so far are: water (acts as the harsh non-solvent), alcohols (act as the soft non-solvent), and mixture of water with various alcohols or with various solvents. For example, the effect of ethanol content of the coagulation bath on PVDF flat membrane structure was investigated by Cao et al [14]. Their results indicated that the degree of crystallization and surface roughness of prepared membranes elevates as a result of further increase of ethanol content in coagulation bath and extended immersion time. In addition, β phase is a dominated crystalline form in these membranes. Deshmukh and Li studied the influence of ethanol in the coagulation bath on PVDF hollow fiber membrane morphology [12]. The structural change of PVDF membranes corresponding to ethanol/water ratio in external coagulation bath was observed. Increasing ethanol concentration in coagulation bath results in decreasing the membrane effective porosity and the rate of precipitation which followed by a morphological changes from finger-like structures to sponge-like structures. Considering their results, comparing two parameters i.e. the process kinetic and the thermodynamic properties, the former is rather controlling the mechanism of membrane formation. Khayet et al reported similar trends of the membrane effective porosity [6].

In order to optimize the additive content in the coagulation bath or dope solution, aiming to achieve the ultimate ultrafiltration structure, manipulation of these parameters by trial and error can be considered as a common method via so called ‘changing one factor at a time approach’. This means keeping all factors unchanged except a single variable for a particular set of experiments. Likewise, optimization of other factors would be done individually through the time consuming single dimensional searches. In such approach reaching the true optimum as interaction among variables is not taken into consideration [15]. On the other hand, a few factors at the same time can be taken into account for optimization through traditional orthogonal method, however, it cannot get a function expression between the factors and the corresponding response values, and it is difficult to find out optimal factor combination and optimal response value in the whole area.

Therefore development of a reliable model which can predict the membrane performance pursuant to various changes of fabrication parameters is considered as an applicable tool for membrane production scale up and greatly improves the economy of the process by elimination of some time-consuming and costly experiments of optimization procedure. In this regards, various computerized approaches based on regression analysis, phenomenology, artificial neural network (ANN), genetic algorithm (GA) and statistical methods such as response surface methodology (RSM) has caught increasing attention in the field of membrane fabrication. In a recent research, chek-ab et al studied phenomenological models to predict cellulose acetate membrane
characteristics [16]. However, accuracy of the generated models using traditional regression techniques decreases when the number of parameters simultaneously affecting a process such as membrane fabrication, increases. For such cases, ANN, GA and RSM are considered as effective alternatives to model nonlinear multivariable systems [17]. In theory, ANN is composed of a group of simple functioning elements based on the structure and processing of biological neural networks which are ordered in parallel layers and internally connected [18]. Indeed, GA which is a bio-inspired optimizer alone [19] or in combination with ANN was introduced as a useful approach to find the best fitness function in PVDF [20], polyethersulfone (PES) and polysulfone (PS) membranes preparation [18]. We found few references to compare ANN and RSM modeling capabilities in membrane science and this makes it a little hard to judge about the pros and cons of each approaches [21, 22]. However, the intrinsic need of ANN to large amounts of training data to recognize a reliable pattern was the reason behind the selection of RSM in this research.

Response surface methodology which is a statistical method includes interactive effects of individual, too and effectively helps researchers to develop models, evaluate the effects of several factors and determine the optimum conditions for suitable responses while performing minimum number of experiments [23]. The design of experiments (DoE) and RSM has been applied successfully in various scientific and technical fields such as applied chemistry and physics, biochemistry and biological, chemical engineering, environmental protection and so on [24–26]. However, to our best knowledge there have been few studies about the function of RSM in membrane fields. For instance Ismail and Lai prepared defect-free asymmetric polysulfone membranes for gas separation and studied the effect of membrane fabrication variables and their manipulation using RSM [27]. Khayet et al used (RSM) to develop predictive models for simulation and optimization of nanofiltration membranes modified by UV-initiated graft polymerization technique [26]. Vatapour et al used RSM to optimize polyamide formation in interfacial polymerization of m-phenylene diamine (MPD)-trimesoyl chloride (TMC) [28].

The present study investigates PVDF concentration and the comparative suitability of PVP and ethanol as additives for dope and coagulation bath, respectively for producing PVDF ultrafiltration membranes with a various range of pore sizes. Central composite design (CCD) and response surface methodology (RSM) were used to design of experiments and fit the models. Pure water flux, mean pore size, mechanical strength and porosity of the prepared membranes were measured as desired responses. Thus, the statistical design was based on three factors (PVDF, PVP and ethanol concentrations) and four responses (pure water flux, mean pore size, mechanical strength and porosity). This method is an economical way of obtaining the maximum amount of information in a short period of time and with the fewest number of experiments.

2. Experimental

2.1. Materials
Polyvinylidene fluoride (PVDF; molecular weight 573,000 Da) supplied by Solvay, France was used as the base polymer in the membrane casting solution. Reagent grade DMAc (99.5% purity) supplied by Merck, Germany, was used as solvent without further purification. Reagent grade PVP (average molecular weight 10,000 Da) was applied as additive in the casting solution and supplied by Sigma-Aldrich, Germany. Ethanol (99.5% v/v purity) supplied by Merck, Germany was used as coagulation bath additive. Deionized water was used as the main non-solvent in the coagulation bath and was provided from our laboratory. Polyethylene glycols (PEGs with Mn = 1000, 6000, 10 000, 20 000 and 35 000 Da) and polyethylene oxides (PEO with Mn = 100 000, 200000 Da) were supplied by Sigma Chemical Co.

2.2. Membrane preparation
For the preparation of the polymeric dopers, PVDF was dissolved in DMAc following PVP addition as the pore former. The polymer concentration and amount of additive in each dope was determined according to experiment design that is presented in table 1. Each dope was kept under constant stirring at 60 °C until a homogeneous solution was obtained. Afterwards, the casting solutions were degassed to allow complete release of the bubbles. The homogeneous casting solutions were cast uniformly on a glass substrate by means of a casting knife with a knife gap adjusted at 220 μm and immediately immersed in a coagulation bath. All other parameters such as coagulation bath temperature, immersion time, ambient humidity etc were kept constant during the manufacturing process for all membranes so as to avoid the influence of these parameters on the membrane structure.

2.2.1. Solution viscosity and cloud point
Viscosities of PVDF solutions with different amount of PVP were measured using a viscometer (Anton paar, model Physica MCR 5,1) at a constant temperature of 25 °C and at a shear rate of 10 s⁻¹.
The method which was presented by Blanco et al. was used for cloud point determination [29]. In this study, components concentration in the dope solution was based on the design of experiment according to table 1. The slow injection of coagulation medium into each casting dope was continued until visually detected turbidity occurred. Afterwards, each one was heated to about 70 °C to dissolve the formed heterogeneous phase then cooled down to 30 °C. The mass balance in the system corresponding to the added volume, at which turbidity started to form upon cooling, was used to calculate the cloud point composition. This protocol was chosen because phases often separate locally at the spot where the non-solvent mixture hits the polymer solution. If the system becomes clear after a heating–homogenization–cooling sequence, then the cloud point had not been obtained at that composition and temperature which was studied. Then, more volume of non-solvent mixture was added to the casting dope and the temperature sequence was repeated until observation of a steady turbidity.

### 2.3. Membrane Characterization

#### 2.3.1. Filtration Experiments

The performance of the prepared membranes was analyzed through a cross-flow setup. Figure 1 represents the scheme diagram of the experimental setup. The effective membrane area was 33.3 cm².

The pure water flux (PWF) of each membrane was measured using deionized water, firstly, under the transmembrane pressure of 1 bar at a feed flow rate of 6 l min⁻¹. A centrifugal pump circulated the feed solution through the membrane module. Aqueous solutions containing non-ionic macro-molecules, i.e., PEG and PEO of various molecular weights were considered as the feed solution following the pure water test, to perform solute rejection experiment. The initial feed solute concentration was 200 ppm. The pure water flux and the rejection are defined by equations (1) and (2), respectively.

\[ J_w = \frac{Q}{A\Delta t} \]  

(1)
\[
\frac{df}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[ -\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right]
\]

Where \(d_p\) is the pore diameter.

2.3.3. Membrane porosity
Gravimetric method was used to determine the membrane porosity, by measuring the weight of water in the membrane pores. The porosity of the membranes \(\varepsilon\) can be calculated using the following equation:

\[
\varepsilon = \frac{W_1 - W_2}{W_1 - W_2 + \frac{W_2}{D_p}}
\]

Where \(w_1\) is the weight of the wet membrane; \(w_2\) is the weight of the dry membrane; \(D_w\) is the water density \((0.998 \text{ g cm}^{-3})\) and \(D_p\) is the polymer density \((1.78 \text{ g cm}^{-3}, \text{as reported in Solvay technical data sheets})\).

2.3.4. Membrane morphology and structure
The membrane’s morphology was observed by using a scanning electron microscope (SEM, Quanta FENG200, FEI Company). Flat sheets cross-sections were prepared by freeze fracturing the samples in liquid nitrogen.

2.3.5. Membrane mechanical properties
The tensile strength of the membranes was measured by means of a ZWICK/ROELL Z 2.5 test unit. The stretching rate for each sample was at a constant value of 5 mm min\(^{-1}\). The initial distance between the clamps was of 5 mm. Five specimens were tested for each sample aiming to achieve an average value. The breaking elongation and elastic or Young’s modulus were determined, too.

3. Results
3.1. Experimental design
A central composite design (CCD) was employed in this study. Polymer concentration \((A)\), PVP content in the casting solution \((B)\), and ethanol content in the coagulation bath \((C)\) were chosen as independent variables. The range and center point values of three independent variables are presented in table 1, which are based on the results of preliminary experiments to prepare casting solution with suitable viscosity to obtain the membranes with pore sizes in the ultrafiltration range (results are not shown). Five replication of the central point, six axial point at a distance of \(\pm 1.682\) from the center and eight factorial points formed our experimental design table (table 2).
Table 2. CCD with the observed response values for PWF, mean pore size, tensile strength and porosity.

| Run | A   | B   | C   | PWF (LMH) | Mean pore size (nm) | Tensile strength (MPa) | Porosity |
|-----|-----|-----|-----|-----------|---------------------|-----------------------|----------|
| 1   | −1  | −1  | −1  | 78.34     | 13.14               | 2.32                  | 0.801    |
| 2   | −1  | −1  | −1  | 22.56     | 8.1                 | 4.03                  | 0.769    |
| 3   | −1  | −1  | −1  | 275.96    | 32.21               | 0.85                  | 0.847    |
| 4   | 1   | 1   | −1  | 261.46    | 28.25               | 1.375                 | 0.830    |
| 5   | −1  | −1  | 1   | 89.58     | 8.26                | 3.075                 | 0.767    |
| 6   | 1   | 1   | −1  | 26.92     | 7.87                | 4.935                 | 0.713    |
| 7   | −1  | 1   | 1   | 105.95    | 17.6                | 1.84                  | 0.813    |
| 8   | 1   | 1   | 1   | 88.44     | 17.22               | 2.435                 | 0.790    |
| 9   | −1.682 | 0   | 0   | 93.34     | 15.73               | 1.775                 | 0.799    |
| 10  | 1.682 | 0   | 0   | 60.96     | 11.93               | 3.045                 | 0.768    |
| 11  | 0   | −1.682 | 0   | 6.34      | 3.55                | 5.39                  | 0.676    |
| 12  | 0   | 1.682 | 0   | 221.93    | 27.81               | 1.46                  | 0.80     |
| 13  | 0   | 0   | −1.682 | 200.38    | 28.52               | 1.345                 | 0.851    |
| 14  | 0   | 0   | 1.682 | 60.5      | 10.65               | 2.32                  | 0.782    |
| 15  | 0   | 0   | 0   | 71.17     | 13.11               | 3.1                   | 0.790    |
| 16  | 0   | 0   | 0   | 68.34     | 13.87               | 3.01                  | 0.780    |
| 17  | 0   | 0   | 0   | 83.27     | 12.58               | 2.95                  | 0.761    |
| 18  | 0   | 0   | 0   | 85.92     | 11.5                | 2.78                  | 0.777    |
| 19  | 0   | 0   | 0   | 75.8      | 12.65               | 3.025                 | 0.781    |
| 20  | 0   | 0   | 0   | 77.49     | 12.84               | 2.89                  | 0.771    |

Three experiments were carried out at each experimental design point and the mean values were stated as observed responses. Experimental runs were randomized, to minimize the effects of unexpected variability on the observed responses. Coded variables were obtained according to the equation blow:

\[ x = \frac{(X_i - X_0)}{\Delta X} \]  

(7)

where \( x \) is the coded value, \( X_i \) is the corresponding actual value, \( X_0 \) is the actual value in the center of the domain, and \( \Delta X \) is the increment of \( X_i \) corresponding to a variation of 1 unit of \( x \). Considering the composite design, the mathematical model used in the study was:

\[ Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j + e \]

(8)

Where \( Y \) is the dependent variables (PWF, tensile strength, mean pore size and porosity), \( \beta_0 \) is the model constant, \( \beta_i \), \( \beta_{ii} \) and \( \beta_{ij} \) are the model coefficients and \( e \) is the error. They show the linear, quadratic and interaction effects of the variables. Analysis of the experimental design data and calculation of predicted responses were carried out using Design Expert software (Version 9.2, Stat-Ease). In order to verify the validity of the statistical experimental design, additional confirmative experiments were subsequently conducted. The effects of three process variables, i.e., PVDF concentration (A: 13–18 wt%), PVP content in casting solution (B: 0–7 wt%) and ethanol content in coagulation bath (C: 0–50 v%), were investigated in this study. Four responses of interest were PWF, mean pore size, tensile strength and porosity. The results of 20 runs using CCD design are shown in table 2, which include the design and the observed responses values. The observed ranges for PWF and porosity were 6.34–275.96 LMH and 0.67–0.85, respectively. The highest PWF (275.96 LMH) was obtained under the experimental conditions of \( A = 14.01 \) wt%, \( B = 5.58 \) wt%, and \( C = 10.13 \) v%; whereas the highest tensile strength (5.39 MPa) was obtained under conditions of \( A = 15.5 \) wt%, \( B = 0 \) wt%, and \( C = 25 \) v%. A wide range of mean pore size was obtained (3.35–32.21 nm) and the maximum point was found under the same conditions of \( A = 14.01 \) wt%, \( B = 5.58 \) wt%, and \( C = 10.13 \) v%. Therefore, a correlation was developed, in order to obtain desirable responses.

3.2. Model fitting

Fitting quadratic models to the results was illustrated in table 3. The contribution of the quadratic model was significant as a results of analysis of variance (ANOVA). The quadratic models for PWF, mean pore size, tensile strength and porosity fitted the coded variables are given in equations (9)–(12) respectively. The significance of each coefficient was determined using the F-test and p-value in table 3. The greater absolute F-value and the
smaller p-value corresponds to more important variables [31]. Lack of fit was also given in table 3 in order to check the quality of the fitted models. The coefficients were removed from the model which were not significant at the 95% confidence level to build a model with less variables and improve its capability of prediction.

\[
PWF = 78.39 - 15A + 64.22B - 41.2C + 10.8AB - 44.83BC + 14.94B^2 + 20.71C^2
\]

\[
\text{Mean Pore Size} = 13.07 - 1.18A + 7.23B - 4.45C - 0.32AC + 2.57BC - 0.99B - 2.38C
\]

\[
\text{Tensile Strength} = 2.96 - 0.5A - 1.06B + 0.39C - 0.31AB - 0.18A^2 + 0.18B^2 + 0.38C^2
\]

\[
\text{Porosity} = 0.78 - 0.013A + 0.032B - 0.02C - 0.011B^2 + 0.016C^2
\]

Table 3. ANOVA results for response surface quadratic model, which show the relationship between responses and independent variables (A), (B), (C).

| Source               | Sum of squares | DF | Mean Square | F-value | P-value |
|----------------------|----------------|----|-------------|---------|---------|
| Pure water flux (LMH)| 1.083E + 005   | 7  | 15476.44    | 211.22  | < 0.0001|
| A-PVDF content       | 3074.40        | 1  | 3074.40     | 41.96   | < 0.0001|
| B-PVP content        | 56316.59       | 1  | 56316.59    | 768.61  | < 0.0001|
| C-ETOH content       | 23183.07       | 1  | 23183.07    | 316.40  | < 0.0001|
| AB                   | 933.77         | 1  | 933.77      | 12.74   | 0.0039  |
| BC                   | 16076.93       | 1  | 16076.93    | 219.42  | < 0.0001|
| B^2                  | 3250.60        | 1  | 3250.60     | 44.36   | < 0.0001|
| C^2                  | 6242.06        | 1  | 6242.06     | 85.19   | < 0.0001|
| Residual             | 879.25         | 12 | 73.27       |         |         |
| Lack of Fit          | 649.71         | 7  | 92.82       | 2.02    | 0.2279  |
| Total                | 1.092E + 005   | 19 |             |         |         |
3.3. PWF response analysis

In this case A, B, C, AB, BC, B², C² were significant model terms (P < 0.05). It can be seen that the variable with the largest effect on PWF was the linear term of PVP content (B) followed by the ethanol content and its interaction with PVP content (BC). Interaction term of PVDF concentration and ethanol content (AC) however did not make any significant influence on PWF. The coefficient of determination (R²) of the predicted models in this response was 0.9765 and p-value for lack of fit was 0.2279. These values would give a relative good fitness to the mathematic model of equation (9) 3D response surface plots of PWF as a function of PVDF content and PVP content at three level of ethanol content (−1 0 + 1) are given at figures 2(a)–2(c).

Figure 2. Response surface plot of predicted pure water flux as function of PVDF and PVP content at (a) level −1 (b) level 0 and (c) level +1 of ethanol content.
Table 4 shows the variation of solution viscosities and additive concentration at cloud point. By adding PVP, the solution viscosity increases and clouding of the solution occur with less amount of non-solvent, also the solution viscosity increases [5].

According to table 4 and figure 2(a), when harsh coagulation bath (water and low amount of ethanol) is applied, PVP addition enhances the demixing of the solution in the thermodynamic point of view. However, as we made the coagulation bath softer, by adding more ethanol, a tradeoff between the thermodynamic enhancement and the kinetic hindrance effects, happened simultaneously. Figure 2(c) shows that at low PVDF concentration by increasing the PVP content, the solution demixing was delayed and the kinetic hindrance due
to viscosity buildup hindered the thermodynamic factor effect, however by further increase of PVP content, the variation in thermodynamic property controls the demixing process and caused the faster phase separation of the solution again, as also reported in the literature \[7, 32, 33\].

The cross-sectional structures of the membranes prepared from the polymer dope numbers 1, 2, 9, 10, 11, 12, 13 and 15 according to numbering of table 2, are shown in figure 3.

As can be observed, addition of PVP in the polymer dopes results in a formation of large finger-like macrovoids and cavities. SEM images also indicate that as ethanol concentration in water bath was increased from 0% to 50%, the long finger-like structure near the bottom wall of the membranes slowly changed to a sponge-like structure. However, the finger-like structures near the inner wall were retained \[32\].

### 3.4. Mean pore size response analysis

The model significant parameters for mean pore size prediction are $A, B, C, AC, BC, B^2, C^2$. The linear term of PVP content ($B$) followed by linear term of ethanol content ($C$) had the largest effect on this response. The coefficient of determination ($R^2$) of the predicted models for this response was 0.9584. Also, p-value for lack of fit was 0.1912, which suggesting a good fit to the mathematical model of equation (10).

The response surface of mean pore size as a function of PVP content and ethanol content at center level of PVDF concentration is shown in figure 4. It is worth noting that the surface trends are nearly the same at other levels of PVDF concentration.

According to equation (10) the interaction term of PVDF concentration and ethanol content (AC) has an increment effect on mean pore size and at high levels of the ethanol content, could neutralize the decreasing...

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**Figure 4.** Response surface plot of predicted mean pore size as function of PVP and Ethanol content at level 0 of PVDF content.

**Table 4.** The Viscosity and composition of the casting solutions at cloud point.

| Solution composition (wt%) | Water content at the cloud point (wt%-ml)* | Ethanol content at the cloud point (wt%-ml)* | Viscosity (Pa.s) |
|---------------------------|-------------------------------------------|--------------------------------------------|-----------------|
| PVDF PVP DMA_C            |                                           |                                           |                 |
| 13 3.5 83.5               | 8.81–2.9                                  | 20.84–7.9                                 | 4.66            |
| 14.01 1.41 84.58          | 7.79–2.6                                  | 20.12–7.6                                 | 7.5             |
| 14.01 5.58 80.41          | 4.15–1.3                                  | 17.35–6.3                                 | 11.9            |
| 15.5 0 84.5               | 9.09–3                                    | 21.05–8                                   | 9.2             |
| 15.5 3.5 81               | 6.25–2                                    | 20–7.5                                    | 9.91            |
| 15.5 7 77.5               | 3.84–1.2                                  | 16.43–5.9                                 | 14.3            |
| 16.98 1.41 81.61          | 5.66–1.8                                  | 18.47–6.8                                 | 14.3            |
| 16.98 5.58 77.44          | 3.22–1                                    | 15.25–5.4                                 | 18.1            |
| 18 3.5 78.5               | 3.33–1.1                                  | 15.49–5.5                                 | 22.4            |

* Weight percentage%—equivalent volume[mL]
effect of the interaction term of PVP and ethanol content (BC) and also could dominate it at low levels of PVP content (figure 4).

Membrane pore size distribution variation ($\sigma_p$) of the prepared membranes was very narrow (1.2–1.88), hence, it is concluded that these ultrafiltration membranes were quite similar in their microstructure, and this result is consistent with Michael’s report for determination of pore size distribution of ultrafiltration membrane [34]. By using the values of mean pore size and geometrical standard deviation for all the membranes prepared in this study, probability density function curves were generated from equation (5). As shown in figure 5, the additives of the membrane dope and coagulation bath can simultaneously shift the curve and change the pore size distribution.

3.5. Tensile strength response analysis

The significant parameters for tensile strength model are A, B, C, AB, $A^2$, $B^2$, and C2. Among them, the linear terms of PVDF PVP concentration have the largest effect on this response; the coefficients of determination ($R^2$) of the predicted model was 0.9176, whereas p-value for lack of fit was 0.0579. Therefore, the predicted models can reasonably represent the observed values and the response were sufficiently explained by the models.

Although the linear term of ethanol content in the coagulation bath was significant and had effect on response but it didn't change the response trend at different levels. Therefore 3D response surface of tensile strength as a function of PVDF and PVP content is only shown at zero level of ethanol content. Figure 6 indicates that the increase in PVDF concentration and decrease in PVP content resulted in tensile strength augmentation but when PVP content was in its maximum ratio, the tensile strength first enhanced with increasing of PVDF concentration due to the kinetic effect and then decreased with further increment due to thermodynamic instability.

3.6. Porosity response analysis

For porosity prediction, a model with significant parameters of A, B, C, $B^2$ and C2 was used ($p < 0.05$). The coefficient of determination ($R^2$) of the predicted models, in this response was 0.8179 and p-value for lack of fit was 0.2773.

Figure 7 shows the surface plot of porosity as a function of PVDF concentration and PVP content at zero level of the ethanol content. The response trend is the same in all other levels of ethanol. According to figure 7 at
constant polymer content, increase in PVP content causes the membrane porosity to augment and at a constant PVP content, polymer concentration enhancement causes the membrane porosity to diminish.

3.7. Verification of predictive models
The regression equations obtained using the experimental data can be used to predict the pure water flux, mean pore size, tensile strength and porosity at any polymer concentration (PVDF), additive content of casting solution (PVP) and additive content of the coagulation bath within the range of the levels defined. In order to validate the veracity of the models, five confirmation runs were conducted. The values of independent variables are shown in table 5. The preparation conditions for three experiments (1–3) were new conditions within the range of the defined levels and other two experiments (4–5) were come from 20 experiments in table 2.

The predicted values and the actual experimental values were compared and the percentage errors between the actual and predicted values for each response were calculated. According to the error percentages illustrated in table 5, it can be concluded that the regression models were in consistent with all responses, as model predictive errors are all in acceptable range with absolute percentage error (MAPE) below 20%. The regression equation can be expected to apply in the preparation of PVDF ultrafiltration membranes and can reasonably predict and optimize the performance of the membranes.
Table 5. Validation data set.

| Run | A: PVDF (w%) | B: PVP (w%) | C: Ethanol (v%) | PWF | Mean pore size | Porosity |
|-----|--------------|-------------|-----------------|-----|----------------|----------|
|     | predicted LMH | Actual LMH  | Absolute Error (%) | predicted MPa | Actual MPa | Absolute Error (%) | predicted nm | Actual nm | Absolute Error (%) | predicted | Actual | Absolute Error (%) |
| 1   | 15.5         | 1.4         | 40              | 54.03 | 65.34 | 17.31 | 4.2 | 3.88 | 8.25 | 7.34 | 8.97 | 18.17 | 0.73 | 0.71 | 2.82 |
| 2   | 18           | 3           | 25              | 34.75 | 42.58 | 18.39 | 3.68 | 3.87 | 4.91 | 9.49 | 11.3 | 16.02 | 0.75 | 0.71 | 5.63 |
| 3   | 17           | 3           | 0               | 155.68 | 134.19 | 16.01 | 1.87 | 1.54 | 21.43 | 21.59 | 19.23 | 12.27 | 0.83 | 0.82 | 1.22 |
| 4   | 16.98        | 1.41        | 10.13           | 22.46 | 26.21 | 14.31 | 4.05 | 3.98 | 1.76 | 8.89 | 9.35 | 4.92 | 0.76 | 0.78 | 2.56 |
| 5   | 14.01        | 5.58        | 39.86           | 96.5  | 110.25 | 12.47 | 1.71 | 1.83 | 6.56 | 16.81 | 17.89 | 6.04 | 0.81 | 0.79 | 2.53 |

Mean Absolute Percentage Error (MAPE):

| Mean Absolute Percentage Error (MAPE) | 15.70 |
|---------------------------------------|-------|
| Absolute Error                        | 8.58  |
| Absolute Error                        | 11.48 |
| Absolute Error                        | 2.95  |
4. Conclusions

Additive incorporation is one of the most recommended methods among physical and chemical techniques that are advised to control membrane morphology and performance. PVP and ethanol are known as suitable additives for casting solution and coagulation bath, respectively. In this method, the response surface methodology (RSM) in conjunction with central composite design (CCD) was applied to investigate the individual and interactive effects of PVDF and PVP concentration on the casting solution and ethanol in the coagulation bath on the membrane performance.

Polymer weight percent (PVDF, 13–18 (wt%)), additive content of the casting solution (PVP, 0–7 (w%/w%)) and additive content of the coagulation bath (ethanol, 0–50 (v%)) were set as variables of the model. The Predicted values of the model equations were found to be in good agreement with observed values according to determination coefficient of $R^2 = 0.9719$, $R^2 = 0.9584$, $R^2 = 0.9181$ and $R^2 = 0.8179$ for PWF, mean pore size, tensile strength and porosity, respectively. 3D response surface graphs were presented to gain a better understanding of the variables effects. The effect of PVP addition on the pore size distribution of the ultrafiltration membranes has been evaluated. This study demonstrated that RSM and CCD can be successfully applied to model the ultrafiltration membranes preparation and that it is the economical way of obtaining the maximum information in a short period of time and with the least number of experiments.

Acknowledgments

The authors would like to thank Dr Mahmoud Hemmati for his guidance regarding the polymeric membrane fabrication.

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