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Application of response surface methodology (RSM) in the optimization of dewetting conditions for flat sheet membrane distillation (MD) membranes

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ABSTRACT

This study focuses on the exploration of the optimum dewetting conditions to remove water in pores in membrane distillation (MD) process. Response surface methodology (RSM) was applied to build statistical models for the analysis of flux and liquid entry pressure (LEP) as a function of dewetting temperature and time. A set of MD experiments based on central composite design of experiments method are carried out. Using these experimental results, two response surface (RS) models were developed to predict flux and LEP. The RS models were further used to optimize the dewetting conditions for desired membrane properties. Moreover, the optimum dewetting condition derived from RSM was experimentally verified.

Keywords: Membrane distillation; Wetting; Dewetting; Liquid entry pressure; Response surface methodology

1. Introduction

As conventional water sources are depleted and polluted, the use of non-conventional water resources has been drawn attention as a viable option. Seawater desalination is one of such non-conventional water resources. However, seawater desalination requires technologies allowing the removal of salt from water. Membrane distillation (MD) is one of the desalination technologies, which is based on the principle of evaporation. However, unlike conventional evaporation technologies such as multistage flash (MSF) and multi-effect distillation (MED), MD uses a hydrophobic membrane as a barrier to separate feed water from treated water or vapor [1,2]. Although this membrane does not directly participate to remove ions from water, it should allow only the vapor passage and block the water penetration [3]. MD has gained popularity due to the recent development of membranes with desired properties, improvements in module design, and better understanding of transport phenomena [4].

MD holds potential as an efficient desalination technology due to the following advantages [3,5]:

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almost 100% rejection of non-volatile solutes such as ions, macromolecules, colloids, virus, and bacterial cells [6]; capability of operation under low operating temperatures and operating pressures; potential use of waste heat as a preferable energy source [7]; possibility of utilizing of alternative energy sources such as solar or geothermal energy [3]; and small foot print compared with MSF and MED.

However, MD still has problems associated with pore wetting [8,9]. Pore wetting is a phenomenon during which the liquid (water) begins to occupy the pores in the membrane. As a result of pore wetting, water in the feed stream penetrates into the distillate stream, leading to a decrease in salt rejection. Pore wetting may occur due to the existence of special chemicals (i.e. detergent or oils), hydraulic pressure, changes in surface properties of the membrane, and vapor condensation inside the pores [10,11]. Due to the hydrophobic properties of the membrane, water cannot penetrate into the pores of the membrane before the applied pressure exceeds the critical pressure, which is called the liquid entry pressure (LEP) [12]. The LEP is defined as the pressure difference from which the liquid penetrates into the pores of the hydrophobic membrane. LEP is correlated with the interfacial tension, the contact angle of the liquid on the surface, and the size and shape of membrane pores. Pore wetting may result from membrane fouling because it may changes the surface properties of the membrane [9,11].

However, relatively few studies have been attempted to solve the wetting problems in MD membranes. Previous studies on wetting of MD membranes mainly focused on the enhancement of hydrophobic properties of membranes using novel materials or implementing surface modification [9,13]. Although these approaches are meaningful, it is also important to remove water in membrane pores to reverse the pore wetting, which is called dewetting. Accordingly, this study intends to develop a dewetting method for MD membrane using hot air flow, which evaporates the water inside the wetted membrane. The optimum dewetting conditions for removing water in pores in MD process were determined by applying response surface methodology (RSM).

2. Materials and methods

2.1. Membrane

A commercially available membrane made of polyvinylidene fluoride (Millipore, USA) was used for the experiments. The pore size, thickness, and porosity of the membrane are 0.22 μm, 125 μm, and 75%, respectively. A laboratory-scale membrane module with the effective membrane area of 3.14 cm^2 was used to hold the membrane.

2.2. Direct contact membrane distillation test

Fig. 1 illustrates the schematic diagram for a laboratory-scale system for direct contact membrane distillation (DCMD) used in this study. The hot solution (feed) was supplied to directly contact with the hot membrane side surface using a gear pump. The vapor was moved by the vapor pressure difference across the membrane to the permeate side and condensed inside the membrane module. An electronic balance connected to a data logger was used to continuously measure water flux through the membrane. Two conductivity meters were immersed into the feed and permeate tanks, respectively, which were also connected to the data logger. The operation conditions of MD are summarized in Table 1.

2.3. Experimental methods for wetting and dewetting

Prior to the dewetting experiments, the membranes were intentionally wetted to fill the water inside the pores. As illustrated in Fig. 2, the wetting of the membranes was done in two steps. First, the membranes were immersed into an ethanol solution to replace air in the pores with ethanol. Then, the membranes were put into a deionized water solution to substitute ethanol with water.

Once the membranes were fully wetted, they were used for the dewetting experiments. The schematic diagram for the dewetting device is shown in Fig. 3. Hot air flow was applied to the surface of the wetted membranes. A vacuum pump was used to assist the penetration of hot air into the pores of the membranes. Table 2 summarizes the conditions for dewetting considered in this study.

Table 1
Operating conditions for DCMD tests

Factor	Condition
Feed solution	3.5 wt.% NaCl solution
Effective area (cm^2)	3.14
Flow rate (L/min)	Feed: 0.6 Permeate: 0.4
Temperature (℃)	Feed: 60 Permeate: 20

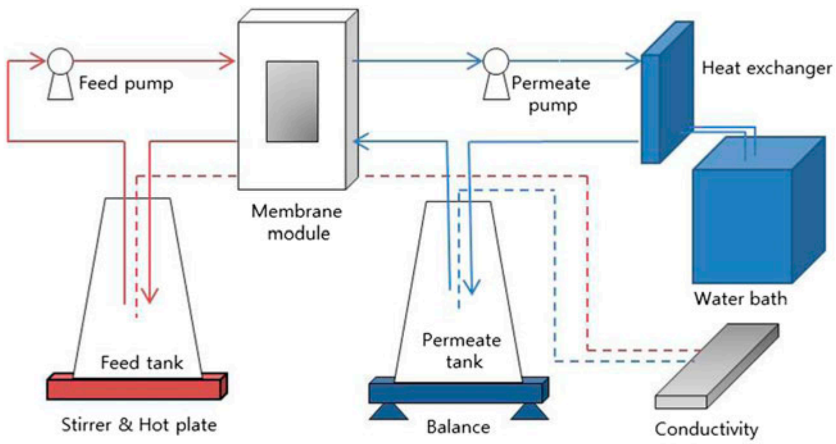

Fig. 1. DCMD process schematic diagram.

Table 2
Operating conditions for membrane dewetting

Factor	Condition
Air temperature (℃)	50–90
Air flow rate (mL/min)	240
Time (min)	3–25

2.4. LEP measurement

The LEP is an important property for MD membranes because it is related to the resistance against the pore wetting. If the feed water exceeds the LEP of the membrane, it penetrates into the pores, leading to pore wetting and poor rejection for solutes. The LEP is theoretically estimated by the following Laplace (Cantor) equation:

$$\mathrm{LEP} = -\frac{2B\gamma\cos(\theta)}{r_{\max}} \qquad (1)$$

where B is a geometric factor for which a value of 1 indicates circular pores, γ is the liquid surface tension, θ is the liquid–solid contact angle, and $r_{\max}$ is the radius of the largest pore. The operation of MD processes at high Reynolds numbers allows an increased mixing and improved mass transfer, but can also lead to operating pressures that exceed the LEP. Additionally, both the process conditions and the compositions of the feed water may affect γ. However, the theoretical calculation of the LEP may not be accurate due to uncertainties in B, γ, and $r_{\max}$. Moreover, if the membrane is partially wetted, the calculation of LEP using Eq. (1) becomes more inaccurate. Accordingly, it is better to determine the LEP by an experimental method.

In this study, the LEP of the membranes was experimentally measured using a device shown in Fig. 4. The system consists of a high-pressure nitrogen cylinder, a pressure regulator, a pressure vessel, a pressure gauge, and a membrane holder. The pressure applied to the membrane increases stepwise until the water penetrates the membrane. The measurements were triplicated to check the reproducibility of the results.

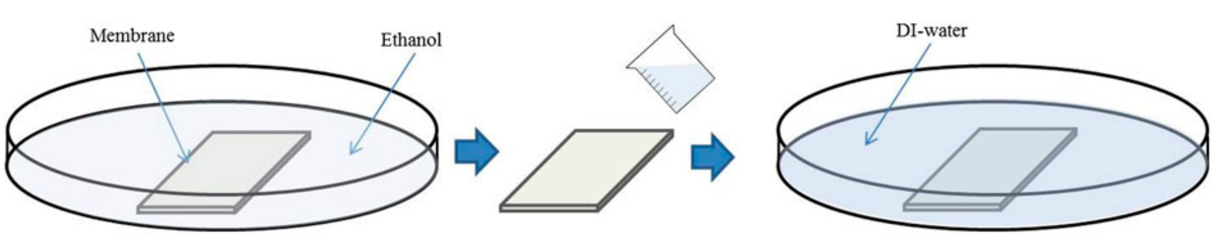

Fig. 2. Schematics for pore wetting of MD membranes.

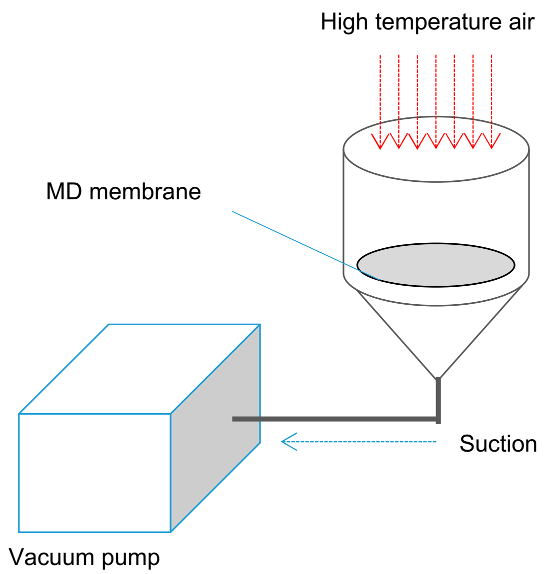

Fig. 3. Schematic diagram for dewetting device using hot air flow.

2.5. Scanning electron microscopy

A field enhanced scanning electron microscopy (FESEM, Hitachi S-4700) was used to examine the surface of the MD membranes after dewetting. The membrane samples were dried overnight at room temperature. Prior to the scanning electron microscope (SEM) analysis, the membranes were coated by platinum.

2.6. Response surface methodology

RSM is the combination of mathematical and statistical techniques. RSM is particularly applicable in situations where several input variables potentially influence the performance of the process or the response of the system [14]. The objective of RSM was to simultaneously optimize the levels of these variables to obtain the best response [15]. This methodology sets the correlation between input and output signals of a process experiment over the range of independent variables (factors) [16]. Application of RSM model requires selection of independent and dependent variables with the greatest effect on response and the choice of the experimental design, carrying out the experiments according to the selected experimental matrix and getting answers [15].

In this study, the central composite design (CCD) was selected for the optimization of condition used for dewetting. This method is suitable for fitting a quadratic surface and helps to optimize the effective parameters with minimum number of experiments, as well as to analyze the interaction between parameters. Each curve represents the evolution of dewetting by varying one variable in the extreme of the CCD model, with its pair variable equal to upper value (+1) and equal to low value (−1) [11]. The level of interaction of one variable on the other is represented between these two situations. A mathematical function is assumed for the response in terms of the significant independent variables. A quadratic model corresponding to the following second-order equation was built to describe the response:

$$Y = b_0 + \sum_i b_i X_i + \sum_i b_{ii} X_i^2 + \sum_{ij} b_{ij} X_i X_j \tag{2}$$

where Y is the response, b_0 the constant coefficient, b_i the linear coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficients, and X_i and X_j the coded values of the variables. In this work, a second-order

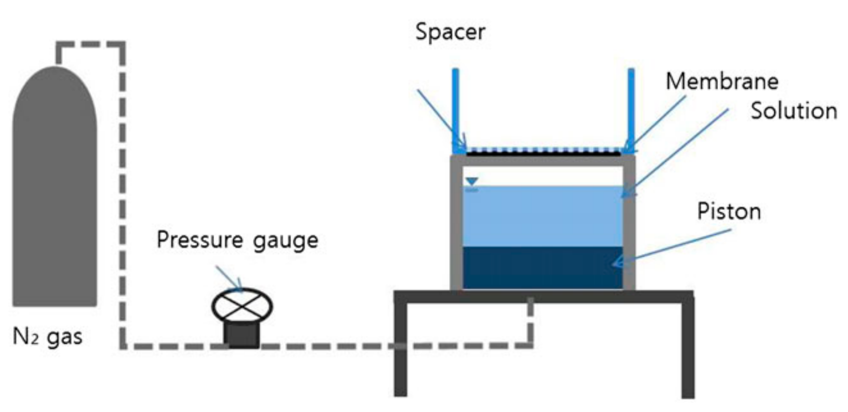

Fig. 4. Schematic diagram for LEP measurement equipment.

polynomial equation was obtained using the uncoded independent variables as below:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_{11}^2 + b_{22}X_{22}^2 + b_{12}X_1X_2 \quad (3)$$

The statistical significance of the models was justified through analysis of variance for polynomial model with 95% confidence level, and residual plots were used to examine the goodness of models fit. The quality of the fit polynomial model was also expressed by the coefficient of determination R^2. Finally, optimum values of factors were obtained by determining a target in dedicated RSM program (response optimizer). Two factors including air temperature and air blowing time with five levels were employed for response surface (RS) modeling and optimization of dewetting condition.

3. Results and discussion

3.1. Application of RSM

The experimental domains and the levels of the variables are given in Table 3. The temperature ranges from 50 to 90℃, and the dewetting time ranges from 5 to 25 min. Based on the CCD, total 13 test runs were implemented. Both LEP and water flux were measured in each test run. The results of CCD experiments are summarized in Table 4.

Fig. 5(a) and (b) show the results of the RSM analysis for LEP. The LEP increases as the dewetting time and temperature increase. According to the experimental design, the result was analyzed and approximating functions (RS model) of LEP was obtained as follow:

$$Y_1 = 3.87 - 0.0303X_1 - 0.0767X_2 + 0.00095X_1X_2 \quad (4)$$

where Y_1 is LEP, X_1 is dewetting temperature, and X_2 is the dewetting time. And R^2 value for RSM equation was 74%.

Table 3
Designed variables and their coded and actual values used for experimental design

		Actual value of coded levels				
Factor	Symbol	−1.414	−1	0	1	1.414
Temperature (℃)	X_1	50	60	70	80	90
Time (min)	X_2	5	10	15	20	25

The results of RSM were analyzed by water flux shown as Fig. 5(c) and (d). Flux was relatively high at intermediate temperature and time. As the temperature for dewetting increases, the flux decreases, indicating that the membrane was damaged by the hot air. However, dewetting at low temperature and short time results in relatively low flux, suggesting that the membrane is not completely dewetted under this condition. This implies that the dewetting conditions should be optimized by considering both the effectiveness of dewetting and intactness of membrane structure.

The experimental results were used to obtain an approximating function of water flux as a function of temperature (X_1) and time (X_2):

$$Y_2 = -12.97 + 0.774X_1 - 0.00474X_1^2 - 0.0153X_1X_2 \quad (5)$$

The R^2 value was calculated to be 83.32% and was higher than the previous case, indicating that the analysis was better than the previous one.

3.2. Pore size distribution analysis

To examine the changes in membrane morphology by dewetting, pore size distributions for original and dewetted membranes were compared. Fig. 6(a) shows the pore size distribution of the original membrane. The average pore size was determined to be 0.227 μm. As the dewetting temperature increases, the pore size distribution curves shift from right to left (Fig. 6(b)–(d)), indicating that the pore size decreases after dewetting at high temperature. The average pore sizes for the membranes dewetted at 50℃ and for 20 min, at 60℃ and for 20 min, and at 70℃ and for 20 min were 0.216, 0.210, and 0.20 μm, respectively. The changes in pore size by dewetting under 70℃ do not seem to be critical. However, it is evident from the results that the dewetting condition is important to minimize the changes in the membrane structure during dewetting.

3.3. Scanning electron microscope analysis

The effect of dewetting conditions on membrane structure was also investigated by SEM analysis. Fig. 7(a) compares the SEM images for the original and dewetted membranes at different temperatures. The changes in the membrane surface structure were not significant for the membranes dewetted at 50 and 60℃. However, the membrane dewetted at 90℃

Table 4
Design and result of experiments

Run	Factors: Temperature (X_1)	Factors: Time (X_2)	Y_1 LEP (bar)	Y_2 Flux (kg/m^2 h)
1	−1	−1	2.39	17.77
2	1	−1	2.37	16.81
3	−1	1	2.38	17.57
4	1	1	2.55	13.56
5	−1.414	0	2.37	17.99
6	1.414	0	2.47	13.37
7	0	−1.414	2.39	17.65
8	0	1.414	2.44	17.00
9	0	0	2.37	17.00
10	0	0	2.36	17.57
11	0	0	2.38	17.96
12	0	0	2.36	17.39
13	0	0	2.37	17.77

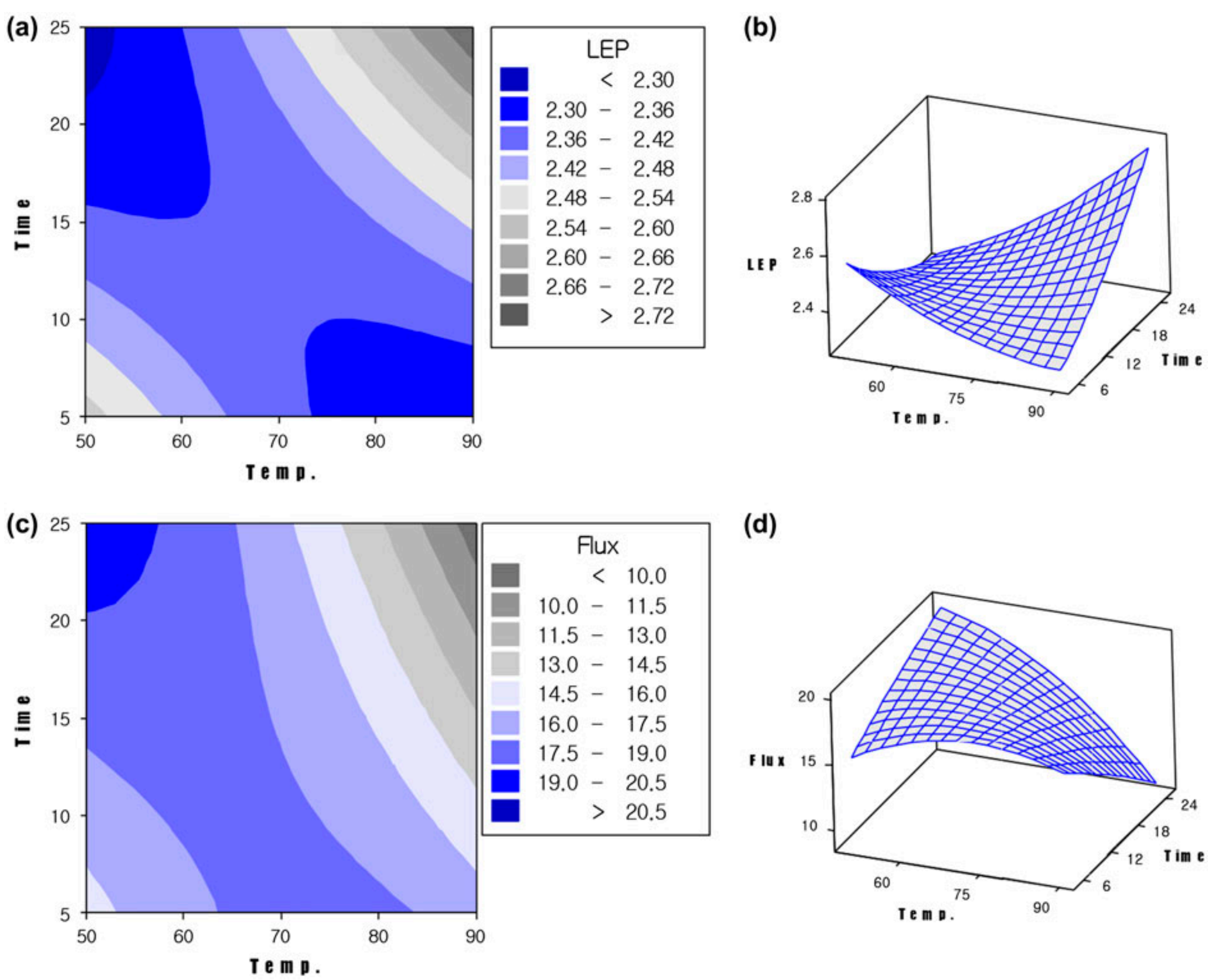

Fig. 5. RS plots of LEP and water flux as function of dewetting temperature and time (50℃ < temperature < 90℃; 5 min < time < 25 min) (a) contour plot of LEP, (b) surface plot of LEP, (c) contour plot of water flux, and (d) surface plot of water flux.

results in irreversible changes in the pore structures. These results suggest that the dewetting should be carefully done under mild conditions to minimize the changes in membrane structure.

3.4. Optimization by RSM

Although the previous RSM analysis was helpful for qualitative understanding of the effect of dewetting conditions on dewetting efficiency, it was limited due to low R^2 values. Accordingly, the experimental runs were redesigned to obtain higher correlations. The new experimental domains and the levels of the variables are given in Table 5. The experimental results obtained under the new design of experiments are summarized in Table 6.

The experimental results were analyzed using the RSM and an approximating function of the LEP was obtained by:

$$Y_1 = -13.83 + 0.218X_1 + 2.02X_2 - 0.0566X_2^2 - 0.0146X_1X_2 \quad (6)$$

Fig. 8 shows the control and surface plots for flux and LEP as a function of dewetting time and temperature. It seems that the optimum temperature for dewetting ranges from 60 to 70℃ and the optimum time ranges from 8 to 10 min. The R^2 values for the RSM equation were over 94%, indicating that the RSM analysis was successful.

The regression equations for water flux were also obtained from the RSM analysis:

$$Y_2 = -279.27 + 5.23X_1 + 26.1X_2 - 0.0228X_1^2 - 0.555X_2^2 - 0.231X_1X_2 \quad (7)$$

Again, the R^2 value was also sufficiently high (>99.9%).

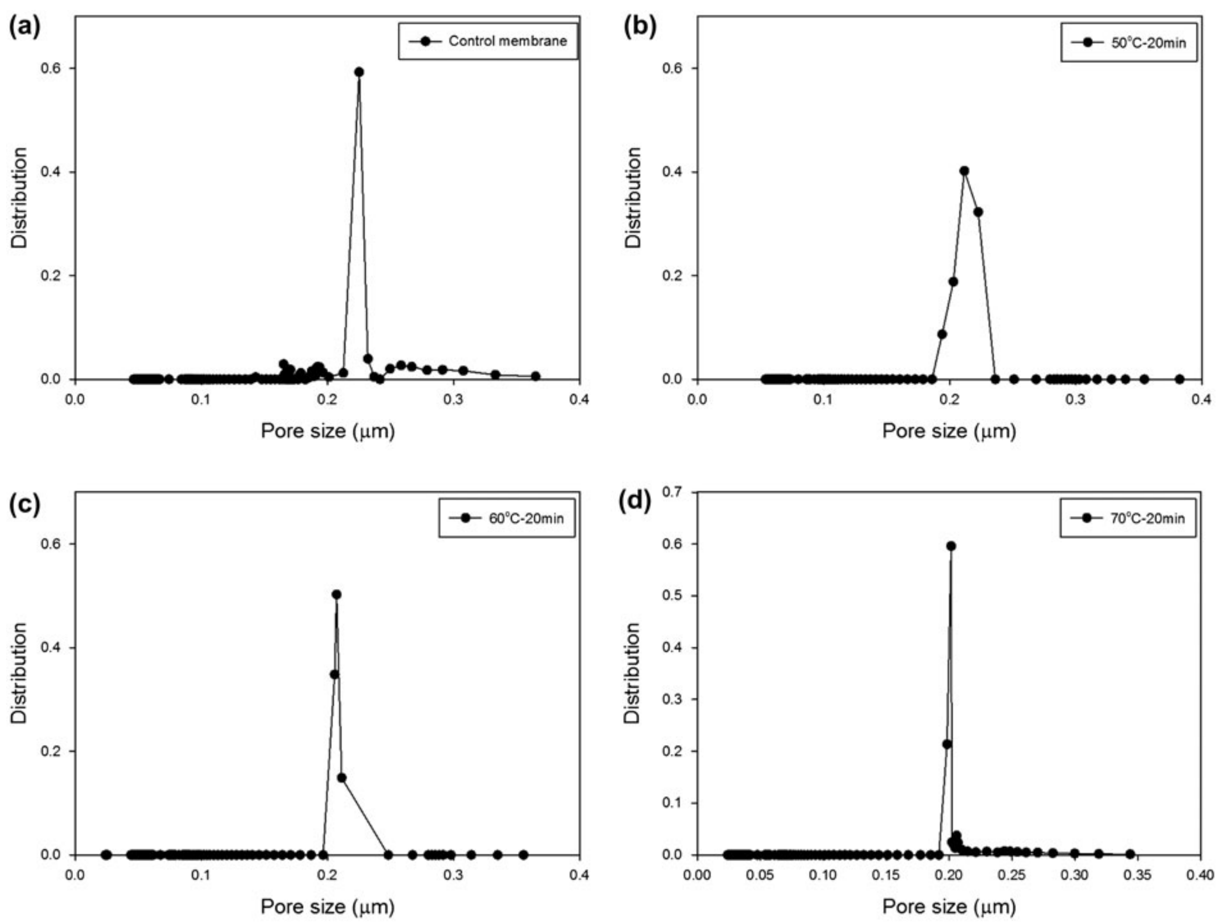

Fig. 6. Pore size distribution of (a) original membrane, (b) membrane after dewetting at 50℃ and for 20 min, (c) membrane after dewetting at 60℃ and for 20 min, and (d) membrane after dewetting at 70℃ and for 20 min.

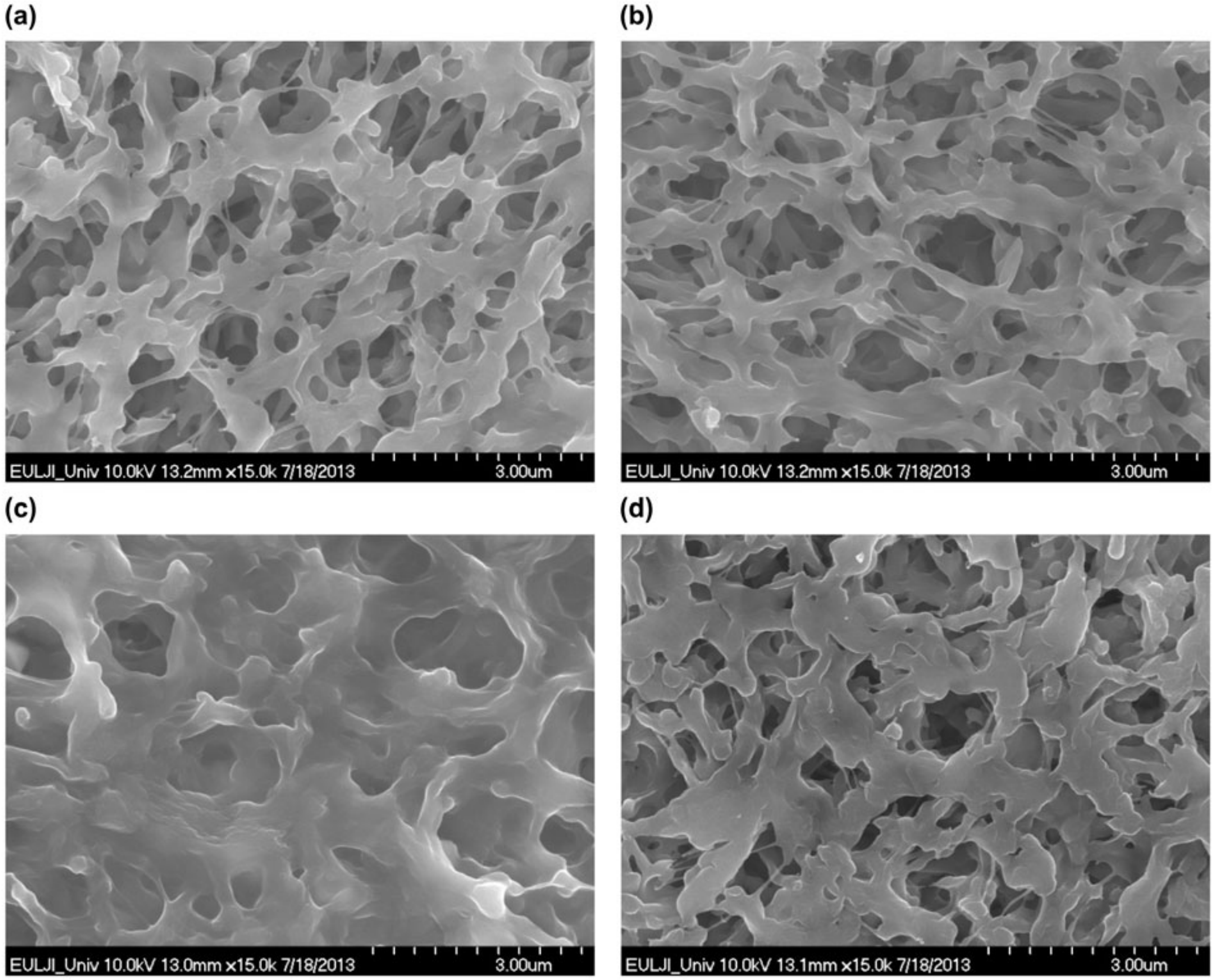

Fig. 7. SEM image of (a) raw membrane, (b) membrane after dewetting at 50˚C and for 20 min, (c) membrane after dewetting at 60˚C and for 20 min, and (d) membrane after dewetting at 90˚C and for 20 min.

To determine the optimum operating conditions for dewetting, response optimization method was applied to identify the combination of variable settings that jointly optimize the flux and LEP. The fitting models in Eqs. (6) and (7) are used to evaluate the impact of multiple variables on a response. The flux and LEP of the original membrane were used as the target value. The results are shown in Fig. 9. The combination of the responses (time and temperature) that produces the best results were determined to be 70.6˚C for temperature and 6.97 min for time. Under this condition, the LEP and flux were predicted to be 2.37 bar and 17.75 kg/m^2 h, respectively.

To confirm the adequacy of optimization proceed, additional experiments were carried out under the optimum conditions suggested by the model (temperature: 70.6˚C; time: 7 min) and the results were compared with the predicted values of model equation. As indicated in Table 7, the model prediction matches the experimental data well, suggesting that the optimization by the model is reliable.

Table 5
Designed variables and their coded and actual values used for experimental design

		Actual value of coded levels				
Factor	Symbol	−1.414	−1	0	1	1.414
Temperature (˚C)	X_1	50	60	70	80	90
Time (min)	X_2	3	5	7	9	12

Table 6
Design and result of experiments

Run	Factors		Y_1	Y_2
	Temperature (X_1)	Time (X_2)	LEP (bar)	Flux (kg/m^2 h)
1	−1	−1	2.39	17.77
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6	1.414	0	2.47	13.37
7	0	−1.414	2.39	17.65
8	0	1.414	2.44	17.00
9	0	0	2.37	17.00
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11	0	0	2.38	17.96
12	0	0	2.36	17.39
13	0	0	2.37	17.77

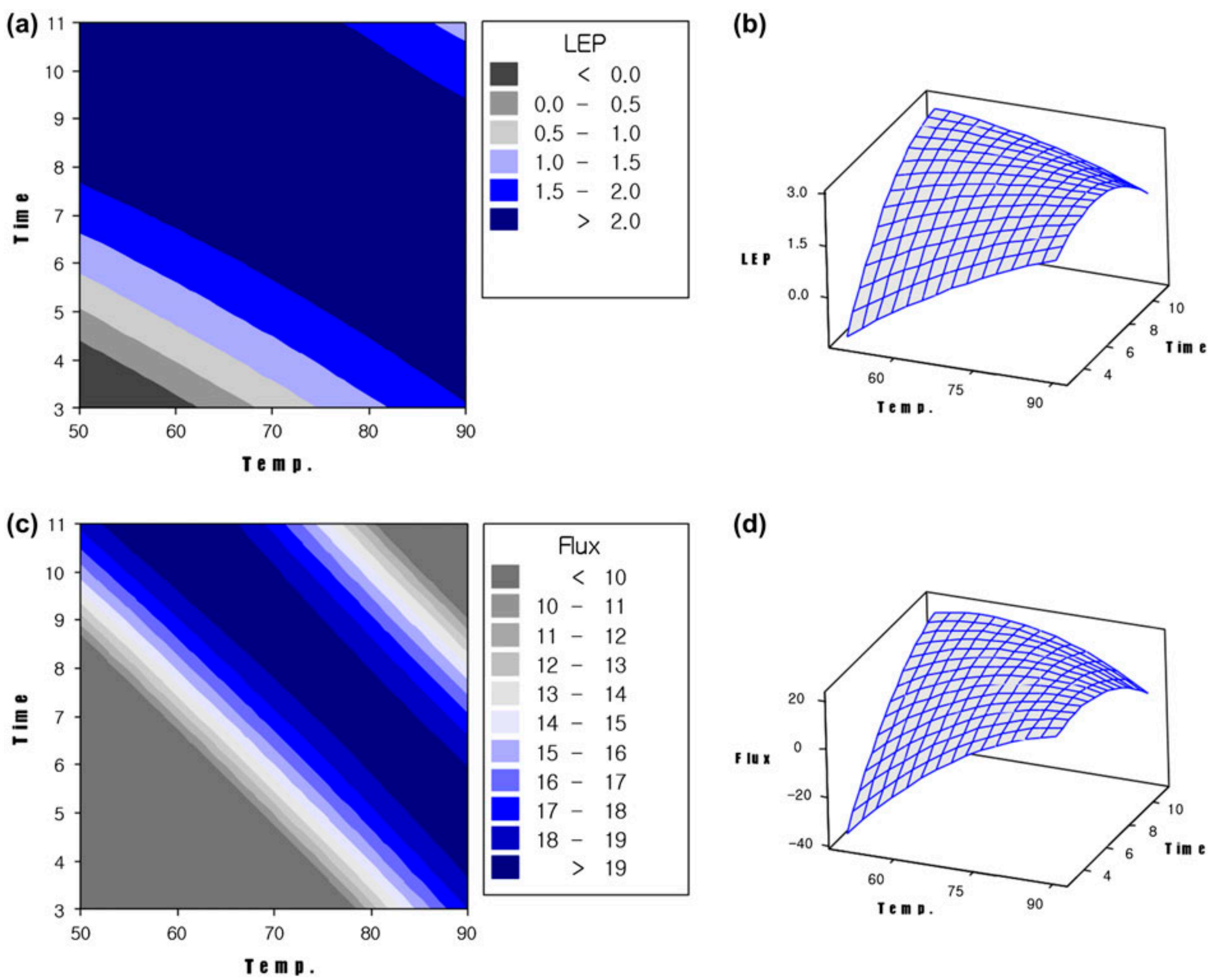

Fig. 8. RS plots of LEP and water flux as function of dewetting temperature and time (50℃ < temperature < 90℃; 3 min < time < 11 min) (a) contour plot of LEP, (b) surface plot of LEP, (c) contour plot of water flux, and (d) surface plot.

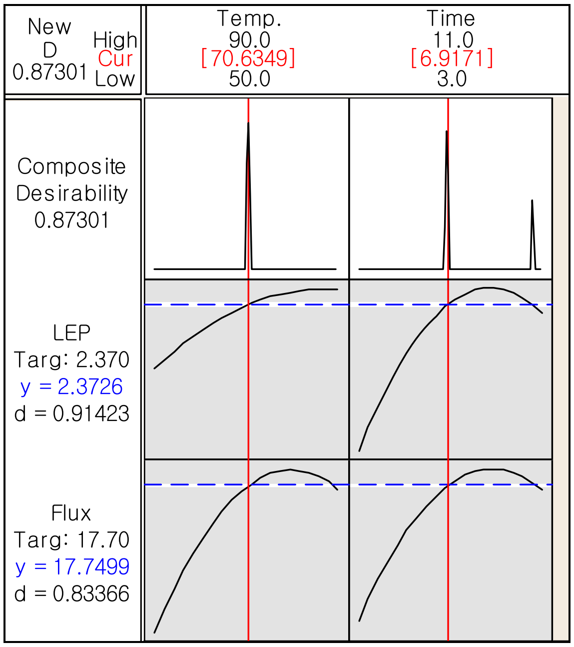

Fig. 9. Optimization of dewetting conditions using response optimization method.

Table 7
Comparison of predicted and measured values

	LEP (bar)	Water flux (kg/m^2 h)
Model prediction	2.38	17.87
Experimental results	2.36	17.77

4. Conclusions

In this study, RSM was applied to explore the optimum dewetting conditions for removing water in pores in MD by blowing high temperature air. The following conclusions were drawn:

(1) The use of hot air blowing was found to be effective for dewetting of MD membranes. Nevertheless, the effectiveness of dewetting was sensitive to the conditions of dewetting, including air temperature and dewetting time.
(2) Two RS models were developed utilizing experimental measurements for flux and LEP. Depending on the ranges of the operating parameter, the R^2 values were different, implying that the selection of proper range is important to derive a reliable model.
(3) The results of RSM indicate that the temperature and time should be adjusted to minimize the risk of membrane damage and maximize the dewetting efficiency. The optimum conditions were determined to be: 70.6˚C for temperature and 7 min for time.

Acknowledgments

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