

# p-ISSN 0852 - 0798 e-ISSN 2407 - 5973

# Acredited: SK No.: 60/E/KPT/2016 Website : http://ejournal.undip.ac.id/index.php/reaktor/

# Reaktor, Vol. 18 No. 1, March Year 2018, pp. 7-15

# Process Parameters Optimization in Membrane Fabrication for Produced Water Treatment Using Response Surface Methodology (RSM) and Central Composite Design (CCD)

# Tutuk Djoko Kusworo<sup>\*)</sup>, Dani Puji Utomo, Annizah Rahmatya Gerhana, and Hanifah Angga Putra

Department of Chemical Engineering, Faculty of Engineering, Diponegoro University Jl. Prof. Soedarto, SH, Tembalang, Semarang

\*)Coresponding author: tdkusworo@che.undip.ac.id

(Received: January 25, 2018; Accepted: March 26, 2018)

## Abstract

Produced water is wastewater from oil production that must be treated well. Membrane is one alternative to water treatment technology based on filtration method. But, in the use of a membrane, there's no exact variable optimal that influences performance of the membrane. This underlying research to assess factors that influences the performance of membrane to be more optimal. Therefore, the objectives of this study determine the optimum variable through Respond Surface Methodology and Central Composite Design. After getting the optimal condition then will check the stability of the membrane. This experiment of optimization of produced water with asymmetric membrane's Polyether sulfone (PES) using Response Surface is done with varying the Zeolite concentration by low level 1% weight and 3% weight, length of UV irradiation time low level 2 minutes and high level 6 minutes, thermal annealing low level 160 °C and high-level 180°C. An analyzer done in this research was by processing data research to make table and charts of the relationship between the result of this experiment with changed variable, namely variation of PES concentration, time of UV ray and thermal annealing by using Response Surface Methodology (RSM) and Central Composite Design (CCD).

**Keywords:** central composite design; membrane hybrid; pes-zeolite; produced water; response surface methodology

*How to Cite This Article:* Kusworo, T.D., Utomo, D.P., Gerhana, A.R., and Putra, H.A., (2018), Process Parameters Optimization in Membrane Fabrication for Produced Water Treatment Using Response Surface Methodology (RSM) and Central Composite Design (CCD), Reaktor, 18(1), 7-15, http://dx.doi.org/10.14710/reaktor.18.1.7-15

## INTRODUCTION

Produced water is petroleum and natural gas industries byproduct that contains organic and inorganic materials. The characteristics of produced water depend on the geographical location of oil well, type of rock structures, type of hydrocarbons, and the additive compounds which are used during oil production enhancement (Fakhru'l-Razi *et al.*, 2009; Alzahrani *et al.*, 2013). Moreover, it also contains high total dissolved solids (TDS), oils and grease, as well as other organic and inorganic contaminants (Mondal *et al.*, 2008; Kusworo *et al.*, 2017). The utilization of membrane for produced water treatment is expected to be more effective in removing the pollutants. However, the separation performance of existing polyether sulfone (PES) membranes must be improved because

it still has low permeability and selectivity performance. Methods of increasing the efficiency of the membrane separation process have been proposed by many researchers (Xie *et al.*, 2011; Ma *et al.*, 2011; Motta *et al.*, 2014). Nevertheless, the optimum condition was rarely studied.

The performance of the membrane includes membrane permeability and selectivity. The performance of the membrane is mostly influenced by its morphology and structure. The structure of the prepared membrane is a result of the influence of several process parameters. The process parameters in membrane fabrication are polymer concentration, the addition of additives, pre-treatment and post-treatment of membrane coagulation. The PES membrane surface is usually modified with electrophoresis, ultraviolet (UV) grafting to produce anti-fouling membrane (Kusworo et al., 2018). Therefore, feed water passes through the membrane barrier with high concentrations of polymer, have a lower permeate flux. This is caused by an increase of membrane density and smaller pore size (Kusworo et al., 2015). The increase in the concentration of the polymer in solution casting will cause an increase in concentration at the interface. Consequently, the resulting membrane has smaller pores size and lower permeate flux (Soroko et al., 2011). The treatment of post-membrane treatment also included one of the factors that greatly affect the performance of the membrane. Polyacrylonitrile (PAN) hollow fiber membrane was heated to higher temperatures to produce structures that are more tightly to improve the performance of pervaporation process (Xu et al., 2004).

The membrane that will be investigated for produced water treatment in this study is PES/zeolite hybrid membrane. The process parameters of membrane fabrication including UV irradiation time, concentration of zeolite filler and temperature of annealing are optimized. Further study is required to optimize in order to obtain the best performance of the membrane that steady in produced water treatment.

Experimental design using Central Composite Design (CCD) technique was considered to simplify the use of the pertinent variables. The use of statistical design of experiments such as factorial designs and Response Surface Methodology (RSM) has been applied in many investigations. Ismail and Lai (2004) researched the influence and interaction factors in the manufacture of membranes using RSM. In their study, they used a factorial design to obtain the most influential factor in the separation performance. The shear rate, the concentration of polymer, and solvent amount are the most prominent factors in the fabrication of the membrane to obtain a membrane with high separation performance. The impact of the aqueous phase composition used in the polymerization connection thin film composite was examined by Idris et al. (2008). CCD and RSM were performed in study to develop mathematical models and to optimize the dope solutions in the hybrid membrane fabrication process to obtain the best membrane for produced water treatment.

#### MATERIALS AND METHODS Materials Selection

Polyethersulfone (Veradel® PESU 3000P) obtained from Solvay Advanced Material (USA), Zeolite powder from Indrasari Chemical Store Semarang, and Original produced water sample from PT. Pertamina E & P Cirebon.

#### **Experimental Design**

Composite Central Design (CCD) was used in the current investigation for designing experimental runs. Three process parameters of membrane fabrication including concentration of zeolite (X1), UV irradiation time  $(X_2)$ , and annealing temperature  $(X_3)$  are independent variables. Lower, upper and the center point of the design is encoded as -1, 1, 0, and  $\alpha$  where +1 indicates a high level, low level -1,  $\alpha = 2^{n/4}$  (n = number of variables or factors) is a star point, and 0 is the center point. Star point added to the design to produce an estimate arch on the mathematic model. It takes 17 times experiment based on the type of trial design used (Kusworo, 2008). Based on this design, the total number of experimental runs are  $2^k + 2k + 2k$  $n_o$ , where 'k' is the number of independent variables and no is the number of repeated experiments at the center point. For statistical calculation, the variables Xi have been coded as xi according to equation (1):

$$x_i = (X_i - X_0)/\delta X \tag{1}$$

Where  $x_i$  is a dimensionless number of variables i,  $X_i$  is the original value of the variable i,  $X_o$  is the value  $X_i$  at the center point, and  $\delta X$  is a step change, respectively (Kusworo, 2008). RSM analysis of the experimental results are performed using Statistica Software V.6.0. The software provides a statistical experimental design of second-degree polynomial equation as a prediction of the effect of experimental variables and their interactions on the response variables. Each response can be presented by Y as the response surface with three independent variables expressed by the quadratic mathematical model as shown in equation (2).

$$Y_{i} = \beta_{0} + \sum_{j=1}^{3} B_{j} x_{i} + \sum_{i < j} \beta_{ij} x_{i} x_{j} + \sum_{j=1}^{3} B_{ij} x_{ij}^{2}$$
(2)

Where  $Y_i$  is the predicted response,  $\beta_o$  is offset term,  $\beta_j$  linear effect,  $\beta_{ij}$  interaction effect, and  $\beta_{ij}$  is squared effect. In this study, the Flux and rejection of Ca<sup>2+</sup>, Mg<sup>2+</sup>, sulfide, and TDS were investigated as the responses to the experimental result. Response contour and surface plots, analysis of variance, and standard deviation were developed using the software. ANO-VA was performed for statistical analysis of the model. This analysis included the Fisher's *F*-test (overall model significance), its associated probability p(F), correlation coefficient *R*, and determination coefficient  $R^2$  which measure the goodness of the fitted regression model. It also includes the student's *t*-value for the estimated coefficients and the associated probabilities p(t). For each variable, the quadratic models were represented as contour plots and surface plots.

From the values of the regression coefficient model, may be prepared matrix b and B :

$$b = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \text{ and } B = \begin{bmatrix} x_1^2 & \frac{1}{2}x_1x_2 & \frac{1}{2}x_1x_3 \\ \frac{1}{2}x_1x_2 & x_2^2 & \frac{1}{2}x_2x_3 \\ \frac{1}{2}x_1x_3 & \frac{1}{2}x_2x_3 & x_3^2 \end{bmatrix}$$
(3)

Then points stationary can be calculated by equation (4):

$$x_0 = -\frac{1}{2}B^{-1}b$$
 (4)

The first stage of this experiment is the production of mixed matrix PES-Zeolite membranes, followed by optimization using RSM for membrane applications in the processing of produced water, and phase characterization. At this stage, fabrication of mixed matrix PES-Zeolite membrane starts with dope solution preparation composed by a variable as presented in Table 1. Factor  $X_1, X_2$ , and  $X_3$  represent for Zeolite concentration, UV irradiation time, and Annealing temperature, respectively.

#### **Membrane Fabrication and Performance Test**

Casting membranes were performed using phase inversion method. This method was done by casting the dope solution on the glass plate using a casting knife. Furthermore, the membrane was immersed into the coagulation bath with distilled water as non-solvent for 1 hour, followed by immersion in a different coagulation bath at ambient temperature (30  $\pm$  2°C) for 24 hours. After that, the prepared membranes were applied for produced water treatment. Rejection and permeate water flux measurement are conducted using dead-end filtration cell system. The effective membrane area in the module was determined to be 12.57 cm<sup>2</sup>. Before performing the permeability test, membrane compaction is done first using distilled water for 30 min, so the membrane polymer chains arrange themselves. After the compaction process, distilled water was replaced with produced water and maintained at  $30 \pm 2^{\circ}$ C. Produced water flux determination is done by measuring the volume of produced water for every 20 min. Membrane rejection was performed by determining the concentration of Cl<sup>-</sup>, S<sup>-</sup>, TDS, COD, Turbidity both of upstream and downstream of the membrane. Determination of TDS was performed using a TDS meter, Turbidity using Turbidimeter, the analysis of Cl<sup>-</sup>, S<sup>-</sup>, and COD ion was analyzed using the titrimetric method. The permeate water flux was calculated by equation (5) (Han et al., 2010):

Table 1. Process variable formulation

Factor	Unit	-α	-1	+1	$+\alpha$
$\mathbf{X}_1$	%wt	0.24	1	3	3.76
$X_2$	Minute	0.47	2	6	7.53
$X_3$	<sup>0</sup> C	152.36	160	180	187.64

$$J = \frac{V}{P.A.t} \tag{5}$$

Where,  $J = \text{Flux} (\text{L.m}^{-2}\text{bar}^{-1}\text{h}^{-1})$ , V = permeate volume (Liter), P = pressure (bar),  $t = \text{time (hour)} A = \text{membrane effective area (m}^2)$ . Determination of the coefficient of rejection is done by analyzing the concentration of pollutants in upstream and downstream of the membrane as in the equation (6).

$$R = \left(1 - \frac{C_p}{C_f}\right) x 100\% \tag{6}$$

Where *R* is the percent of rejection,  $C_p$  is permeated concentration and  $C_f$  is feed concentration. Manufacture parameter of membranes is optimized using a technique called RSM (Cornell, 2011).

## **RESULTS AND DISCUSSION Permeate Flux Optimization**

Filtration test of produced water using prepared membranes has been conducted. The experimental results are presented in Table 2. A mathematical model is generated as the second order of polynomial equation. Statistica software V.6.0 generates the equation. A mathematical model is presented in equation (7), prediction value and errors are tabulated in Table 2.

<b>Ypred</b> = $704.4725 - 64.6368 X_1 + 80.2463$	X2 –
$8.7289 X_3 + 3.7943 X_1^2 + 2.0053 X_2^2 + 0.0294$	$X_3^2 -$
$2.2437 \ X_1 X_2 + 0.3188 \ X_1 X_3 - 0.5531 \ X_2 X_3$	(7)

Table 2 imposed the difference between the observation and prediction response as shown in column error (% error). The statistical analysis of variant was used to evaluate significance and accuracy of the results of experimental results through F-test. The accuracy test of the regression model was done by dividing the mean of squares of regression ( $M_{sreg}$ ) and mean of squares of residuals ( $MS_{Res}$ ) later than the fisher (F) Table, where  $MS_{Reg}$  or  $MS_{Res}$  is the sum of squares divided by degree of freedom. The results of

Table 2. Membrane flux in 16 runs

					Flux	
Run	$\mathbf{X}_1$	$X_2$	$X_3$	$Y_{\text{obsrv}}$	$\mathbf{Y}_{\text{pred}}$	% eror
1	1.00	2.00	160.00	34.2	38.32	12.03
2	1.00	2.00	180.00	42.7	48.08	12.60
3	1.00	6.00	160.00	59.8	60.49	1.16
4	1.00	6.00	180.00	29.7	26.01	12.43
5	3.00	2.00	160.00	26.9	32.42	20.53
6	3.00	2.00	180.00	53.8	54.94	2.11
7	3.00	6.00	160.00	40.2	36.65	8.83
8	3.00	6.00	180.00	17.2	14.91	13.29
9	2.00	4.00	170.00	30.4	24.22	20.33
10	0.24	4.00	170.00	46.3	43.51	6.02
11	3.76	4.00	170.00	28.1	28.53	1.54
12	2.00	0.47	170.00	65.3	57.04	12.65
13	2.00	7.53	170.00	35.4	41.31	16.68
14	2.00	4.00	152.36	41.6	38.65	7.08
15	2.00	4.00	187.64	27.5	28.09	2.16
16	2.00	4.00	170.00	18.3	24.22	32.35

the analysis of variant will be used to determine the proposed hypothesis withdrawal, namely:

 $H_0 = \beta_i$  value is zero

#### $H_1 =$ at least one $\beta_i$ value is zero

The accuracy of this model also can be seen from the value of the determination coefficient ( $\mathbb{R}^2$ ). The model can be expressed accurately when the value of  $\mathbb{R}^2$  is higher than 70% so that it can be said that estimated values by model approaching the observed values obtained from the experiments. ANOVA calculation was conducted using Statistica software V.6.0; the results are shown in Table 3.

From the Table 3, the value of the *F*-value for the regression is defined as  $MS_{reg}/MS_{res}$ , where  $MS_{reg}$ is a mean square of regression which is obtained by dividing the sum of squares of regression with a degree of freedom.  $MS_{res}$  is the mean square of the residuals. From the Table 3, F-value shows the influence of variables for the model with the hypothesis  $H_0$  (there is no influence of variables to the model); and  $H_l$  (there is the influence of variables to the model). F value of the calculation  $(F_{model})$  is 6.16, this result is higher than  $F_{table}$  value ( $F_{0.05}$ ;  $_{9.10} = 3.34$ ) (Dougherty, 2012). According to the value of  $F_{model}$  is higher than  $F_{table}$ , then the decision was taken to reject  $H_0$ , which it means that the independent variables  $x_i$ gives effects to the proposed model (Kusworo, 2008). Table 3 also shows that p-value in the lack of fit worth 0.738 or greater than the  $\alpha$  value. Then the decision is taken to receive  $H_0$  which means the generated model represents the experimental results. While the coefficients of determination  $(\mathbf{R}^2)$ , reached 0.89. This indicates that 89% of the total variation to the results represented in the model. Thus in general model said in accordance they have met three parameter testing.

In addition, the effect of every factor on the response of Y based on the equation 7 is evaluated using ANOVA test. The linear first order effect, quadratic effect and interaction effect. The effect is considered influential when  $P \le 0.05$ . The influence of the third effect is known of the value of the coefficients and the values of p which are presented in Table 4.

Based on Table 4, it can be seen that the most significant effect is the quadratic effect of UV irradiation time variable and the interaction between UV irradiation and annealing treatments. From statistical analysis, the equation shows that the coefficients of  $X_2^2$  and  $X_2$  are positives, while the coefficient of  $X_3$  is negative. These signs indicate that the response in term of permeate flux will increase along with UV ir-

radiation time. While in the outcome of the experiment showed the increase of UV irradiation reduces the response in term of flux. The difference perhaps can be possible because of other factors like linear first order effects of zeolite concentration (X-1). The P-value of X<sub>1</sub> is more than 0.05 (0.065) while in terms of the model coefficients is -64.6368 which indicates the zeolite addition in higher concentration reduces permeate flux rate significantly.

Optimization using RSM methods was performed using Software STATISTICA V.6.0. The optimum variables were obtained as  $X_1 = 2.9180$ ,  $X_2 =$ 0.3363 dan  $X_3 = 135.6794$ . RSM modeling for flux response surface plot and contour plot are presented in Figure 1.

#### **Solute Rejection Optimization**

The optimization of membrane performance is also done in term of membrane selectivity. The selectivity of the membrane in this study is represented by the rejection efficiency of sulfide ion, chloride ion, COD, TDS, and Turbidity. The experimental solute rejection efficiencies are shown in Table 5. The mathematic models are generated to estimate the value of response as a function of independent variables. The software gives the models. Mathematical equations of polynomial second order for each response in term of solute rejection are presented in equations 8 to 12, and the value of predicted responses are presented in Table 5.

$$\begin{split} \mathbf{Y}_{\text{Sulfide}} &= -5.82230 \, + \, 0.04900 \, \, \mathrm{X_1} \, - \, 0.01196 \, \, \mathrm{X_2} \, + \\ 0.07386 \, \, \mathrm{X_3} \, - \, 0.00496 \, \, \mathrm{X_1}^2 \, - \, 0.00337 \, \, \mathrm{X_2}^2 \, - \, 0.00022 \\ \mathrm{X_3}^2 \, + \, 0.01040 \, \, \mathrm{X_1X_2} \, - \, 0.00030 \, \, \mathrm{X_1X_3} \, + \, 0.00017 \, \, \mathrm{X_2X_3} \end{split} \end{split}$$

$$\begin{split} \mathbf{Y_{Chloride}} &= -\ 6.63906\ +\ 0.03900\ X_1 - 0.05838\ X_2 + \\ 0.08244\ X_3 - 0.00234\ {X_1}^2 - 0.00241\ {X_2}^2 - 0.00024 \\ {X_3}^2 + 0.01392\ X_1 X_2 - 0.00034\ X_1 X_3 + 0.00037\ X_2 X_3 \end{split}$$

Tabel 4. Signification of each Model Factor

Fa	ctor	Р
<b>X</b> <sub>1</sub>		0.065062
$\mathbf{x}_1^2$	2	0.135221
x <sub>2</sub>		0.055705
$\mathbf{x}_2^2$	2	0.010740
X3		0.163219
X3	2	0.229364
X <sub>1</sub> .	. X <sub>2</sub>	0.124268
X <sub>1</sub> .	. X3	0.251478
X2.	. X3	0.004550

Table 3. ANOVA membrane flux

Source	Sum of squares	Degree of freedom	Mean square	F Value	F <sub>0.05</sub> Value (Table)	р	$R^2$
SS regression	2800.56	9.00	311.173	6.16	3.34		0.89
S.S. error	302.891	6.00	50.482				
Lack of fit	229.686	5.00	45.9372			0.738	
S.S. total	2871.98						

 $\begin{array}{l} \mathbf{Y_{COD}} &= 7.145993 - 0.022020 \ X_1 - 0.035425 \ X_2 - \\ 0.079917 \ X_3 \ + \ 0.005011 \ X_1{}^2 \ + \ 0.007893 \ X_2{}^2 \ + \\ 0.000237 \ X_3{}^2 \ + \ 0.000841 \ X_1X_2 - \ 0.000002 \ X_1X_3 - \\ 0.000136 \ X_2X_3 \end{array}$ 

 $\begin{array}{l} \mathbf{Y_{Turbidity}} = 2.370497 + 0.023028 \; X_1 - 0.004731 \; X_2 - \\ 0.017348 \; X_3 \; + \; 0.003401 \; X_1{}^2 \; + \; 0.004085 \; X_2{}^2 \; + \\ 0.000054 \; X_3{}^2 - \; 0.001705 \; X_1X_2 - \; 0.000177 \; X_1X_3 - \\ 0.000123 \; X_2X_3 \; \end{array}$ 

Analogous to the previous discussion, the ANOVA is also used as a method to evaluate the empirical conformity model. The model will be expected to meet three terms in testing that expressed as a model appropriate and accurate. The calculations of ANOVA to predict the responses in term of solutes rejection efficiency are shown in Table 6 to 10.

The statistical analysis results show that in general, the alleged models predicted accurately with experimental results, although in several data show significant errors. Based on the ANOVA analysis results in Table 6 to 7, the determination coefficient of S<sup>-2</sup>, Cl<sup>-</sup>, COD, TDS, and Turbidity are 0.93, 0.93, 0.90, 0.89, and 0.89, respectively. But two parameter, from fisher test and regression test are customarily enough to prove that model can predict the responses significantly. All rejection data stated that value F<sub>calc</sub> is greater than  $F_{table}$ . The decision is to reject the  $H_0$ hypothesis. This proved that independent variables (x<sub>i</sub>) give significant impacts on the response (dependent variables). The average value of determination coefficient  $(R^2)$  is 90%. It indicates that the variant has interpreted the proposed models.

The steady condition is set based on the stationary value of every model. The stationary values are the variables which give the highest response, in other words, the selected variables are the optimal



Figure 1. Surface Plot and Contour Plot Fluks Optimum

Table 5.	Mem	brane	selecti	ivity	in	16	run
----------	-----	-------	---------	-------	----	----	-----

					Selectiv	vity				
Run	S	2-	C	1-	CC	DD	T	DS	Turbi	ditas
	Y <sub>obsrv</sub>	Ypred	Y <sub>obsrv</sub>	Ypred	Y <sub>obsrv</sub>	Y <sub>pred</sub>	Y <sub>obsrv</sub>	Ypred	Y <sub>obsrv</sub>	Ypred
1	0.47	0.47	0.30	0.31	0.33	0.33	0.30	0.30	0.95	0.94
2	0.49	0.47	0.32	0.31	0.34	0.33	0.31	0.30	0.96	0.96
3	0.49	0.47	0.32	0.30	0.36	0.35	0.32	0.32	0.97	0.97
4	0.49	0.48	0.33	0.33	0.37	0.35	0.33	0.32	0.98	0.97
5	0.49	0.48	0.33	0.32	0.32	0.32	0.31	0.31	0.95	0.95
6	0.47	0.47	0.30	0.30	0.34	0.33	0.31	0.31	0.96	0.96
7	0.56	0.56	0.42	0.41	0.37	0.36	0.31	0.31	0.97	0.97
8	0.58	0.56	0.46	0.43	0.37	0.35	0.32	0.31	0.96	0.96
9	0.53	0.54	0.39	0.38	0.28	0.28	0.28	0.28	0.94	0.93
10	0.48	0.48	0.31	0.32	0.28	0.30	0.28	0.29	0.94	0.95
11	0.54	0.56	0.40	0.42	0.29	0.30	0.29	0.29	0.94	0.94
12	0.45	0.45	0.30	0.30	0.36	0.36	0.31	0.32	0.97	0.97
13	0.52	0.53	0.36	0.39	0.38	0.40	0.33	0.34	0.99	1.00
14	0.45	0.47	0.28	0.29	0.35	0.35	0.32	0.32	0.94	0.95
15	0.46	0.47	0.29	0.31	0.34	0.36	0.31	0.32	0.95	0.96
16	0.53	0.54	0.36	0.38	0.28	0.28	0.27	0.28	0.93	0.93

Source	Sum of squares	Degree of freedom	Mean square	F Value	F <sub>0.05</sub> Value (Table)	$\mathbb{R}^2$
SS regression	0.023632	9.00	0.002626	9.31	3.34	0.93
S.S. error	0.001693	6.00	0.000282			
Lack of fit	0.001693	5.00	0.000339			
S.S. total	0.023888					

Table 6. ANOVA Selectivity S<sup>2-</sup>

Table 7. ANOVA Selectivity Cl<sup>-</sup>

Source	Sum of squares	Degree of freedom	Mean square	F Value	F <sub>0.05</sub> Value (Table)	Р	$\mathbb{R}^2$
SS regression	0.035646	9.00	0.003961	5.62	3.34		0.93
S.S. error	0.004230	6.00	0.000705				
Lack of fit	0.003878	5.00	0.000776			0.470	
S.S. total	0.039920						

# Table 8. ANOVA Selectivity COD

Source	Sum of squares	Degree of freedom	Mean square	F Value	F <sub>0.05</sub> Value (Table)	Р	$\mathbb{R}^2$
SS regression	0.018852	9.00	0.002095	6.88	3.34		0.90
S.S. error	0.001826	6.00	0.000304				
Lack of fit	0.001826	5.00	0.000365			0.01	
S.S. total	0.017935						

## Table 9. ANOVA Selectivity TDS

Source	Sum of squares	Degree of freedom	Mean square	F Value	F <sub>0.05</sub> Value (Table)	Р	$R^2$
SS regression	0.005217	9.00	0.000580	6.73	3.34		0.89
S.S. error	0.000517	6.00	0.000086				
Lack of fit	0.001826	5.00	0.000365			0.39	
S.S. total	0.004549						

# Table 10. ANOVA Selectivity Turbidites

Source	Sum of squares	Degree of freedom	Mean square	F Value	F <sub>0.05</sub> Value (Table)	Р	$R^2$
SS regression	0.004218	9.00	0.0004687	5.42	3.34		0.89
S.S. error	0.000519	6.00	0.0000865				
Lack of fit	0.000483	5.00	0.0000966			0.43	
S.S. total	0.004546						

formulation for obtaining the best membrane performance. Position point of stationary value will be identified mathematically with the matrix methods in software. The mathematical calculations of the steady parameter for every parameter are presented in Table 11.

The response surface methodology was used to illustrate the effect of zeolite concentration, UV irradiation, and annealing treatment on the rejection response. Figure 2 to 6 show the surface plot and contour plot of solute rejection response in function of two factor (zeolite concentration and UV irradiation), keeping the other variable constant it its center value.

Tabel 11. Membrane optimum parameter towards selectivity

Selectivity parameters	$x_{I}$	$x_2$	<i>x</i> <sub>3</sub>
Sulfide	4.113	3.763	171.419
Chloride	0.105	1.409	170.058
COD	1.934	3.605	169.697
TDS	1.939	3.621	169.862
Turbidity	1.831	3.471	167.149



The The effect of Zeolite concentration and UV irradiation shows a synergistic effect on S<sup>-2</sup> and Cl<sup>-</sup> rejection responses. A higher S<sup>-2</sup> and Cl<sup>-</sup> rejections at 60-65% were obtained with concentration of zeolite (4 wt-%) and longer UV irradiation (6 minute). While in the other solute rejection responses show different profiles. The highest rejection was achieved with longer UV irradiation at any point of Zeolite concentration. It indicates that the zeolite concentration doesn't give a significant effect on COD, TDS, and turbidity rejection. This phenomenon could explain that S<sup>-2</sup> and Cl<sup>-</sup> were mainly rejected through molecular sieving mechanism provided by zeolite particles. While other solutes were mainly rejected by the repulsion of the membrane surface charge. The UV irradiation modified the membrane surface become more hydrophilic which more effective in rejecting hydrophobic pollutants in produced water. Based on the generated model, the critical value of process parameters that may produce membrane with excellent performance can be determined. The concentration zeolite 1.35 wt-%, UV irradiation time at 3.55 min, and thermal annealing at 160.25°C exhibited the best separation performance.

## CONCLUSION

This study confirmed that the concentration



Figure 2. (a) Surface Plot and (b) Contour Plot of sulfide rejection response



Figure 3. (a) Surface Plot and (b) Contour Plot chloride selectivity response

zeolite 1.35 wt-%, UV irradiation during 3.55 min, and thermal annealing 160.25°C exhibited the best separation performance regarding flux and rejection for produced water treatment using hybrid membrane zeolite/PES. The main effects and interactions effect was successfully developed using response surface methodology. The value of  $R^2$  between the performance of permeability and selectivity is 96,6%. The value of  $R^2$  acceptable limit (90%). Therefore, the RSM with CCD are useful tool for estimating the optimal process variable in the fabrication of flat sheet cellulose acetate membrane.



Figure 4. (a) Surface Plot and (b) Contour Plot of COD rejection response



Figure 5. (a) Surface Plot and (b) Contour Plot of TDS rejection response





## REFERENCES

Alzahrani, S., Mohammad, A.W., Hilal, N., Abdullah, P., and Jaafar, O., (2013), Comparative Study of NF and RO Membranes In The Treatment Of Produced Water - Part I: Assessing Water Quality, *Desalination*, 315, pp. 18-26.

Cornell, J.A., (2011), *Experiments with Mixtures: Designs, Models, and the Analysis of Mixture Da- ta* (Vol. 895), John Wiley & Sons.

Dougherty, (2012), *Introduction to Economics*, Second Edition, University Press, Oxford.

Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L.C., Biak, D.R.A., Madaeni, S.S., and Abidin, Z.Z., (2009), Review of Technologies for Oil and Gas Produced Water Treatment, *Journal of Hazardous Materials*, 170(2), pp. 530-551.

Han, J., Lee, W., Choi, J.M., Patel, R., and Min, B.R., (2010), Characterization of Polyethersulfone/Polyimide Blend Membranes Prepared by a Dry/Wet Phase Inversion: Precipitation Kinetics, Morphology and Gas Separation, *Journal of Membrane Science*, 351(1), pp. 141-148.

Idris, A., Yet, L.K., Noordin, M.Y., and Kee, C.M., (2008), Response Surface Methodology Approach to Study the Influence of PEG and Water in Cellulose Acetate Dialysis Membranes, *Jurnal Teknologi*, 49(F), pp. 39-49.

Ismail, A.F. and Lai, P.Y., (2004), Development of Defect-Free Asymmetric Polysulfone Membranes for Gas Separation using Response Surface Methodology, *Separation and Purification Technology*, 40(2), pp. 191-207.

Kusworo, T.D., (2008), Fabrication and Characterization of Flat Sheet and Hollow Fiber Mixed Matrix Membrane for Gas Separation, *Doctoral Dissertation*, Universiti Teknologi Malaysia.

Kusworo, T.D., Ismail, A.F., and Mustafa, A., (2015), Experimental Design and Response Surface Modeling of PI/PES-ZEOLITE 4A Mixed Matrix Membrane for CO<sub>2</sub> Separation. *Journal of Engineering Science and Technology*, 10(9), pp. 1116-1130.

Kusworo, T.D., Aryanti, N., Anggita, R.A., Setyorini, T.A.D., and Utomo, D.P., (2017), Surface Modification and Performance Enhancement of Polyethersulfone(PES) Membrane Using Combination of Ultra Violet Irradiation and Thermal Annealing for Produced Water Treatment, *Journal of Environmental Science and Technology*, 10, pp. 35-43.

Kusworo, T.D., Hadiyanto, H., Deariska, D., and Nugraha, L., (2018), Enhancement of Separation Performance of Asymmetric Cellulose Acetate Membrane for Produced Water Treatment Using Response Surface Methodology, *Chemical Industry and Chemical Engineering Quarterly*. In Press.

Ma, Y., Shi, F., Ma, J., Wu, M., Zhang, J., and Gao, C., (2011), Effect of PEG Additive on the Morphology and Performance of Polysulfone Ultrafiltration Membranes, *Desalination*, 272(1), pp. 51-58.

Mondal, S., (2016), Polymeric Membranes for Produced Water Treatment: An Overview of Fouling Behavior and Its Control, *Reviews in Chemical Engineering*, 32(6), pp. 611-628.

Motta, A., Borges, C., Esquerre, K., and Kiperstok, A., (2014), Oil Produced Water Treatment for Oil Removal by an Integration of Coalescer Bed and Microfiltration Membrane Processes, *Journal of Membrane Science*, 469, pp. 371-378.

Soroko, I., Lopes, M.P., and Livingston, A., (2011), The Effect of Membrane Formation Parameters on the Performance of Polyimide Membranes for Organic Solvent Nanofiltration (OSN): Part A. Effect of Polymer/Solvent/Non-Solvent System Choise., *Journal of Membrane Science*, 381(1), pp. 152-162.

Xie, F., Chen, W., Wang, J., and Liu, J., (2015), Fouling Characteristics and Enhancement Mechanisms in a Submerged Flat-sheet Membrane Bioreactor Equipped with Micro-channel Turbulence Promoters with Micro-Pores, *Journal of Membrane Science*, 495, pp. 361-371.

Xu, Z.L. and Qusay, F.A., (2004), Polyethersulfone (PES) Hollow Fiber Ultrafiltration Membranes Prepared by PES/Non-solvent/NMP Solution, *Journal of Membrane Science*, 233(1), pp. 101-111.