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Application of response surface methodology for the composition optimization of polycaprolactone based composite membrane

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Response surface methodology is successfully utilized for the optimization of the composition of Polycaprolactone based nanocomposite membrane. The amount of nanoclay used as the additive and Polyethylene glycol as the pore former is optimized based on the membrane properties porosity and hydrophilicity. The quadratic equations are obtained using the central composite design and the ANOVA results are validated. The values for the coefficient of determination (R-squared), adjusted R-squared, adequate precision and coefficient of variance describe the significance of the model developed for the responses, porosity and contact angle. Eigen value analysis of the Hessian matrix for each response has been carried out and the nature of optimum is found maximum for porosity and minimum for contact angle. Residual plots have been analysed to validate the obtained models and the combined interaction of the variables was analysed using contour plots and surface plots. The independent variables and their levels have been determined using batch studies with one parameter optimization. Also, the optimized composition obtained using one parameter optimization and RSM analysis is compared and the composition optimized using RSM is found to be less with better membrane porosity and contact angle.

Keywords: Contour plot, Hessian matrix, Membrane, Optimization, RSM, Surface plot

Membrane filtration is a proven technology for the treatment of wastewater and water purification. However, optimization of membrane composition is the key factor for the successful utilization of any membrane for the picked applications. The term optimization refers to the condition at which a stated process or a technique produces the best possible response. Initially, single variable optimizations were carried out, in which one variable is studied keeping the other variables constant at a time. The major drawback of this method is that the interactive effects within the variables cannot be determined. Also, this way of optimization needs to conduct more experiments and hence more time consumption. This problem is overcome by the optimization of multi variables at a time using mathematical and statistical techniques and among them, the most relevant and effective method is response surface methodology (RSM)[1,2].

RSM is a commonly used method to determine the combined effect of variables on one or more responses and to optimize the responses[3] with a reduced number of experimental trials. RSM identifies the influence of variables on the responses[4] and also recognizes those variables which significantly affect the responses. As the name suggests, the method evaluates the topography of the response surfaces and determines the region of optimum response (either maximum or minimum based on the desirability). RSM can provide global or local optimum based on the experimentally designed range of independent variables[5]. The most important experimental designs in RSM are Box-Behnken design (BBD) and central composite design (CCD)[6]. CCD is a two-level fractional factorial design whereas BBD is a three-level fractional factorial design. The selection of appropriate points where the response lies is important in RSM design, which is related to the design of experiments (DoE). Hence, experiments need to be carried out to screen the variables and to identify those variables which are having a large effect on the response. Therefore, DoE can be stated as an important aspect of RSM.

The experimental data is evaluated and RSM fits the data to a statistical model, linear, quadratic, cubic or 2FI (two-factor interaction) respectively. The adequacy of the models is examined using the coefficient of determination (R-squared), adjusted R-squared, adequate precision (AP) and coefficient of variance (CV). The obtained model is adequate when the p-value<0.05, lack of fit p-value> 0.05, R^2> 0.9, AP>4 and CV > 10%[6]. The independent variables which significantly affect the responses are identified using the statistical tool, Analysis of Variance (ANOVA). In this analysis, the effect of independent variables on the process is determined using F-test at 95% confidence level[7].

RSM is utilized for the optimization of process parameters in the treatment methods such as electrochemical processes as well as advanced oxidation processes[4]. This paper presents the composition optimization of PCL based membrane incorporated with PEG as a pore former and nanoclay as an additive. The combined effects of PEG concentration and nanoclay concentration on the membrane properties are investigated, and the variables were optimized using central composite design (CCD) in conjunction with the RSM method. A model was developed by using the design of experiment (DoE) to determine the optimum composition of the membrane with maximum porosity and minimum contact angle.

Experimental Section

The base polymer used was Polycaprolactone (PCL, Mn=80,000), purchased from Sigma-Aldrich. Surface modified nanoclay containing 25–30 wt% methyl dihydroxy-ethyl hydrogenated tallow ammonium, purchased from Aldrich chemistry was used as an additive. The pore former PEG 400 and the solvent N,Ndimethylformamide (DMF) were obtained from Sisco Research Laboratories Pvt. Ltd. and Merck, respectively.

The method adopted for membrane preparation is the immersion precipitation phase inversion technique. After the dispersion of nanoclay in the solvent by sonication, PCL pellets (17 wt%) were dissolved at a temperature of 70°C. After attaining homogeneity, the solution was kept air tight to remove air bubbles for 20-30 min and then the bubble-free solution was casted using an automatic film applicator. The obtained film is immediately immersed in the water bath to get membranes.

Single variable optimization was carried out to determine the effect of PEG 400 and nanoclay on membrane properties such as porosity, hydrophilicity and pure water permeability. Membrane porosity was calculated according to the dry-wet weight method, explained by Nikos *et al*.[8] and hydrophilicity is determined by contact angle values made by the water droplet on the membrane surface. Pure water permeability of the membrane is determined using cross-flow filtration in total recycle mode at pressures ranging from 2-8 bars. Before filtration, the membranes were compacted for one hour to obtain steady-state flux values[9].

It is assumed that the pure water permeability of a membrane depends on its porosity and hydrophilicity and hence optimization was carried out based on these two properties. Therefore, the objective function can be written as

$$\text{Response} = f(PEG\ conc., nanoclay\ conc.) \quad ...(1)$$

The independent variables are kept in the specified range and the response, porosity is subjected to maximisation and contact angle is subjected to minimisation. Using the independent variables, the responses are fitted to a polynomial function containing quadratic terms, to determine the critical point (maximum, minimum or saddle)[1], given in Eqn.2.

$$Y = \beta_o + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j \quad ...(2)$$

where Y is the predicted response, β_o is the constant coefficient, β_i is the linear coefficients, β_{ii} the quadratic coefficients, β_{ij} the interaction coefficients and X_i, X_j are the independent variables[10,11]. The results were analysed using Design Expert 17 software, in which RSM is coupled with central composite rotatable design. All the design points were analysed in triplicate and the solution with the highest desirability function was experimentally validated.

Results and Discussion

The concentration ranges of the membrane components studied and the prepared membrane properties are given in Table 1. It is observed that the porosity and hydrophilicity of the membrane increased with the increasing content of nanoclay, with increase in permeability. The membrane with addition of 1.5 wt% nanoclay exhibited higher permeability with maximum porosity. The contact angle values were found to be comparable for the membranes with 1 wt% and 1.5 wt% added nanoclay. At the nanoclay concentration of 2 wt%, the porosity was decreased and the contact angle was increased. Hence, the concentration of nanoclay is optimized at 1.5wt% based on the observed results. At this fixed concentration of nanoclay, the effect of PEG on the composite membrane was studied. The porosity of the membrane increased with the addition of PEG upto

Table 1 — Membrane properties with the addition of nanoclay and PEG at varied concentrations (single variable optimisation study)

PCL (wt%)	DMF(wt%)	Nanoclay(wt%)	PEG(wt%)	Porosity(%)	Contact angle (degrees)	Permeability ($l/m^2h.bar$)
17	83	-	-	26 ± 2	87 ± 2	
17	82.5	0.5	-	31 ± 2	64 ± 2	68
17	82	1	-	33 ± 2	62 ± 2	77
17	81.5	1.5	-	38 ± 2	63 ± 2	95
17	81	2	-	28 ± 2	73 ± 2	50
17	78.5	1.5	3	44 ± 2	72 ± 2	84
17	76.5	1.5	5	47 ± 2	72 ± 2	90
17	74.5	1.5	7	40 ± 2	79 ± 2	80
17	72.5	1.5	9	38 ± 2	83 ± 2	75

Table 2 — Variables, responses and range studied for RSM analysis

Parameter	Variable/Response	Minimum value	Maximum value	Variability
PEG concentration (wt%)	Variable	2	10	Continuous
Nanoclay concentration (wt%)	Variable	0.5	4	Continuous
PCL concentration (wt%)	Variable	-	17	Fixed
Porosity (%)	Response	-	-	-
Contact angle (degrees)	Response	-	-	-

5wt% loading. However, at higher PEG dosages, the porosity of the membrane was found to decline, causing the membrane denser. This shows that PEG acts as a pore suppressor agent in the PCL matrix. The contact angle values were observed to increase with the addition of PEG showing the resistance of the membrane against liquid water. The permeability results were observed to be in accordance with the porosity and hydrophilicity results, showing higher membrane permeability at higher porosity and higher hydrophilicity. Therefore, the composition of PCL-PEG-nanoclay composite membrane is optimized at the concentration of nanoclay and PEG at 1.5 and 5wt% respectively. Based on the results obtained, the independent variables and levels were chosen for DoE to conduct RSM-based optimization.

Application of RSM for optimization

Porosity and hydrophilicity was found to be the key parameters for the analysis of membrane performances based on the batch studies and hence those two parameters were selected as the responses or dependent variables. The independent variables are PEG concentration and nanoclay concentration with a selected range chosen from batch studies. These independent variables were considered as continuous variables, whereas PCL concentration is fixed. The ranges and variability of all the parameters are given in Table 2.

Mathematical interpretation of RSM

The statistical analysis produced a quadratic model which shows the effect of variables on the selected responses. The model for porosity showed the coefficient of determination (R-squared) value of 0.959 and the R^2 value close to one shows the better predictability of the model[12]. This confirms the high similarity between the experimental and predicted results by the model[13] and its close proximity with adjusted R-squared (value of 0.930) indicates the absence of insignificant terms[14]. On the other hand, the model produced for contact angle gives a value of 0.958 for R-squared and 0.928 for adjusted R-squared. Adequate Precision (AP) quantified by signal to noise ratio gives a comparison between the range of predicted values at the design points and the average prediction error. For RSM models, AP value above four is desirable. The obtained AP values for porosity and contact angle are 16.51 and 17.37 respectively and these values indicate an adequate signal and this model can be used to navigate the design space. The coefficient of variance (CV) obtained for porosity and contact angle is 3.36% and 2.56%. CV represents the ratio of the standard error of predicted value to the mean value of the observed response and it should not be greater than 10%[15].

The quadratic equation developed to fit the data are given in Eqn. 3 for porosity and in Eqn. 4 for contact angle, where X_1 is PEG concentration and is X_2nanoclay concentration.

$$\text{Porosity} = 48.20 - 2.45\ X_1 - 1.82\ X_2 + 2.25\ X_1X_2 - 6.16\ X_1^2 - 0.91\ X_2^2 \quad ...(3)$$

$$\text{Contact angle} = 77.60 + 6.95\ X_1 + 5.13\ X_2 + 2.75\ X_1X_2 + 2.32\ X_1^2 + 1.57\ X_2^2 \quad ...(4)$$

From the analysis of variance (ANOVA), the quadratic model obtained for porosity presented a F-value of 33.04 and p-value of 0.0001. The probability value (p-value) at 95% confidence interval is used to analyse the significance of the model terms[16]. A larger F-value with p-value less than 0.05 indicates the significance of the model. Correspondingly in the model for contact angle, the values 32.28 and 0.0001 for F-value and p-value show the significance of terms in the model. The "Lack of Fit F-value" of 2.89 and 2.92 for the model of porosity and contact angle implies the Lack of Fit is not significant relative to the pure error. Non-significant lack of fit is good for the model to fit.

Hessian matrix and Eigen values

The square matrix of second-order partial derivatives of a multi variable function is the hessian matrix, and the Eigen values calculated from the Hessian matrix predicts the nature of the optimum points. For a multi variable function z = f (x_1, x_2), the Hessian matrix (H) is

$$H = \begin{bmatrix} \frac{\partial^2 z}{\partial x_1^2} & \frac{\partial^2 z}{\partial x_1 \partial x_2} \\ \frac{\partial^2 z}{\partial x_2 \partial x_1} & \frac{\partial^2 z}{\partial x_2^2} \end{bmatrix}$$

And the Eigen values were calculated using the Eqn. 5, where 'e' represents Eigen values and 'I' is the 2×2 unit matrix. The quadratic equation obtained by expanding the determinant is solved to yield the two Eigen values (e_1 and e_2)[17]. If both the Eigen values are positive, then the quadratic surface has a minimum value and if both the values are negative the quadratic surface has a maximum value. When the Eigen values are of mixed signs, a saddle point is identified[18].

$$|H - (e \times I)| = 0 \qquad ...(5)$$

Table 3 shows the Hessian matrix of the response surface model equations, calculated Eigen values for each Hessian matrix and the nature of optimum based on the Eigen values.

Residual plots

The residual diagnostic plots obtained from the RSM analysis are shown in Fig. 1. Diagnostic plots of predicted vs. actual help to determine the model satisfactoriness.Close proximity of all the data points to a straight line indicated a high agreement with the predicted and actual values[19]. Residuals vs. predicted plots show that the residuals for both responses were distributed within a very narrow range. This observation indicates that there were no outliers present outside the set limit of ±3. Hence, it can be stated that the quadratic models obtained are suitable for the prediction of responses, porosity and contact angle.

Two-D Contour plots and three-D surface plots

Regression equations are graphically represented two-dimensionally as contour plots and three-dimensionally as surface plots[20]. Figure 2 shows the contour plots for the responses porosity and contact angle respectively. The value for each response at different concentrations of the variables can be predicted using contour plots. Each contour curve represents an infinite number of combinations of the two variables and the maximum predicted value is indicated by the surface confined in the smallest ellipse in the contourdiagram[20]. A significant mutual interaction between the independent variables can be observed and an optimum concentration for nanoclay and PEG can be read from these plots. The contour plot of desirability is also shown in Fig. 2. The maximum desirability that can be achieved is 1. Desirability above 0.8 is represented by the red coloured region of the contour plot[21]. Desirability was found to be decreasing with the increase in concentration of PEG and nanoclay. RSM predicted a maximum value of 49% for porosity and a minimum value of 72^{o} for contact angle at an optimum concentration of 1 wt% and 3.7 wt% for nanoclay and PEG respectively, with desirability of 0.996.

3D surface plots

Additional analysis of the effect of operating parameters on the responses was done using surface

Table 3 — Hessian matrix and Eigen values of each response equations

Response equations	H	e_1	e_2	Nature of optimum
Equation 3	$\begin{bmatrix} -12.32 & 2.25 \\ 2.25 & -1.82 \end{bmatrix}$	-1.36	-12.78	Maximum
Equation 4	$\begin{bmatrix} 4.64 & 2.75 \\ 2.75 & 3.14 \end{bmatrix}$	6.74	1.04	Minimum

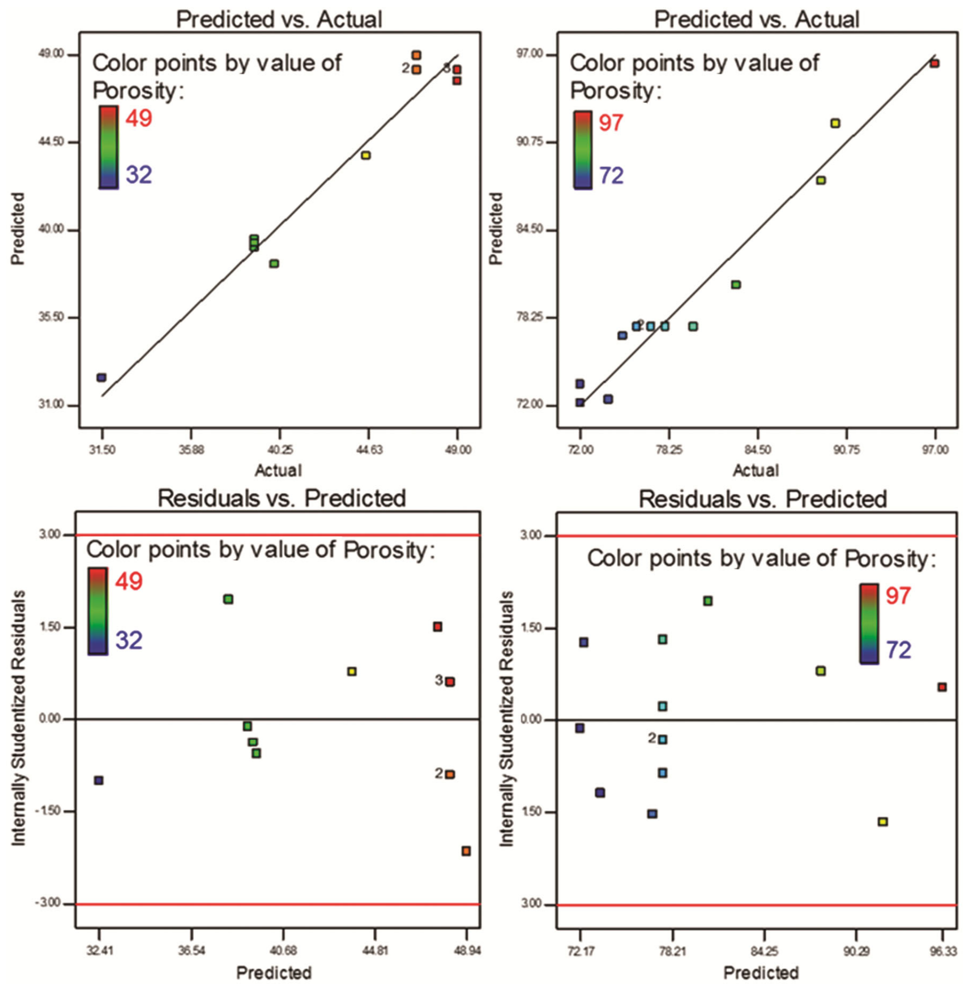

Fig. 1 — Predicted vs. actual values plot and residuals vs. predicted plot for (left) porosity and (right) contact angle for the optimisation of membrane composition

plots, shown in Fig. 3. Since PEG is a pore-forming agent, the porosity of the membranes increased with the increase in PEG concentration. However, after a particular concentration of PEG, the porosity was found to decline. This observation is due to the agglomeration of PEG particles at higher concentrations. But with the addition of nanoclay, the porosity is declining continuously. This reduction in porosity is due to the reduction in pore size by nanoclay. The surface plot for contact angle shows that lower the concentration of PEG and nanoclay, lower is the contact angle. Hence it can be said that the combined effect of nanoclay and PEG decreases the contact angle of the membranes. The red coloured dome-shaped area depicts the maximum desirability in the surface plot of desirability and the blue colour area shows zero desirability. The surface plots for both the responses are combined in the surface plot of desirability based on the criteria set for each response. The curvature area satisfies the optimality criteria of both responses simultaneously.

Validation of the model

It is necessary to validate the effect of responses on the independent variables determined theoretically by calculating an experimental error between theoretical and experimental values[6]. Based on the RSM analysis, the concentration of PEG and nanoclay at maximum desirability is chosen and the response values predicted by RSM are compared with the experimental values. The results are shown in Table 4. The experimentally observed responses were found to be in good agreement with the theoretical values predicted by RSM. This confirms the accuracy and precision of the RSM models[4].

Table 5 presents the comparison between the optimized composition of nanoclay and PEG obtained using single variable batch optimization and combined multivariable optimization using central composite

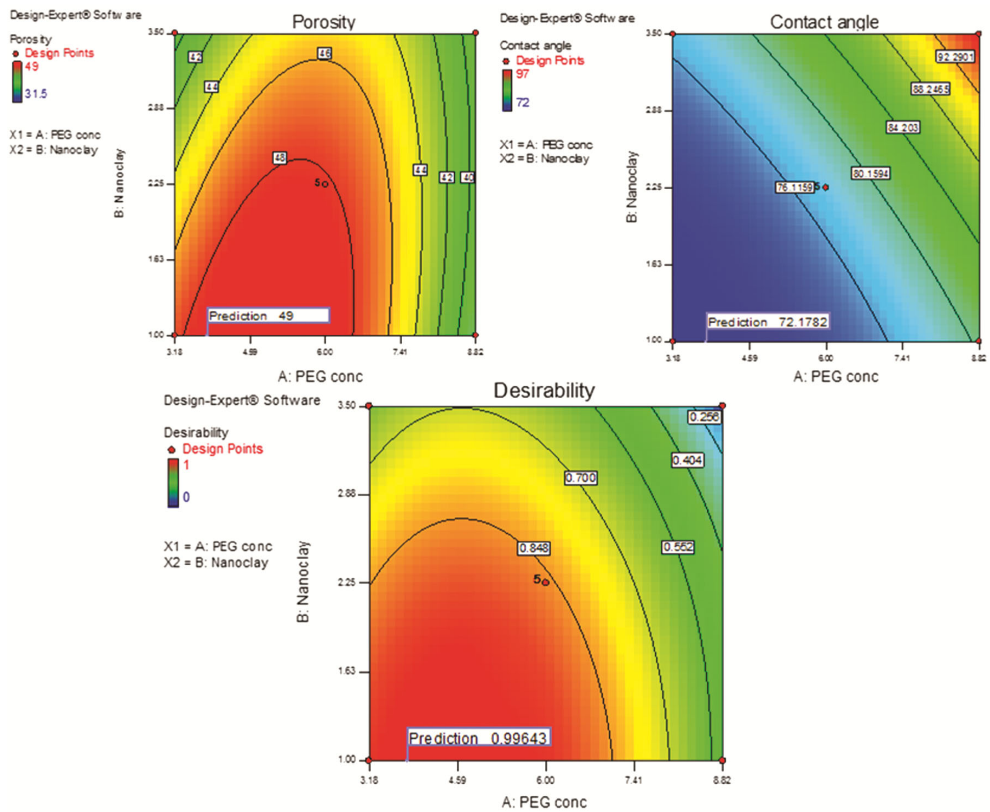

Fig. 2 — Contour plots describing the effects of PEG and nanoclay concentration on (a) porosity, (b) contact angle and (c) desirability (clockwise from top left)

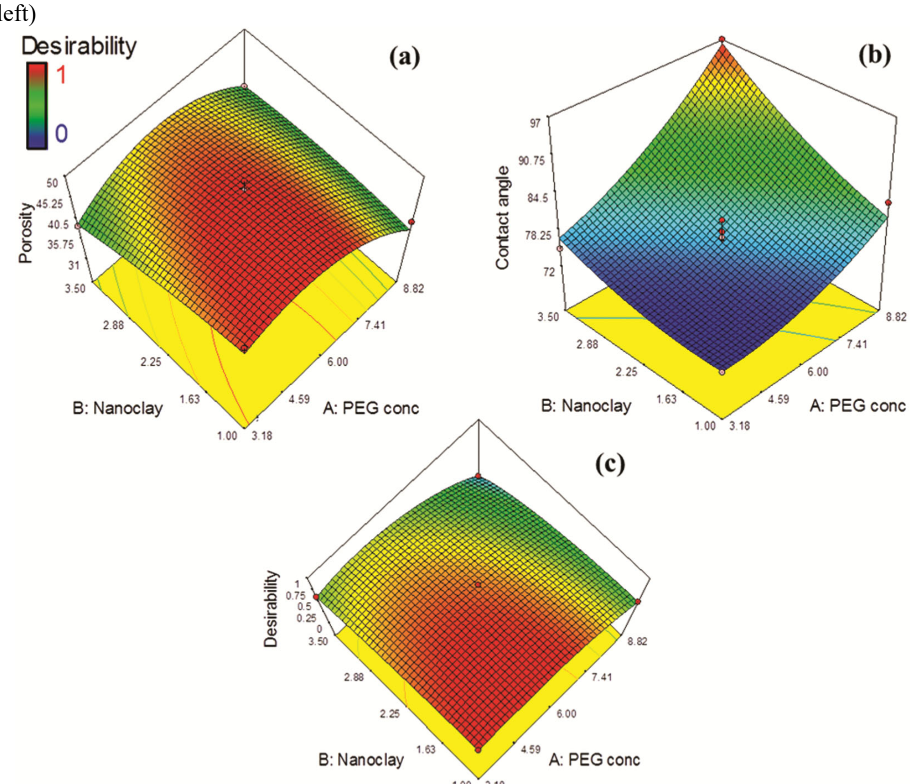

Fig. 3 — 3D surface plots for (a) porosity (b) contact angle and (c) desirability for varied PEG and nanoclay concentration

design (CCD) in conjunction with RSM method. The composition optimized RSM method which analyses the combined effect of independent variables was found to be lower than that of single variable optimization at improved membrane properties.

Conclusion

The composition of membrane for filtration operations was optimized using response surface methodology and compared with that of the single variable optimization. By analysing the batch study results, it was found that the membrane permeability has a direct relation to porosity and hydrophilicity of the membranes. RSM analysis was carried out by choosing the concentration of membrane components as independent variables and porosity and contact angle (a measure of hydrophilcity) as dependent variables or responses. The quadratic models obtained were analysed and the significance of model terms was determined from R-squared, adjusted R-squared and ANOVA results respectively. The Eigen value analyses were also carried out from the Hessian matrix to determine the nature of the optimum obtained. The optimum composition of nanoclay and PEG obtained from RSM is found to be less than that of batch study with better membrane properties. This is due to the fact that, RSM identifies the interaction between the variables, as their combined interactions at varying levels have a significant effect on the responses. Hence, it can be concluded that RSM is a better optimization technique and can be effectively utilized for polymer optimization, especially for the fabrication of polymeric membranes.

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References

1 Bezerra M A, Santelli R E & Oliveira E P, *Talanta* 76 (2008) 965.
2 McDonald D B, Grantham W J, Tabor W L & Murphy M J, *Appl Math Model*, 31 (2007) 2095.
3 Şenaras A E, *Sustain Eng Prod Manuf Technol*, (2019) 187.
4 Kumari M & Gupta S K, *Sci Reports Nat Res*, 9 (2019) 1.
5 Wang X, Wang S, Pan D, *Eng Life Sci*, 18 (2018) 611.
6 Aydar A Y, *Statistical Approaches with Emphasis on Design of Experiments Applied to Chemical Processes*, (2018) 157.
7 Dutta P, Mandal S & Kumar A, *Adv Model Anal C*, 73 (2018) 23.
8 Koromilas N D, Anastasopoulos C, Oikonomou E K & Kallitsis J K, *Polym Basel*, 11 (2019) 1.
9 Srivastava H P, Arthanareeswaran G, Anantharaman N & Starov V M, *Desalination*, 282 (2011) 87.
10 Yiew T, Ling E & Fadhil M, *J Environ Manage*, 228 (2018) 13.
11 Zulkali M M D, Ahmad A L & Derek C J C, *Desalination*, 179 (2005) 381.
12 Bandara P C, Nadres E T & Rodrigues D F, *ACS Appl Mater Interf*, 11 (2019) 17784.
13 Banerjee A & Ray S K, *J Memb Sci*, 549 (2018) 84.
14 Gadekar M R & Ahammed M M, *J Environ Manage*, 231 (2019) 241.
15 Sadeghian M, Sadeghi M, Hesampour M & Moheb A, *Desalin Water Treat*, 55 (2014) 615.
16 Behera S K, Meena H, Chakraborty S & Meikap B C, *Int J Min Sci Technol*, 28 (2018) 621.
17 Kumar M M & Karthikeyan R, *Asian J Chem*, 28 (2016) 1561
18 Shankar T J, Sokhansanj S, Bandyopadhyay S & Bawa A S, *Food Bioprocess Technol*, 3 (2010) 498.
19 Ahmadi M, Masoumi S, Hassanajili S & Esmaeilzadeh F, *Chinese J Chem Eng*, 26 (2018) 2503.
20 Elibol M, *Process Biochem*, 39 (2004) 1057.
21 Arun V V, Saharan N & Ramasubramanian V, *Sci Rep*, 7 (2017) 1.