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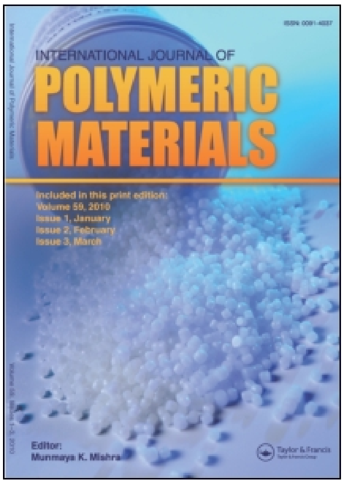

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Studies on Performance of Cellulose Acetate and Poly(Ethelene Glycol) Blend Ultrafiltration Membranes Using Mixture Design Concept of Design of Experiments

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Cellulose acetate (CA) membranes have several advantages over other membranes due to their moderate flux, high salt rejection properties, renewable source of raw material, etc. Membrane compositions containing different concentrations of CA, polyethylene glycol (PEG 600) as additive and N,N–dimethyl formamide (DMF) as solvent have been prepared using phase inversion technique based on the mixture design concept of design of experiments. The prepared membranes have been characterized for permeate flux, membrane hydraulic resistance, and separation of proteins such as pepsin, egg albumin (EA), and bovine serum albumin (BSA). Using statistical techniques, the experimental data have been analyzed and a suitable model was suggested for predicting the optimal level of response as a function of the input variable. The influence of variation of the CA, DMF, and PEG 600 on the asymmetric membrane properties has also been reported.

Keywords: cellulose acetate, design of experiments, phase behavior, polymeric membranes, separation techniques

INTRODUCTION

Polymeric materials and their blends have played an important role in many separation applications such as ultrafiltration (UF), microfiltration, and nanofiltration [1–3]. The basic principles of membrane

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separation and its commercial importance have been extensively reported [4–5]. For preparation of membranes with better performance, the raw material should be tolerant to wide temperature range and pH apart from yielding membranes with wider range of pore sizes. Michaels has discussed the chemical constitution of these polymer membranes and their potential biomedical applications [6]. It is also a pressure driven process used to separate or concentrate macro solutes. Cellulose acetate (CA) is one of the most universally used materials for preparing ultrafiltration and reverse osmosis (RO) membranes. Cellulose acetate membranes have been prepared by many researchers and characterized for their compaction, hydraulic permeability, and osmotic permeability properties [7–8]. Cellulose acetate and its derivatives are suitable raw materials for membrane preparation, because of advantages such as moderate flux, high salt rejection properties, cost effectiveness, relatively easy manufacture, renewable source of raw material, and non-toxicity. The effect of cast solution thickness on the formation of macro voids in the membrane forming ternary cellulose acetate/acetone/water system by wet phase inversion technique has been reported [9].

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Ever since the membrane synthesis results reported by Loeb and Sourirajan in the early sixties [10], many studies have been carried out for better understanding of the phenomena involved in the phase inversion process. Many studies have been done to improve the thermal or ultrafiltration properties of the CA membranes by the addition of organic or inorganic substances [11–12]. Recently, it has been shown that the addition of borates and phosphates improves the thermal properties of CA [11]. Generally, additives are added to improve the polymer properties thus enabling wider application of CA.

Using statistical techniques, a set of combinations that variables which influence the properties of interest can be designed without the need for studying all possible combinations practically [13]. Based on the experimental results, using suitable models, the effect of variables on the properties can be predicted. Several studies have been carried out to design experiments, primarily process parameters, based on response surface methodology using Box-Behnken design of experiments [14–17]. Among the different techniques available for optimizing inputs with constraints, mixture design technique is highly appropriate. Mixture design technique is preferred because it requires relatively few experimental combinations of the variables to estimate potentially complex response functions [18]. In the present investigation, the effect of addition of polyethylene glycol 600 (PEG 600) with CA in the preparation of membranes on permeate flux and hydraulic resistance for pure water as well as rejection of proteins such as pepsin

(35 kDa), egg albumin (45 kDa), and bovine serum albumin (66 kDa) have been studied using a set of experiments based on mixture design technique.

METHODOLOGY AND DESIGN OF EXPERIMENTS

The classical approach of changing one variable at a time (OVAT) and studying the effect of that variable on the response is a complicated technique, particularly in a multivariable system, or if more than one response are of importance. Design of experiments comprises a group of statistical techniques, which can be used for model building, model exploitation, and optimizing such multivariable systems [19–22].

Two such techniques are the mixture design and response surface methodology, where the primary approach to the general problem is to optimize a mixture whose properties depend on the proportions of the component materials. In these techniques, a set of trial batches covering a chosen range of proportions for each component is set up according to established statistical procedure, rather than selecting one starting point. Trial batches are performed and results are analyzed using standard statistical methods that yield reliable estimates of parameters from empirical models for each performance criterion. Each response is expressed as an algebraic function of factors. Once a response is characterized by an equation, any number of analyses is possible. It allows calculations to be made of the response at intermediate levels, which were not experimentally studied and shows the direction in which to move, if one wishes to change the input levels so as to decrease or increase the response. For instance, the user could determine which mixture proportions would yield a desired response. Similarly, the user could optimize any response function subject to constraints on the others like determining the lowest cost mixture with strength greater than the specified strength.

In mixture design approach, the total amount of the product is fixed and is constrained to sum 1. For each statistical combination, all properties of interest would be measured and empirical models for each property as a function of the variables would be determined from regression analysis. The advantage of the mixture approach is that the experimental region of interest is more naturally defined. To simplify calculations and analysis, the actual variable ranges are usually transformed to dimensionless coded variables with a range of ± 1. Intermediate values are also translated similarly.

Use of an appropriate mixture experiment design allows estimation of a full quadratic model for each response. The mathematical

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relationship between three independent variables and the response can be approximated by the second order polynomial:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

where β_0 is a constant; β_1, β_2, β_3 are linear coefficients; β_{12}, β_{13}, β_{23} are cross product coefficients; β_{11}, β_{22}, β_{33} are quadratic coefficients; and $X_1 = (A - X_0)/\Delta X$, X_1 = coded value of the variable A; X_0 = value of A at the center point; ΔX = step change; $X_2 = (B - X_0)/\Delta X$ and so on where A, B, and so on are the input variables.

MATERIALS AND METHODS

Materials

Commercial grade cellulose acetate (acetyl content 39.99 wt%) was procured from Mysore Acetate and Chemicals Company Ltd., India. Analar grade N,N-dimethyl formamide (DMF) from Qualigens Fine Chemicals, Glaxo India Ltd. was procured and dehydrated through molecular sieves (Type—4 Å) for removing moisture, and stored in dried condition prior to use. Other solvents such as acetone and methanol as well as surfactant, sodium lauryl sulphate (SLS), of AR grade were procured from Qualigens Fine Chemicals Ltd., India. PEG 600 was procured from Merck (India) Ltd. and used as such, as an additive for the whole study. Proteins, namely, bovine serum albumin (BSA), $M_w = 69$ kDa, and pepsin, $M_w = 35$ kDa, were purchased from SRL Chemicals Ltd., India and used as received. Egg albumin (EA), $M_w = 45$ kDa was obtained from CSIR Biochemical Centre, New Delhi, India. Deionized and distilled water was used for all the studies.

Design of Experiments

Mixture design technique was employed in this investigation to discover the optimal formulation of CA, additive, and solvent. The chosen variables CA, solvent, and additive were coded as X_1, X_2, and X_3, respectively. The lower and upper level of each variable were designated as 0 and +1, respectively, and listed in Table 1. A design expert software (State-Ease Inc., Minneapolis, MN) employing multiple regression analysis was used to find different combinations of CA, solvent, and additive. A total of 14 experiments were necessary to estimate the 9 coefficients of the model. The mixture design combinations for experimentation and their corresponding responses from

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TABLE 1 Range of Variables and Their Coded Form

Variable	Lower limit		Upper limit	
	%	Code	%	Code
CA	10	0	25	+1
Solvent	72.5	0	82.5	+1
Additive	2.5	0	10	+1

various studies are listed in Table 2. The responses studied were permeate flux, hydraulic resistance, and rejections of pepsin, egg albumin, and bovine serum albumin. Using the design expert software, the coefficients for different responses and optimum values were predicted.

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Preparation and Characterization of the Membrane

Sets of 14 membranes were prepared using the following procedure based on the combinations (Table 2) derived from design expert software. In each trial, CA was dissolved in DMF solvent containing PEG 600 as additive. The components were mixed for 3 to 4 h at around $80 \pm 5^{\circ}$C to attain homogeneous solution. The solution was allowed to stand for 0.5 h to eliminate air bubbles. The casting of the membranes was carried out as reported [23]. Each prepared membrane was cut in to desired size needed for fixing it up in the ultrafiltration kit of 38.5 cm^2 area. Each membrane was initially hydrostatically compressed in the ultrafiltration test cell at a pressure of 414 kPa for 5–6 h. This makes the membrane to attain steady flux.

Permeate Flux

Membranes after compaction were subjected to pure water flux at transmembrane pressure of 345 kPa. The flux was measured under steady state flow, that is after every 1 h for 4 h. The permeate flux was determined using Eq. 2:

$$J_w = \frac{Q}{A \cdot \Delta T} \tag{2}$$

where, J_w = permeate flux, $l\,m^{-2}\,h^{-1}$; Q = quantity of permeate, l; A = membrane area, m^2; ΔT = sampling time, h.

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TABLE 2 Mixture Design Combinations

	Variables (%)				Responses			
Combination reference	CA	Solvent	Additive	Permeate flux ($lm^{-2}h^{-1}$)	Hydraulic resistance ($kPa/lm^{-2}h^{-1}$)	% Rejection of Pepsin	% Rejection of EA	% Rejection of BSA
1	10	80	10	120.9	8.0	4.0	11.6	15.4
2	10	80	10	115.1	12.0	7.8	11.6	15.5
3	10	82.5	7.5	98.7	10.0	13.5	19.2	28.9
4	12.5	82.5	5	51.7	20.1	20.0	29.7	40.8
5	13.75	76.25	10	80.3	4.5	16.0	30.7	33.9
6	15	82.5	2.5	14.1	30.0	15.0	21.5	32.2
7	15	82.5	2.5	13.1	31.1	18.5	22.4	32.4
8	15.5	78	6.5	43.6	9.6	21.0	55.6	64.5
9	17.5	72.5	10	43.9	9.0	36.2	37.5	41.0
10	17.5	72.5	10	42.5	9.4	33.2	36.8	40.8
11	20	77.5	2.5	15.5	25.9	36.2	48.1	59.4
12	21.25	72.5	6.25	20.7	23.7	49.4	64.3	76.5
13	25	72.5	2.5	8.3	40.0	40.0	54.1	66.8
14	25	72.5	2.5	8.9	39.8	42.5	53.6	66.7

Membrane Hydraulic Resistance (R_m)

Membrane hydraulic resistance is an important parameter, that decides the productivity of the membranes at a given pressure [24]. This would be more useful to apply the membrane for a particular environment and to identify the suitability of the membranes for a particular membrane process. Membrane hydraulic resistance (R_m) was evaluated by measuring permeate flux at different transmembrane pressures such as 69, 138, 207, 276, and 345 kPa after compaction. The resistance of the membrane was evaluated from the slope obtained by plotting the transmembrane pressure difference (ΔP) vs. permeate flux (J_w) using Eq. 3:

$$R_m = \frac{\Delta P}{J_w} \tag{3}$$

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Protein Rejection

After mounting the membrane in the UF cell, the chamber was filled with individual protein solution and immediately pressurized under nitrogen atmosphere to the desired level (345 kPa) and maintained constant throughout the run. Proteins such as BSA, EA, and pepsin were dissolved (0.1 wt%) in phosphate buffer (0.5 M, pH 7.2) and used as standard feed solutions.

For all experiments, the concentration of feed solution was kept constant. Permeate was collected over measured time intervals in graduated tubes and the tube contents were analyzed for protein content by UV-visible spectrophotometer (Shimadzu, Model UV-160A) at 280 nm ($\lambda_{\max}$). The percent protein separation, %SR, was calculated from the concentration of feed and permeates [25] using Eq. 4:

$$\%SR = 1 - \left(\frac{C_p}{C_f}\right) \times 100 \tag{4}$$

where, C_p and C_f are concentrations of permeate and feed, respectively.

RESULTS AND DISCUSSION

The purpose of this investigation is to derive optimal composition of inputs for improved membrane properties such as permeate flux, hydraulic resistance, and rejections of proteins using mixture design technique. The statistically designed combinations were experimentally studied and the responses analyzed statistically. The responses (properties) studied were permeate flux, hydraulic resistance, and rejections of pepsin, EA, and BSA, which are designated as Y_1, Y_2, Y_3, Y_4, and Y_5. The individual responses have been predicted by the following regression equations, which give the relationship between the input variables and the response.

$$\begin{aligned} Y_1 = {} & 9.993 * X_1 + 24.576 * X_2 + 140.401 * X_3 - 21.498 * X_1 * X_2 \\ & - 127.863 * X_1 * X_3 + 144.904 * X_2 * X_3 \end{aligned} \tag{5}$$

$$\begin{aligned} Y_2 = {} & 40.362 * X_1 + 45.254 * X_2 + 25.100 * X_3 - 63.479 * X_1 * X_2 \\ & - 89.162 * X_1 * X_3 - 108.714 * X_2 * X_3 \end{aligned} \tag{6}$$

$$\begin{aligned} Y_3 = {} & 69.666 * X_1 + 86.039 * X_2 + 85.616 * X_3 - 1.483 * X_1 * X_2 \\ & + 3.140 * X_1 * X_3 + 6.582 * X_2 * X_3 \end{aligned} \tag{7}$$

$$\begin{aligned} Y_4 = {} & 43.225 * X_1 + 12.656 * X_2 - 36.771 * X_3 - 18.841 * X_1 * X_2 \\ & + 123.586 * X_1 * X_3 + 69.530 * X_2 * X_3 \end{aligned} \tag{8}$$

$$\begin{aligned} Y_5 = {} & 53.530 * X_1 - 28.14 * X_2 - 138.83 * X_3 + 102.463 * X_1 * X_2 \\ & + 318.714 * X_1 * X_3 + 380.882 * X_2 * X_3 \end{aligned} \tag{9}$$

The equations are based on the quadratic model because it fits well with the experimental data unlike other models such as linear, cubic, and two factor interactions. The fitness of the model for each response can be explained using model summary statistics and analysis of variance.

Model Summary Statistics

Model summary statistics provide several comparative measures for model selection. R squared statistics is the correlation coefficient between the experimental response and the predicted response, which should be nearly 1 for a particular model to be significant [19]. Adjusted R squared parameter provides similar correlation after ignoring the insignificant model terms. It should also have good agreement with predicted R squared parameter for the model to be fit. Model summary statistics for the selected models for different responses are given in Table 3. It is seen that the special cubic model has higher R squared statistics than quadratic model; however, the correlation between adjusted R squared and predicted R squared values is good in quadratic model compared to special cubic, as clearly

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TABLE 3 Model Summary Statistics

Property	Source	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared
Permeate flux	Linear	18.38138	0.821156	0.788639	0.685671
	Quadratic	3.553564	0.995139	0.992101	0.980485
	Special cubic	3.264807	0.99641	0.993332	0.978275
	Cubic	2.169222	0.999094	0.997056	—
Hydraulic resistance	Linear	4.575826	0.881712	0.860205	0.823676
	Quadratic	2.765076	0.968587	0.948953	0.896754
	Special cubic	2.932978	0.969074	0.942566	0.836182
	Cubic	1.495581	0.995405	0.985066	—
Rejection of pepsin	Linear	5.7323	0.859424	0.833865	0.772856
	Quadratic	4.306711	0.942291	0.906223	0.823285
	Special cubic	3.328219	0.969843	0.943995	0.768626
	Cubic	2.277776	0.991929	0.973768	—
Rejection of EA	Linear	9.79945	0.728953	0.679672	0.614174
	Quadratic	0.733963	0.998894	0.998203	0.99628
	Special cubic	0.607271	0.999338	0.99877	0.995495
	Cubic	0.439218	0.999802	0.999356	—
Rejection of BSA	Linear	10.95435	0.73633	0.68839	0.618975
	Quadratic	0.222261	0.999921	0.999872	0.999672
	Special cubic	0.192308	0.999948	0.999904	0.999689
	Cubic	0.122014	0.999988	0.999961	—

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seen in hydraulic resistance and rejection of pepsin. Similarly in the case of cubic model, although the R squared values are higher than the quadratic model, the predicted R squared values are not generated by the design and hence not in good agreement with the adjusted R squared values. Thus, the design software suggests quadratic model for further navigation of the design space. It is observed that the correlation coefficient (R squared) is 0.99 for permeate flux, 0.97 for hydraulic resistance, 0.94 for pepsin, 0.99 for EA, and 0.99 for BSA in the quadratic model indicating high degree of correlation between the experimental and predicted response. It can also be seen from the model that predicted R squared is in good agreement with adjusted R squared [19].

Analysis of Variance (ANOVA)

ANOVA for each response for the selected quadratic model is given in Tables 4–8. Prob $>$ F values are much less than 0.05, indicating that the model is significant for all the responses confirming the fitness of the selected model. Prob $>$ F values for AB in permeate flux

TABLE 4 ANOVA for Quadratic Model of Permeate Flux

Source	Sum of squares	DF	Mean square	F value	Prob > F
Model	20680.36	5	4136.073	327.5366	< 0.0001
Linear mixture	17064.76	2	8532.38	675.6812	< 0.0001
AB	11.41207	1	11.41207	0.903724	0.3696
AC	150.0133	1	150.0133	11.87959	0.0087
BC	132.8199	1	132.8199	10.51804	0.0118
Residual	101.0225	8	12.62782		
Lack of fit	82.20044	4	20.55011	4.36723	0.0912
Pure error	18.8221	4	4.705525		
Cor total	20781.39	13			

TABLE 5 ANOVA for Quadratic Model of Hydraulic Resistance

Source	Sum of squares	DF	Mean square	F value	Prob > F
Model	1885.949	5	377.1898	49.33395	<0.0001
Linear mixture	1716.794	2	858.3969	112.2727	<0.0001
AB	99.49933	1	99.49933	13.01386	0.0069
AC	72.9456	1	72.9456	9.540807	0.0149
BC	74.76107	1	74.76107	9.778259	0.0141
Residual	61.16514	8	7.645643		
Lack of fit	52.21809	4	13.05452	5.836347	0.0579
Pure error	8.94705	4	2.236763		
Cor total	1947.114	13			

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and AB and BC in pepsin rejection are higher than 0.05, which indicates that the interaction between the respective inputs are not significant. The predicted response obtained from the regression Eqs. 5 to 9 by substituting the coded values of the variables corresponding

TABLE 6 ANOVA for Quadratic Model of Pepsin Rejection

Source	Sum of squares	DF	Mean square	F value	Prob > F
Model	2422.843	5	484.5686	26.12545	<0.0001
Linear mixture	2209.773	2	1104.887	59.56982	<0.0001
AB	8.765342	1	8.765342	0.472582	0.5112
AC	140.1459	1	140.1459	7.555947	0.0251
BC	30.58039	1	30.58039	1.648738	0.2351
Residual	148.3821	8	18.54776		
Lack of fit	127.629	4	31.90725	6.149892	0.0532
Pure error	20.75305	4	5.188263		
Cor total	2571.225	13			

TABLE 7 ANOVA for Quadratic Model of Egg Albumin Rejection

Source	Sum of squares	DF	Mean square	F value	Prob > F
Model	3892.885	5	778.5769	1445.284	<0.0001
Linear mixture	2840.873	2	1420.436	2636.777	<0.0001
AB	259.2364	1	259.2364	481.2244	<0.0001
AC	932.0587	1	932.0587	1730.194	<0.0001
BC	917.659	1	917.659	1703.464	<0.0001
Residual	4.309614	8	0.538702		
Lack of fit	3.537964	4	0.884491	4.584933	0.0847
Pure error	0.77165	4	0.192913		
Cor total	3897.194	13			

to different combinations are compared with the experimental values in Table 9. The predicted values are found to be in good correlation with the experimental values, proving the fitness of the selected model [19].

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Effect of Variables on Response

Contour plots are response surface plots that help in the identification of the type of interaction between the test variables and the responses [19]. 3-D contour plots facilitate to visualize the effect of variables on the responses in a three-dimensional space. The effects of variables on responses such as permeate flux, hydraulic resistance, and rejection of pepsin, EA and BSA are given in Figures 1–5. The converging contour lines indicate that the interaction between the variables and response is significant, which is well pronounced in EA and BSA as shown in

TABLE 8 ANOVA for Quadratic Model of Bovine Serum Albumin Rejection

Source	Sum of squares	DF	Mean square	F value	Prob > F
Model	5005.762	5	1001.152	20266.33	<0.0001
Linear mixture	3686.182	2	1843.091	37309.69	<0.0001
AB	209.0313	1	209.0313	4231.42	<0.0001
AC	1237.171	1	1237.171	25044.06	<0.0001
BC	1170.99	1	1170.99	23704.34	<0.0001
Residual	0.395198	8	0.0494		
Lack of fit	0.335648	4	0.083912	5.636412	0.0613
Pure error	0.05955	4	0.014888		
Cor total	5006.157	13			

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TABLE 9 Experimental and Predicted Responses

Combination reference	Permeate flux ($lm^{-2}h^{-1}$)		Hydraulic resistance ($kPa/lm^{-2}h^{-1}$)		Pepsin rejection (%)		EA rejection (%)		BSA rejection (%)	
	Actual value	Predicted value	Actual value	Predicted value	Actual value	Predicted value	Actual value	Predicted value	Actual value	Predicted value
1	120.9	118.7	8.0	7.9	4.0	5.3	11.6	11.7	15.4	15.5
2	115.1	118.7	12.0	7.9	7.8	5.3	11.6	11.8	15.5	15.5
3	98.7	95.4	10.0	14.4	13.5	11.6	19.2	19.6	28.9	29.1
4	51.7	51.6	20.1	19.5	20.0	18.6	29.7	29.6	40.8	40.9
5	80.3	79.6	4.5	5.3	16.0	18.6	30.7	30.8	33.9	33.9
6	14.1	14.9	30.0	29.5	15.0	18.7	21.5	21.9	32.2	32.3
7	13.1	14.9	31.1	29.5	18.5	18.7	22.4	21.9	32.4	32.3
8	43.6	48.9	9.6	10.2	21.0	27.0	55.6	54.5	64.5	64.1
9	43.9	43.2	9.0	10.4	36.2	34.1	37.5	37.0	41.0	40.9
10	42.5	43.2	9.4	10.4	33.2	34.1	36.8	37.0	40.8	40.9
11	15.5	10.1	25.9	27.9	36.2	28.9	48.1	49.1	59.4	59.7
12	20.7	18.6	23.7	19.8	49.4	46.4	64.3	65.2	76.5	76.7
13	8.3	9.9	40.0	40.1	40.0	43.2	54.1	53.5	66.8	66.7
14	8.9	9.9	39.8	40.4	42.5	43.2	53.6	53.5	66.7	66.7

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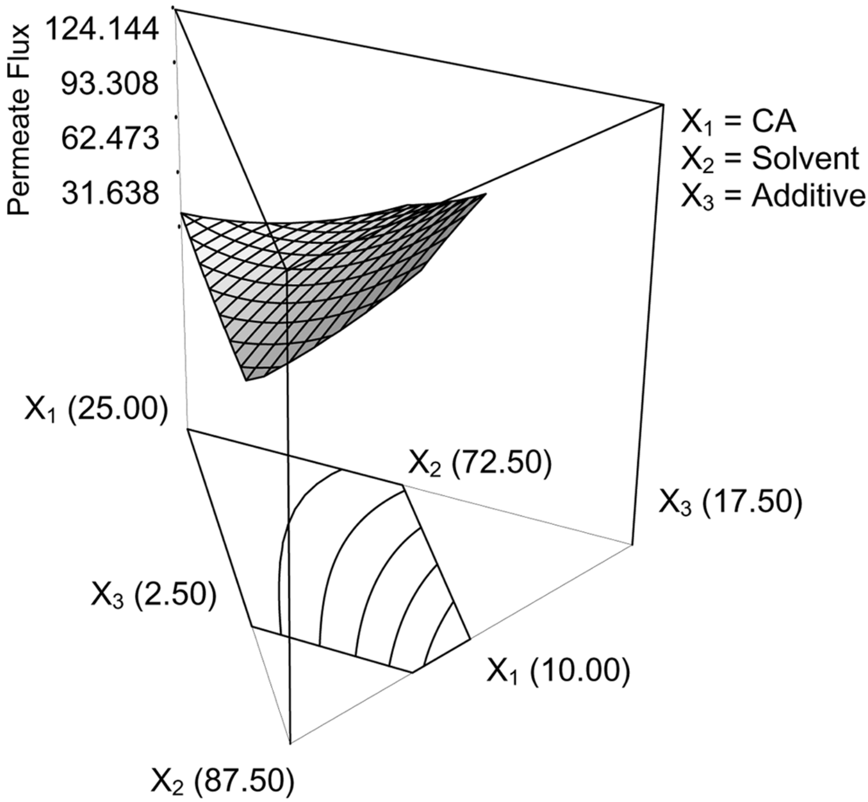

FIGURE 1 3-D contour diagram showing effect of individual variables on the permeate flux.

Figures 4 and 5. The linear contours show that the interaction of the input variables on the response in not much significant, which is slightly expressed in permeate flux as seen in Figure 1.

Permeate Flux and Membrane Hydraulic Resistance

Piepel graphs of coded input variables for all the responses are shown in Figures 6–10. It is seen that in the case of permeate flux (Figure 6), as the CA content increases the permeate flux decreases; however, the change in solvent content does not alter the permeate flux significantly. It is essential to mention that an increasing additive content increases the permeate flux linearly.

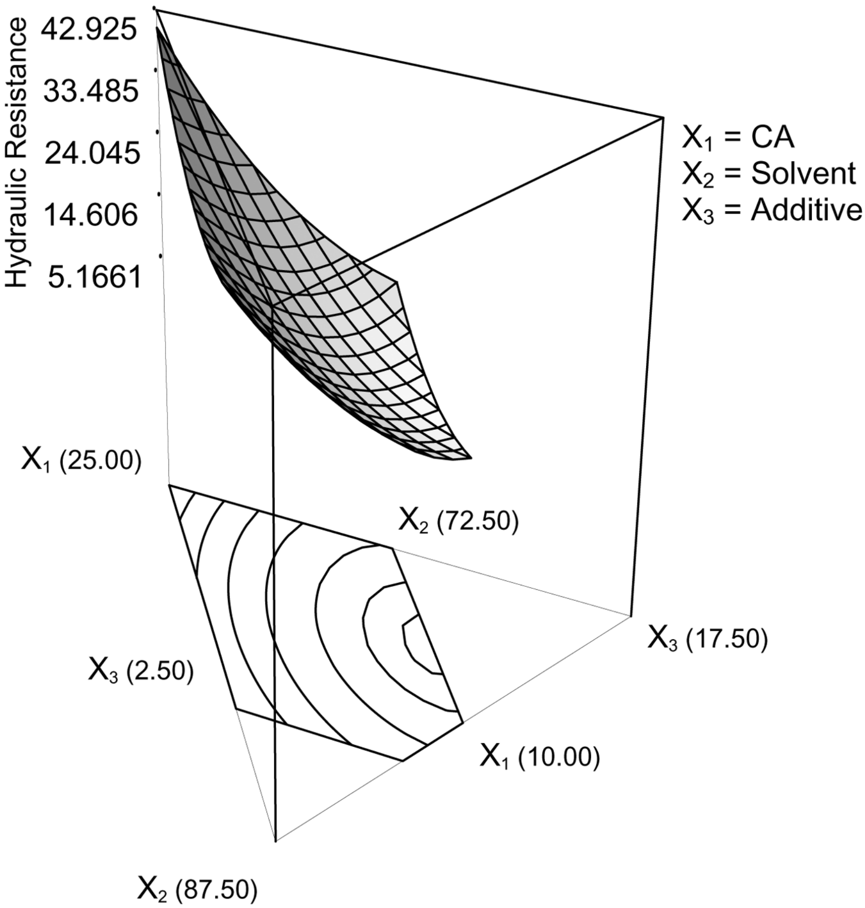

FIGURE 2 3-D contour diagram showing effect of individual variables on hydraulic resistance.

This increase in flux upon increase in additive concentration may be due to the fact that PEG 600 being hygroscopic are leached out of the membranes upon gelation, leading to the formation of macrovoids [26–27]. The relatively high flux in the presence of additive may be due to the increase in the network pore size. The lower flux of CA without any additive may be due to higher packing density of the polymer, which results in reduced size of the pores. In the case of hydraulic resistance, the response is significantly influenced by the variables CA and solvent, as seen from Figure 7. With increasing CA and solvent, the hydraulic resistance

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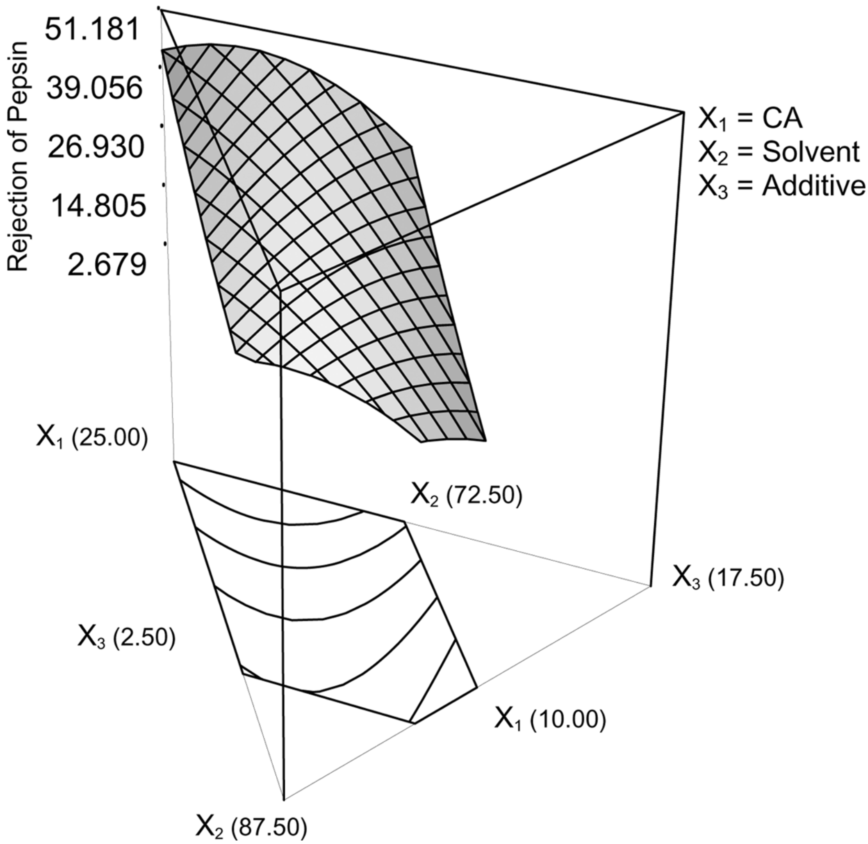

FIGURE 3 3-D contour diagram showing effect of individual variables on pepsin rejection.

decreases up to an optimum level and thereafter increases linearly. The additive is inversely contributing to the hydraulic resistance. The increase in additive concentration results in significant decrease in the hydraulic resistance. The reduced resistance is due to the instability of pores, which are formed by leaching out the PEG 600 during the coagulation process in membrane casting technique. Furthermore the presence of PEG increases this gap further due to the formation of macro voids on the membrane surface resulting from faster rate of leaching of PEG at higher concentration gradient from casting solution during gelation. Similar observations have also been observed by [28–29].

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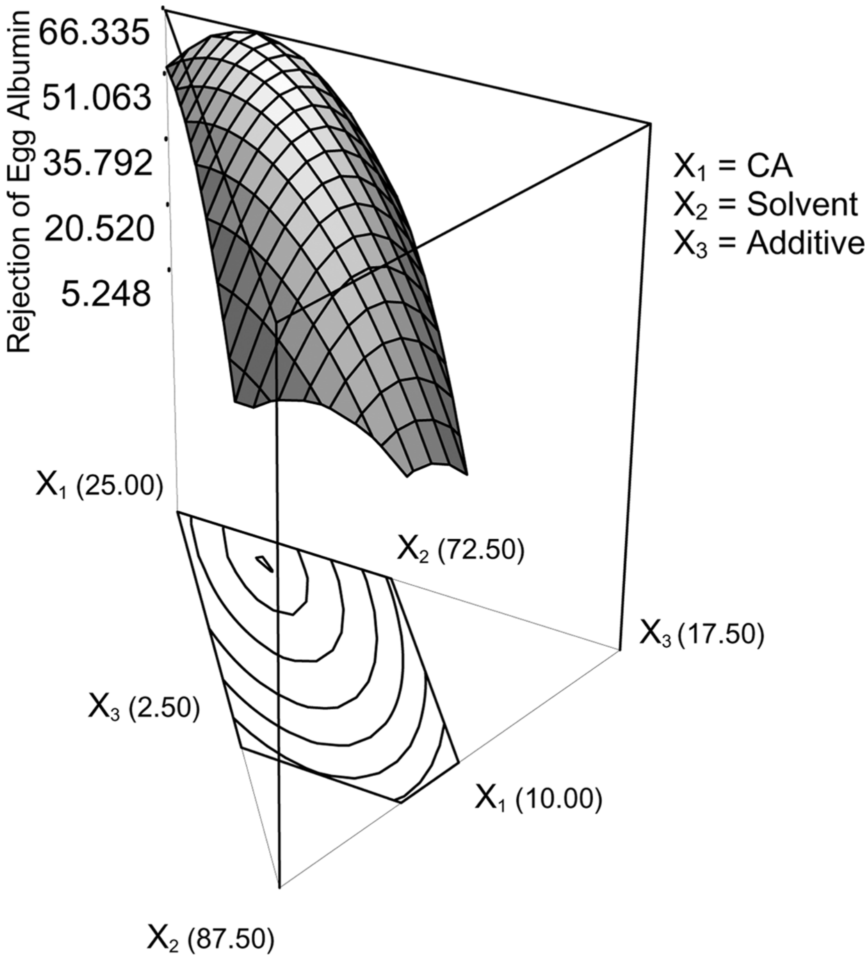

FIGURE 4 3-D contour diagram showing effect of individual variables on egg albumin rejection.

Protein Rejection

Fractionation of proteins using ultrafiltration membrane has not been successfully scaled up to industrial level because selectivity poses a threat to the industry. The interaction of the solutes with the membrane results in adsorptive fouling and interferes with the performance of the membranes. From Figure 2, among the proteins studied, BSA was found to have higher rejection. These trends may be due to the molecular weights of BSA, EA, and pepsin, which are 69, 45, and 35 kDa, respectively. The rejection of pepsin is significantly

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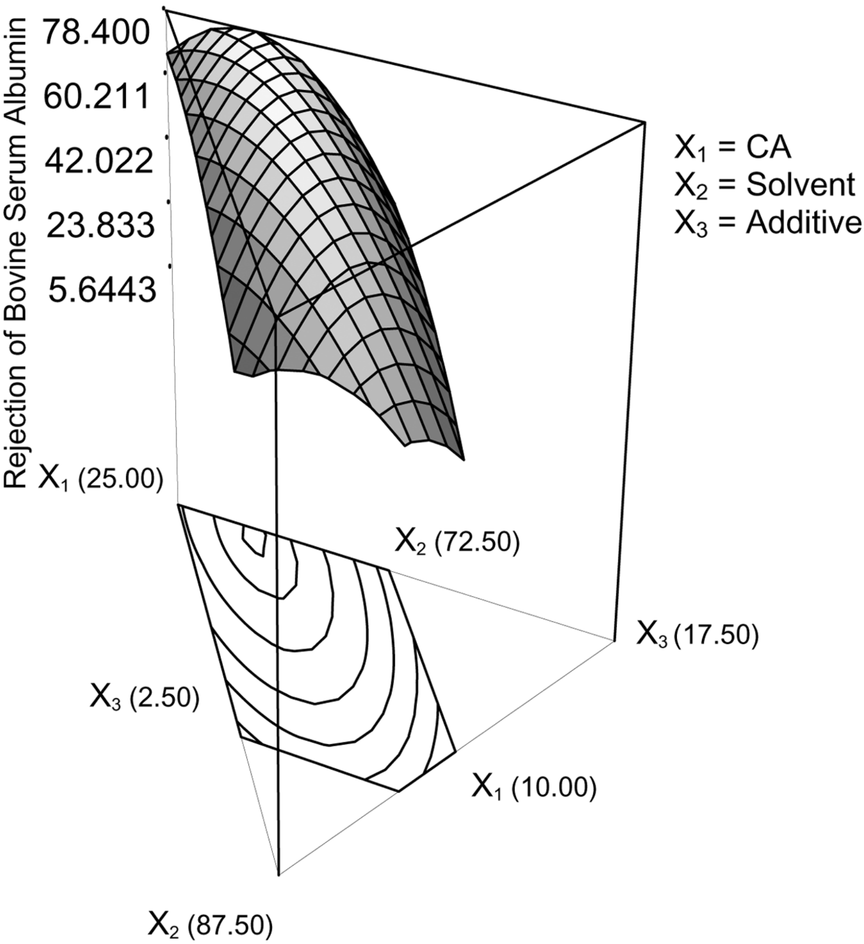

FIGURE 5 3-D contour diagram showing effect of individual variables on bovine serum albumin rejection.

increased upon increase in the concentration of CA and decrease in the concentration of solvent as seen in Figure 8. However, the presence of additive increases the pepsin rejection up to an optimum level after which the rejection decreases abruptly. This may be due to the formation of bigger pores in the membranes in the presence of additive and CA in an optimum ratio. In the case of EA and BSA rejection, the increase in CA and solvent as well as additive results in the increase of rejection of proteins up to optimum levels, after which the rejection decreases appreciably as shown in Figures 9 and 10.

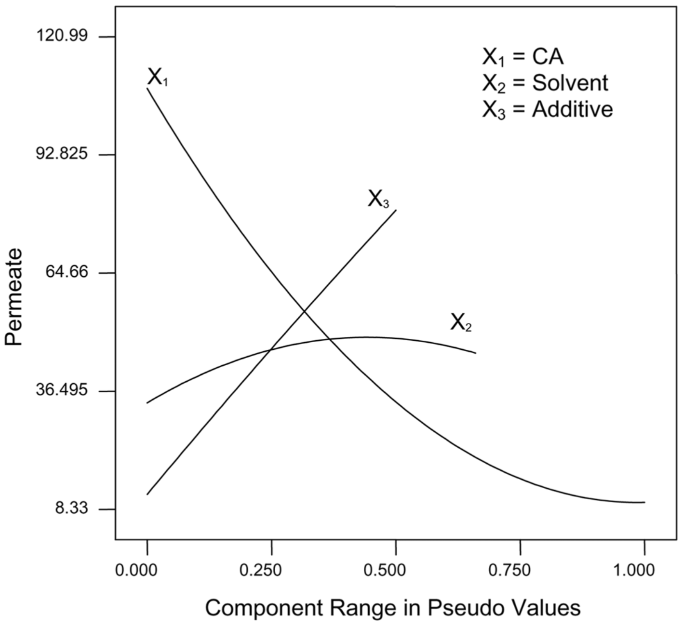

FIGURE 6 Trace plot (Piepel) for permeate flux.

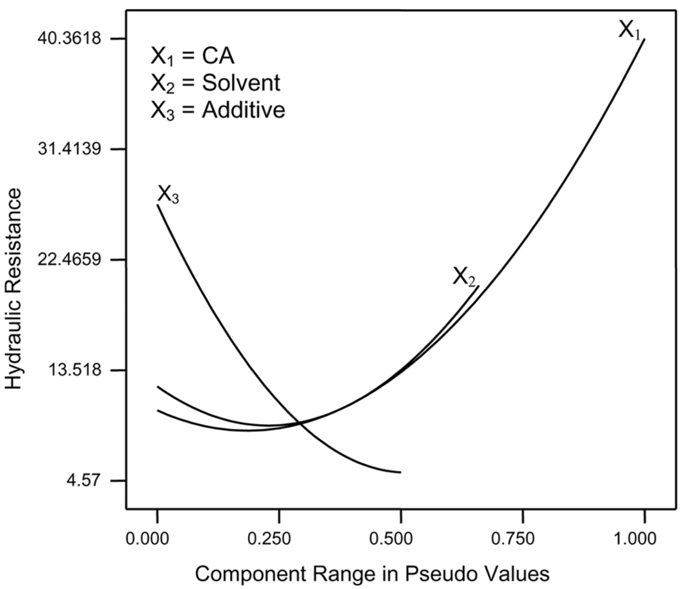

FIGURE 7 Trace plot (Piepel) for hydraulic resistance.

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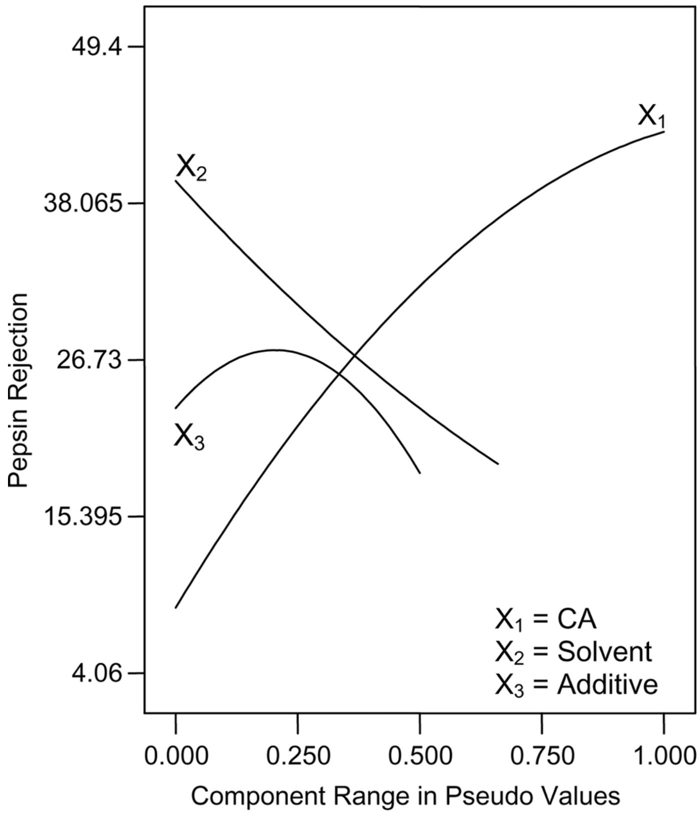

FIGURE 8 Trace plot (Piepel) for pepsin rejection.

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The predicted optimum level of combinations of input variables along with predicted individual responses are given in Table 10. It is seen that the input combinations for the individual responses corresponding to the predicted optimum are different from the experimental maximum and also different from the practically studied combinations, except in the case of permeate. Thus, statistical techniques helps in predicting optimum combinations of input variables by analyzing the experimental data using suitable mathematical models and provides the best combination, which otherwise requires numerous experimental studies. In all the membranes, irrespective of PEG 600 concentration, the order of percentage protein rejection was found to be BSA > EA > Pepsin. The reason for this trend may be explained by the fact that the flux of the proteins is inversely proportional to their size [30].

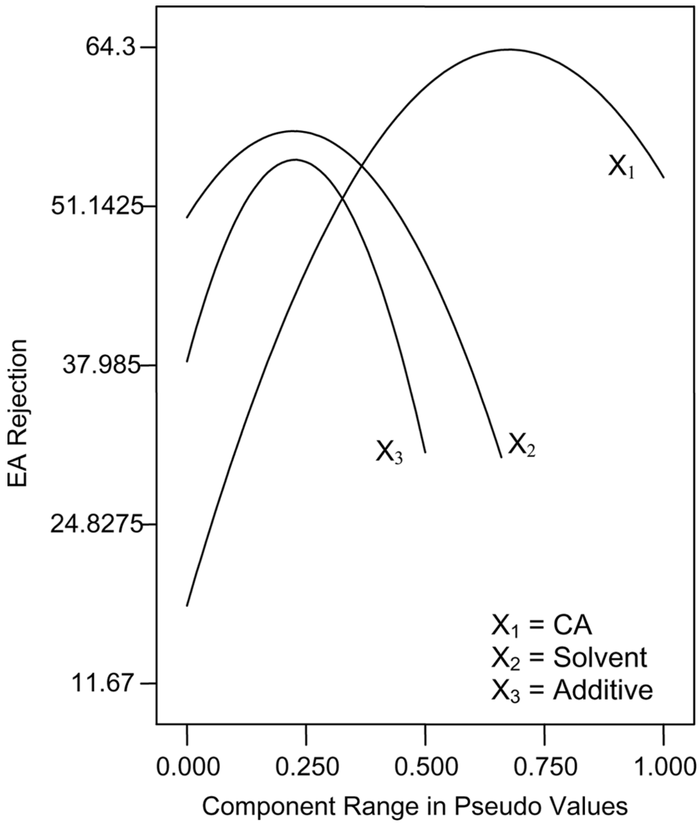

FIGURE 9 Trace plot (Piepel) for EA rejection.

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CONCLUSION

A series of cellulose acetate membranes was prepared based on mixture design concept of design of experiments, using three input variables namely cellulose acetate, solvent, and additive. The prepared membranes were characterized by studying permeate flux and hydraulic resistance. Separations of proteins of different molecular weights were also carried out. All the responses were statistically analyzed. The effects of variables on the responses were discussed. Among the different models analyzed, quadratic model fitted well with the experimental data. Equations were suggested for individual responses, based on which optimum values could be predicted with high degree of accuracy, within the experimental range of variables studied. Depending on the application requirements, any particular

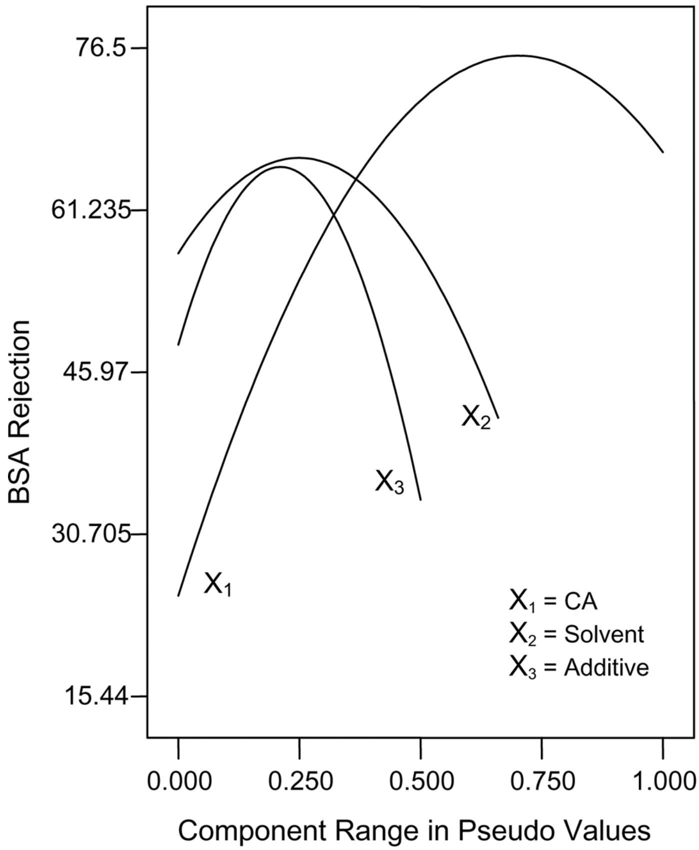

FIGURE 10 Trace plot (Piepel) for BSA rejection.

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TABLE 10 Optimum Combinations of Input Variables Suggested for Individual Properties

		Variable (%)		
Response	Predicted optimum	CA	Solvent	Additive
Permeate flux ($lm^{-2}h^{-1}$)	118.7	10	80	10
Hydraulic resistance ($kPa/lm^{-2}h^{-1}$)	40.1	24.94	72.53	2.53
Rejection of pepsin (%)	47.1	22.35	72.5	5.15
Rejection of EA (%)	65.1	19.25	75.01	5.74
Rejection of BSA (%)	77.9	20.61	74.23	5.16

response can be chosen, optimized, and the corresponding input combinations could be arrived at, thus proving the significance of statistical methods in model building and prediction of experimental data with limited number of experiments.

REFERENCES

[1] Balakrishnan, M. and Agarwal G. P., *J. Membr. Sci.* **75**, 112 (1996).
[2] Lentsch, S., Aimar, P. and Orozco, J. L. *Biotechnol. Bioeng.* **41**, 1039 (1993).
[3] Sundareva, N. N., Kurenbin, O. I., and Belenki, B. G. *J. Membr. Sci.* **68**, 263 (1992).
[4] Crull, A. (1990). *Membrane for the Nineties: Highlighting Surface Modification Technology*, Business Communications Co., Norwalk, CT.
[5] Harris, J. E., and Johnson, R. N. (1989). In *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, **13**, p. 196.
[6] Michaels, A. S. *Pure Appl. Chem.* **46**, 193 (1976).
[7] Prabhakar, S., and Misra, B. M., *J. Membr. Sci.* **29**, 143 (1986).
[8] Johnsson, G., *Proceedings of the 6th International Symposium in Fresh Water from Sea*, Athens, 3 (1978).
[9] Vogrin, N., Stropnik, C., Musil, V., and Brumen, M., *J. Membr. Sci.* **207**, 139 (2002).
[10] Loeb, S. and Sourirajan, S., *Adv. Chem. Ser.* **38**, 117 (1962).
[11] Lucena, M. C. C., Alencar, A. E. V., de, Mazzeto, S. E., and Soares, S. A., *Polym. Degrad. Stab.* **80**, 149 (2003).
[12] Tirthankar, J., Bidham, C., and Sukumar, M., *Polym. Degrad. Stab.* **69**, 79 (2000).
[13] Muthukumar, M., Mohan, D., and Rajendran, M., *Cement Concrete Comp.* **25**, 751 (2003).
[14] Annadurai, G. and Sheeja, R. Y., *Bioprocess Eng.* **18**, 463 (1998).
[15] Kapat, A., Rokshi, S. K., and Parda, T., *Bioprocess Eng.* **15**, 13 (1996).
[16] Annadurai, G., Raju, V., Chellapandian, M., and Krishnan, M. R. V., *Bioprocess Eng.* **16**, 13 (1996).
[17] Sattur, A. P. and Karanth, N. G., *Biotechnol. Bioeng.* **34**, 863 (1989).
[18] Stowe, R. A. and Mayer, R. P., *Ind. Eng. Chem.* **58**, 36 (1966).
[19] Hicks, C. R. and Turner, K. V. (1966). *Fundamental Concepts in the Design of Experiments*, Oxford University Press, London.
[20] Box, G. E. P. and Draper, N. (1987). *Empirical Model Building and Response Surfaces*, Wiley, New York.
[21] Box, G. E. P., Hunter, W. G., and Hunter, J. S. (1978). *Statistics for Experiments—An Introduction to Design, Data Analysis and Model Building*, Wiley, New York.
[22] Box, G. E. P. and Wilson, K. B., *J. Roy. Stat. Soc.* **B13**, 1 (1951).
[23] Sivakumar, M., Mohanasundaram, A. K., Mohan, D., Balu, K., and Rangarajan, R., *J. Appl. Polym. Sci.* **67**, 1999 (1998).
[24] Bhattacharyya, D., McCarthy, J. M., and Grieves, R. B., *AIChE J.* **20**, 1206 (1974).
[25] Sarbolouukki, M. N., *Sep. Sci. Technol.* **17,** 381 (1982).
[26] Sivakumar, M., Malaisamy, R., Sajitha, C. J., Mohan, D., Mohan, V., and Rangarajan, R., *J. Membr. Sci.* **169**, 215 (2000).
[27] Han, W., Gregor, H. P., and Pearce, E. M., *J. Appl. Polym. Sci.* **74**, 1271 (1999).
[28] Cabasso, I., Klein, E., and Smith, J. K., *J. Appl. Polym. Sci.* **21**, 165 (1977).
[29] Munari, S. S., Bottino, A., Capanelli, G., Moretti, P., and PetitBon, P., *Desalination* **70**, 265 (1988).
[30] Mahendran, R., Malaisamy, R., Arthanareeswaran, G., and Mohan D., *J. Appl. Polym. Sci.* **92**, 3659 (2004).

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