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Optimization of preparation conditions for polydimethylsiloxane (PDMS)/ceramic composite pervaporation membranes using response surface methodology

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Abstract

We used response surface methodology (RSM) to optimize the preparation conditions that had great effects on the performance of the polydimethylsiloxane (PDMS)/ceramic composite membranes for pervaporation. Good performance of membranes could be realized through manipulating three variables, which were polymer concentration, crosslink agent concentration, dip-coating time. In our study, we established the regression equations between the preparation variables and the performance of the composite membranes. We investigated main effects, quadratic effects and interactions of the three variables on the flux and the selectivity of composite membranes. The results showed that polymer concentration was the most significant variable that influenced the permeation flux and the selectivity among three variables and the experimental results were in good agreement with those predicted by the proposed regression models. At a feed temperature of 333 K under a pressure of 500 Pa in an ethanol concentration of 4.2 wt.%, the maximum flux of the 12.95 kg m^{-2} h^{-1} was obtained by employing the model under the following preparation conditions: polymer concentration 7.4 wt.%, crosslink agent concentration 10.6 wt.%, dip-coating time 60 s. One can expect to apply the regression equations in the preparation of PDMS/ceramic membranes and reasonably predict and optimize the performance of the composite membranes.

Keywords: Response surface; Pervaporation; Polydimethylsiloxane; Ceramic support; Composite membrane

1. Introduction

Bio-fuels are generally considered as offering many advantages, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture, security of supply [1]. In the process of biomass-to-ethanol, there is a growing trend towards employing the bioreactor-pervaporation coupled technology that removes ethanol from the fermentation [2]. The coupled process can overcome the disadvantage of conventional ethanol fermentation systems and is becoming competitive in cost.

Good performance of ethanol-permselective pervaporation membrane is a key in realizing the competitive coupled process. The ethanol-permselective ones are mainly silicalite-1 [3,4] and silicalite-silicone rubber mixed matrix membranes [5–7], polydimethylsiloxane (PDMS) [8–10], poly[1-(trimethylsilyl)-1-propyne] (PTMSP) [11–13], their derivatives [14–19] and so on. Vane [20] thought that PDMS at least would continue to be the dominant hydrophobic membrane material for the recovery of alcohols from aqueous solutions for the near future. But so far, the performance of composite PDMS membranes employing pervaporation for ethanol recovery from fermentation broths cannot meet the commercial cost-effective requirement.

Composite membrane has a thin dense skin layer on a porous support generally which serves to increase the performance of the membrane. However, thin-skinned composite membrane would result in defect or pinhole on skin surface due to irregular packing of polymer chains and incomplete coalescence of polymer molecules in skin layer [21]. Preparation conditions can determine the membrane structure and performance ultimately. Thus, the good performance of composite membrane can be obtained by manipulating preparation conditions. In the past, researchers used one-factor-at-a-time experimental method, which not only consumed more time and more cost

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but also neglected the effect of interaction between factors [22]. Although traditional orthogonal method is capable of considering a few factors at the same time, it cannot get a function expression between the factors and response values, and it is difficult to find out optimal factor combination and optimal response value in the whole area.

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine multiple regression equations between the factors and experimental results. In recent years, RSM has played an important role in the biotechnology. However, there have been few investigations of the function of RSM in membrane field. Ismail and Lai [23] studied the preparation of defect-free asymmetric polysulfone membranes for gas separation through the manipulation of membrane fabrication variables using RSM. Idris et al. [24] used RSM to investigate the composition effect of the aqueous phase on the interfacial polymerization of reverse osmosis membrane. So far, No one has reported research on using RSM to optimize the preparation conditions of polydimethylsiloxane (PDMS)/ceramic composite membranes for pervaporation.

In our previous study [8], we prepared cross-linked PDMS/ceramic composite membranes with great high flux, and investigated the effects of feed concentration and the operating temperature on the performance of membranes and found that the preparation conditions affected the performance of composite membranes. But the detailed relationship between the preparation condition and the performance was not investigated. Therefore, to elucidate this relationship, we prepared the cross-linked PDMS layer on the top of tubular asymmetric ZrO_2/Al_2O_3 ceramic support and optimized preparation conditions using RSM in this work. We established the regression equations between the preparation parameters and the performances of the composite membranes. Polymer concentration, cross-linking concentration and dip-coating time were considered as dominant preparation parameters in controlling performance. Main effects, quadratic effects and interactions of the three variables on the flux and the selectivity of composite membrane were investigated.

2. Theory

2.1. Response surface methodology (RSM)

RSM is a statistical and mathematical method that gives an effective practical means for design optimization [25]. Two goals of RSM are to find an approximating function for predicting future response and to determine factor values that optimize the response function. When behavior (response) (y), which should be taken into consideration for design, is determined as a function of multiple variables x_i, the behavior in response surface method is expressed by a polynomial $y=f(x)$ on the basis of observation data. In the case of a quadratic response function by a multiple linear regression model, it is expressed by Eq. (1):

$$y = \beta_0 + \sum_{i}^{p}\beta_i x_i + \sum_{i}^{p}\beta_{ii} {x_i}^2 + \sum_{i<j}^{p}\beta_{ij} x_i x_j + \cdots + \varepsilon \qquad (1)$$

where $x_1, x_2, \ldots, x_i$ are the variables, which influence the response y, β_0 the constant coefficient, β_i the liner coefficients, β_{ii} the quadratic coefficients, β_{ij} the second-order interaction coefficients and ε the approximation error.

In developing the regression equation, the test variables were coded according to the following equation:

$$x_i = \frac{(X_i - X_i^*)}{\Delta X_i} \qquad (2)$$

where x_i is the coded value of the ith independent variable, X_i is the uncoded value of the ith independent variable, X_i^* is the uncoded ith independent variable at the center point and ΔX_i is the step change value.

Response surfaces and contour plots are developed using the fitted quadratic polynomial equations obtained from the response surface regression analysis. The fitted surface may attain a maximum, a minimum, or a saddle point in the region. At an optimal point, the rates of change $\partial y/\partial x_i$ are equal to 0. Central composite designs are response surface designs that can fit a full quadratic model. The general form of a central composite design is composed of Nc cube points, Na axial points and No center points for a total of $N = \mathrm{Nc} + \mathrm{Na} + \mathrm{No}$ experimental units. The 2^3 full factorial design for three independent variables, each at five levels with eight cube points, six axial points and six replicates at the center points, was employed to fit a second order polynomial model, which indicated that 20 experiments were required.

2.2. Resistances-in-series model

Pervaporation is a separation process in which a multicomponent liquid is passed across a membrane that preferentially permeates one or more of the components. According to solution-diffusion Model [26], the flux of a component i through a pervaporation membrane can be expressed in terms of the partial vapor pressures on either side of the membrane, by the equation

$$J_i = \frac{P_i^{\mathrm{G}}}{l}(p_{i\mathrm{o}} - p_{i\mathrm{l}}) \qquad (3)$$

$$P_i^{\mathrm{G}} = D_i K_i^{\mathrm{G}} \qquad (4)$$

where J_i is the flux, l the membrane thickness, P_i^{G}, D_i and K_i^{G} the gas separation permeability coefficient, diffusion coefficient, gas-phase sorption coefficient, $p_{i\mathrm{o}}$ and $p_{i\mathrm{l}}$ the partial vapor pressures of component on feed side and permeate side.

Pervaporation can be described by a popular resistance-in-series model, which analyzes the relative resistances involved in the process. Transport of components from the feed solution to the vapor mixture involves several stepwise processes [27]: mass transfer from the feed bulk to the feed membrane interface; partition of penetrants between feed and membrane; diffusion through the membrane; and desorption at the membrane-permeate interface (usually neglected if a high vacuum is maintained on the permeate side). Based on the above steps, the total transfer resistance is the sum of the boundary layer resistance, the membrane resistance and the support layer resistance. An expression for the flux of a given component