

Preparation of Cation Exchange Resin Filled EVAL Hollow Fiber Membrane Adsorbent

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Abstract

This paper presents a generic technology allowing the incorporation of functional entities into a porous substrate. Ion exchange particles were incorporated into an ethylene vinyl alcohol (EVAL) copolymer porous matrix by a dry-wet spinning process and a heterogeneous matrix, composed of solid particles surrounded by a polymeric film, was formed. Hydrophilic ethylene vinyl alcohol copolymer (EVAL) and cation exchange resin D061 powder used as matrix material for hollow fiber membrane and functional particles, respectively, resins with different loading were prepared to fill EVAL hollow fiber membrane adsorbents. The membrane adsorbents were characterized with respect to their morphology, porosity, pure water flux (PWF), and rejection rate. Micro morphology was observed by the scanning electron microscope method. Effects of resin load on the performance of membrane adsorbents were mainly discussed. The experimental results showed that PWF and porosity increased and retention coefficient decreased with higher resin loading.

Keywords: EVAL, Hollow fiber membrane adsorbent, Cation exchange resin

1. Introduction

In order to prepare a kind of hollow fiber membrane with large adsorption of protein, hudropholic

membrane matrix materials and ion exchange resin with good function of adsorption. Polymeric membrane materials with hydrophilic groups have been increasingly developed in recent years, especially in biological and biomedical applications. Incorporation of hydrophilic groups reduces the hydrophobic interaction between the biological compound and the membrane surface and increases the water-wettability of the membranes. Especially in protein separation, hydrophobic interactions between proteins and hydrophobic surfaces are generally responsible for non-selective (irreversible) adsorption and membrane fouling (Avramescu, 2003, PP. 155-173). In order to avoid the fouling of membrane adsorbents due to solute adsorption, hydrophilic polymer membranes was applied in the present study. Ethylene vinyl alcohol (EVAL), a semi-crystalline random copolymer consisting of hydrophobic ethylene and hydrophilic vinyl alcohol segments, has become a promising biomedical material, since it is water insoluble and can prevent membrane fouling in the membrane separation application. EVAL also displays a good mechanical strength, has high thermal stability, good chemical and biological resistance, and is easy to sterilize using (Matsuyama, 2001, PP. 2583-2589, Young, 1998, 717-724). Moreover, cation exchange resins (CER) D061 were incorporated as particulate material into an EVAL porous structure to prepare heterogeneous membranes with high protein adsorption capacity.

Avramescu (2003, PP. 171-183, 2003, PP. 219-233, 2003, PP. 177-193) have reported that EVAL panel membrane and fiber adsorbents filled by ion exchange resins were prepared by the phase inversion process and modified to separate and purify protein mixtures. The mixed-matrix adsorber membranes developed in the study feature high protein adsorption and desorption capacities of model protein, BSA. Zhang Yuzhong (2005, PP. 224-232) reported that incorporated with resin powder in fiber matrix, the resin CNP80ws filled EVAL fibrous adsorbents with some extent of open pore on its surface were prepared by the method of controlled phase transition with some external liquids. The more open structure on its surface was obtained with higher resin loading and the resin filled EVAL fibrous adsorbents had good adsorption capacity and desorption. EVAL hollow fiber membrane assorbents filled by resins were prepared by a dry-jet wet spinning process, Hydrophilic EVAL and cation exchange resin D061 powder used as matrix material for hollow fiber membrane and functional particles, respectively. In this method, most suitable particles have, in combination with the porous matrix morphology, rapid adsorption kinetics, a capacity and selectivity commensurate with the application and allows for desorption of the molecule with an appropriate agent. The affinity of suitable adsorptive particles for specific molecules can be defined in terms of hydrophobic, hydrophilic or charged functionalities, in particular ion exchange functionalities, molecular (imprinted) recognition, or other specific interactions.

2. Materials and methods

2.1 Materials

EVAL (a random copolymer of ethylene and vinyl alcohol) with an average ethylene content of 44 % was purchased from Kuraray, Japan and used as membrane material without further modification. Dimethylsulfoxide (DMSO, Tianjin) was employed as solvent and 1-octanol (Tianjin) as non-solvent-additive in the casting solution. Water was used as non-solvent in the coagulation bath. Cation exchange resins D061 kindly supplied by Nankai University, China, were used as adsorbent particles. Buffer solutions were freshly prepared in ultrapure water. BSA was used as a model protein in the adsorption/desorption experiments. Ultrapure water was prepared using a Millipore purification unit Milli-Q plus. All other chemicals were of chemical reagent grade and used as received.

2.2 Adsorbent preparation

Due to large size of the resins purchased, the spinning solution obtained was unstable and declined to deposit with lower absorption capacity, and therefore the resins should be further processed.

2.2.1 Drying

The resin beads with high water content and impurity were washed with demiwater in a stirred vessel until neutral pH and dried at 80 °C in a conventional oven until constant weight.

2.2.1 Grinding

Cation exchange resin particles are crushed mainly by the apparatus of Super Fine Pulverizer HMB-701 (Beijing Huanya Tianyuan Machinery technology Co., ltd, China). It has a dynamic plate and static plate. The material is pulverized with the impact, friction and cutting forces on the static plate by the high-speed rotation of the dynamic plate. Due to the impact, if the particles were too large to control the biotechnology conditions, ant thus fail to obtain the expected effects, all the resins were primarily crushed from large size to lower size (above 325 mesh). At the influence of negative pressure, the qualified powder $(10\mu m)$ enters into classifying zone and gathers in the collector while the coarse material returns for further pulverizing. Through above resin processing, micron resin particle sample was prepared for study.

2.3 Analysis of resin particle size distribution

The particle size distribution of different particle fractions was measured using LA-300 Laser Scattering Particle Size Distribution Analyzer. Using a concentric multiple photo-diode array detectors, which act as receptors for light refracting off of particles suspended in the flow cell, the analyzer measures particles ranging anywhere between 0.1 and 1000 μ m in diameter with unprecedented precision. Electrical signals corresponding to the intensity of the scattered light are used to calculate the size distribution of the particles. Based on the Mie scattering theory and fraunhofer diffraction theory patterns, this measurement method consistently yields superior repeatability with astounding precision. Before performance, the analyzer was first filled with solvents (usually water), then resin samples were scattered in the solvents, and immediately transferred to evaluating pool to measure, in order to avoid the formation of agglomerates and swellings.

2.4 EVAL hollow fiber membrane preparation

Cation exchange particles D061 were successively added to a solution containing EVAL polymer in DMSO in order to obtain membranes with different adsorptive properties. Ten percent 1-octanol was added to the casting solution in order to improve the membrane morphology. The mixtures were stirred over night to break the clusters of particles. The blend hollow fiber membranes were fabricated through a wet spinning process, as schematically represented in Figure 1. The clear and homogeneous blend dope solution was then forced through a stainless steel spinneret comprising an annular ring and extruded into an external coagulation bath. A bore liquid coagulant was simultaneously delivered through the inner core of the spinneret by a high pressure syringe pump. The hollow fiber membranes were collected by a drum from the external coagulation tank. All prepared membranes were washed by water, followed by rinsed with ethanol to remove the additives and solvents and immersed in 30% glycerin solution for 24 hours, and afterwards dried in air.

2.5 EVAL hollow fiber membrane characterization

2.5.1 Scanning electron microscopy

The structure and morphology of membranes were observed by scanning electron microscopy (SEM), cross-sections of the membranes freeze-fracturing under liquid nitrogen, and the membrane samples were coated with gold-palladium. A QUANTA200 SEM (FEI, Netherlands) with an accelerating voltage set to 20 kV was used to examine the membrane cross-section.

2.5.2 PWF measurement

The pure water flux was determined using a dead-end ultrafiltration cell connected to a gas cylinder of compressed

nitrogen to apply the feed pressure (Tianjin, China). The filtration experiments were carried out at room temperature and a applied pressure of 0.1MPa. The pure water flux was determined after steady state conditions were reached. Average values were obtained from several different samples. PWF Q was calculated according to the formula:

$$Q = \frac{V}{At}$$
(2-1)

Where V is volume flow (L), A is membrane area (m^2) , and t is tested time (s).

2.5.3 Porosity measurement

The porosities of the blend hollow fibers were measured by the dry–wet weighing method. The dried hollow fibers were equilibrated with pure water for 24 h. The porosity was then determined by dividing the amount of water adsorbed (mL) with the amount of the wet hollow fibers (mL). The experiment was done for several samples and the average porosity was used for each type of the blend hollow fibers. The porosity was calculated according to the formula:

$$P_r = \frac{W_w - W_d}{S \cdot d \cdot \rho} \times 100\%$$
(2-2)

Where Ww is membrane weight with water adsorbed(g), Wd is membrane weight without water(g), S is membrane area(cm²), d is average membrane thickness(cm), and ρ is solvent density (pure water density, 1.0g/cm³).

2.5.4 Rejection rate measurement

For the rejection rate measurements, a freshly prepared BSA (67,000Da) solution (0.1% acetate buffer at pH 7.4) was permeated through the membrane. The BSA concentration in the feed and the permeate samples was determined by measuring the absorbance at 280 nm with a spectrophotometer UV2450. All the filtration experiments were carried out at room temperature. The retention coefficient R was calculated according to the formula:

$$R = \frac{E_i - E_s}{E_i} \times 100\%$$
(2-3)

Where, R is the rejection rate (%), E_i is the absorbency of the initial liquid (mg/ml) and E_s is the absorbency of the filtered liquid (mg/ml).

3. Results and discussion

3.1 Configuration and particle size distribution of D061

Milling is a simple way to reduce the size of sorbent particles and potentially a method to increase the surface area. As seen from Figure 2, resin D061 showed an irregular configuration with coarse surface and equal particle distribution. Data on particle size distribution and total surface area are presented in Figure 3. According to particle size distribution of D061 (Figure 1), the size of the ion exchange resins was reduced from an average particle diameter of 100 μ m to less than 0.5 μ m, mostly ranged from 10 to 30 μ m. The mean size of resin particle was 17.17 μ m in diameter.

As seen from Figure 4, there was no difference in resins with or without grinding, which indicated that after grinding, functional groups of resins haven't changed. Moreover, specific surface area of resins increased, and thus adsorption capacity increased.

3.2 Structure and morphology of hollow fiber membrane adsorbent

An important parameter for the preparation of adsorber membranes is the amount of resins incorporated into the polymeric matrix. By increasing of the resin loading, the amount of adsorptive-sites increases and a higher protein adsorption capacity is expected. The morphologies of the adsorber membranes prepared in the solid fiber geometry with different loading capacities of D061 cation exchange resins are shown in Figure 5. Both surfaces became coarser and the pores of outer surface became wider and increased with increasing the resin loading. Meanwhile, finger-like pores of cross-section decreased and became denser and denser. We interpret the solid particles to act as a nucleus in the casting solution limiting the grow size of the macrovoids. The solid particles also increase the viscosity of the polymer solution and therefore decrease the macrovoid formation. Moreover, outer surface possessed an open, interconnected porous structure which allowed the protein to permeate free in favor of protein adsorption.

3.3 Effects of resin loading on PWF and porosity of membrane adsorbents

As seen from Figure 6 and Table 1, with increasing resin loading, PWF and porosities of EVAL hollow fiber membrane adsorbents increased. The ion-exchange particles are tightly held together within the porous polymeric matrix. The solid particles also increase the viscosity of the polymer solution and therefore decrease the macrovoid formation. The

presence of resin inhibited the processing of solvent to coagulating bath, decreased the speed of membrane separation and formed a dense membrane. However, a further increase in the resin content leads to an increase of viscosity, formation of a stack of resins. Membrane became looser with more and more pores inside, so porosity increased with increasing PWF.

3.4 Effects of resin loading on retention coefficient of membrane adsorbents

As seen from Figure 7, with increasing resin loading, retention coefficient of BSA decreased. Retention function of membrane was ascribed to pore size of surface, which was interfered by adsorption when ion exchange resin was involved. Proteins constitute in amino acid groups which posses amino and carboxyl groups, and thus belong to ampholyte with isoelectric point (pI). When amino acid become zwitterions and have no net charge, the pH of solvents is its isoelectric point. When pH is lower than pI, amino acids in the presence of cations and could be adsorbed by cation exchange resins; when pH is higher than pI, amino acids in the presence of anion could be adsorbed by anion exchange resins. Therefore buffer solution (pH 7.4) higher than pI was applied and resin have a lower adsorption capacity of proteins, mainly due to the function of pore size of surface. With increasing resin load, configuration of EVAL hollow fiber membrane adsorbents filled with resins have changed, large voids of cross section appeared, and thus retention coefficient decreased.

4. Conclusions

In the present paper, cation exchange resins D061 were incorporated into EVAL copolymer porous matrix by a dry-wet spinning process and a heterogeneous matrix, composed of solid particles surrounded by a polymeric film, was formed. When the content of EVAL and 1-octanol was stable, by increasing the resin loading, configuration of EVAL hollow fiber membrane adsorbents filled with resins have changed, and its PWF and porosity increased while retention coefficient decreased.

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Table 1. Effects of resin loading on porosities of membrane adsorbents

Resin loading(%)	Porosity(%)
50	65
55	70
60	73
65	77



Coagulation bath (H₂O)

(a) Spinning machine



(b) Spinneret Figure 1. Spinning machine and spinneret



Figure 2. The surface morphological structure of D061



Figure 3. Particle size distribution of D061



Figure 4. Infrared spectrum of D061before or after grinding



 $(A_1 \sim A_3 \text{ resin loading 50\%}, B_1 \sim B_3 \text{ resin loading 55\%}, C_1 \sim C_3 \text{ resin loading 60\%}, D1 \sim D_3 \text{ resin loading 65\%})$



Figure 6. Effects of resin loading on PWF of membrane adsorbents



Figure 7. Effects of resin loading on retention coefficient of BSA