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β-Cyclodextrin modified PES hollow fiber membrane, a new strategy for bilirubin separation

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ABSTRACT

The aim of this study was to synthesis and evaluates the capability of modified polyethersulfone (PES) hollow fiber membrane for bilirubin separation from patients' blood. Cyclodextrin (CD) was grafted on the membrane surface via ester bond between hydroxyl groups in CD and sulfonate functional groups on the membrane surface. Surface modification not only improved the membrane hydrophilicity, but also inhibited bovine serum albumin (BSA) and platelets adhesion on the surface. Moreover, the modified membrane could adsorb bilirubin up to 51 mg/g membrane. In conclusion, the proposed system could be a promising candidate to be used instead of resins in hemoperfusion column.

1. Introduction

Bilirubin (BR) is an oxidative metabolite of heme, which is usually conjugated with glucuronic acid to form a water-soluble complex. Hyper-bilirubinemia happens as a result of high concentration of free bilirubin in blood, which can damage brain cells [1]. Different procedures such as phototherapy, hemodialysis and hemoperfusion were followed to separate free (unconjugated) bilirubin from patients' blood. Among these treatments, hemoperfusion was recognized as an effective and reasonable treatment in which blood is circulated through a column containing appropriate adsorbents to remove excessive unconjugated BR. Different kinds of adsorbents were employed to separate free BR from plasma [2–4]. One of the common adsorbent, which is widely used to separate toxins, was active charcoal. But, due to its poor biocompatibility, it needed to be coated with a biocompatible polymer which consequently could affect adsorption efficiency [5]. Also, anion exchange resins like Dowex I [6] that contain amine groups were good candidates for BR adsorption. However, due to the release of metallic ions during exchange process and influencing the balance of electrolytes in plasma, these resins could not be applicable in hemoperfusion.

In recent years, some researchers focused on employing porous membrane adsorbents in hemoperfusion column instead of particles due to their high mass-transfer efficiency [7,8]. Different strategies were applied to modify the membranes surface and enhance BR removal [9,10].

Cyclodextrins (CDs) are commercially available cyclic oligopolysaccharides composed of several glucose units. CD molecules structure composed of a hydrophobic cavity surrounded by a hydrophilic outer shell, which enable them to form inclusion complexes with many hydrophobic compounds. CDs were immobilized on polymeric supports and demonstrated to have inclusion ability to adsorb bilirubin [11,12]. Due to the size of β-CD cavity (6–6.5 °A), the pyrole rings of bilirubin can be accommodated into the cavity [13]. In this study, capability of immobilized β-CD on the PES hollow fiber membrane for bilirubin separation was evaluated. Polyethersulfone was chosen as the membrane material due to its mechanical, thermal and chemical stability [14]. In order to form a covalent bond between β-CD and the membrane surface, sulfonated polyether ether ketone (SPEEK) was synthesized and mixed with PES to form hollow fiber membrane by using the phase inversion technique. Membrane characteristics as well as blood compatibility were studied. The BR adsorption capacity of the modified membrane was also investigated through static adsorption experiment.

2. Experimental

2.1. Materials

Polyethersulfone (PES, Veradel® A-301) and β-CD were supplied by Solvay Advanced Polymers (USA) and Merck respectively.

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Polyvinylpyrrolidone (PVP, k90), N-methylpyrrolidinone (NMP), and poly (etherether ketone) (PEEK) were obtained from Fluka and Victrex USA, Inc. respectively.

2.2. Preparation of hollow fiber membrane

PES/SPEEK hollow fiber membranes were fabricated according to our previous publication [15]. The cleaned hollow fiber membrane was soaked in a solution of 10 wt% β-CD for 24 h. CD molecules was immobilized on the membrane surface due to the formation of ester bond between CD and available sulfonate groups on the surface. The surface characteristics of the Hollow fiber membranes were characterized by FTIR (Nicolet-Magna 560 IR spectrometer) and contact angle measurement instrument. Morphology of the prepared membranes were observed by SEM microscope (TM3000, HITACHI, Japan) and hemocompatibility was investigated via protein adsorption and platelet adhesion assays.

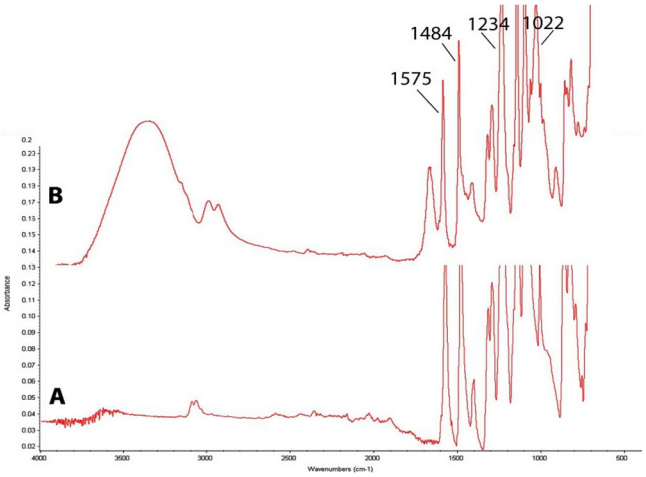

Fig. 1. ATR-IR spectra of (A) pristine PES membrane (B) CD-coated PES membrane.

2.3. Preparation of BR solution

Considering that BR solubility in water is low [16], therefore, NaOH solution (2.5 mL, 0.1 M) was used as the medium to dissolve BR. In order to preserve the pH value of the prepared alkaline suspension [9], phosphate buffer (10 mL, 0.2 M) was mixed with the solution under moderate swirling to obtain a BR buffered solution. Then, 50 mL deionized water was employed to dilute the solution and the final pH was 7.5. The achieved solution was used as stock solution in BR adsorption tests.

2.4. Batch experiments of bilirubin adsorption

Small piece of membrane (15 mg) was soaked in 10 mL bilirubin buffered solution in a covered cuvette. An aluminum foil was used to cover the cuvette to protect the solution from light exposure. The sample was shaken and adsorption capacity of membrane was evaluated in various conditions such as adsorption time and BR initial concentration. The amounts of the adsorbed bilirubin have been measured by using Eq. (1).

$$q = \frac{C_i - C_t}{m} V_s \quad (1)$$

Where q is the quantity of adsorbed bilirubin onto unit mass of the membrane (mg/g); C_i and C_t are the bilirubin concentrations in the initial and in the final solution after adsorption, respectively (mg/l); V is the volume of the bilirubin solution; and m is the mass of the membrane (g). The concentration of unbound bilirubin in the solution was detected by HITACHI 7060 automated analyzer.

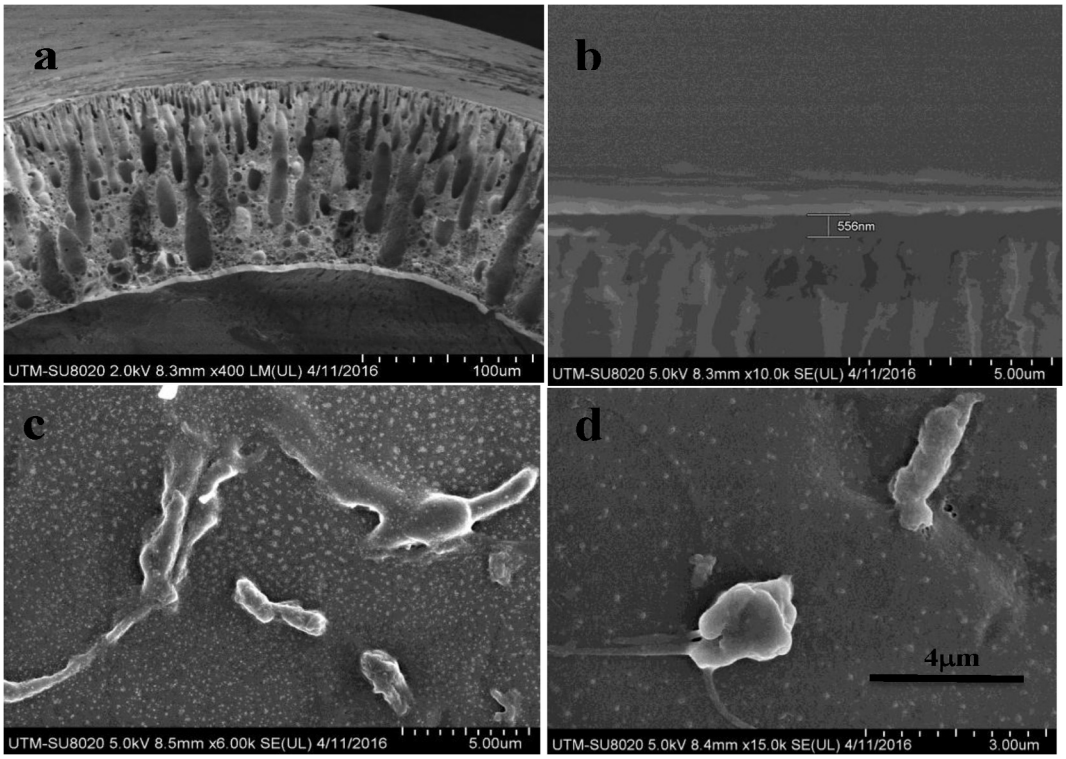

Fig. 2. FESEM images of (a) pristine PES membrane cross section, (b) modified PES membrane cross section, (c) adhered platelets on the pristine PES membrane surface and (d) adhered platelets on the modified PES membrane.