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Immobilization of Cibacron blue F3GA on electrospun polysulphone ultra-fine fiber surfaces towards developing an affinity membrane for albumin adsorption

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Abstract

Non-woven polymer membrane with nano- or micro-scaled fiber diameter prepared by electrospinning technique is a potential material for affinity membrane application. In this work, electrospun polysulphone (PSU) fiber membrane was surface modified and studied as a novel affinity membrane, using Cibacron blue F3GA (CB) and bovine serum albumin (BSA) as a ligand–ligate research model. Methacrylic acid (MAA) was graft polymerized on the PSU fiber surface initiated by Ce(IV) to introduce carboxyl groups. With carbodiimide as coupling agent, the carboxyl groups were reacted with diamino-dipropylamine (DADPA) to introduce amino groups. Finally, CB was covalently attached on the PSU fiber surface through reaction with the amino groups. The surface of the membrane was characterized by ATR-FTIR, XPS and other colorimetric methods. The novel PSU affinity membrane showed higher water permeability than commercial microporous membranes. BSA adsorption isotherm curve on the CB immobilized PSU membrane was tested. The CB functionalized PSU membrane showed a capturing capacity of 22 mg/g for BSA. Regeneration of the membrane using elution buffer with increased ionic strength and pH value made the membrane reusable. To understand the dynamic adsorption and desorption of BSA, breakthrough curve and elution curve of the affinity membrane were tested. This work demonstrated that electrospun polymer fiber membrane has potential for affinity membrane applications.

Keywords: Electrospinning; Affinity membrane; Polysulphone; Cibacron blue F3GA; Surface modification; Fiber membrane; Affinity membrane chromatography

1. Introduction

Discovered about 70 years ago, electrospinning provides a simple way to prepare ultrafine polymer fibers with nano/micro-scaled diameters [1,2]. In electrospinning, polymer solution is stretched and elongated into fibers by a voltage sufficient to overcome its surface tension force, and collected as an interconnected non-woven fiber membrane. Electrospun polymer fiber membranes received extensive research interests in such diverse fields as tissue engineering scaffold [3], protective cloth and air filtration [4,5] and electronic and semi-conductive materials [6], etc.

Our interest for the electrospun polymer fiber is its potential application as affinity membrane or adsorptive membrane. Affinity membrane chromatography was introduced as an integrative technology for purification of biomolecules [7,8]. Instead of operating purely on sieving mechanism, the separation of affinity membrane is based on the selectivity of the membrane to 'capture' molecules, by attaching active ligands to the inner surface through pores of the membrane. Advantages of the affinity membrane over column chromatography resins include reduced pressure drop, high volumetric flow and absence of pore diffusion [9]. In response to an increasing demand for preparative amounts of biomolecules in the rapid developing biotechnologies, affinity membrane chromatography is becoming an attractive and competitive method for purifying proteins or other biomolecules [7,8].

The idea of using electrospun fiber membrane as affinity membrane is based on the fact that the electrospun non-woven membrane has properties like high porosity, micro-scaled pore size and high interconnectivity of the interstitial space, and above all, the small fiber diameter give rise to an increased surface area as compared with the conventional non-woven filter with typical diameters of several microns. A large surface area to volume

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ratio is one of the most important requirements for an ideal affinity membrane.

In chromatographic separation, dye-ligands for protein purification have been developed extensively because they offer chances of simple and rapid isolation of proteins. There are now about 30 different types of dyes for purification of a great variety of protein molecules ranging from recombinant polypeptides to many kinds of enzymes. One of the mostly utilized dye-ligands is a reactive dye, Cibacron blue F3GA (CB). This dye is a general purpose ligand for purification of many enzymes and blood proteins, among which the most well known is serum albumin [10]. In a previous work, we have showed that electrospun cellulose fiber membrane immobilized with CB can capture serum albumin with a capacity of 13 mg BSA per gram membrane [11]. Although the cellulose membrane has a big advantage of being easy-to-be surface modified, a big disadvantage of the material is its poor mechanical strength and chemical instability, especially in acidic or basic aqueous solutions. In this work, to develop a practical affinity membrane with strong chemical stability, a strong polymer, polysulphone (PSU) was chosen. Electrospun PSU non-woven fiber membrane was first prepared and then surface modified with CB. The CB functionalized membrane was then studied in terms of its filtration property and bovine serum albumin (BSA) capturing abilities.

2. Experiments

2.1. Materials and reagents

Polysulphone ($M_n = 26{,}000$), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDAC), *N*-hydroxysuccinimide (NHS), 2-(*N*-morpholino) ethanesulphonic acid (MES), diamino-dipropylamine (DADPA), ammonium cerium(IV) nitrate (Fluka), CB and bovine albumin serum (Sigma–Aldrich) were all purchased from Sigma–Aldrich company and used as received. Methacrylic acid (MAA, Sigma) was purified by vacuum distillation.

Two commercial membranes, cellulose nitrate–acetate membranes (Cartoon®, Zhejiang China, Ø25 mm, pore size 0.22 μm, thickness ~100 μm) and PVDF (polyvinyl chloride) membrane (Durapore®, Milllipore, Ø25 mm, pore size 5 μm, thickness ~135 μm), were used in this work. Comparisons were made between physical structures and water permeability of the electrospun PSU fiber membranes and that of the commercial membranes.

2.2. Membrane preparation

Non-woven PSU fiber membranes were fabricated by electrospinning method. Briefly, 5 ml PSU solution (25 wt%) in pyridine was ejected out of a 27G needle (inner diameter, 0.21 mm) at a speed of 1 ml/h. A 15 kV voltage was loaded between the needle and an aluminum plate (10 cm × 10 cm). The polymer solution was drawn into fibers and deposited on the aluminum plate to form a non-woven fiber membrane. The electrospun fiber membranes were then heat treated under 188 °C for 6 h to increase the integrity and mechanical strength. The heat-treated membrane was then peeled off from the aluminum plate. The white-colored and paper-like PSU membranes with thickness of ~300 μm were cut into 3 cm × 3 cm pieces for later use.

Specific surface area of the membrane was measured on a N_2 BET system (ASAP 2020 V3.00H, Micromeritics Co.). Pore size of the membrane was measured by the Bubble Point method on a Porometer 3G (Xonics Co., USA). To know the porosity of the PSU membrane, the apparent density of the membrane was first obtained by dividing the mass of the membrane by

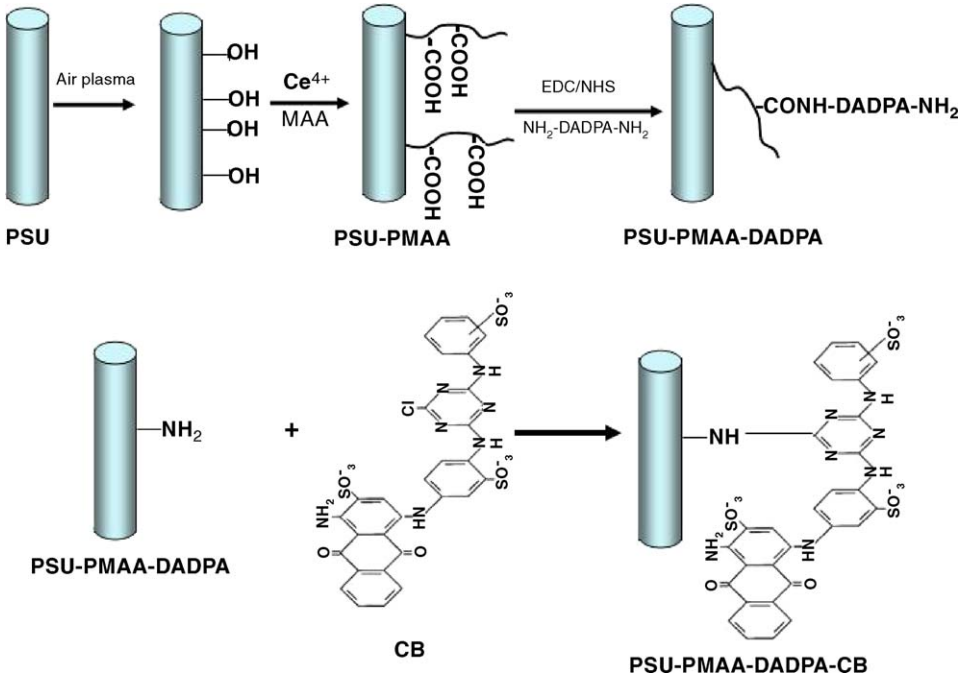

Fig. 1. Schematic representation of the surface modification procedures, where NH_2–DADPA–NH_2 equals to $NH_2CH_2CH_2CH_2NHCH_2CH_2CH_2NH_2$.