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Full Length Article

High flux nanofiltration membranes based on layer-by-layer assembly modified electrospun nanofibrous substrate

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ABSTRACT

Herein, high flux nanofiltration (NF) membranes were fabricated by combined procedures of electrospinning, layer-by-layer (LBL) assembly, and phase inversion. The membranes displayed three-dual structure constituted polyether sulfone (PES) coating layer, LBL assembly modified electrospun polyester (PET) nanofibrous mats, and non-woven supports. High flux NF membranes thus prepared are characterized by ultrathin phase inversion layer (~10 μm) while that of conventional membranes are 100–150 μm, implying that very high flux could be expected. Various factors including electrospinning conditions, chitosan (CHI)/alginate (ALG) concentration, PES concentration, exposed time, coagulating temperature, thermal treatment, and sulfonated poly ether ketone (SPEEK) content were systematically investigated. Structures of the membranes were characterized by field emission scanning electron microscopy (FESEM), mechanical properties test, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and static contact angle measurements. The separation experiments indicated that thus prepared membranes exhibited high flux of as high as ~75 L m^{-2} h^{-1} with Mg SO_4 rejection of ~80%.

1. Introduction

With first exploration in late 1980‘s [1], Nanofiltration (NF) is a process driven by the pressure with the filter fineness between ultrafiltration (UF) and reverse osmosis (RO). Initially, the operating pressure for NF is initially in the range of 5–20 bar [2] and nowadays can be as high as 40 bar [3]. Variety of advantages such as low operating pressures, high fluxes, and high rejections towards multivalent salts, low investment, and operating cost are making NF being used in various areas [4]. In recent years, NF membranes are mainly used in water purification processes [5], accompanied with some novel applications such as solvent resistant nanofiltration (SRNF) [3].

Currently the most used NF membranes are mainly based on polyamide separating layer fabricated by interfacial polymerization using piperazine (PIP) and trimesoyl chloride (TMC) as the monomers supported by polymeric substrates [6–8]. Nevertheless, for this kind of NF membranes, the surface polyamide layer displays distinct heterogeneity in perpendicular direction towards the outside of the membrane, which is induced by the diffusion determined interfacial polymerization mechanism [9–11]. The heterogeneity might be detrimental to their structure stability and separation performance. Alternatively, phase inversion is a good candidate for fabrication of NF membranes due to the easy operation, stability, and low cost [12–14]. The structure of conventional NF membranes fabricated via phase inversion comprises ultrathin layer (<0 μm) and sublayer characterized by large thickness, low porosity, and nonuniform pore diameters which provides mechanical strength. Nevertheless, thus prepared NF membranes are always restricted by low flux and high operating pressures.

Electrospun nanofibrous membranes (ENMs) have demonstrated great potential and practical applications in water reuse because of their unique properties, such as controllable nanofibers diameters, high Brunauer-Emmett-Teller (BET) surface areas between 9 and 51 m^2/g, high porosity varied from 25% to 80%, and the adjustable pore size in the range of 2.7–0.17 μm. Due to these characteristics, ENMs have displayed variety of applications in water purifications [15]. ENMs can be directly used as microfiltration membranes just by altering the nanofibers diameters through choosing different polymers [16–18]. With hydrophilic coatings (e.g., polyvinyl alcohol (PVA) [19] and chitosan [20]) on top of ENMs, they can be used as ultrafiltration membranes [21]. Moreover, ENMs has made breakthrough in fabrication of novel NF membranes. By interfacial polymerization using various monomers on the surface of pristine [22–25] or hydrophilic coatings (e.g., chitosan [26] and cellulose [27]) modified ENMs could fabricate thin

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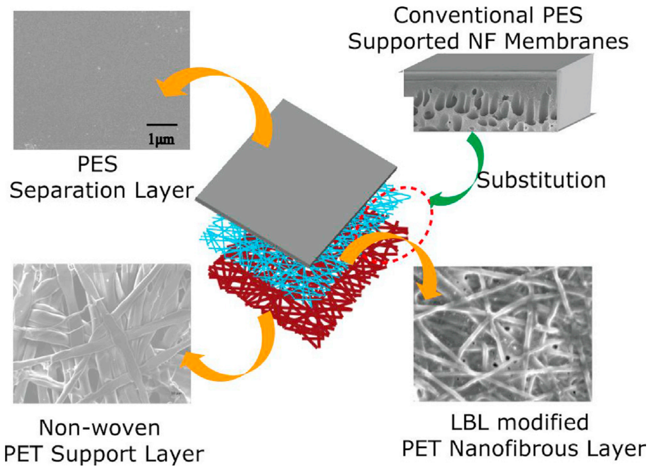

Fig. 1. Distinction between the conventional PES NF membranes and High flux NF membranes supported by ENMs.

film nanocomposite NF or RO membranes ENMs. It should be noted that all these ENMs supported membranes are characterized by their high permeations.

Thus, introduction of ENMs into the phase inversion induced NF membranes might be a feasible strategy to enhance their water flux and decrease the operating pressures while retain the advantages. The critical point in fabricating such membranes is controlling the thickness of the separating layer with nanofibrous mats underneath [28]. Nevertheless, one point needed to be paid attention is the penetration of casting solutions into the pores of ENMs due to the large pores [29]. Thus, modification is always used before the applications for the ENMs. LBL assembly, which was invented by Decher [30,31], has been widely used as strategy to modify the filtration membranes [32], including ENMs [33–35]. LBL assembly is a versatile, simple, reproducible, and environmentally friendly method to fabricate ultrathin films with controlled thickness on the matrix substrate. In the LBL assembly process, polyelectrolytes with opposite charges are alternatively deposited on the matrix surface through various interactions including electrostatic attraction, hydrogen bonding, etc. [36]. Moreover, the repulsion between the hydrophilic polyelectrolytes and the PES surface would effectively alleviate the penetration of the cast solution and leads to a separation layer with ideal thickness [37].

Inspired by the thinking above, herein, a novel strategy is explored to fabricate a new kind of NF membranes supported ENMs. As shown in Fig. 1, the new NF membranes are characterized by the three-dual structures. ENMs were fabricated on top of non-woven fabric mats by electrospinning. Subsequently, the LBL assembly was carried out on ENMs surface. Finally, separating layer was obtained by phase inversion on LBL assembly modified ENMs. This concept integrates the superiorities of ENMs and phase inversion induced NF membranes, which might pave the path for exploring novel NF membranes with advanced properties.

2. Experimental

2.1. Materials and agents

Polyester (PET, with intrinsic viscosity of 0.8) was purchased from Shanghai Jin-shan Co., Ltd. Chitosan (CHI, B.R., $M_w = 30{,}000$) with the degree of deacetylation (DD) of 80.0–95.0 and sodium alginate (SA, C.P., $M_w = 3000$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyether sulfone (PES, 4800G grade) was purchased from Sumitomo Chemical. Poly(ether ether ketone) (PEEK) powder of the grade 450 PF was purchased from Vitrex plc. Polyvinylpyrrolidone (PVP, Mw ~10,000, A.R.,) was purchased from Beijing Tongguang Fine Chemical Co., Ltd. Magnesium sulfate anhydrous ($MgSO_4$, A.R., ≥99.5%) and sodium hydroxide (NaOH, A.R., ≥99.5%) were obtained from Tianjin Damao Chemical Works. Trifluoroacetate acid (TFA, A.R., ≥99.5%), dichloromethane (DCM, A.R., ≥99.5%), 1-Methyl-2-pyrrolidone (NMP), acetic acid (HAc, A.R., ≥99.5%) were all supplied by Beijing Chemical Works. All the materials and reagents were used as received without any purification.

2.2. Fabrication of ENMs supported NF membranes

The preparation of ENMs supported NF membranes includes three steps. In the first step, electrospinning was carried out on the PET non-woven fabric to obtain PET ENMs. Afterwards, LBL assembly was executed on the ENMs surface. Finally, separating layer of PES was fabricated on the substrate of ENMs by phase inversion. Moreover, SPEEK was used as additives during the phase inversion to investigate their improvement on the separation performance of ENMS supported NF membranes. The detailed experimental procedures are as follows.

In electrospinning process, the homogeneous solution of PET in bi-solvent systems of TFA and DCM was stirred for one day (TFA: DCM = 4: 1, volume ratio). Then the prepared solution was electrospun onto a PET non-woven fabric which was fixed on a grounded rotating metallic drum. The applied voltage was +19 kV and the solution feed rate was 20 μL/min. The distance between spinneret and the grounded drum was 20 cm. Moreover, in order to obtain a uniform electrospun mat, a stepping motor was utilized to control the translational oscillatory motion, which was perpendicular to the collector direction. In order to enhance the pressure tolerance and mechanical performance of the supporting substrate, the PET nanofibrous/non-woven substrates were hot pressed at 80 °C for 6 min.

Afterwards, the ENMs was modified via LBL assembly method. Before LBL assembly, the mat was firstly immersed into 0.5 M NaOH solution for 0.5 h to minimize the penetration of CHI solution into the nanofibrous support and help the polyelectrolyte to bridge the pores of mats [38]. The mats were subsequentially immersed into the polycation (CHI) and polyanion (ALG) solution with soaking times of 5 min. Each immersion was followed by rinse with deionized water for 2 min. The procedure was repeated six times to produce a LBL assembly layer consists 6 bilayers on the ENMs surface and the whole assembly were completed in 1 h.

Finally, the separating layer was fabricated on the LBL assembly modified ENMs surface via phase inversion method. The casting solution was prepared by dissolving a certain amount of PES and PVP powder (PES: 20–25 wt%, PVP: 2 wt%) in NMP solution followed by magnetic stirring and ultrasonic bath to make the complete dissolution of PES and PVP and eliminate the air bubbles. The LBL assembly modified ENMs was fixed onto a plate and the casting solution was poured on the substrate. The casting solution was then spread over the substrate using a self-made casting blade film applicator with the thickness in the range of 10–50 μm by adjusting the lifting height of casting blade. The casting speed was 50 mm/s. After an exposed time of 5–60 s, the casted membrane was moved into a water coagulating bath for 6 h and then immersed into excessive water for 24 h to remove the residual additives and solvents. After being dried at 60–120 °C for 20 min, the ENMs supported NF membranes were obtained.

Considering the fact that sulfonic acid groups ($-SO_3H$) and sulfonated poly (ether ketone) (SPEEK) were always used for modifying the surface hydrophilicity and salt rejections of NF membranes [39,40], SPEEK was used as an additive in the casting solution to investigate their effect on the separation performance of the NF membranes. SPEEK was self-made by the following procedure. 3.0 g PEEK was dissolved in 100 mL concentrated sulfuric acid and stirred