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Preparation of thin film nanofibrous composite NF membrane based on EDC/NHS modified PAN-AA nanofibrous substrate

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Abstract. A novel kind of thin-film nanofibrous composite (TFNC) nanofiltration (NF) membranes consisting of a polyamide (PA) barrier layer were successfully fabricated by interfacial polymerization (IFP) based on electrospun double-layer nanofibrous substrates, which have an ultrathin poly (acrylonitrile-co-acrylic acid) (PAN-AA) nanofibrous layer as top layer and a thicker polyacrylonitrile (PAN) nanofiber layer as bottom porous support layer. Immersing PAN/PAN-AA nanofibrous substrates into 1-ethyl-(3-3-dimethylaminopropyl) carbodiimide hydrochloride/N-hydroxysuccinimide (EDC/NHS) aqueous solution and piperazine (PIP) aqueous solution (0.20 wt%) sequentially for a period of time, the carboxyl groups on PAN-AA nanofibers were activated by carbodiimide and then reacted with the amide groups. The as prepared composite membrane has an integrated structure with high rejection rate (98.0%); high permeate flux (40.4 L/m^{2}h) for $MgSO_4$ aqueous solution (2 g/L).

1. Introduction

TFNC membranes have been proven to be an effective media for nanofiltration (NF) and reverse osmosis (RO), which structure with a thin and dense functional barrier layer supported on a reinforced porous substrate [1-4]. The ultra-thin dense barrier layer is usually obtained through interfacial polymerization (IFP), by which the filtration performance of TFNC membranes is mainly determined. The conventional reinforced porous matrix is a less porous dense asymmetric membrane made by phase inversion methods. In recent decades, electrospun nanofibrous membranes have been used as supporting materials in composite membranes due to its high porosity (up to over 80%), interconnectivity, micro scale interstitial space, and a large surface-to-volume ratio [5-7]. But it is difficult to fabricate a structure-integrated nanofibrous composite NF membrane because the pore size of electrospun nanofibrous support is relatively large (submicron level) to support strugglingly the ultrathin barrier layer (~ 100 nm thickness) prepared IFP method [8].

In this study, a new kind of TFNC membrane was fabricated by introducing a PAN-AA intermediate layer between PA barrier layer and PAN nanofibrous substrate. Carboxyl groups on PAN-AA nanofibers were activated by EDC/NHS and reacted with secondary amine group on PIP,

which could form covalent linkage with PA barrier layer. The nanofiltration performance of the resultant TFNC membrane was evaluated by the rejection of $MgSO_4$ from salt water using a cross-flow filtration device.

2. Experimental

2.1. Materials

PAN (Mw = 1.36×10^5) 2-Morpholinoethanesulfonic acid (MES), 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), and N-hydroxysuccinimide (NHS) were purchased from J & K Scientific Ltd. N,N'-dimethyl formamide (DMF), n-hexane, piperazine (PIP), trimesoyl chloride (TMC) and magnesium sulfate ($MgSO_4$) were purchased from China State Medicinal Group Chemical Reagent Co., Ltd. PAN-AA with a viscosity-averaged molecular weight (Mη) of 2.4×10^5 was synthesized by radical polymerization [9].

2.2. Preparation of PAN-AA/PAN nanofibrous substrate

Dried PAN and PAN-AA powder were dissolved in DMF respectively with gentle stirring at 50 ºC in oil bath for 12 h to get homogeneous solutions respectively. PAN solution (10 wt%) was electrospun on a grounded rotating metal drum until the thickness of the PAN nanofibrous substrate reached to 40 μm (electric voltage: 20 kV, solution feed rate: 16.6 μL/min, spinneret diameter: 0.7 mm, distance between the spinneret and the grounded drum: 15-20 cm, environment temperature: 40 ºC, humidity ~40%, diameter of drum: 10 cm, length of drum: 30 cm and rotating speed: 300rpm) [6]. Then an ultrathin layer of PAN-AA nanofibers was electrospun above the PAN nanofibrous substrate for 20 min (Electric voltage: 24kV, solution feed rate: 8.0 μL/min). The distance between the spinneret and the grounded drum was 15 cm. The as-prepared nanofibrous membranes were dried at 50 ºC in vacuum for 24 h to remove the remained solvent.

2.3. Preparation of TFNC membrane

TFNC membrane was prepared through IFP technique. To begin with, the PAN/PAN-AA nanofibrous substrate was clamped with a Teflon holder, and activated in an MES buffer solution (50 mmol, pH 6.0) containing EDC and NHS (concentration of EDC range from 50-200 mmol, concentration ratio fixed at 2:1, w/w) for 4 h at room temperature [10]. Then the activated membranes were washed and immersed in PIP aqueous solution (0.2 wt%) for 1 h to impregnate the nanofibrous substrates. The surface was rolled with a glass rod to eliminate any little bubbles formed in the process of soaking. Excess solution was drained off the surface by air knife (EXAIR, USA). The n-hexane solution of TMC (0.2 wt%) was poured into the holder. After a certain period of reacting time (60 s), the excess organic solution was removed off the surface and the membrane were held in oven for 1.0 h at 60 ºC, so that a dense PA barrier layer was formed on the support membrane. Finally, the resultant membranes were successively washed and stored in deionized water for testing [11].

2.4. Characterization

The morphology of TFNC membrane was investigated by scanning electron microscopy (SEM) system (Phenom G2 pro, FEI, USA). The nanofiltration (NF) performance of the resulting membranes was measured by using a cross-flow membrane filtration system with 5 parallel filtration cells (effective area: 3.8 cm^2). Membranes were pressured at 0.2 MPa for 30 min with distilled water before the NF tests to obtain stable permeate flux. After that, the permeate flux and salt rejection of TFNC membranes were tested with $MgSO_4$ aqueous solution (2 g/L) under certain operating pressure at 100 psi; The permeate flux was calculated using the equation: J (L/m^2h) = $V/(A\cdot\Delta t)$, where V is the volume of permeate flow during the test time, A is the effective membrane area, Δt is the collecting time of permeate flow. The $MgSO_4$ rejection rate was calculated using the following equation: R (%) = $(Cf\text{-}Cp)/Cf\times100\%$, where Cf and Cp were conductivity of feed and permeate

solution, respectively, which were measured by using a conductivity detector (FE30, Mettler Toledo) [9].

3. Results and discussion

3.1. Membrane morphology characterization

The prepared PAN/PAN-AA double-layer nanofibrous substrates were fabricated via electrospinning technique. The typical SEM image of PAN nanofibers (average diameter ~ 342 nm) and PAN-AA nanofibers (average diameter ~ 173 nm) was shown in figure 1(A) and 1(B) respectively. The combined PAN/PAN-AA double-layer nanofibrous substrates were fabricated by depositing an ultrathin PAN-AA nanofibrous layer in 20min (thickness < 0.2 μm) on the surface of PAN nanofibrous substrate (thickness ~ 40μm) as shown in figure 1C.

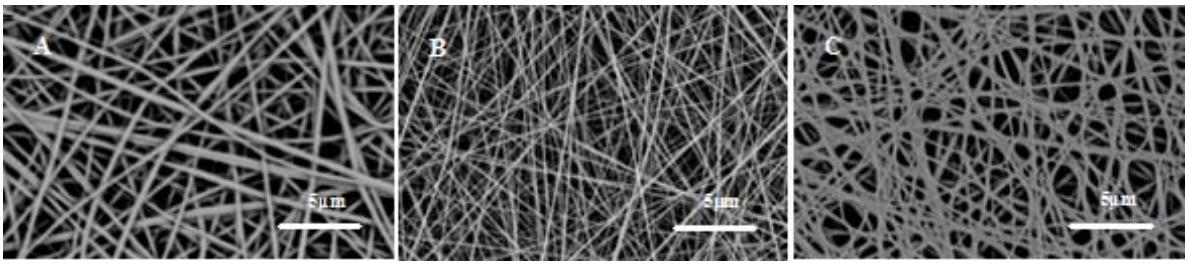

Figure 1. SEM images of electrospun nanofibers: A) PAN, B) PAN-AA and C) PAN/PAN-AA double-layer nanofibrous substrate

In figure 2(A) and 2(B), the surface and cross section morphologies of PAN-AA/EDC100/PATFNC membranes show that a PA barrier layer (thickness ~150 nm) was coated on PAN/PAN-AA nanofibrous substrate modified with EDC/NHS solution (100/50 mmol).

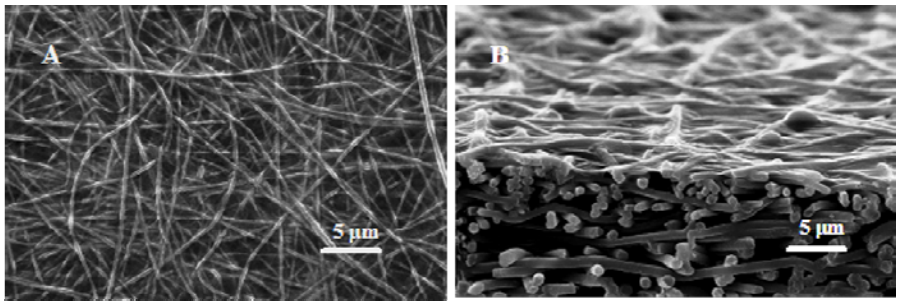

Figure 2. SEM images of surface (A) and cross section (B) of PAN-AA/EDC100/PA TFNC membrane

3.2. Filtration performance of PAN-AA/PA membrane

A series of TFNC membranes were prepared by interfacial polymerization (IFP) based on PAN-AA nanofibrous substrate modified with different concentration of EDC/NHS solutions (50-200 mol), while other IFP conditions is fixed (TMC 0.2 wt%, reacting time was kept at 60s, heat-treated in oven at 60℃ for 1h) as shown in figure 3. As the concentration of EDC/NHS solutions increased, the permeate flux of the PAN-AA/EDC/PA TFNC membrane decreased from 43.5 L/m^{2}h to17.3 L/m^{2}h, and the rejection of TFNC membrane increased from 96.3 % to 98.5 %/. When the concentration of EDC was 100 mmol, the rejection of TFNC membrane was above 98.3% and the permeate flux could obtain 40.4 L/m^{2}h. Compared with the TFNC membrane prepared by same IFP conditions (PIP 0.2

wt%, TMC 0.2 wt%, 60s reacting time, 60 ^{o}C for 1h) based on single-layer PAN nanofibrous substrate, the rejection of PAN/PA TFNC membrane is just 97.8 % and the permeate flux of that is 41.5 L/m^{2}h.

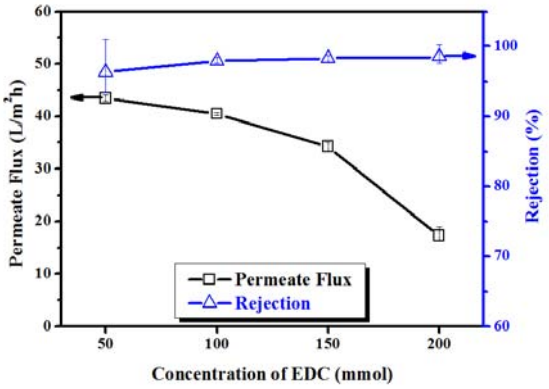

Figure 3. Filtration performance of PAN-AA/EDC/PA TFNC membrane effect with concentration of EDC

4. Conclusions

In this study, a novel kind of TFNC membranes was prepared by interfacial polymerization on electrospun double-layer PAN-AA/PAN nanofibrous substrates, which were activated with EDC/NHS to react with aqueous monomer PIP. The EDC/NHS modified PAN-AA med-layer generated an interconnection linkage between PA barrier layer and PAN nanofibrous substrate. The resulting TFNC membranes were evaluated for nanofiltration using $MgSO_4$ aqueous solution at 2 g/L. The PAN-AA nanofibrous layer modified with different concentration of EDC/NHS solution (50-200 mmol) played a critical role in interfacial polymerization, which changed the permeate flux decreasing from 43.5 L/m^{2}h to 17.3 L/m^{2}h. When the EDC concentration was 100 mmol, the filtration properties of TFNC membrane based on EDC/NHS modified double-layer PAN/PAN-AA nanofibrous substrate were better than that of TFNC membrane based on PAN nanofibrous substrate.

Acknowledgments

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