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Polypiperazine-amide nanofiltration membrane containing silica nanoparticles prepared by interfacial polymerization

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ABSTRACT

Silica/polypiperazine-amide nanofiltration (NF) membranes were prepared by interfacial polymerization on polyethersulfone (PES) supporting membrane. Different preparation conditions and NF membrane performances were discussed, including silica concentrations, monomer concentrations, reaction time and salt rejections. The chemical structure characterizations of polyamide composite membrane were carried out by attenuated total reflectance infrared (ATR-IR). The surface images and cross sections were observed by scanning electron microscope (SEM) and atomic force microscopy (AFM). The results showed that polypiperazine-amide NF membrane prepared under the optimum conditions exhibited Na_2SO_4 rejection of 97.4% and water flux of 46.8 $l.m^{-2}.h^{-1}$. After addition of silica sol in the aqueous phase, the rejection of the resulting membrane changed slightly, but the water flux increased 21.1% than polypiperazine-amide NF membrane. According to the rejection of polyethylene glycols (PEGs), the molecular weight cut-off (MWCO) of the resulting membrane was under 600 Da.

1. Introduction

Nanofiltration (NF) is a liquid separation membrane technology positioned between reverse osmosis (RO) and ultrafiltration (UF), which is a technique prospered over the past few years [1–4]. The function of NF is similar to RO, but is generally targeted to remove only divalent and large ions. Monovalent ions such as sodium and chloride will pass through a NF membrane. NF refers to a membrane process that rejects solutes approximately 1 nm in size with molecular weight cut-off above 200 Da. NF membranes generally have a thin skin layer enabling higher fluxed and lower operating pressures than RO membranes and are able to reject organic compounds and multi-valent ion salts. Today, NF is mainly applied in drinking water purification process steps, such as water softening [5–7] and micro pollutant removal [8]. During industrial processes NF is applied for specific components and organics, such as pesticides [9,10], heavy metal [11,12], dyeing [13–15], pharmacy [16] and food [17–19].

For most synthetic membranes, the pure water flux is a very important parameter. Under the same conditions, low water flux leads to an increase of operation cost. Energy consumption of NF membranes will be reduced if the membranes are with high water flux and keep the high rejection at the same time. In academic research, studies have been focused on choosing different nano-materials with special feature to prepare the TFC membranes [20–25] to enhance the performance of the membrane. Nanotechnology is the engineering of functional systems at molecular scale. This covers both current works and concepts. It will offer better built, longer lasting, cleaner, safer and smarter products [26–29]. Silica nanoparticles as very important inorganic materials have attracted much interest in the modification of composite membranes. Ma et al. [20] prepared the functional silica/polyamide-imide composite films via simple ultrasonic blending, after the silica nanoparticles were modified by cationic surfactant cetyltrimethyl ammonium bromide (CTAB). Jadav and Singh [22] described a synthesis method of polyamide nanocomposite film of about 400–800 nm thickness coated over porous polysulfone support via interfacial polymerization. Silica nanoparticles have rapidly become the research focus of membrane modification because of their special physical and chemical properties, such as their small size, strong surface energy, high scattered performance, and thermal resistance [30–34]. However, the applications of silica nanoparticles are largely limited because of their high energetic hydrophilic surface, which causes the nanoparticles to be easily agglomerated [35]. Fortunately, this problem could be resolved by using silica sol directly.

The goal of this study was to investigate the effect of silica sol addition on improving the permeation performance. It was believed that the polypiperazine-amide compound with adding silica sol in aqueous phase would produce the polyamide processing an improved water flux. In this study, PES UF membranes were used as a support membrane. Trimesoyl chloride (TMC) and piperazine (PIP) were used as monomers for interfacial polymerization. The polypiperazine-amide TFC NF membranes were prepared by interfacial polymerization and adding silica sol in aqueous phase. The NF membrane performances in terms of pure water permeability and salt rejection were evaluated by

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using stainless steel system with salt aqueous, and the membrane structures and chemical alterations were characterized by attenuated total reflectance infrared (ATR-IR), scanning electron microscope (SEM) and atomic force microscopy (AFM). Different polymerization conditions on membrane performance were investigated. The rejection of different inorganic electrolytes, polyethylene glycols and dye for TFC NF membrane was also discussed in this study.

2. Experimental

2.1. Materials

Polyethersulfone (PES) UF membrane with molecular weight cut-off (MWCO) of 50,000 Da was fabricated in our lab. TMC (purity > 98%) was bought from Qingdao Ocean Chemical Company; PIP (chemical grade) was purchased from Sinopharm Chemical Reagent company; and silica sol (20% SiO_2, particle size: 11 nm) was supplied by Zhejiang Yuda Chemical Industry Company.

2.2. Fabrication of the composite membrane

The TFC membranes were prepared by interfacial polymerization of TMC and PIP. The UF support membrane was first cleaned with de-ionized water then clamped between two Teflon frames. An aqueous phase containing different concentrations of PIP and silica sol was poured on the top of the support membrane and allowed to soak for 2 min in the ambient temperature. The excess monomer on the membrane surface was eliminated by air knife. Then this membrane was dipped in the organic phase prepared by mixing monomer TMC (0.05–0.30%, w/v) in hexane and left in the organic solution for interfacial polymerization. After a predetermined time, the excess organic solution was poured off the surface, and the frame with membrane was held at 80 °C for several minutes for further polymerization. Finally, the resulting membrane was washed with de-ionized water and stored in $NaHSO_3$ solution (1.0 wt.%). For short term storage (i.e. one week or less) 1% $NaHSO_3$ solution is adequate for preventing biological growth.

2.3. Membrane characterization

ATR-IR (Nicolet, Magna-IR 550) was used to characterize the chemical alteration of the TFC membrane surface. For ATR-IR analysis of membrane samples, Irtran crystal at 45° angle of incidence was employed. The measured wavenumber range was 4000–500 cm^{-1}.

The surface and cross section morphologies of the TFC membrane and PES supporting membrane were observed with SEM (JEOL JSM-6360LV).

Quantitative surface roughness analysis of the TFC membrane was measured using AFM (Veeco, Nanoscope IIIa Multimode AFM). Air-dried membrane sample was fixed on a specimen holder and 5μm × 5μm areas were scanned by tapping mode in air. In the AFM analysis, RMS is defined as the mean of the root for deviation from the standard surface to the indicated surface.

TFC NF membrane performance tests of the resulting membranes were performed using stainless steel system. The effective membrane area is around 75 cm^2. Before the permeation tests, the membranes were soaked in de-ionized water for 4 h to eliminate the $NaHSO_3$, and then pressured at 0.6 MPa for 1 h with de-ionized water before the water flux and salt rejection were measured. The experiments were conducted with Na_2SO_4 aqueous solution of 2000 $mg.l^{-1}$ (ppm) at a pressure of 0.6 MPa, a temperature of 25 ± 0.5 °C, and pH of 7.0. The water flux was determined by direct measurement of permeate flow. The permeation flux (F) of membranes was obtained as follows: $F = V/(A \times t)$, where V is the total volume of the obtained permeate during the experiment, A is the membrane area and t is the operation time. The salt rejection rate was calculated using the following equation: $R(\%) = 100 \times (1 - (C_p/C_f))$, where C_p and C_f represent permeate and feed concentrations, respectively. The salt concentration in permeate and feed solutions was measured by DDS-11A conductance meter (Shanghai Neici Instrument Company) and compared the calibration plot drawn between salt concentration and conductivity.

3. Results and discussion

3.1. Structure and morphology characteristics of TFC NF membranes

The polypiperazine-amide TFC NF membrane and the silica/polypiperazine-amide TFC NF membrane prepared under optimum conditions were characterized by structure and morphology.

The chemical composition of the TFC membrane surfaces is investigated by ATR-IR and the results are presented in Fig. 1. The ATR-IR spectrum indicates that the interfacial polymerization occurred since strong bands at 1565.9 and 1623.8 cm^{-1} are present, which are the characteristic bands of C–N and C═O [36]. The bands at 653.8 and 1030.8 cm^{-1} suggest the stretching vibration and anti-stretching vibration of Si–O band.

The morphologies of the membranes were characterized by SEM and AFM. Fig. 2 shows the SEM micrographs of PES supporting membrane and silica/polypiperazine-amide TFC NF membrane. Compared with PES supporting membrane, the surface morphology of modified TFC membrane is dense but not smooth. The photograph (d) shows that the active layer around 200 nm in thickness could be clearly observed from the cross-section. Fig. 3 shows the AFM image of surface morphologies of polypiperazine-amide TFC NF membrane and silica/polypiperazine-amide TFC NF membrane, which cover an area of 5μm × 5μm. The RMS of polypiperazine-amide TFC NF membrane and silica/polypiperazine-amide TFC NF membrane are 6.5 and 42.0 nm respectively, indicating the modified membrane surface is rougher than the unmodified membrane, which increases the contact area of the membrane to a certain extent.

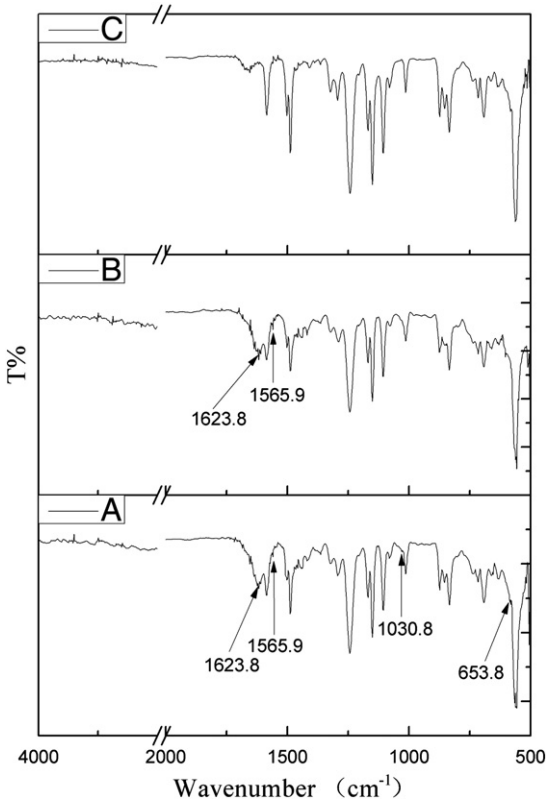

Fig. 1. ATR-IR spectra of (a) silica/polypiperazine-amide TFC NF membrane, (b) polypiperazine-amide TFC NF membrane and (c) PES supporting membrane.