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Studies on a novel nanofiltration membrane prepared by cross-linking of polyethyleneimine on polyacrylonitrile substrate

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ABSTRACT

In this study, composite nanofiltration membranes with positive charges comprising of polyethyleneimine (PEI) active layer and polyacrylonitrile (PAN) substrate were prepared by cross-linking modification. PAN substrate was first hydrolyzed to create carboxyl groups with negative charges, followed by supramolecular assembly of PEI on the substrate surface. Afterwards, PAN/PEI membrane was impregnated in aqueous phase containing cross-linking agent to fabricate the PAN/PEI$_c$ membrane. While the hydrolyzed PAN substrate was negatively charged, the surface modification led to a charge reversal due to the skin layer of PEI. Surface property and morphology of the membrane were characterized by contact angle, scanning electron microscope (SEM) and atomic force microscope (AFM). Effects of cross-linking conditions (e.g. agent type, agent concentration and cross-linking temperature) and operating parameters (e.g. feed type, feed concentration and operating pressure) on the membrane performance were systematically investigated. The results showed that a PAN/PEI$_c$ membrane from PEI layer cross-linked with 12.0 wt% epichlorohydrin (ECH) at 65 °C for 15 h has an optimum NF performance (relatively high salt rejection and high permeation flux). This membrane so formed exhibited salt rejections of 92.82%, 69.76% and 61.31% for a feed $MgCl_2$, $MgSO_4$ and NaCl concentration of 2000 mg/L, respectively, and the corresponding permeation fluxes of 16.26, 16.03 and 17.88 L/(m^2 h) at 1.0 MPa. The rejections to different salt solutions follow a decreasing order of $MgCl_2$, $MgSO_4$ and NaCl, which reveals typical characteristics of a positively charged NF membrane.

1. Introduction

Nanofiltration (NF) membrane is a new burgeoning pressure driven membrane, whose characteristic pore size lies between those of ultrafiltration membrane and reverse osmosis membrane [1]. Thus, nanofiltration enables the rejection of small organics or multivalent ions [2] along with a relatively high water flux at low operating pressure, resulting in the extensive utilization in industrial fields such as water softening [3–5], waste water treatment [6–8], dye reclamation [9] and whey demineralization [10]. At present, polyamide is one of the most widely used materials for manufacturing active layer of composite NF membranes with generally neutral or negative charged. However, there are not many studies on positively charged NF membrane, which have unique benefits, such as resistances to acids, alkalis, microbes and high rejection of multivalent cations.

In recent years, chitosan and its derivatives were used as membrane materials to form a positively charged active layer. Huang et al. [11] reported such a NF membrane prepared by grafting trimethylallyl ammonium chloride onto chitosan by epichlorohydrin (ECH) cross-linking. At 25 °C and 1.2 MPa, the rejections of 1000 mg/L $MgCl_2$, $MgSO_4$ and NaCl solutions were 97.6%, 89.7% and 40.7%, with permeation fluxes of 6.8, 6.12 and 5.51 L/(m^2 h), respectively. They [12] also prepared a quaternized chitosan/poly(acrylonitrile) composite NF membrane from ECH cross-linking, which exhibited the salt rejection of 96.7% and permeation flux of 7.04 L/(m^2 h) for a feed $MgCl_2$ concentration of 1000 mg/L. These studies indicated that the active layer from chitosan and its derivatives could indeed yield a high salt rejection, while the ultra-low permeation flux was considered as the main disadvantage to limit its real application in water treatment. Xu et al. [13] developed a novel thin-film-composite polyamide membrane by supramolecular assembly of chitosan on the polyamide membrane surface. Though permeation flux of this membrane increased obviously, it cannot be used in NF process because of its high salt rejection of 95%. Therefore, a novel positively charged NF membrane with relatively high performance, especially the permeation flux, should be explored, which could be used in seawater softening for offshore oilfield and polymer flooding.

Polyethyleneimine (PEI) was widely used as cationic polyelectrolyte in the preparation of layer-by-layer membrane due to its

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good hydrophilicity and large positive charge density. Many studies showed that a modification using PEI could improve membrane performance in pervaporation or gas separation [14] and ultra-/nano-filtration processes [15]. Ba et al. [16] modified a P84 copolyimide membrane by PEI to investigate NF performance. The results showed that the optimized membrane achieved a salt rejection of 50.9% and a permeation flux of 50.0 L/(m^2 h) at 1.4 MPa when 2000 mg/L NaCl solution was used as feed solution. Moreover, PEI molecules can be cross-linked because of its long carbon chains and a large number of amino groups, which can be used to form a relatively dense active layer on a porous substrate.

In this study, inspired by the abovementioned PEI properties, we fabricated a positively charged PAN/PEI$_c$ membrane with cross-linked PEI as the active layer, and we expected that the resultant membrane would exhibit an improved NF performance in terms of permeation flux and rejection compared to the membrane with an active layer from chitosan. First, hydrolyzed PAN substrate was modified by the surface deposition of PEI layer, followed by a cross-linking process. A commercial PAN substrate was chosen due to its outstanding thermal tolerance, mechanical properties and the ability to generate large number of carboxyl groups by hydrolysis under alkaline conditions [17]. PEI was selected as the material of active layer because of its large positive charge density, which could deposit on the substrate surface with negative charges through supramolecular assembly, and many primary and secondary amino groups on the long carbon chains, which could be cross-linked to form a dense active layer. Self-assembly of PEI on the PAN substrate was studied in the previous literature [15]. As well known, the cross-linking condition can tune the active layer structure and thus the separation performance of a composite membrane. Therefore, effects of the cross-linking conditions (e.g. agent type, agent concentration and cross-linking temperature) on membrane performance were systematically investigated. The contact angle, scanning electron microscope (SEM) and atomic force microscope (AFM) were employed to characterize the surface property and morphology of the composite membrane.

2. Experimental

2.1. Materials

PAN substrate (MWCO ≈ 50 KDa) was provided by Lanjing Membrane Co. Ltd. (Shanghai, China). PEI (MW ≈ 10000, 99%) was purchased from Aladdin Reagent (Shanghai, China). Sodium hydroxide (NaOH), magnesium chloride ($MgCl_2$), magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), ethanol, glutaraldehyde (GA), ECH, propanetriol glycidyl ether (PTGE) and toluene diisocyanate (TDI) were supplied by BASF Chemical Co. Ltd. They were of analytical grade and used without further purification. Molecular structures of various cross-linking agents included GA, ECH, PTGE and TDI and structures of polymers used included PAN and PEI which are shown in Fig. 1.

2.2. Membrane preparation

PAN substrate was hydrolyzed by immersing into 2.0 M NaOH solution at 50 °C for 40 min. It can be readily functionalized to generate carboxyl groups with negative charges. Hydrolysis was terminated by rinsing the membranes with deionized water until the pH value of the rinsed water reached about 7.0. Subsequently, supramolecular assembly of PEI on the substrate surface was performed in the same fashion by contacting the membrane with the 2000 mg/L PEI solution for 4 h. After PEI deposition, PAN/PEI membrane was washed with deionized water using a shaker for 30 min to remove excess amount of PEI on the membrane surface. Afterwards, PAN/PEI membrane was impregnated in aqueous phase containing ECH with a concentration of 6.0, 8.0, 10.0 and 12.0 wt% at 50 °C for 15 h. When cross-linking temperature was investigated, it was changed to 20, 35 and 65 °C. Finally, the PAN/PEI$_c$ membrane with an active layer of cross-linked PEI was fabricated.

2.3. Surface characterization

Hydrophilicity of the membrane surface was characterized by contact angle meter (Germany, KRUSS DSA100). The membrane sample was fixed flat on a glass slide using a double-sided tape after drying in a vacuum oven at 40 °C overnight before the measurements. A drop of water (5 μL) was placed onto the sample surface and the digital image of the droplet was immediately recorded. The data of contact angle reported in this study represent the mean value of more than 10 measurements at different points on each membrane sample.

SEM (Japan, HITACHI S4800) was applied to investigate the surface structure. The membrane sample was glued on a round substrate after drying in a vacuum oven at 40 °C overnight. Gold was sprayed on the sample surface before the measurements and the image of membrane surface with magnification of 100,000 was taken.

AFM (America, VEECO Nano-3D) was used to measure the surface roughness of the membrane. The membrane sample was glued on a round metal substrate after drying in a vacuum oven at 40 °C overnight, and then was examined in tapping mode. The surface roughness was measured in terms of the mean roughness (R_a) and the root mean square roughness (R_q). All roughness measurements were based on scans of at least three different areas.

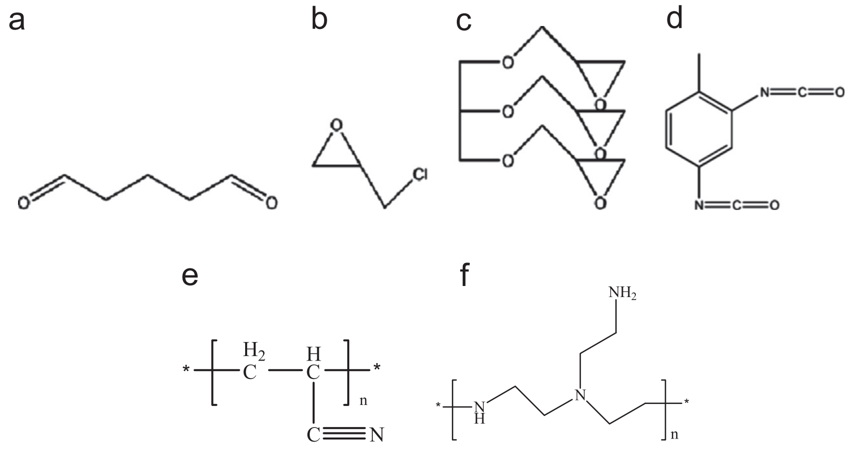

Fig. 1. Molecular structures of various cross-linking agents. (a) GA, (b) ECH, (c) PTGE, and (d) TDI. Structures of polymers used. (e) PAN and (f) PEI.