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Poly (vinyl alcohol)/carboxymethyl cellulose sodium blend composite nanofiltration membranes developed via interfacial polymerization

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ABSTRACT

A novel negatively charged blend composite nanofiltration (NF) membranes were prepared via interfacial polymerization (IP), occurring between poly (vinyl alcohol) (PVA) blending with carboxymethyl cellulose sodium (CMC-Na) and 1, 6-hexamethylene diisocyanate (HDI) at ambient temperature. It was found that the increases in the total concentration of PVA and CMC-Na and the surfactant concentration could reduce the contact angles of the resultant membrane surfaces significantly, while the prolonged IP time increased the contact angle under the test conditions. The performance of the obtained PVA-CMC/PS composite membranes was tested by permeation of different inorganic electrolyte solutions with 5 mM concentration. The rejections of different salts by the optimized membrane were as follows: Na_2SO_4 93.7%, NaCl 32.6%, $MgSO_4$ 24.5%, and $MgCl_2$ 8.6%. Obviously, the difference in the rejections to Na_2SO_4 and NaCl is above 60%, especially beneficial to the removal of hardness and partial desalination. In contrast to other PVA NF membranes, the blend composite NF membrane had the relatively high pure water permeability (*PWP*) and high permeate flux (*F*) while maintaining proper balance between permeate flux and salt rejection.

1. Introduction

Water scarcity is one of the most serious global challenges of our time. With nearly 98% of the world's available water supply being seawater or brackish water, the major ways to increase water supply beyond what is available from the hydrological cycle are desalination and water reuse.

Nanofiltration (NF) is a relatively new membrane separation technique, which is a pressure-driven membrane process normally applicable for separation of dissolved components, widely employed as pretreatment process in reverse osmosis (RO) desalination plants. NF membranes are capable of passing small, uncharged solutes while retaining inorganic salts. While NF has been already applied widely in various industries, including textile wastewater treatment [1], pulp and paper industries [2], pharmaceutical industries [3,4], etc., it will have a broad application prospect in the coming years.

Poly (vinyl alcohol) (PVA) polymer, with high hydrophilicity, good film-forming ability, and outstanding physical and chemical stability, is a kind of excellent material for the preparation of hydrophilic membranes. To create stable membranes with good mechanical properties, and to improve the selective permeability, PVA must be insolubilized by cross-linking or other modification methods due to its water solubility [5]. There have been numerous literatures reported on the membranes based on cross-linked PVA, including microfiltration (MF) [6], ultrafiltration (UF) [7–13], NF [14–17], and RO membranes [18–23]. However, the permeate fluxes of the resultant PVA membranes were rarely satisfactory: most of the RO or NF membranes showed low permeate flux at high operating pressure. For example, PVA was cross-linked in the temperature range of 90–120 °C with bicarboxylic acids to fabricate PVA-PS RO composite membranes [22]. The rejection of the best resultant PVA-PS RO membrane to 3500 ppm NaCl solution was about 95%, but the water permeate flux was only in the range of ʟ-3 gfd (1.7–5.1 kg m^{-2} h^{-1}) at 25 °C and 4.0 MPa. Gohil et al. [16] prepared PVA NF membranes through the method of cross-linking with maleic acid (MA) as the cross-linker. After cross-linking, the PVA membranes were cured at 125 °C for 30 min. The resultant PVA NF membrane showed about 84% rejection to

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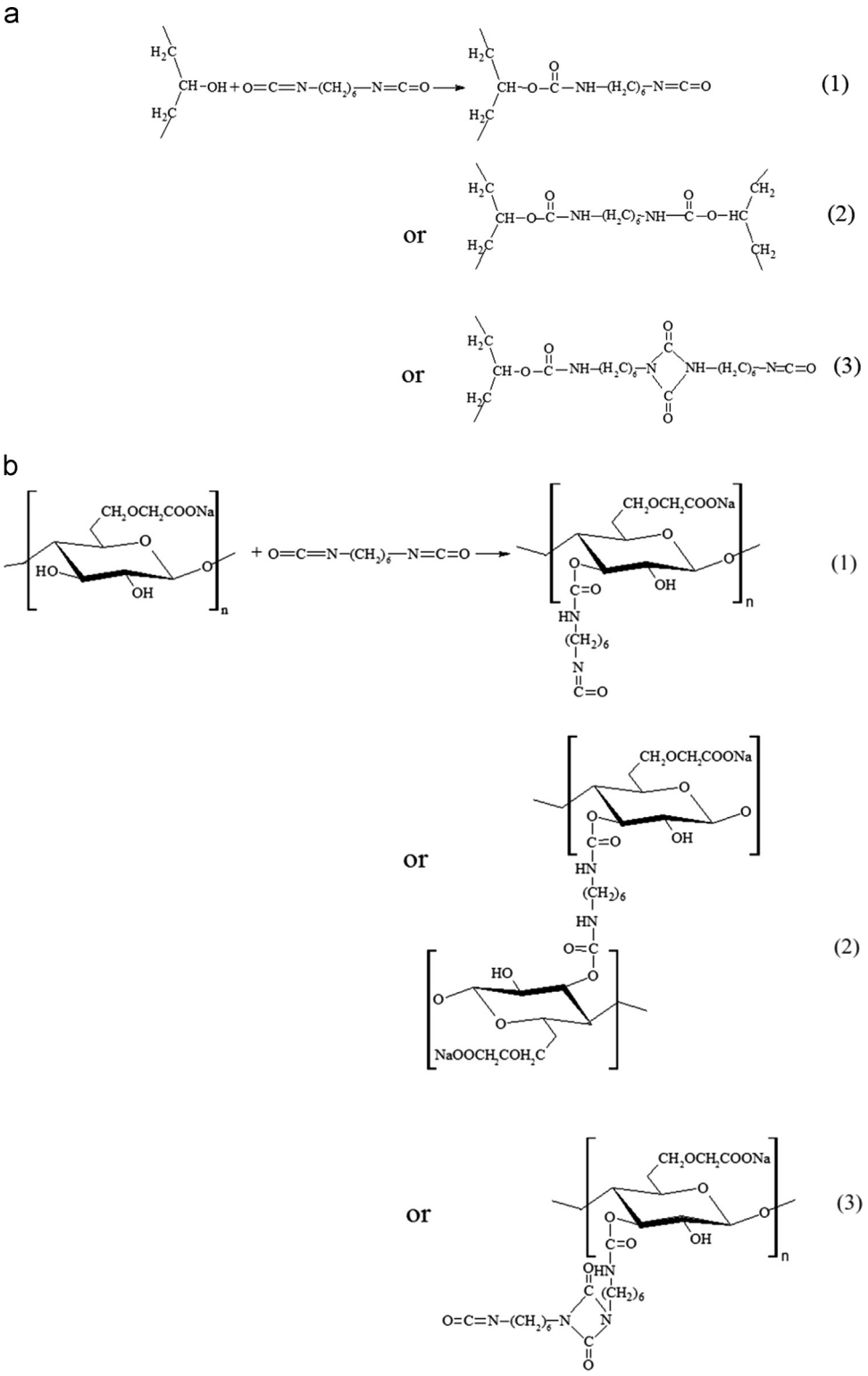
$MgSO_4$ solution and 6 kg m^{-2} h^{-1} permeate flux under 1.03 MPa operating pressure. The heat treatment, the thickness of the PVA layer, and the thermal cross-linking reaction at high temperature were the reasons for the low permeate fluxes of the resultant RO or NF membranes based on PVA.

Interfacial polymerization (IP) is the most important process for the fabrications of commercial composite NF membranes. Typically, a UF membrane is firstly immersed in a polymer or monomer aqueous solution. After immersion, the wetted UF membrane is then contacted with one or more cross-linking agents dissolved in an immiscible organic solvent(s). A dense, cross-linked polymer layer forms at the solution interface. Since the cross-linking reaction occurs mostly at the solution interface, such interracially polymerized active layer is extremely thin. A less cross-linked, more permeable layer forms under the surface layer and fills the pores of the support membrane [24–26]. The keys to



Scheme 1. Schematic representation of the interfacial polymerization reactions: (a) PVA and HDI; (b) CMC-Na and HDI.