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Positively charged composite nanofiltration membrane from quaternized chitosan by toluene diisocyanate cross-linking

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Abstract

2-Hydroxypropyltrimethyl ammonium chloride chitosan/polyacrylonitrile (HACC/PAN) positively charged composite nanofiltration (NF) membrane was prepared using HACC as active layer, PAN ultrafiltration (UF) membrane as support layer, and toluene diisocyanate (TDI) as cross-linking reagent. FTIR-ATR spectrum was employed to characterize the cross-linking on the resultant membrane surface. Besides, some characteristics such as the permeability of pure water and the rejection performance to different salt solutions were evaluated. At 20 °C and 30 L h^{-1} of cycling flow, the permeability of pure water through this membrane was 8.96 kg m^{-2} h^{-1} MPa^{-1}. The rejection to different salt solutions increased in the order of Na_2SO_4, $MgSO_4$, NaCl and $MgCl_2$.

Keywords: 2-Hydroxypropyltrimethyl ammonium chloride chitosan; Positively charged composite nanofiltration membrane; Toluene diisocyanate; Cross-linking

1. Introduction

Nanofiltration (NF) is increasingly gaining attention in many separation and treatment processes such as water softening, color removal, chemical oxygen demand (COD) reduction [1–3]. Now many negatively charged NF membranes are available in the market such as Nitto Denko NTR series, Filmtec NF series and osmonics DK series, etc. However, in some cases, such as for the retention of multi-valent cations and the recovery of cathode electrophoresis lacquer, positively charged nanofiltration membrane is actually needed. Therefore it is of great realistic significance to study positively charged NF membrane. And some work has been placed on its preparation and application [4–7].

Xu and Yang [4] prepared a novel positively charged composite membrane with poly(2,6-dimethyl-1,4-phenylene oxide) as a support to separate divalent salt from monovalent salt. The rejections for 1000 mg L^{-1} $MgCl_2$ and NaCl were 32–73 and 6–36%, respectively, and the pure water flux changed from 32 to 38 kg m^{-2} h^{-1}. Du and Zhao [5] prepared (*N*,*N*-dimethylaminoethyl methacrylate)/polysulfone (PDMAEMA/PSF) positively charged nanofiltration membrane by the interfacial cross-linking polymerization. The rejection of $MgSO_4$ (1000 mg L^{-1} aqueous solution) is almost 90% and the rejection of NaCl (1000 mg L^{-1} aqueous solution) is almost 78% at 0.8 MPa and 30 °C. The rejection of the following inorganic salts to this membrane is decreasing in the order of $MgCl_2$, $MgSO_4$, NaCl and Na_2SO_4.

At present, the most commonly utilized routes to prepare positively charged membranes include chloromethylation and quaternation processes [8]. But chloromethyl methyl ether—a carcinogen substance and potentially harmful to human health is often used in chloromethylation [9]. To avoid the use of chloromethyl methyl ether, we applied quaternization to prepare positively charged membrane. Chitosan is a natural polymer with good membrane-forming characteristic. And there are many active groups such as hydroxy and amino in chitosan, so it is modified easily. In recent years, there are many reports available where chitosan or its derivatives have been used in the preparation of reverse osmosis [10], NF membrane [11–13], ultrafiltration (UF) membrane [14] and pervaporation membrane [15].

In this research, quaternation is employed to modify chitosan in order to improve its hydrophilicity and introduce

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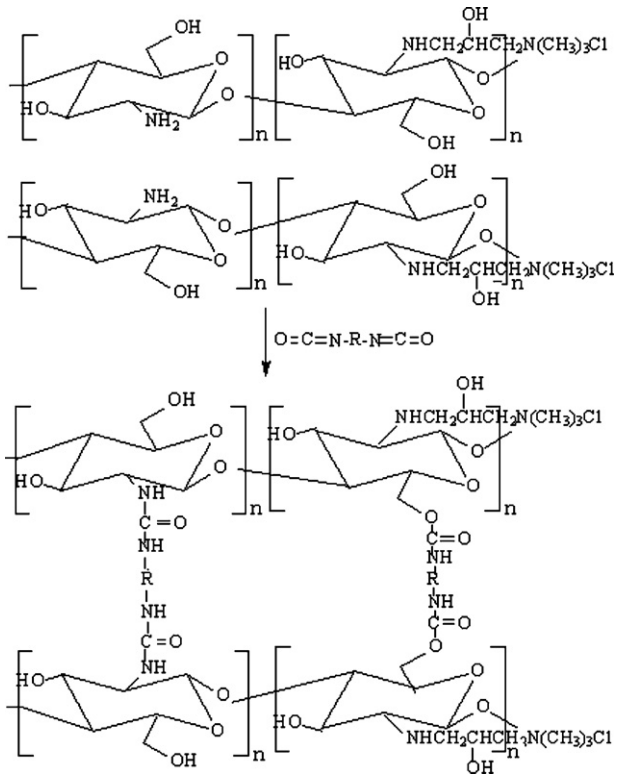

Fig. 1. The cross-linking reaction between HACC and TDI.

positively charged groups in this polymer. What is mentioned is that quaternized chitosan means 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC), which was prepared according to the synthesized procedure in the lecture [13]. A HACC/polyacrylonitrile (PAN) composite NF membrane is developed by using PAN UF membranes as support layer, HACC as the material of active layer, and toluene diisocyanate (TDI) as cross-linking reagent. The effects of its preparation conditions such as HACC concentration, TDI concentration and cross-linking time, etc. on membrane performance were investigated. And some characteristics about this membrane including water permeability, streaming potential and rejection behavior, etc. were also measured. The cross-linking reaction between HACC and TDI is illustrated in Fig. 1; R denotes  .

2. Experiment

2.1. Materials and apparatus

HACC was prepared in our laboratory; sulfuric acid, NaCl, KCl, $MgCl_2$, Na_2SO_4, etc. were of analytical grade; PAN UF membrane with molecular weight cut-off (MWCO) of 1.0×10^5 Da was provided by the Development Center of Water Treatment Technology, State Oceanic Administration (Hangzhou, China). Salt concentrations were evaluated by a Model DDS-11A conductivity meter (Shanghai Leici Instrument, China). Membrane evaluation apparatus was provided by the Development Center of Water Treatment Technology, State Oceanic Administration (Hangzhou, China). The plat-sheet membrane with an effective surface area of 19.6 cm^2 was applied in all permeation experiments.

2.2. Membrane preparation

The casting solution was prepared by dissolving a certain amount of HACC in de-ionized water. The solution was cast on a surface-dried PAN UF membrane, and it was coated on the whole PAN UF membrane with the aid of a glass rod uniformly. The wet composite membrane was allowed to stay at 50 °C for 2 h to evaporate the solvent, then placed in a sealed container with TDI solution. Here the cross-linking reaction between HACC and TDI would be carried out. The membrane cross-linked was heat-treated at 50 °C again, then washed thoroughly with de-ionized water and stored in de-ionized water until ready to use.

2.3. Membrane characteristics

2.3.1. Permeation characteristic

The permeation performance was investigated by determining the fluxes and rejections for NaCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$ solutions at a concentration of 1000 mg L^{-1} at an operating pressure of 1.0 MPa, 30 L h^{-1} of cycling flow and room temperature. Flux (F) and rejection (R) were measured as follows. F was calculated as Eq. (1):

$$F = \frac{W}{At} \times 600 \tag{1}$$

where F (kg m^{-2} h^{-1}) is the flux, A (cm^2) is the effective area of the membrane; t (min) and W (g) are the time and the weight of permeation through the membrane, respectively. R was calculated as Eq. (2):

$$R = 1 - \frac{C_p}{C_f} \tag{2}$$

where C_p (mg L^{-1}) and C_f (mg L^{-1}) are the concentrations of the permeation and the feed, respectively. The datum presented was the average of two measurements conducted with standard deviation of 5%.

2.3.2. Determination of water permeability

The water permeability through HACC/PAN NF membrane was obtained by measuring the fluxes for pure water at these operating pressures varying from 0.5 to 1.4 MPa, 30 L h^{-1} of cycling flow and room temperature.

2.3.3. Streaming potential of membrane measurement

The experimental cell used for the measurement of streaming potential had two compartments separated by a membrane of circular shape of 7.0 cm^2 or so. To minimize the effect of boundary layers on potential, the solutions in both compartments were vigorously stirred by magnetic stirrers. The potential difference across the membrane was recorded with the help of a digital multi-meter using saturated calomel electrodes and salt bridges. For the measurement of streaming potential, the solution applied