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Preparation of nanofiltration membranes from polyacrylonitrile ultrafiltration membranes

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Abstract

Polyacrylonitrile (PAN) membranes display some unusual features for ultrafiltration (UF). The meso-macropores of PAN UF membranes can be easily reduced into the range of micro-mesopores by taking advantage of surface tension forces within the capillary pores during heat treatment in the presence of $ZnCl_2$. Asymmetric PAN nanofiltration (NF) membranes with controlled highly dense pore surface functional groups were prepared by hydrolysis of the nitrile groups with NaOH. The combined effects of heat treatment and the presence of $ZnCl_2$ on the formation of nanofiltration membranes were investigated. In addition, membrane post-treatment with NaOH was studied.

The effect of counterion species on the membrane performance was also investigated. A simple new method, which utilized univalent alkaline ions as probes, was developed to derive the average pore size of cationic nanofiltration PAN membranes from pure water permeability coefficients.
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Keywords: Polyacrylonitrile; Nanofiltration; Pore size characterization; Pure water permeability coefficients; Zinc chloride

1. Introduction

Nanofiltration (NF), defined by many “as a process between ultrafiltration (UF) and reverse osmosis (RO)”, is a relatively recent technology, largely developed over the past decade. Typically, NF membranes have sodium chloride rejections between 20 and 80% and molecular weight cutoffs for dissolved organic solutes of 200–1000 Da. Their separation mechanisms frequently involve both size and Donnan exclusion effects. NF membranes have found many applications in a variety of industries. In water treatment, for example, NF membranes are promising for the treatment of both organic and inorganic pollutants. Their low-pressure operation (4–14 bar) provides increased energy savings with significantly lower installation and operating costs [1,2].

Polyacrylonitrile (PAN), because of its high degree of solvent resistance, is widely used as an UF membrane. Due to its highly hydrophilic properties, it has been known as a low fouling membrane for aqueous filtration. Compared to other polymer materials, PAN also has good resistance against chlorine [3]. Usually, PAN UF membrane is prepared via the phase separation technique. Average pore size and effective porosity of PAN membranes can be controlled by the polymer concentration in the casting solution. However, it is not practical to reduce the pore size of PAN membrane into the range of micro-mesopores by phase separation technique due to poor solubility of PAN in various solvents. PAN UF membranes have been modified to improve permeation behavior or create NF membranes by various methods such as chemical conversions of the nitrile groups [4–6], photoinitiation [7,8], heterogeneous [9] or plasma [10,11] graft polymerization of acrylic monomers.

Here, we demonstrate a novel technique to conveniently prepare an asymmetric cationic PAN NF membrane from PAN UF membranes. This conversion is achieved by taking advantage of the interaction of surface tension forces at the vapor–liquid interface within the capillary pores during the heat treatment of UF membranes that are saturated with a $ZnCl_2$ aqueous solution. Continuous micro-mesopores with controlled highly dense pore surface functional carboxylic acid groups were formed by post-treatment with 1 M NaOH. We also investigated the effect

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of different counter ions on the permeability properties of the cationic PAN NF membranes and developed a simple method, which uses univalent alkaline ions as probes, to estimate the average pore radius of the cationic NF membranes.

2. Experimental

2.1. Materials

PAN (homopolymer, $T_g = 85\,^\circ\mathrm{C}$, average M_w 150,000), polyvinylpyrrolidone (PVP, $M_w = 29{,}000$) and DMF were received from Aldrich. All the salts were used as received from Fisher Scientific.

2.2. Preparation of asymmetric PAN UF membrane

The UF membranes were prepared by the phase separation technique using water as a coagulant. PAN was used as a membrane material and PVP as an additive to make the membrane more porous. PAN and PVP powder were dissolved at 80–90 °C with stirring in DMF to form a 15:5 wt.% PAN:PVP casting solution. The solution was cast onto a Hollytex® polyester nonwoven fabric using a laboratory membrane-casting machine (Separation Systems Technology, USA). The nascent membrane was immersed in a room temperature tap water coagulation bath without evaporation of solvents in the air. After precipitation, the membrane was kept in a water bath for several days and then washed with deionized water before further experiments.

2.3. Preparation of asymmetric PAN NF membrane

The PAN UF membrane was soaked in $ZnCl_2$ aqueous solution for several days. After saturation with the $ZnCl_2$ solution, the membrane was heat treated in air at varying temperatures and times. Following heating, the membrane was allowed to cool to room temperature in air. By soaking the membrane in a very dilute HCl aqueous solution (pH = 3–4), $ZnCl_2$ was removed and a half-transparent PAN membrane that was two to three times thinner was formed. The membrane was then hydrolyzed with 1 M NaOH at room temperature for a controlled time. After the reaction was complete, the hydrolyzed membrane was treated with 1 M HCl at room temperature overnight. The color of the hydrolyzed yellowish red PAN membrane turned to yellowish white. Following that, the membrane was infiltrated with a dilute NaOH solution (pH = 8–9) to convert it into a NF membrane with highly dense pore surface functional groups (–COONa, –CN and $–CONH_2$). The preparation process was described in Fig. 4.

2.4. Membrane performance measurement

The membranes were cut into disks appropriate for use in a filtration cell (Sterlitech™ HP4750 Stirred Cell). A standard magnetic stirrer (Corning Stirrer/Hot Plate, Model PC-420) was used and the stirrer speed was set to achieve a reasonable rate of stirring. Rejection was determined using a NaCl solution. The salt solution flux and salt rejection were measured at 13.79 bar and room temperature. The feed concentration was typically 2000 mg/L in pure DI water. The permeated samples were collected for a few minutes and the concentration of permeates were determined, using a Corning pH/ion analyzer 455. Every point of membrane performance including flux and salt rejection was measured at least three times to get an average value.

2.5. Measurement of pure water permeability coefficients of NF membranes with different counterions

One molar solutions of the chloride salts in Table 5 were passed through the membrane at 13.79 bar for 1 h to form different carboxylic acid salts on the membrane pore surfaces. The membrane was then washed with DI water for at least half an hour to flush the membrane and permeate flow channel. Pure water flux experiments were performed by applying pressures of 6.89, 10.34 and 13.79 bar. The purpose of this experimental technique was to track any changes to the water flux that would indicate changes in the membrane porous structure.

2.6. Elemental analysis, scanning electron microscope, attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FTIR) and nitrogen adsorption

A Model CE440 Elemental Analyzer was used to directly determine the C, H, and N (wt.%) in the samples.

The morphology of membranes (cross-section and surface) was observed with a scanning electron microscope (Hitachi S-4700). Membranes were pretreated by the solvent-exchange method to prevent the structure from collapsing upon drying. Water in the membrane was replaced first with *iso*-propanol and then with *n*-hexane. Samples were cryogenically fractured in liquid nitrogen to form a suitable cross-section and then coated with gold.

ATR/FTIR spectra were collected in the range 4000–600 cm^{-1}, on a Nexus 670 FT-IR (Thermo Electron Corporation, Madison, WI) with a Golden Gate™ MKII Single Reflectance ATR (Specac Inc., Woodstock, GA). The spectrometer was installed with a deuterated triglycine sulfate–potassium bromide (DTGS–KBr) detector and KBr beamsplitter. Spectra collection was performed using FT-IR software (OMNIC, Thermo Electron Corporation, Madison, WI) and analyzed using spectrum software (KnowItAll Informatics System 5.0 Academic Edition, Bio-Rad Laboratories, Inc.). Spectra were recorded by positioning the samples on a cell platform operating at room temperature (64 scans, 4 cm^{-1} resolution).

The adsorption was carried out with an Autosorb-1 volumetric sorption analyzer controlled by Autosorb-1 for Windows 1.19 software (Quantachrome Corp.). All samples were pretreated by the solvent-exchange method and outgassed at 80 °C until the test of outgas pressure rise was below 5 $\mu\mathrm{m\,Hg\,min}^{-1}$ prior to their analysis. N_2 isotherm data from the appropriate relative pressure ranges were used for subsequent calculations. The surface areas were determined using the standard BET equation for N_2 adsorption at 77 K with correlation coefficients $R > 0.99$ in all cases. The DR method was used to estimate the micropore volume from nitrogen adsorption isotherms. The volume of