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Tuning the performance of polypyrrole-based solvent-resistant composite nanofiltration membranes by optimizing polymerization conditions and incorporating graphene oxide

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Solvent-resistant nanofiltration (SRNF) is considered an emerging process capable of replacing conventional energy-consuming methods of separating organic mixtures in diverse industrial fields. This study optimized the performance of polypyrrole (PPy) composite SRNF membranes by varying the polymerization conditions, including the types and concentrations of oxidants and pyrrole concentrations, forming integral selective layers on hydrolyzed polyacrylonitrile (PAN-H) support membranes with better separation properties. The PAN-H support was partially hydrolyzed as indicated by the FTIR spectrum and was compatible with the PPy selective layer, as demonstrated by the apparent lack of an interfacial phase observed in the cross-sections of the composite membranes. The PPy/PAN-H composite SRNF membrane fabricated by reacting 0.5 mol L^{-1} $(NH_4)_2S_2O_8$ and 5.0 wt% pyrrole exhibited a Rose Bengal (RB) rejection of 99.2% in isopropanol (IPA), with a relatively high solvent permeance. For the first time, graphene oxide (GO) was incorporated into the PPy/PAN-H composite SRNF membrane by dispersing GO into the pyrrole ethanol solution before polymerization. GO led to a significant enhancement in solvent permeance without compromising RB rejection. Compared with pure PPy/PAN-H composite SRNF membranes, the methanol (MeOH), ethanol (EtOH), and isopropanol (IPA) permeances of the GO-PPy/PAN-H membrane were approximately 945%, 635% and 302% higher, respectively. In a long term experiment, the GO-PPy/PAN-H composite SRNF membrane exhibited a constant IPA permeance of 1.21 L m^{-2} h^{-1} bar^{-1} and an RB rejection of approximately 99.0%. Therefore, the newly developed GO-PPy/PAN-H composite SRNF membranes in this study have significant potential for practical applications.

1. Introduction

In many industrial fields, processes must be designed to separate active molecules while limiting organic solvent waste, which can lead to high energy consumption and significant environmental contamination. The emerging approach of membrane separation technology may be able to effectively alleviate such critical issues [1–5]. Among various membrane separation processes, solvent-resistant nanofiltration (SRNF) seems to be the most suitable strategy to solve such issues in production processes requiring large amounts of organic solvents. SRNF is a recently developed membrane process applied in non-aqueous media that can replace traditional separation systems. SRNF uses a membrane with a pore size diameter between 0.5 and 2.0 nm and is typically a pressure-driven separation process without phase transfer. Highly efficient SRNF is required to ensure the recovery of organic solvents and the purification of active molecules such as catalysts and pharmaceutically active ingredients. SRNF can be used to significantly reduce energy consumption and solvent contamination while retaining profits. Therefore, SRNF has attracted increasing attention over the last several decades [6–15]. The performance of SRNF membranes has received less investigation than traditional NF membranes. The lack of high-performance and low-cost membrane materials has been the major problem for SRNF. The membrane materials for commercial SRNF are primarily cross-linked polyimides (PI) or polydimethylsiloxane (PDMS). The typically high price of PI and the serious swelling of PDMS limit the practical applications of SRNF. Therefore, recent studies have explored the development of new types of low cost membrane materials and the fabrication of composite membranes consisting of thin selective layers for SRNF [16].

Sirkar and co-workers have studied polyamide (PA) composite SRNF membranes (on polypropylene (PP) supports) via IP (interfacial polymerization) of polyethyleneimine (PEi) and isophthaloyl

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dichloride (IPD) [17,18]. They found that brilliant blue R rejection of PA composite SRNF membranes could reach 88% in methanol, with a high permeance of 1.2 $L\,m^{-2}\,h^{-1}\,bar^{-1}$. After continuous monitoring for ten weeks, the composite SRNF membrane demonstrated high stability in alcohols and aromatic hydrocarbons [17]. Furthermore, multi-walled carbon nanotubes were incorporated into the PA selective thin layer, and the methanol permeance of the CNTs/PA/PP composite membrane was close to an order of magnitude higher than that of the PA/PP composite membrane [18]. Vankelecom and colleagues have performed a series of research studies on layer-by-layer assembly of SRNF membranes using polyelectrolytes (PEs). Under optimized preparation conditions, they obtained composite SRNF membranes with an isopropanol permeance in the range of 0.12–1.57 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ and Rose Bengal retention up to 99% [19–22]. Other materials such as polyurethane (PU), poly[1-(trimethylsilyl)-1-propyne] (PTMSP) on a porous polyacrylonitrile (PAN) support and PANI have been investigated for use in the fabrication of composite SRNF membranes [23–32].

The conducting polymer polypyrrole (PPy) is highly chemically stable but is insoluble in most organic solvents [33,34]. PPy has been used as the selective layer material for gas separation and pervaporation [35,36]. However, only Vankelecom's group [37] initiated a pioneering study using PPy as the SRNF membrane material, investigating the effects of support type and the concentration of the pyrrole monomer on the performance of PPy composite SRNF membranes. They reported that PPy composite SRNF membranes exhibited a high selectivity (over 96%) for negatively charged solutes with a greater flux (over 0.79 $L\,m^{-2}\,h^{-1}\,bar^{-1}$) than that of commercial SRNF membranes. Although Vankelecom's study is interesting and the results are promising, the effects of oxidant types and oxidant concentrations have not yet been investigated, and these parameters are expected to exhibit significant effects on the membrane performance from the point of view of the PPy polymerization process.

This study presents a detailed investigation of oxidant types, oxidant concentrations and PPy concentrations on the pore structures of PPy/PAN-H composite SRNF membranes to obtain the optimal performance. For the first time, graphene oxide (GO), the 2-D particle [38–40] previously used in the synthesis of GO-PPy/PAN-H composites for high-performance electrochemical supercapacitors [41–44], has been incorporated into PPy selective layers to enhance the performance of PPy composite SRNF membranes. The resulting SRNF membranes have been physicochemically characterized, and their solvent permeance and RB rejection have been investigated.

2. Experimental

2.1. Materials

Methanol (MeOH), ethanol (EtOH), isopropanol (IPA) (Xilong Chemical Industrial Co., Ltd.), pyrrole (Sinopharm Chemical Reagent Co., Ltd.), Rose Bengal (RB) (Aladdin Industrial Co., Ltd.), N-methyl-2-pyrrlione (NMP) (Tianjin Guangfu Fine Chemical Research Institute), NaOH, HCl (35%), $(NH_4)_2S_2O_8$, $FeCl_3$, and H_2O_2 (30%), (Xilong Chemical Co., Ltd.) were used as received. Graphite powder was manufactured by Qingdao Baichuan Graphite Co., Ltd. The PAN was provided by Qilu Petrochemical Company with Mw ≈ 90,000 and used to prepare the support membranes.

2.2. Preparation of GO, PAN support and the composite SRNF membranes

Graphene oxide was synthesized using a modified Hummer's method as reported in the literatures [45,46]. The detailed procedure was as follows: 5 g graphite powder and 5 g $NaNO_3$ were added into a 1000 ml three-neck bottle. Then, after slowly adding 240 ml H_2SO_4 (98 wt%) to the mixture, 30 g $KMnO_4$ was added slowly while stirring in an ice-water bath to keep the temperature under 10 °C. After 4 h, the ice-water bath was removed, and the resulting mixture was heated to 35 °C for 30 min. Then, 200 ml H_2SO_4 (5 wt%) was added slowly under stirring. The temperature of the mixture was then held at 98 °C for 30 min. To reduce the residual $KMnO_4$ and MnO_2, 400 ml distilled water and 50 ml H_2O_2 (30 wt%) were added to the mixture, which was then stirred for 30 min. The resulting mixture solution was left to stand for a certain period of time, and then the supernatant was poured. Then, 250 ml HCl (3 wt%) and 250 ml H_2O_2 (0.5 wt%) were added to the mixture to wash the product. The obtained mixture was rinsed and centrifuged repeatedly in distilled water until the pH of the solution reached approximately 7.0. Finally, the mixture was dried in a vacuum freeze drier for 24 h.

PAN membranes were obtained by the phase inversion method from an 18 wt% NMP solution, with a steel blade used to obtain a thickness of 200 μm. The PAN-H membrane was prepared via hydrolysis of the original PAN membranes in 10 wt% NaOH for 3 h at room temperature. Before fabricating PPy or GO-PPy composite SRNF membranes on the PAN support, the PAN-H support membrane was immersed in 0.2 $mol\,L^{-1}$ HCl for approximately 3 h for activation. The PAN-H membranes were stored in distilled water before the fabrication of SRNF composite membranes.

The GO-modified PPy composite SRNF membrane was fabricated by casting the GO/pyrrole monomer mixture on the PAN-H support, followed by polymerization using selective oxidants. First, 0.05 g GO was dispersed into 100 g ethanol with the aid of ultrasound to obtain a homogenous solution. Then, pyrrole monomers were added, and a certain amount of the GO/pyrrole monomers/ethanol solution was poured into a 15 × 15 cm^2 steel ring fixed firmly on top of the support membranes. After immersion for approximately 2 h, the solution was removed and the residual ethanol on the membrane was evaporated. Then, the PPy was polymerized by immersing the membrane in the oxidant for approximately 3 h. The GO-modified PPy composite SRNF membrane was rinsed and immersed in distilled water for more than 12 h to remove all residual oxidants. Finally, the GO-PPy/PAN-H composite SRNF membrane was submerged in methanol overnight. The fabrication process of PPy/PAN-H composite membranes without GO was similar to that of the GO-PPy/PAN-H composite membranes. The fabrication process of composite SRNF membranes and the polymerization mechanism are described in Fig. 1. Each fabrication condition was repeated at least twice to improve the reliability of the results.

2.3. Characterization

FTIR-ATR was performed using a Spectrum One instrument (Perkin Elmer, USA). ZnSe was used as the crystal plate and the penetration depth was approximately 50 Å with a 45° incident angle. All spectra were recorded over the wave number range from 4000 to 600 cm^{-1}. XPS measurements were carried out using an AXIS ULTRA DLD spectrometer (SHIMADZU, Japan) with a monochromatized Al K_α X-ray source (1486.6 eV photons) at a constant dwell time of 250 ms and a pass energy of 40 eV. Wide-angle X-ray diffraction (WAXD) spectra were recorded using a RINT D/MAX-2500/PC XRD instrument (Cu $K_{\alpha 1}$ (λ=0.154 nm), 40 kV × 30 mA, Rigaku, Japan). The samples were measured from 5° to 60° with a 0.02° step. The d-spacing can be calculated by Bragg's Law, Eq. (1):

$$d = \frac{\lambda}{2\sin\theta} \tag{1}$$