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Solvent resistant nanofiltration membrane based on polybenzimidazole

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ABSTRACT

Polybenzimidazole (PBI) membranes with different morphology were prepared via traditional phase inversion method and applied in solvent resistant nanofiltration (SRNF) application. The morphology of the membranes was tuned via changing polymer concentration and adding volatile solvent in cast solutions. The morphology of the membranes was studied in detail by scanning electronic microscopy (SEM). The membranes show less macrovoids sublayer and denser skin layer with increasing polymer concentration in cast solution. The evaporation of volatile solvent is beneficial to forming a thicker skin layer. In this paper, PBI based membranes were also applied in the filtration of organic solvents, where dyes with different charge and size were selected to study the role of charge in solvent filtrations. The membranes showed more than 95% retention on positive charged MB (MW = 160) in alcohol based medium, which is very promising for SRNF application.

1. Introduction

Membranes are effective tools to separate mixtures in an efficient and environmentally friendly way. Nanofiltration (NF) is a process, which allows for the separation and purification of compounds with molecular weight cut-offs (MWCOs) between 200 and 1000 Da over a membrane [1,2]. The membrane pore diameter is normally in the range from 0.5 to 2 nm and the operating pressure is in between 5 and 30 bar. Currently, most NF processes are applied in water purification [3,4] and waste water treatment [5–7]. A great challenge of NF is to extend this process to organic feed, so called solvent resistant nanofiltration (SRNF).

SRNF process is widely applied in catalysis [8,9], the petrochemical industry [10], pharmaceutical industry [11,12] and treatment of organic solvent waste streams. These applications cover the recovery of the organometallic complexes from various organic solvents, fractionation of oligomers, recovery of oils from their extraction solvents and purification of drug precursors etc. Since most of polymers are not stable in organic solvents, exploring high-performance and low-cost membrane materials becomes one of the most challenging issues for SRNF. Therefore, most of researches are still in exploring new membranes with high stability and low cost. Currently, the SRNF membranes are mainly divided into two types, the thin film composite membrane fabricated by interfacial polymerization, dipcoating, in-situ polymerization or plasma polymerization and the integrally skinned membranes fabricated by phase inversion [13–17]. Until now, most of the polymeric SRNF membranes possess the integrally skinned asymmetric structure [18]. The crosslinked polyimide and polydimethylsiloxane (PDMS) composite membranes are among the two mostly studied systems, other polymers like poly(sulfone), poly (ether ether ketone) and polyamide (PA) can also be used in SRNF in certain solvents [19]. Even though, the low chemical stability of most polymers in different organic solvents inspires extensive work on the development of new SRNF membranes.

As a class of heterocyclic polymers, polybenzimidazole (PBI) was commercially developed by the Celanese Corporation in 1983. And PBI was widely used in different fields like protective apparel, electronic devices due to its exceptional high thermal and chemical stability [20,21]. In membrane field, PBI has been used for various separation processes like electrodialysis, forward osmosis and nanofiltration [17,22–24]. Recently, PBI membranes have also been used for gas separation [25] and fuel cell application [26], due to their close chain packing and the feature of high proton conductivity when doping with acid. However, the traditional commercial PBI polymers, especially with high molecular weight, normally show very poor solubility in solvents, therefore, it is very difficult to make them into membranes. In this paper, PBI polymers with ether groups were designed and prepared, the polymers show very good solubility in apolar solvent. And PBI asymmetric membranes with different morphology were fabricated by traditional

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Nomenclature

List of symbols

PBI	polybenzimidazole
THF	tetrahydrofuran
SEM	scanning electronic microscopy
MB	Methylene Blue
MV	molar volume (cm^3/mol)
SRNF	solvent resistant nanofiltration
NF	nanofiltration
MW	molecular weight (g/mol)
MWCOs	molecular weight cut-offs
PDMS	polydimethylsiloxane
PA	polyamide
DABz	3,3′-Diaminobenzidine
DCDPE	4,4′-Dicarboxydiphenyl ether
DMAc	N, N-dimethylacetamide
IPA	2-propanol
RB	Rose Bengal
BTB	Bromothymol Blue
MSA	methansulfonic acid
FTIR	Fourier transform infrared spectroscopy
UV	ultraviolet radiation
J	permeance (l/m^2 h bar)
V	total volume of permeated solvent (l)
A	the effective filtration area (m^2)
Δt	flow time across the membrane (h)
ΔP	the operative pressure (bar)
C_p	permeate concentration (μmol/l)
C_f	concentration of the original feed solution (μmol/l)
R	rejection (%)

phase inversion method and applied in SRNF application. The morphology of prepared membranes was tuned via changing polymer concentration and via adding volatile solvents. The relation between morphology and performance was investigated in detail.

2. Experimental

2.1. Materials

3,3′-Diaminobenzidine (DABz) and 4,4′-Dicarboxydiphenyl ether (DCDPE) were purchased from Acros Organics and Peakchem. N,N-dimethylacetamide (DMAc) was supplied by DAMAO chemical reagent factory (Tianjin, China) and was used as received. Tetrahydrofuran (THF) was purchased from Kermel and used as volatile solvent. Methylene Blue (MB), Rose Bengal (RB) and Bromothymol Blue (BTB) with analytical grade are used as solutes. Ethanol, 2-propanol and acetone with analytical grade were purchased from Tianjin BODI Chemical Limited Corporation.

2.2. Polymer synthesis

Scheme 1 shows the structure and synthesized route of PBI. The detailed procedure was described in literature [27]. The PBI was obtained via aromatic nucleophilic substitution condensation of DCDPE and DABz. The mixture of phosphorus pentoxide and MSA was used as solvent, the temperature was kept at 140 °C.

2.3. Membrane preparation

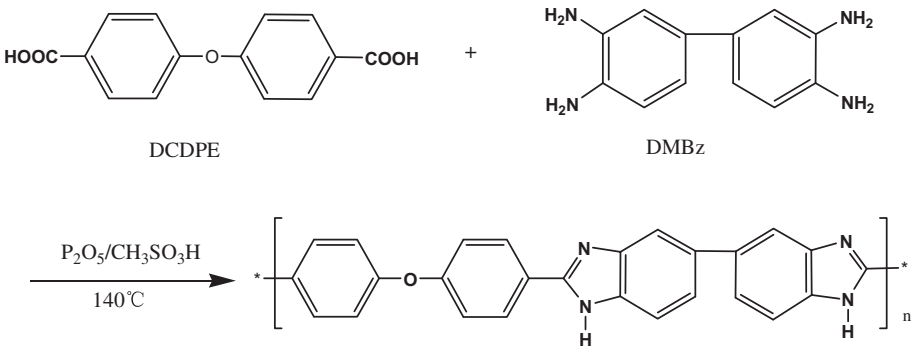
The membranes were prepared via the phase inversion method from casting solutions with predetermined amounts PBI, dimethylacetamide (DMAc) and tetrahydrofuran (THF). The polymer solutions were cast on a glass plate by using an automatic film applicator (Elcometer), afterward, the cast film with wet thickness of 250 μm was immersed in de-ionized water. The addition of the volatile co-solvent THF allows to create a thicker skin layer, hence to increase membrane selectivity. The composition of the resulting membranes is shown in Table 1. The number in the membrane code refers to as the concentration of polymers and the evaporation time of volatile THF.

2.4. Scanning electron microscopy

SEM (JEOL JCM-6000) was applied to observe the cross-section and surface morphology of the membranes. The cross-section was obtained by breaking membranes in liquid nitrogen. Samples were coated with gold before SEM analysis. The surface morphology of membranes with different solution concentration was characterized by field emission scanning electron microscopy (FE-SEM, SUPRA 55).

2.5. Chemical characterization

The chemical structure of membranes was characterized by Fourier Transform Infrared Spectroscopy (FTIR) (BRUKE TENSOR 27) in attenuated total reflectance mode (FTIR-ATR). The dynamic viscosity of polymer solutions was measured by using a NDJ-8S



Scheme 1. The synthesis of PBI.