Chemical Engineering Science 64 (2009) 1577 – 1584

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Enhanced forward osmosis from chemically modified polybenzimidazole (PBI) nanofiltration hollow fiber membranes with a thin wall

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ARTICLE INFO

Article history:
Received 31 July 2008
Received in revised form 23 December 2008
Accepted 23 December 2008
Available online 6 January 2009

Keywords:
Forward osmosis
Polybenzimidazole
Nanofiltration
Hollow fiber
Membranes
Separation
Desalination

ABSTRACT

To develop high-flux and high-rejection forward osmosis (FO) membranes for water reuses and seawater desalination, we have fabricated polybenzimidazole (PBI) nanofiltration (NF) hollow fiber membranes with a thin wall and a desired pore size via non-solvent induced phase inversion and chemically cross-linking modification. The cross-linking by *p*-xylylene dichloride can finely tune the mean pore size and enhance the salt selectivity. High water permeation flux and improved salt selectivity for water reuses were achieved by using the 2-h modified PBI NF membrane which has a narrow pore size distribution. Cross-linking at a longer time produces even a lower salt permeation flux potentially suitable for desalination but at the expense of permeation flux due to tightened pore sizes. It is found that draw solution concentration and membrane orientations are main factors determining the water permeation flux. In addition, effects of membrane morphology and operation conditions on water and salt transport through membrane have been investigated.

1. Introduction

Along with the global water scarcity, less and less access to clean water has become a world-wide issue afflicting people, especially in the developing and industrialized nations (Shannon et al., 2008). More and more effort has been put into evaluating the potential techniques to recover fresh water from wastewater and sea water/brine desalination with low capital costs. Even though the reverse osmosis (RO) process has replaced conventional thermal distillation processes as the dominant desalination technology after 40 year development, the high oil prices have shadowed its future potential because high hydraulic pressures must be provided in the RO process to overcome the osmotic pressure of feed solutions. In addition, the low water recovery by RO is another disadvantage during sea water desalination.

Forward (direct) osmosis (FO) is an emerging desalination technology. It is based on the osmotic pressure as a driving force. As a result, it can operate without high pressures and high temperatures. FO has drawn much attention from researchers and its applications have been explored in wastewater treatment (Cath et al., 2006; Holloway et al., 2007), desalinating seawater (Kessler and Moody, 1976; McCutcheon et al., 2005), water purification in arid environments (Salter, 2005) and the potable water reuse in space (Cath et al., 2005a,b). In addition, FO may offer the advantages of high rejection of a wide range of contaminants and lower membrane-fouling propensities than traditional pressure-driven membrane processes. Because the osmotic driving forces from draw solutions in FO can be much greater than the trans-membrane pressures used in RO, potentially higher water productivity and recoveries may be achieved.

Similar to the RO process, the semi-permeable membrane as the barrier plays an important role on the realization of FO, in which membrane acts as the interface between draw solution and feed solution to transport water and reject solutes. Presently, most available membranes used in the FO are composite RO membranes except the commercialized FO membrane developed by Hydration Technologies Inc. (McCutcheon et al., 2006; Cath et al., 2006; Holloway et al., 2007). Because nanofiltration (NF) membranes have active nano-scale pores, with the estimated pore sizes of around 0.5–2 nm in diameter, they can produced higher water permeation than RO membranes in the pressure-driven process. NF membranes have been widely used for the separation of small neutral and charged molecules in aqueous solutions. For example, NF has become an effective means for the removal of heavy metals ions, divalent anions and harmful organic carbons from wastewater (Raman et al., 1994; Schäfer et al., 2005). In view of effective nano-scale pores, we have conducted the pioneering study to explore the potential of using NF membranes for FO applications (Wang et al., 2007).

Generally, NF membranes are mainly in the configurations of composite flat sheet membranes and hollow fiber membranes.

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doi:10.1016/j.ces.2008.12.032

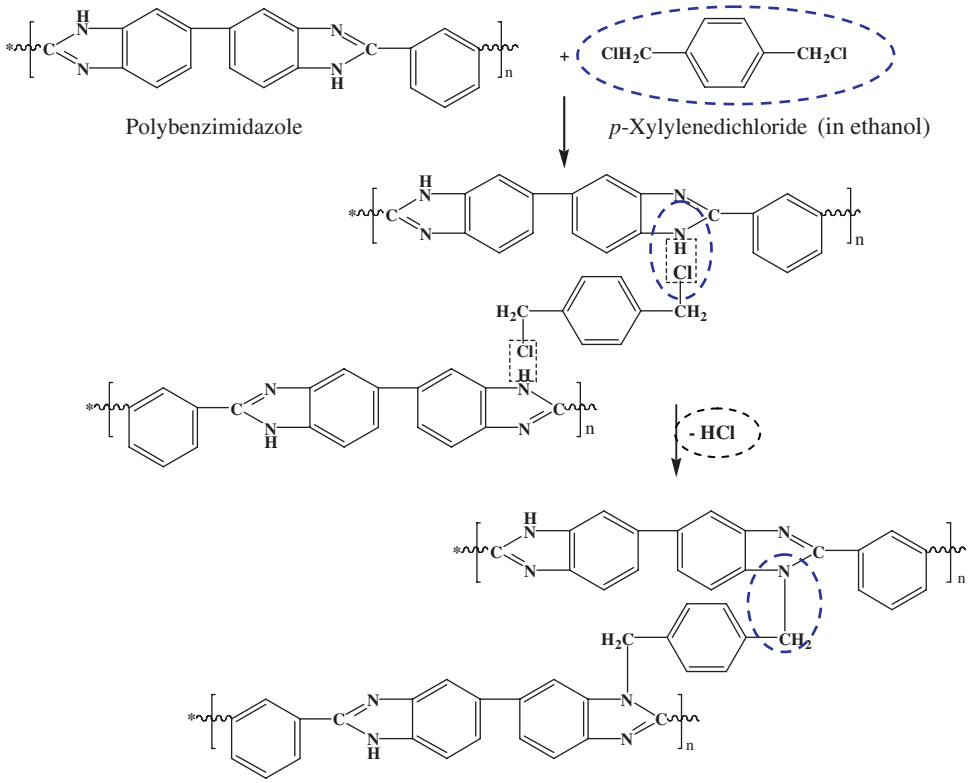

Fig. 1. Possible mechanism of polybenzimidazole modification by *p*-xylylene dichloride.

Hollow fiber membranes have been widely used for liquid phase separation due to their high surface area to volume ratio and self-support capability. Moreover, the relatively low cost of fabricating hollow fibers makes it of interest for large-scale industrial applications. However, because of the asymmetric structure in hollow fiber membrane, the internal concentration polarization within the porous support layer may result in a greatly decrease in water permeation flux (McCutcheon et al., 2006; McCutcheon and Elimelech, 2006). Therefore, to apply NF hollow fiber membranes in FO, the fiber wall thickness should be made as thin as possible to reduce the water transport resistance.

This paper will investigate the fabrication of thin-wall polybenzimidazole (PBI) NF hollow fiber membranes and their uses in the FO process. PBI is chosen because it is a class of heterocyclic polymers commercially developed by the Celanese Corporation in 1983 (Choe and Choe, 1996; Chung, 1997). The heterocycle imidazole ring makes it possible for both inter and intra-molecular hydrogen bonding to occur between PBI molecules. As a result, PBI may become self-charged in aqueous solutions because the adjacent benzene ring delocalizes the proton of the imidazole group (Staiti et al., 2001). The charged property makes PBI membrane applicable in water separation together with its high hydrophilicity for antifouling. Further surface modification may enhance the PBI membrane separation performance. It has been verified that the functionality of –NH-group of the heterocyclic imidazole ring can be directly performed by reacting with *p*-xylylene dichloride (Wang et al., 2006). The possible mechanism of PBI/*p*-xylylene dichloride is given in Fig. 1. As a result, the effective mean pore size and pore size distribution of PBI membranes can be finely adjusted. With a thin wall and a desired pore size, the chemically modified PBI NF hollow fiber membrane may have better performance in FO.

Table 1
Spinning conditions of PBI nanofiltration hollow fiber membranes.

PBI dope solution (wt%)	PBI/DMAc/LiCl (22.0:76.3:1.7)
Dope flow rate (ml/min)	3.0
Bore fluid composition (wt%)	Ethylene glycol/DMAc (50:50)
Bore fluid flow rate (ml/min)	3.0
Air gap (mm)	10
Take-up speed (m/min)	39.2
External coagulant	Tap water, 26 ± 1 °C
Room humidity	65–70%
Dimension of spinneret (mm)	i.d./o.d. (0.66/1.6)
Dimension of PBI HFM (μm)	i.d./o.d. (213 ± 5/293 ± 6)

2. Experimental

2.1. Chemicals

The PBI dope was purchased from Hoechst Celanese Corporation, NJ, with the composition of PBI 25.6 wt%, DMAc 72.4 wt%, LiCl 2.0 wt%. *N*-dimethylacetimide (DMAc), *p*-xylylene dichloride, ethanol, ethylene glycol, $MgCl_2$, $MgSO_4$, Na_2SO_4 and NaCl was purchased from Merck, Germany. Uncharged neutral solutes of glycerol, glucose, saccharose, raffinose and α-cyclodextrin were purchased from Aldrich, USA. All chemicals were used as of received. Deionized (DI) water (Milli-Q, 18.2 MΩ cm) was used for the preparation of solutions.

2.2. Fabrication of PBI NF hollow fiber membrane

The hollow fiber spinning process through the dry-jet wet phase inversion was schematically described elsewhere (Wang and Chung, 2006). The detailed spinning parameters are listed in Table 1. The