



Effect of additives on the performance and morphology of sulfonated copoly (phthalazinone biphenyl ether sulfone) composite nanofiltration membranes[☆]

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ABSTRACT

Sulfonated copoly (phthalazinone biphenyl ether sulfone) (SPPBES) composite nanofiltration membranes were fabricated by adding low molecular weight additives into SPPBES coating solutions during a dip coating process. Three selected additives: glycol, glycerol and hydroquinone were used in this work. The effect of additives on the membrane performance was studied and discussed in terms of rejection and permeation flux. Among all the composite membranes, the membrane prepared with glycol as an additive achieved the highest Na_2SO_4 rejection, and the membrane fabricated with glycerol as an additive exhibited the highest flux. The salts rejection of SPPBES composite membranes increased in the following order $\text{MgCl}_2 < \text{NaCl} \leq \text{MgSO}_4 < \text{Na}_2\text{SO}_4$. The morphologies of the SPPBES composite membranes were characterized by SEM, it was found that the membrane prepared with hydroquinone showed a rough membrane surface. Composite membrane fabricated with glycol or glycerol as the additive showed very good chemical stability.

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1. Introduction

It is well known that polymer membranes have been widely applied in desalination, drinking water production, wastewater treatment and many other industrial applications. Membrane separation process appears to be an economical and environmentally friendly approach, which has been paid extensive attention due to its specific characteristics, e.g. separation process without phase change, more competitive operating cost, relatively low energy consumption, operation at ambient temperature and easy scale-up [1–5]. Among all types of membranes, nanofiltration (NF) membrane possesses the separation characteristics in the intermediate range between reverse osmosis (RO) membrane and ultrafiltration (UF) membrane [6]. By virtue of their characteristic properties, nanofiltration membranes are sometimes referred to as tight ultrafiltration or loose reverse osmosis membranes [7–10]. Most of the nanofiltration membranes developed so far are composite in nature, with a selective layer on the top of a micro-porous substrate [11]. The characteristics of the selective layer material determine

separation properties of the membrane, and the support structures give mechanical strength [12,13].

A lot of polymers have been successfully used as the selective layer of composite nanofiltration membranes in order to optimize membrane performance, such as polyamide [14,15], poly(vinyl alcohol) [16,17], chitosan [18], sulfonated polysulfone [19–21], sulfonated poly(2,6-dimethyl-1,4-phenyleneoxide) [22] and sulfonated poly(ether ether ketone) [23–25]. In our previous work, sulfonated poly(phthalazinone ether sulfone ketone) [26,27] and sulfonated copoly(phthalazinone biphenyl ether sulfone) (SPPBES) [28] were used as the active layer materials for composite NF membranes. The SPPBES composite nanofiltration membranes were prepared by coating SPPBES solutions onto poly (phthalazinone ether sulfone ketone) (PPESK) ultra filtration membranes. As the feed temperature increased from 20 °C to 90 °C, the permeate flux of SPPBES membrane increased from 32 to 94 L/m²h, while the rejection of the membrane decreased from 89.7% to 87.8%. SPPBES composite membranes had high thermal stability and good chlorine tolerance [28].

It has been well known that the membrane morphology and performance can be controlled by the addition of appropriate additive [23,29]. Petersen [29] reported that cross linking can be increased via additives such as polyols or polyphenols which are reactive with the sulfonic acid groups. Various membrane examples were

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Nomenclature

GL	Glycol
HQ	Hydroquinone
NF	Nanofiltration
RO	Reverse osmosis
UF	Ultrafiltration
GLE	Glycerol
SEM	Scanning electron microscopy
EGME	Ethylene glycol monomethyl ether
PPESK	Poly (phthalazinone ether sulfone ketone)
SPPBES	Sulfonated copoly (phthalazinone biphenyl ether sulfone)
ATR-FTIR	Attenuated total reflectance fourier transform infrared
SPPBES–GL	SPPBES composite membranes prepared with glycol as the additive
SPPBES–HQ	SPPBES composite membranes prepared with hydroquinone as the additive
SPPBES–NA	SPPBES composite membrane without additive in coating solution
SPPBES–GLE	SPPBES composite membranes prepared with glycerol as the additive

produced that showed high rejections. M. Dalwani [23] developed sulfonated poly (ether ether ketone) membranes by using 1,4-benzenedimethanol as cross linker, no irreversible changes in membrane performance have been observed after prolonged exposure (up to several weeks) of this membrane to solutions with a pH in the range 0–14. In addition, SPPBES membranes were prepared by solvent evaporation phase inversion technique, which is that SPPBES coating solution on PPESK substrate is cured in an oven. During the process, the solvent in the coating solution is evaporated and phase separation occurs in the membrane. After membrane formation, the membrane was further washed in a bath of distilled water. By washing the membrane with water, the residual water-soluble additive was removed and then the micropore was retained [30], so the molecular weight and physical properties of additives also can affect the membrane performance. Therefore, polyols and polyphenols: glycol, glycerol and hydroquinone were selected as additives in this work, we have made first attempt to study systematically the relationships between additives and membrane properties.

Sulfonated copoly (phthalazinone biphenyl ether sulfone) (SPPBES) was used as the active layer material for composite NF membrane. The separation properties and chemical stability of composite membranes have been investigated by dead-end filtration. SPPBES membranes were characterized using scanning electron microscopy (SEM) and infrared spectroscopy.

2. Experimental

2.1. Materials and instrument

PPESK (S:K=1:1) was provided by Dalian new polymer co. ltd. (PR China). SPPBES with degree of sulfonation 0.86 was prepared in our lab, and its chemical structure was showed in Fig. 1. Acetone, ethylene glycol monomethyl ether (EGME), glycerol, glycol, hydroquinone and other chemicals used in the experiments are all analytical purity grade and used as received. Na₂SO₄, NaCl, MgSO₄ and MgCl₂ were used as solutes for the membrane characterization. A stainless flat sheet dead-end filtration set-up, which was described in our previous work [31], was used to evaluate the composite membrane. Magnetic

stirring heater (Jiangsu Jiangyin Science Research Instrument Plant) was installed in the membrane feed side to reduce concentration polarization. Electrical conductivity meter (DDS-11A, Shanghai Rex Instrument Factory, China) was used to measure the concentration of salt in the feed and permeate solutions.

2.2. Membrane preparation

An appropriate solvent for coating should be able to dissolve coating material, while the support polymer cannot be dissolved in the solvent system. A mixed solvent system EGME-acetone was selected in this work, and the quality ratio of EGME to acetone was 5:1. SPPBES showed good solubility in the mixed solvent system, and PPESK was insoluble in the mixed solvent system. Then, glycol, glycerol and hydroquinone were dissolved in the mixed solvent system of EGME-acetone using mechanical stirring, respectively. After that, SPPBES powder was added under continuous stirring to produce a SPPBES coating solution. Additive concentration was 25 wt.%, SPPBES concentration was 3 wt.%.

Preliminary investigations revealed that PPESK has excellent comprehensive properties as sub-layer of NF and RO [26,27]. PPESK ultra filtration membrane was prepared according to our previous work [28]. Composite membranes were prepared by coating SPPBES solutions on PPESK ultra filtration support membranes. Firstly, the coating solution was poured onto the PPESK support and let sit for 5 min. Then, the excess solution on the PPESK membrane surface was drained, leaving a thin SPPBES layer on the membrane surface. The SPPBES coated PPESK membranes were then cured for 30 min. Finally, the SPPBES composite membranes were washed with water to remove residual additives and solvent.

2.3. Performance of composite membrane

Composite membrane was pre-compressed at 1.2 MPa for 30 min with deionized (DI) water before the permeation tests, and then it was evaluated under a pressure of 1.0 MPa in a stainless flat sheet dead-end filtration set-up. The permeate flux was calculated by the following equation:

$$F = \frac{Q}{At}$$

where F is the permeate flux (L/m²h), A is the effective area of the membrane (m²), Q is the volume of permeate solution (L), and t is the time (h). The salt rejection was evaluated using the following equation:

$$R(\%) = 100 \times \left(1 - \frac{C_p}{C_f}\right)$$

where C_p and C_f are the salt concentrations in permeate and feed, respectively. The salt concentration was determined by measuring the electrical conductivity of the salt solution using a conductance meter.

2.4. Characterization of composite membrane

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was employed to analysis the functional groups of the membranes. Membrane samples were thoroughly rinsed with deionized water and dried before characterization. The ATR-FTIR spectra were recorded on a Nicolet-20DXB spectrometer.

Samples were prepared for SEM by freezing the membranes in liquid nitrogen and subsequently breaking them. After drying

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