

# Preparation of thermally stable composite forward osmosis hollow fiber membranes based on copoly(phthalazinone biphenyl ether sulfone) substrates



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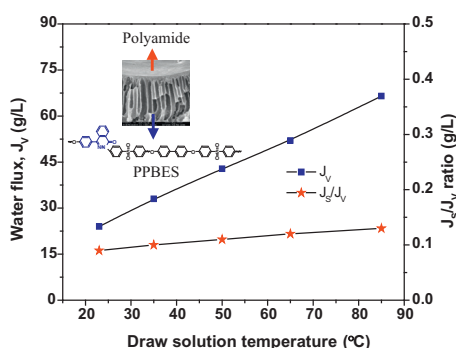
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## HIGHLIGHTS

- Novel composite FO hollow fiber membranes were developed via interfacial polymerization.
- Composite FO membranes were prepared from PPBES hollow fiber membranes as substrates.
- Effect of IP preparation conditions on the membrane performance was investigated.
- The novel PPBES composite FO membranes exhibited excellent thermal stability.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A series of composite forward osmosis (FO) hollow fiber membranes were developed using interfacial polymerization (IP) on the lumen side of copoly(phthalazinone biphenyl ether sulfone) (PPBES) substrates. The effect of the PPBES substrate and IP preparation conditions on composite FO membranes performance was evaluated. Water flux of the FO membranes increased with an increase in flux of PPBES substrates. The IP preparation parameters such as solvents, monomer concentrations, reaction time, and curing conditions had a great influence on the properties of composite FO membranes. The novel PPBES composite FO hollow fiber membranes exhibited high thermal stability. The water flux of composite FO membranes improved from 24.0 L/m<sup>2</sup> h to 66.5 L/m<sup>2</sup> h without significant change of  $J_s/J_v$  ratio when the draw solution temperature was elevated from 23 °C to 85 °C.

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## 1. Introduction

With the accelerating population growth, environmental deterioration and economic development, pervasive water scarcity

and energy shortage have become two of the most serious universal challenges (Elimelech and Phillip, 2011; Klaysom et al., 2013). Membrane technology has been extensively applied to water treatment fields. However, traditional pressure-driven membrane processes such as reverse osmosis (RO) have high energy consumption, low water recovery, and negative environmental effects (Linares et al., 2014). Therefore, there is an urgent

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need to search for an alternative novel sustainable technology of water treatment with low energy consumption.

As an emerging energy-effective water treatment technology, forward osmosis (FO) has gained significant attention recently with various advantages such as relatively lower prime energy demand, less membrane fouling behaviors and higher rejections toward contaminants (Lee et al., 2010; Zhao et al., 2012). Instead of using hydraulic pressure, forward osmosis utilizes an osmotic pressure difference between draw solution and feed solution to extract water automatically (Cath et al., 2006). The unique performance shown by FO processes have improved the development of its potential applications including wastewater treatment, seawater desalination, food processing, power generation and so forth (Thiruvenkatachari et al., 2016; Roy et al., 2016; Coday et al., 2014; Anna et al., 2012; Han et al., 2013).

Despite the various advantages and many potential applications of FO technology, the absence of desirable FO membranes with appropriate separation performance is a significant hurdle deterring further advancements of this revolutionary process (Chung et al., 2012). Water flux of conventional RO membranes applied to FO process is significantly lower than theoretical values. Furthermore, the commercially available FO membrane not only shows relatively low water permeability and rejection, but also exhibits poor resistance to hydrolysis which restricts its application scope (Yip et al., 2010). Therefore, it is necessary to develop a new type of FO membrane with low reverse solute leakages, high water permeability and high thermal stability.

Many composite membranes have been studied for FO applications. Unlike composite RO membranes, both the substrate and active layer properties play a key role in the performance of composite FO membranes. Selecting suitable substrate materials is critical for the development of composite FO membranes (Liu and Ng, 2014; Wang et al., 2010; Chou et al., 2010). Copoly(phthalazinone biphenyl ether sulfone) (PPBES) is a novel amorphous copolymer, and its chemical structure is presented in Fig. 1. PPBES materials have relatively high chemical resistance, good solubility, mechanical properties, membrane-forming ability, and excellent thermal stability. PPBES has exhibited good performance as a membrane material in ultrafiltration and as a sub-layer of nanofiltration (Liu et al., 2015; Han et al., 2011). So PPBES may be a suitable candidate for the substrate material of composite FO membranes. Compared to flat sheet membranes, hollow fiber membranes show more promising properties such as larger surface areas and a preferable flow pattern for FO processes (Sukitpaneevit and Chung, 2012). However, to the author's knowledge, there is few report on the development of composite FO hollow fiber membranes based on copoly(phthalazinone biphenyl ether sulfone) substrates.

Interfacial polymerization (IP), one of the most frequently used methods for thin-film composite membranes, has been widely adopted for preparing composite FO hollow fiber membranes because it allows both substrate porosity and the active layer to be individually tailored (Lau et al., 2012). However, many challenges must be overcome to promote the development of novel composite FO hollow fiber membranes based on IP technology. Although in a similar way to technology employed in

nanofiltration and RO processes, the fabrication schemes utilizing IP method for composite FO hollow fiber membranes may be quite different because of extremely different application environments and performance requirements (Li et al., 2012). Furthermore, many studies have focused on researching novel FO substrate membranes (Sun et al., 2014; Zhong et al., 2013), but relatively few research reports have been published on the development of novel composite FO membranes by simultaneously optimizing substrate and IP preparation conditions. In light of these concerns, there is an urgent need to evaluate the effects of substrate properties and IP fabrication schemes on composite FO membranes performance.

In the current work, PPBES composite FO hollow fiber membranes were prepared by optimized IP fabrication schemes on the lumen side of tailored PPBES substrates. Effects of substrate and IP preparation conditions on separation performance of composite FO membranes were evaluated. Moreover, thermal stability of novel PPBES composite FO membrane was investigated by raising the temperature of draw solution up to 85 °C.

## 2. Experimental

### 2.1. Membrane materials and chemicals

PPBES material was obtained from Dalian New Polymer Co., Ltd (PR China). N,N-dimethylacetamide (DMAc) was obtained from Tianjin Bodi Chemical Co., Ltd (PR China) as solvents. To optimize composite FO membranes performance, the 1,3,5-benzenetricarbonyl trichloride (TMC) was synthesized from 1,3,5-benzenetricarboxylic acid and purified via a series of distillation steps. The commercialized m-phenylenediamine (MPD) was purified via reduced pressure distillation.

### 2.2. Fabrication and characterization of PPBES hollow fiber substrates

PPBES hollow fiber substrates were prepared by phase inversion at room temperature (Liu et al., 2015; Yang et al., 2006a) By varying PPBES concentrations in the dope solution from 16 wt.% to 22 wt.%, four different hollow fiber substrates were fabricated. The substrates containing different amounts of PPBES (16, 18, 20 and 22 wt.%) were labeled as Sub-16, Sub-18, Sub-20 and Sub-22, respectively. Fabrication conditions are briefly described as follows: The homogeneous dope solutions were poured into the hollow fiber spinning machine. Subsequently, the dope solutions were extruded from the spinneret at the flow rate of 1.5 ml/min under the pressure of nitrogen. The nascent hollow fibers were then formed in the external coagulation bath at room temperature. The air gap distance was kept at 15 cm. Finally, the resultant PPBES hollow fiber substrates were taken up, and stored in water bath.

Ultrafiltration experiments were measured using a lab-scale circulating test instrument described as reported previously (Yang et al., 2006b). After a pretreatment process under 0.15 MPa for 30 min, the properties of substrate membranes was tested under 0.1 MPa. The water permeation flux ( $F$ , L/m<sup>2</sup> h) was calculated from Eq. (1):

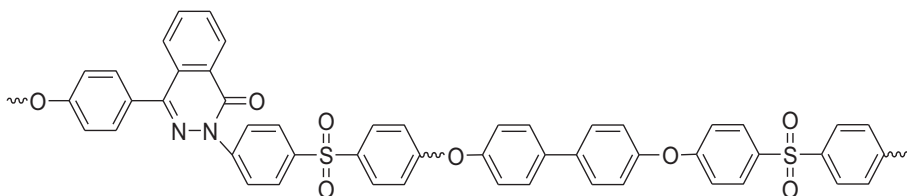


Fig. 1. Chemical structure of PPBES.

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