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## Controlled surface morphology of polyamide membranes via the addition of co-solvent for improved permeate flux

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## ABSTRACT

Polyamide membranes with a controlled surface morphology were prepared by the interfacial polymerization of 1,3-phenylenediamine (MPD) with 1,3,5-benzenetricarbonyl trichloride (TMC) on polysulfone ultrafiltration supports. In a novel polymerization method, co-solvents, which included acetone, ethyl acetate, diethyl ether, toluene, isopropyl alcohol (IPA) and *N,N*-dimethyl formamide (DMF), were added into the organic phase which made it possible to control the surface morphology and polyamide network structures. As-prepared, the membranes showed multi-layered ridge-and-valley structures, and the types of co-solvent successfully controlled permeate flux and rejection. Polyamide membranes prepared by the addition of 2 wt% ethyl acetate, showed the best performance with NaCl rejection of 99% and permeate flux of more than 1 m<sup>3</sup>/(m<sup>2</sup> d) at 1.5 MPa, which was about twice that of a membrane prepared without a co-solvent.

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## 1. Introduction

Due to rapid growth in population and an increased demand in the amount of water needed for life, industry and agriculture, water demand has constantly increased, although the amount of usable water, such as surface water, is decreasing. Therefore seawater and wastewater have drawn a great deal of attention as new water sources [1]. Thus far, membrane manufacturers and researchers have developed a great number of reverse osmosis and nanofiltration membranes, which have shown both good desalination performance and permeate flux [2–5].

Reverse osmosis (RO) membranes were developed to obtain safe and clean water and for application to various types of separation targets. Separation targets of RO membranes include inorganic monovalent ions, and RO membranes have the highest level of rejection of solutes among the separation membranes, such as monovalent ion, hardness components (eg. calcium, magnesium) and organic matters (eg. trihalomethane precursor, pesticides and deodorants). Several types of RO membranes have been developed and operated at pressures of approximately 0.5–6.0 MPa [6].

In general, the composite RO membranes are divided into 3 layers. A bottom layer of polyester unwoven cloth with an approximate thickness of 100–200 μm is used for mechanical strength in the PA separation layer. The middle layer which is composed of polysulfone (PSf) or polyethersulfone (PES) with an approximate thickness of 30–50 μm is used for support of a top layer. A top layer of polyamide (PA) or polyetherimide (PEI) with an approximate thickness of 100–200 nm is used for the separation of solutes from feed water [3,6]. Polyamide membranes were fabricated on the middle-layer PSf supports by interfacial polymerization between diamine in the water phase and acid chloride in the organic phase, such as 1,3-phenylenediamine (MPD) and 1,3,5-benzenetricarbonyl trichloride (TMC). FT-30 is one of the industry standard RO membranes, which has a highly cross-linked structure that imparts a high degree of salt rejection and flux, the values of which are more than 99% and more than 1 m<sup>3</sup>/(m<sup>2</sup>/d), respectively, for 2000 ppm NaCl at 1.55 MPa [3,6,7].

However, the following challenges persist for RO membranes: (1) a great deal of energy (electricity costs) must be used for pressurizing feed water in order to obtain permeate; (2) membrane materials have a lower resistance to chemicals when used as a disinfectant and in cleaning; (3) a great deal of energy (electricity costs) must be used for pretreatment. Therefore, extensive investigation has been focused on the development of novel RO membranes that have both a higher chemical resistance and a higher degree of permeate flux, which will lead to a lowering of both the energy costs and the impact on the environment.

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One method to achieve high permeate flux is to improve monomer diffusivity by adding additives to the water phase (diamine solution). For example, Hirose et al. reported [8,9] that adding alcohol and ether in the water phase led to higher permeate flux and higher salt rejection. Polyamide membranes prepared by the addition of 20 wt% isopropyl alcohol, showed the best performance with a rejection of 99.7% for 1500 ppm NaCl and permeate flux of more than  $1.7 \text{ m}^3/(\text{m}^2 \text{ d})$  at 1.5 MPa, which is about 1.7-fold higher than that of a membrane prepared without isopropyl alcohol. Zhao et al. also reported [10] that adding hydrophilic additives to the water phase led to higher permeate flux and higher salt rejection. Polyamide membranes prepared by the addition of 2.85 wt% *o*-aminobenzoic acid with post-treatment by soaking in an aqueous solution of 5 wt% glycerol and 6 wt% CSA-TEA salt followed by drying at  $90^\circ\text{C}$  for 14 min showed the best performance with a rejection of 98.8% for 2000 ppm NaCl and permeate flux of more than  $2.1 \text{ m}^3/(\text{m}^2 \text{ d})$  at 1.55 MPa, which was more than twice that of a membrane prepared without hydrophilic additives. Xie et al. reported [5] that optimizing the concentrations between diamine and acid chloride led to higher permeate flux and higher salt rejection. Polyamide membranes that were interfacially polymerized using 1.5% MPD and 0.05% TMC showed the best performance with a rejection of 99.6–99.7% for 2000 ppm NaCl and permeate flux of from 0.94 to  $1.08 \text{ m}^3/(\text{m}^2 \text{ d})$  at 1.55 MPa, which was about twice that of a membrane prepared under un-optimized conditions. But only a few papers have reported membranes fabricated with additives in the organic phase.

Another novel method used to achieve a high degree of permeate flux has been the introduction of a water path into a polyamide structure by the addition of either inorganic or organic materials. For example, Hoek et al. reported [11] a new membrane concept whereby fabrication was accomplished by adding inorganic nano-sized particles (eg. zeolite) to an organic phase, which led to higher permeate flux. Polyamide membranes, prepared by the addition of 0.4% (w/v) 100 nm-diameter zeolite NaA nanoparticles, showed the best performance with a negligible rejection loss (94% for 2000 ppm NaCl) and a permeate flux of  $0.4 \text{ m}^3/(\text{m}^2 \text{ d})$  at 1.24 MPa, which was approximately twice that of a membrane prepared without zeolite type A [LTA] nanoparticles. Kong et al. also [12] reported higher permeate flux organic–inorganic hybrid membranes by adding zeolite nanoparticles to the organic phase. Polyamide membranes, prepared by the addition of 0.4 wt% 150 nm-diameter zeolite HY nanoparticles, showed the best performance with a negligible rejection loss (95% for 2000 ppm NaCl, 1.5 MPa) and a permeate flux of  $0.8 \text{ m}^3/(\text{m}^2 \text{ d})$  at 1.5 MPa, which was approximately twice that of a membrane prepared without zeolite HY type nanoparticle. Furthermore, Kong et al. reported [13] higher permeate flux from organic–inorganic hybrid membranes by adding metal alkoxides to the organic phase. Polyamide membranes prepared by the addition of 5 wt% of phenyltriethoxysilane showed the best performance with a negligible rejection loss (95% for 2000 ppm NaCl) and a permeate flux of  $0.6 \text{ m}^3/(\text{m}^2 \text{ d})$  at 1.5 MPa, which was approximately twice that of a membrane prepared without the addition of PhTES. Zhao et al. reported [14] robust, high performance biomimetic membranes using aquaporin by interfacial polymerization. Aquaporin is a well-known water channel protein with excellent permeate flux and solute rejection qualities [15]. Polyamide membranes prepared using 10 mg/mL proteliposomes with the addition of aquaporin to the water phase showed the best performance with a negligible rejection loss (96% for 10 mg/L NaCl) and a permeate flux of  $0.48 \text{ m}^3/(\text{m}^2 \text{ d})$  at 0.5 MPa, which was approximately 1.3-fold higher than that of a membrane prepared without aquaporin.

Recently, we reported [16,17] that the addition of a co-solvent into the organic phase enhanced the miscibility at the interface,

and led to high degree of permeate flux using the model type of polyamide, which was a MPD/TMC polyamide without the addition of some of the additives in the water phase. Polyamide membranes prepared by the addition of 2 wt% acetone to the organic phase showed the best performance with a glucose rejection of 99.4% and a permeate flux of more than  $1.4 \text{ m}^3/(\text{m}^2 \text{ d})$  for 500 ppm glucose at 1.5 MPa, which was approximately 4-times higher than that of a membrane prepared without acetone. However, the preparation conditions, including the types of added solvents, have not yet been investigated in detail.

In the present study, novel RO membranes, which had high values for both salt rejection and permeate flux, were developed using the model type of polyamide, which was a MPD/TMC polyamide without the addition of some of the additives in the water phase, with the addition of various types of organic solvents, including acetone, ethyl acetate, diethyl ether, toluene, isopropyl alcohol (IPA) and *N,N'*-dimethyl formamide (DMF) into the organic phase. To clarify the effects of co-solvents for membrane performance, the model polyamide, which was prepared from a MPD and a TMC without the addition of any additives in the water phase was used in the present study. These membranes also showed a specific surface morphology formed by organic solvents. Furthermore, we found that salt rejection and permeate flux could be controlled widely by changing the types of organic solvents. For these membranes, FT-IR (for amide binding content), surface morphology, desalination performance, the diffusivity of diamine to the organic phase, and the degree of separation for the active layer (polyamide skin layer) were evaluated using different types of added organic solvents.

## 2. Experimental

### 2.1. Fabrication of a novel RO membrane

Polyamide membranes were fabricated on ultrafiltration polysulfone (PSf) supports with an approximate top-surface diameter of 20–30 nm [13] by interfacial polymerization of 1,3-phenylenediamine (MPD) with 1,3,5-benzenetricarbonyl trichloride (TMC). The detailed process of membrane preparation was as follows [16,17]. First, the PSf supports was placed in an aqueous solution of 2 wt% MPD and 0.15 wt% sodium lauryl sulfate for 2 min, and then the excess of the solution was removed. Subsequently, the polysulfone support was immersed in a hexane solution of 0.1 wt% TMC with 2 wt% co-solvent. In this study, 6 types of solvents, including acetone, ethyl acetate, diethyl ether, toluene, isopropyl alcohol (IPA) and *N,N'*-dimethyl formamide (DMF) were selected and added as co-solvents. After a polymerization reaction of approximately 60 s, the solution of the TMC was poured off, and then the membrane was dried in air for 5–10 min. Finally, the as-prepared membranes were rinsed with deionized (DI) water. In this study, three sheets of membrane were prepared for each preparation condition in order to confirm the repeatability of the RO performances.

### 2.2. Characterization

Different types of co-solvents that were added during formation of the separation active layer by interfacial polymerization reaction were examined using the following procedure for visual observation. Hexane added with 0.1 wt% of TMC and 2 wt% of co-solvent was poured slowly onto an aqueous solution of 2 wt% MPD and 0.15 wt% sodium lauryl sulfate, and the formation of the polyamide layer at the interface was observed by the naked eye and was recorded with a digital photograph.

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