



# Dual layer composite nanofiltration hollow fiber membranes for low-pressure water softening



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## ABSTRACT

Nanofiltration (NF) membrane process has become increasingly attractive due to their unique characteristics to selectively remove specific compounds or ions. The most commonly NF membranes are negatively charged which is unsuitable for hardness removal. Therefore, the development of novel NF membranes with a positively charged skin has become a key issue for low pressure water softening.

In this study, dual layer microporous hollow fiber membranes were fabricated using Torlon poly(amide-imide) (PAI) as the material of the selective outer layer and polyethersulfone (PES) as the material of the porous support inner layer. A positively charged NF-like selective layer was developed by a simple polyelectrolyte cross-linking using polyallylamine (PAAm). The newly developed (PAI–PAAm)–PES dual layer hollow fiber membranes show a salt water permeability of 15.8 L/m<sup>2</sup> h bar and high Mg<sup>2+</sup> and Ca<sup>2+</sup> rejections of 94.2% and 92.3%, respectively, at operating pressure of 2 bar using a 3000 ppm TDS feed solution. This study provides a simple and effective approach to produce positively charged NF hollow fiber membranes for water softening applications with low energy consumption.

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## 1. Introduction

It is well recognized that the presence of certain metal ions, such as calcium, magnesium and other metal cations (e.g. iron (II) manganese (II)), in water creates a variety of problems. The removal of hardness from water, which is referred to as water softening, can be beneficial as it improves the compatibility of water with soap, resolves the esthetic issue, and increases the life expectancy of plumbing due to less residues built up in water pipes, etc. The reduced build-up of scale inside hot water pipes also helps to prevent the loss of heat transfer efficiency in heat exchangers [1,2]. Conventionally, hardness can be removed by lime softening or ion-exchange resins. Lime softening, which is a chemical method to precipitate multivalent metal cations from aqueous solutions, is less attractive as it requires a significant land use and results in the production of waste sludge. Moreover, it is difficult to expand the capacity of the process in response to increased demand [3]. The resins in an ion exchanger contain sodium/potassium, which can be displaced by calcium/magnesium. This results in the capture of calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) and the release of sodium

(Na<sup>+</sup>) until the material becomes saturated. The saturated material is regenerated using a highly concentrated sodium chloride solution. The disadvantages of this process include an overall increase in total dissolved salts in the water as the ion exchanger releases two sodium ions for every one calcium or magnesium ion captured. It also consumes the salt brine that is used for regeneration [4].

In contrast, membranes offer a possible way to solve the above-mentioned problems. Nanofiltration (NF) as a membrane-based separation process has drawn much attention in recent years. This is attributed to their merit features (e.g. low operating pressure, high retentions to multivalent ions and low molecular weight of organic materials, high salts selectivity, etc.) for water softening [2,5], water treatment and waste water reclamation [6–8], separation of salts from dye solutions [9,10] and heavy metal recovery [11–13], etc. An NF membrane process is basically a low pressure reverse osmosis (RO) with pore sizes in a range of about 0.5–5 nm and thus it has flux and solute rejection values between those of ultrafiltration (UF) and RO processes [14–16]. The solute rejection mechanisms of NF membrane process are based on size exclusion (sieving effect) and Donnan exclusion (charge interactions and repulsion) [16].

In the past decades, many attempts have been made in the development of high performance NF membranes both in hollow fiber and flat sheet configurations. Generally, an NF membrane consists of an NF-like selective layer supported by a permeable layer providing necessary mechanical support with the least mass

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transfer resistance. The selective layer can be fabricated by integrally connecting it to the support layer. This method allows simultaneous fabrication of the NF-like skin and the support, though it depends critically on the rate of phase separation which requires a fine dope formulation and precise control of fabrication parameters [17–21]. On the other hand, composite membrane fabrication method is rather attractive as it allows more room to customize and optimize each layer depending on the requirement. The support layer can be made based on the phase inversion method or electrospinning of nanofibers, while several techniques can be used to fabricate the NF-like selective layer.

Thin film composite by interfacial polymerization of polyamide is the most commonly used technique. Commercially available NF membranes such as UTC series from Toray Industries, NF series from Filmtec Corporation, etc., are polyamide-based composite membranes. Specific formula and optimum conditions are needed in order to form a homogeneous covalent bond between the carboxyl group from acyl halides as the organic monomer and the amine group from amine aqueous monomer [22–26]. Despite having high water permeability and good separation performance, however, the polyamide layer is vulnerable to the chemicals used for sterilization (i.e. chlorine). It is thus desirable to improve the stability of NF membranes.

Multilayer polyelectrolyte deposition has been gaining interest as a simple technique to form a thin NF-like skin layer with high selectivity. The thickness of the skin layer, the charge carried by the skin and the charge density can be easily controlled by varying the number of deposited layers, the sequence of polyelectrolyte layers and the molecular structure of polyelectrolytes, respectively [27–29]. However, the membrane charge (zeta potential) and the dissociation of polyelectrolytes which are pH dependent restrict the stability of each layer due to the electrostatic interaction [30].

Surface grafting such as ultra-violet (UV) induced grafting grows a new polymer on the membrane surface modifying the properties of a base polymer. In spite of its simplicity and low cost [31–33], only photosensitive polymers can be used as the support materials, otherwise a photoinitiator is needed in order to perform the reaction. Moreover, UV, which possesses high energy at low wavelength, may damage the membrane.

Surface modification by chemical cross-linking exploits the unique feature of reactive groups in some membrane materials. It offers simplicity and flexibility in fabricating an NF-like skin. For example, the cross-linking reaction between an asymmetric microporous hollow fiber membrane made from Torlon poly(amide-imide) (PAI) material and polyethylenimine (PEI) could be carried out to produce hollow fiber membranes with a positively charged NF-like selective layer [34]. It was reported that the water permeability of the modified membrane decreased and the isoelectric point of the membrane surface changed after cross-linking. However, for the cross-linking modification through immersion, the cross-linking solution was able to penetrate inside the membrane. Consequently, the cross-linking reaction was performed not only on the surface but also inside the support and hence, the membrane resistance increased [34].

Dual layer hollow fiber membrane is made by a novel fabrication technique involving a single-step simultaneous extrusion of two different polymer solutions to develop two layers connected to each other by using a triple orifice spinneret [35,36]. The drawback of the entire membrane cross-linking can be overcome by utilizing a reactive polymer as the selective layer and a non-reactive polymer as the support layer. As such, the substrate of the membrane remains intact and thus, the increase in membrane resistance due to the cross-linking can be avoided.

The current study describes a development of novel composite dual layer NF hollow fiber membranes by co-extrusion method

using a triple orifice spinneret, followed by a simple chemical treatment for water softening applications at low pressure. The porous inner layer was made of polyethersulfone (PES) that provides mechanical support and low trans-membrane resistance. The selective outer layer was constructed from cross-linked Torlon® polyamide-imide (PAI) membrane, which presents positive charges on the surface of the hollow fiber. The performance of positively charged dual layer NF hollow fiber membranes was then tested for the removal of multivalent cations in water softening process using mixed salts solutions at low pressure (<2 bar).

## 2. Experimental

### 2.1. Materials

Dual layer hollow fiber membranes were made from Torlon® 4000T-MV (copolymer of amide and imide) (PAI, Solvay Advanced Polymers, Alpharetta GA) and Gafone™ polyethersulfone (PES, Solvay Advanced Polymers, Gujarat) as the outer and inner layer materials, respectively. N-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4) from Merck Chemicals, Singapore was used as a solvent. Lithium chloride (LiCl, anhydrous, CAS#7447-41-8, Merck) and polyethylene glycol 400 (PEG400, CAS#25322-68-3, Merck) were used as an additive in both the outer and inner dope solutions. Glycerol (85%, Merck) was used to post-treat the membrane for storage purposes. Purified water by a Milli-Q system (18 MΩ cm) was used in preparing all the solutions and as the bore fluid. Tap water was used as the external coagulant. Polyallylamine (PAAm, molecular weight of 15, 17, 65 kDa) (Polysciences) was used as the cross-linker. Sodium hypochlorite (NaOCl, Merck) was used to observe the chlorine resistance of the membranes. Magnesium chloride (MgCl<sub>2</sub>), calcium chloride (CaCl<sub>2</sub>), and sodium chloride (NaCl) were purchased from Merck (analytical grade). All chemicals were used without further purification.

### 2.2. Fabrication of polyamide-imide (PAI)–polyethersulfone (PES) dual layer UF hollow fiber membranes

PAI–PES dual layer UF hollow fiber membranes were fabricated by dry jet-wet spinning technique based on non-solvent induced phase separation. Details can be found elsewhere [35]. Briefly, the polymers (PAI and PES) and the additives (LiCl, PEG 400, and water) were completely dissolved in NMP in two different jacket flasks equipped with an overhead stirrer connected to a circulator bath at 70 °C. The detailed compositions of the polymer dope solutions are shown in Table 1. The solutions were then filtered and degassed at

**Table 1**  
Dope composition and spinning conditions.

Outer dope composition (wt.%)	PAI/LiCl/PEG400/H <sub>2</sub> O/NMP 16/3/3/3/75
Inner dope composition (wt.%)	PES/LiCl/PEG400/NMP 15/5/10/70
Outer dope flow rate (g/min)	2
Inner dope flow rate (g/min)	6
Coagulant	Water
Coagulant temperature (°C)	23
Bore fluid composition	Water
Bore fluid flow rate (mL/min)	8
Take up speed (m/min)	5.68
Air gap (cm)	0.5
Ambient temperature (°C)	23
Room humidity (%)	80

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