

Preparation and characterization of positively charged polyamide composite nanofiltration hollow fiber membrane for lithium and magnesium separation



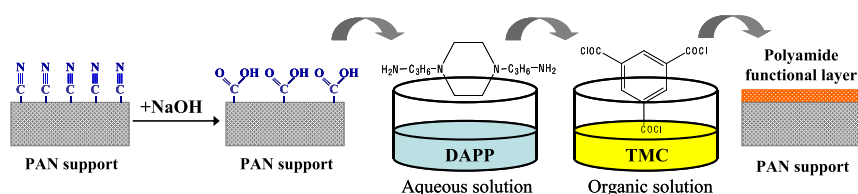
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HIGHLIGHTS

- A positively charged NF membrane was prepared by interfacial polymerization.
- The membrane performance was related to DAPP concentration rather than that of TMC.
- The surface of resultant membrane was positively charged at pH < 9.5.
- The difference between the rejection rates of MgCl₂ and LiCl reached to 47.5%.
- The mass ratio of Mg²⁺/Li⁺ decreased from initial 20:1 to 7.7:1 after NF.

GRAPHICAL ABSTRACT



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ABSTRACT

A positively charged polyamide composite nanofiltration (NF) hollow fiber membrane for lithium and magnesium separation was fabricated by the interfacial polymerization of 1,4-Bis(3-aminopropyl)piperazine (DAPP) and trimesoyl chloride (TMC) on the polyacrylonitrile (PAN) ultrafiltration hollow fiber membrane. The chemical structure, morphology and surface charge of the composite membrane were characterized by using ATR-FTIR, XPS, SEM, AFM and zeta potential analyzer. The performance of the composite membrane was tested with various salts in aqueous solution (2000 ppm) at the operating pressure of 0.3 MPa. The results showed that the membrane performance was related to the changes of the monomer content in the aqueous phase rather than that in the organic phase. Furthermore, the salt rejection order of the membrane was MgCl₂ > MgSO₄ > NaCl ≥ LiCl. The difference between the rejections of MgCl₂ and LiCl reached to 47.5%. The zeta potential measurements indicated that the surface of the resultant membrane was positively charged at pH values below 9.5. Moreover, the mass ratio of Mg²⁺/Li⁺ decreased from initial 20:1 in the feed of 2.0 g/L MgCl₂ and LiCl mixture to 7.7:1 in the permeate after the filtration by the composite membrane.

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1. Introduction

Nanofiltration (NF) is a pressure driven membrane separation technology with characteristics between ultrafiltration (UF) and reverse osmosis (RO). NF membrane has separation capability for mono- and multivalent ions, and offers low operating pressures and operating

costs [1]. Hence, it has been widely applied for water softening, wastewater reclamation, dyes and biochemical substances separation [2–4].

One attractive application for NF membranes is the recovery of lithium from lithium-containing waters, especially in the mixed lithium–magnesium solutions [5,6]. This is because lithium, as one of the significant and rare elements on earth, is naturally coexisting with many other minerals such as magnesium in brine or seawater. However, the selectively separation behavior of NF membrane not only relies on size exclusion, but also is mainly governed by the Donnan exclusion theory

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[7]. Thus, the positively charged NF membranes are more efficient for the separation and recovery of multi-valent cations such as Mg^{2+} and Ca^{2+} removal. This property is particularly important for the separation between Li^+ and Mg^{2+} . However, commercially available NF membranes are mostly negatively charged [8]. Therefore, the preparation of positively charged NF membranes is of great importance for the efficient lithium and magnesium separation.

In recent years, many researchers have devoted to the preparation and characterization of positively charged NF membranes using interfacial polymerization, chemical crosslinking and UV photografting [9–14]. However, these studies only focus on the preparation of positively charged flat-sheet NF membrane. Compared to the flat-sheet configuration, the membranes in hollow fiber configuration have obvious advantages such as high packing density, lower energy and maintenance cost, and so on. At present, there is a growing interest to develop positively charged NF hollow fiber membranes. For instance, Zheng et al. [15] developed a positively charged thin-film composite NF hollow fiber membranes by the dip-coating method using polypropylene hollow fiber microfiltration membrane as support, polyvinyl alcohol (PVA) and polyquaternium-10 as coating materials, and glutaraldehyde as cross-linking agent. The resultant NF membrane had a molecular weight cut-off of about 650 Da and a pure water flux of 8.6 L/(m^2 h bar). Wang et al. [16] successfully fabricated a positively charged NF hollow fiber membrane by the phase inversion method. The asymmetric microporous hollow fibers made of polyamide-imide (PAI) material were used as the porous substrate, and followed by polyelectrolyte post-treatment using polyethyleneimine (PEI). Wang et al. [17] further prepared a thin-film selective layer of the composite hollow fiber membrane formed on the inner surface of a polyethersulfone (PES) UF membrane substrate with branched PEI and trimesoylchloride (TMC) employed as the monomers in aqueous and organic phases, respectively. On the basis of above studies, Wang and co-workers [18] further described a development of novel composite dual layer positively charged NF hollow fiber membranes by co-extrusion method. The PES and PAI were used as the materials of the porous support inner layer and the selective outer layer, respectively. The positively charged NF-like selective layer was developed by a simple polyelectrolyte cross-linking using polyallylamine (PAAm). In order to provide insightful guidelines for developing high-performance positively charged NF membrane, Chung and co-workers [19,20] investigated the influence of the PEI molecular weight and structure of membrane substrate on the properties of positively charged NF membranes, respectively. The results showed that NF membrane modified by a high molecular weight PEI of 60 kg/mol exhibited the higher rejection of ciprofloxacin above 90%, the lower fouling tendency compared to that modified by low molecular weight PEI of 2 kg/mol. And with the decrease of the pore size of membrane substrates, the pore size of cross-linked NF membranes first decreased, and then increased.

Although these studies have provided novel preparation method for positively charged NF hollow fiber membrane, only few studies focus on the application of interfacial polymerization technique. So far, the interfacial polymerization is the most widely commercial technique for the preparation of NF membranes owing to the high-efficiency and self-inhibition of reaction [21]. Moreover, the structure of monomers has a great influence on the performance of the membranes in the interfacial polymerization process. The piperazine as well as its derivatives is the most widely-used aqueous phase monomer [22,23]. Among the different piperazine derivatives, 1,4-bis(3-aminopropyl)-piperazine (DAPP) has a similar molecular structure to piperazine except for the presence of two aminopropyl groups bounded to the N atoms of the ring. Thus, DAPP was successfully used for the preparation of positively charged NF membranes by interfacial polymerization technique on the PEI flat-sheet membrane [23].

The aim of the present study is to prepare a novel positively charged NF hollow fiber membrane for lithium and magnesium separation by the interfacial polymerization of DAPP and TMC on the polyacrylonitrile

(PAN) support membrane. The effects of the reaction time of polymerization and the concentration of reactive monomers on the performance of the composite membrane were investigated. The chemical structure, morphology and surface charge of the composite membrane were characterized by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), atom force microscopy (AFM) and zeta potential analyzer, respectively.

2. Materials and methods

2.1. Materials and reagents

Polyacrylonitrile (PAN) UF hollow fiber membranes provided by Tianjin Aisheng Membrane Filtration Co. Ltd. (Tianjin, China) were used as the support membrane in this study. The detailed specifications of the PAN hollow fibers including pure water permeability (L_p), molar weight cut-off (MWCO), and inner and outer diameters (d_{in} and d_{out}) were presented in Table 1. In addition, a commercial NF membrane (NF-90) from Filmtec (DOW, USA) was used to compare the separation performance of the Li^+/Mg^{2+} mixture with the composite NF hollow fiber developed in the current work.

Trimesoyl chloride (TMC) (99%, CAS#4422-95-1, J&K), 1,4-Bis(3-aminopropyl) piperazine (DAPP) (98%, CAS#7209-38-3, TCI), dodecyl sulfonic acid sodium salt (DDS) (Guangfu Fine Chemical Co., Ltd., China), dimethyl sulfoxide (DMSO) (Kermel Chemical Reagent Co., Ltd., China), triethylamine (TEA) (Kermel Chemical Reagent Co., Ltd., China) and cyclohexane (Kermel Chemical Reagent Co., Ltd., China) were used for interfacial polymerization as received without further purification. The analytical grade sodium hydroxide (NaOH) (Kermel Chemical Reagent Co., Ltd., China) was used for the hydrolysis modification of PAN ultrafiltration membranes.

The analytical grade polyethylene glycol (PEG) with molecular weights of 200, 300, 400, 600 and 1000 (Kermel Chemical Reagent Co., Ltd., China) was used as the model solutes to determine the molecular weight cut-off (MWCO) and mean pore size of the composite NF hollow fiber membranes.

Several analytical grade inorganic salts including magnesium chloride ($MgCl_2$, anhydrous), sodium chloride (NaCl), lithium chloride ($LiCl$, anhydrous) and magnesium sulfate ($MgSO_4$, anhydrous) purchased from Tianjin Kermel Chemical Reagent Co., Ltd. were used to prepare various feed solutions. Deionized water was utilized for the preparation of aqueous solutions.

2.2. Preparation of composite NF hollow fiber membranes

PAN hollow fiber membrane was hydrolyzed by immersing into 1.0 M NaOH solution at 60 °C for 15 min. It can be readily functionalized to generate carboxyl groups. After hydrolysis, the membranes were rinsed with deionized water until the pH value of the rinsed water reached approximately 7.0. The ion exchange capacity (IEC) could be used as an important value to characterize hydrolysis degree of the hydrolyzed PAN membrane [24]. In this study, the IEC of the hydrolyzed PAN membrane is 0.347 mmol/g after hydrolysis. Subsequently, the active skin layer of the composite NF hollow fiber membrane was prepared using interfacial polymerization technology. First, the modified PAN hollow fiber membrane was immersed in the DAPP aqueous

Table 1
Characteristics of the PAN support hollow fibers.

Parameters	Value
Pure water permeability (L_p), L/(m^2 h bar)	40–50
Molar weight cut-off (MWCO), kDa	20–50
Inner diameter (d_{in}), mm	0.85
Outer diameter (d_{out}), mm	1.30

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