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Positively charged capillary nanofiltration membrane with high rejection for Mg2 + and Ca2 + and good separation for Mg2 + and Li +

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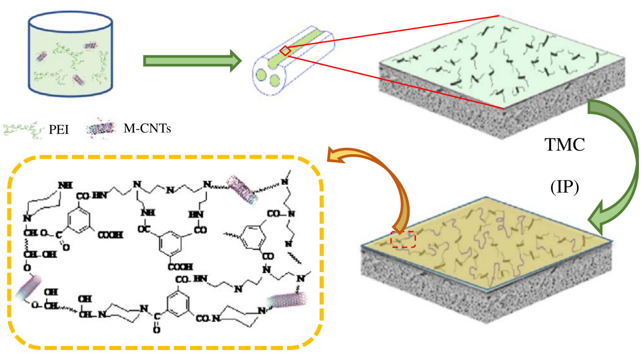
GRAPHICAL ABSTRACT



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ABSTRACT

High water permeability and good separation property are greatly desired in water production due to energy concerns. To explore nanofiltration (NF) membrane with high permeability for cations separation, a positively charged NF membrane was fabricated via interfacial polymerization using polyethersulfone (PES) three-channel capillary ultrafiltration (UF) membrane as substrate, polyethyleneimine (PEI) as the aqueous precursor. The NF membrane preparation conditions were optimized. To enhance the permeability of the prepared NF membrane, modified hydroxyl contained multi-walled carbon nanotubes (MWCNTs-OH), grafting with piperazine (PIP), were utilized. The resultant NF membrane showed increased water flux from 20.8 $L{\cdot}m^{-2}{\cdot}h^{-1}$ to 56.1 $L{\cdot}m^{-2}{\cdot}h^{-1}$ at 4 bar after adding 0.01 wt% modified MWCNTs-OH in aqueous solution. Interestingly, $MgCl_2$ rejection of the membrane also increased from 94.2% to 96.9%. The positively charged NF membrane exhibited above 97% rejection for divalent cations (Mg^{2+} and Ca^{2+}) and low rejection (< 70%) for monovalent cations (Na^+ and Li^+), and it also showed long durability and good separation for Mg^{2+} and Li^+ when the membrane was used to separate mixed salts solution simulated the composition of salt lake brine. The fabricated membrane would have potential for effective water softening and for reclamation of lithium from brine or seawater with high Mg^{2+}/Li^+ ratio.

1. Introduction

Freshwater and energy scarcity become worldwide problems due to the rapid development of global industry, the overgrowth of population and the pollution of available water resources. Membrane technology, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse

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osmosis (RO) or forward osmosis (FO) and membrane distillation (MD), are extensively adopted for water treatment in the past decades [1–4]. In which, NF process has widespread applications in desalination, water softening and separation, and concentration of solutes, etc. [5–7]. Many researchers focus on developing and constructing composite NF membrane with high performance and long life-span. Nevertheless, most of the composite NF membranes are negatively charge currently, and NF membrane with negative charge has better rejection performance for anions according to Donnan effect [8]. However, the separation effect is unsatisfactory when these NF membranes are utilized in dealing with positively charged solutes such as cationic dyes and metal ions from electroplating wastewater. Thus, it is essential to fabricate NF membrane with positive charge.

Various approaches have been used to fabricate the positively charged active layer on substrate surface, such as interfacial polymerization (IP) [9,10], chemical cross-linking [11,12], layer-by-layer assembly [13] and UV-induced photografting polymerization etc. [5]. IP has been a dominating method for fabricating composite NF membrane because the performance of the obtained membrane could be fine-tuned by varying the preparation conditions, e.g. the concentration of monomers, immersion time, reaction time and also the heat treatment temperature [14,15]. For the monomers, polyethyleneimine (PEI), a positively charged polymer, has been broadly employed to fabricate positively charged composite NF membranes [16–19]. However, the permeation of the composite NF membrane prepared using PEI should be improved considering energy efficiency [18]. Therefore, many efforts have been attempted to enhance the water permeability of this positively charge NF membrane through introducing a surfactant or co-reactant in the aqueous phase. Fang et al. added sodium dodecyl sulfate (SDS) in PEI aqueous and investigated the additive amount on the permeation and salt rejection of NF membrane [20]. The membrane prepared under optimized conditions shows pure water permeability and $MgCl_2$ rejection of 16.5 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ and 96.5%, respectively. Bera et al. used dextran (Dex) conjugate of PEI (PEI-Dex) as the co-monomer in PEI aqueous solution to prepare composite NF membrane via IP [21], and the pure water permeate flux of membrane improved significantly without sacrifice of salt rejection. In addition, PIP was also employed as co-monomer with PEI to fabricate high-permeable NF membrane [22].

Carbon nanotubes (CNTs) are promising materials for the preparation of nanohybrids and nanocomposites with polymers [23]. At present, MWCNTs are widely used in improving the permeation performance of NF membrane for they can afford transport channels for water molecular [24]. However, the pristine MWCNTs cannot be used directly because of their poor dispersion. Many efforts have been tried to improve the dispersion of MWCNTs by introducing hydrophilic groups on the wall edge of MWCNTs. Liu et al. modified CNTs with hydroxyl and applied them in biomedical area [25]. Chan et al. synthesized zwitterionic CNTs and incorporated them into polyamide thin film composite membranes to improve the permselectivity [26]. The permeation flux of membrane increased by approximately three-fold after introducing zwitterionic CNTs. Zhao et al. adopted poly(dopamine) (PDA) to modified MWCNTs, and the PDA-MWCNTs show admirable dispersion in water [27]. Moreover, even a little amount of PDA-MWCNTs can enhance membrane permeability greatly. In addition, sulfonated MWCNTs were synthesized from hydroxyl-functionalized multiwall carbon nanotube for the improvement of membrane water flux [28]. Although there are a number of publications using different CNTs to improve the permeability of membranes, to the best of our knowledge, there are no reports about the modification of hydroxyl contained MWCNTs with PIP.

Recent years, more and more researchers focus on constructing composite NF membrane with hollow fibers as substrate [8,29,30]. The selective layer can be located at both the shell side and the lumen side of hollow fibers. The hollow fiber NF membrane with outer selective layer would have larger surface area, but the composite layer is vulnerable during module fabrication and nanofiltration process [31]. While the effective area is relatively small for NF membrane with inner selective layer. Capillary NF membrane with inner selective layer does not have the problems aforementioned [32]. In this work, a positively charged NF membrane was fabricated via IP using PES three-channel UF capillary membrane as substrate, PEI and TMC as aqueous precursor and organic monomer, respectively. The membrane preparation conditions have been systematically investigated. To improve the permeation of the prepared NF membrane, MWCNTs-OH were modified via grafting with PIP, the characteristics of the modified MWCNTs were analyzed by FTIR, TGA, TEM. Then the modified MWCNTs-OH were incorporated into the selective layer by adding them in the aqueous solution. Finally, the morphology and the permeation and rejection performance of the resultant membrane were observed and determined, respectively.

2. Experimental

2.1. Materials and chemicals

Polyethersulfone (PES) capillary UF membrane with three-channel was prepared via non-solvent phase inversion method as reported in our previous work [32]. The inner diameter and outer diameter of this capillary membrane are about 1.39 ± 0.03 mm and 3.92 ± 0.08 mm, respectively, and the pure water permeability of the PES membrane is 161 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$. The hydroxyl-functionalized MWCNTs (purity > 95 wt%, –OH content 5.58%, outer diameter < 8 nm) were purchased from Shenzhen Nanotech Port Co. Ltd. Polyethyleneimine (PEI) with a molecular weight of 70,000 Da was provided from Aladdin Reagent Co., LLC, Shanghai, China. Trimesoyl chloride (TMC, ≥ 98%), the active monomer in organic phase, was purchased from Qingdao Benzo Chemical Co., China. Piperazine (PIP, GR) was obtained from Sigma-Aldrich. Glutaraldehyde (GA), n-Hexane, PEG 400 (AR), PEG 600 (AR), sucrose (AR), raffinose (AR), glucose (AR), sodium sulfate (Na_2SO_4, AR), magnesium sulfate ($MgSO_4$, AR), magnesium chloride ($MgCl_2$, AR), calcium chloride ($CaCl_2$, AR), sodium chloride (NaCl, AR), lithium chloride (LiCl, AR) and lithium sulfate (Li_2SO_4, AR) were provided from Sinopharm Chemical Reagent Co. Ltd. (China).

2.2. Modification of MWCNTs

The hydroxyl-functionalized MWCNTs were modified via grafting with PIP using glutaraldehyde (GA) as the cross-linking agent. The modification process is described as follows: MWCNTs-OH powder (50 mg) was added into a conical flask with 100 mL pure water, and dispersed by 5 min sonication (KQ100DB, 100 W, Kunshan Ultrasonic Instruments). Subsequently, PIP (50 mg), 25% GA (0.5 g) and 0.1 mL hydrochloric acid (pH = 2) were added, then the mixture was strongly stirred in water bath at 50 °C for 12 h. Afterward, the mixture was centrifuged (10 min, 4000 rpm) to eliminate assembled residues. Finally, the modified MWCNTs powder was collected by filtration supernatant (washed with DI water), and dried at 40 °C under vacuum for 24 h. The hydroxy contained MWCNTs and the modified MWCNTs were denoted as CNTs and M-CNTs respectively in this paper. The diagram of the grafting reaction is shown in Fig. 1.

2.3. Membrane fabrication

The NF membranes with inner selective layer were fabricated via IP, and the schematic preparation of the NF membranes is shown in Fig. 2. Prior to IP, the PES capillary membrane was first sealed in a module using epoxy resin, and each module contained one piece of membrane with an effective length of 50 cm. As described in our previous work [32], the fabrication procedure started with one membrane module that was held vertically. PEI contained aqueous solution was guided inside the PES substrate with a rotary pump at a flow rate of 0.3 L/min. Excess