Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Chelating polymer modified P84 nanofiltration (NF) hollow fiber membranes for high efficient heavy metal removal

Jie Gao, Shi-Peng Sun, Wen-Ping Zhu, Tai-Shung Chung *

Department of Chemical & Biomolecular Engineering, National University of Singapore, 10 Kent Ridge, Crescent, Singapore 119260, Singapore

ARTICLE INFO

Article history:
Received 9 April 2014
Received in revised form
30 May 2014
Accepted 4 June 2014
Available online 21 June 2014

Keywords:
P84 polyimide
Hyperbranched polyethyleneimine
Cheating polymer
Nanofiltration
Hollow fiber membrane
Heavy metal ions

ABSTRACT

High performance nanofiltration (NF) membranes for heavy metal removal have been molecularly designed by adsorption of chelating polymers containing negatively charged functional groups such as poly (acrylic acid-co-maleic acid) (PAM), poly (acrylic acid) (PAA) and poly (dimethylamine-co-epichlorohydrin-co-ethylenediamine) (PDMED) on the positively charged polyethyleneimine (PEI) cross-linked P84 hollow fiber substrates. Not only do these chelating polymers change the membrane surface charge and pore size, but also provide an extra mean to remove heavy metal ions through adsorption in addition to traditional steric effect and Donnan exclusion. The adsorbed membranes have comparable water permeability and superior rejections to heavy metals, for instance, $Pb(NO_3)_2$, $CuSO_4$, $NiCl_2$, $CdCl_2$, $ZnCl_2$, $Na_2Cr_2O_7$ and Na_2HAsO_4, with rejections higher than 98%. The membranes also display excellent rejections to mixed ions with rejections more than 99%. The newly developed membranes show reasonably stability during 60-h tests as well as multiple washes.

1. Introduction

Water scarcity is a severe worldwide problem to be solved urgently (Vorosmarty et al., 2010). Therefore, many efforts have been made to safely discharge and reuse the reclaimed wastewater. One of the major contaminates in industrial wastewater is heavy metals. Heavy metals have high toxicity. Even extremely low concentrations of heavy metals in human body can disrupt the body's normal physiological activities. They can also accumulate in certain organs in human body, resulting in pathological changes ranging from odd diseases (such as water Minamata disease, bone disease, etc.) to even death (Athar and Vohora, 2001). Thus, heavy metal pollution has drawn increasing attentions throughout the world. Many countries have set-up more and more stringent standards to control heavy metal concentrations in discharged water (Xu and Zhao, 2005), which opens huge opportunities for water treatment technologies.

Compared to conventional technologies, membrane separation has many advantages such as cost effective, energy saving, no phase change, environmental friendly and high removal efficiency (Deon et al., 2013; Escobar and Van der Bruggen, 2011). Since the majority of heavy metal ions are

* *Corresponding author*. Tel.: +65 6516 6645; fax: +65 6779 1936.
E-mail address: chencts@nus.edu.sg (T.-S. Chung).
http://dx.doi.org/10.1016/j.watres.2014.06.006
0043-1354/

multivalent, one of the promising membrane filtration methods to treat heavy metals is nanofiltration (NF), owing to its unique rejection mechanisms - steric effect and Donnan exclusion (Chiang et al., 2009; Zhou et al., 2009). Compared to reverse osmosis (RO), NF requires a lower pressure while giving a higher flux without much compromise in rejection (Abu Qdais and Moussa, 2004).

Recently, there is a growing interest on the positively charged polyethyleneimine (PEI) cross-linked polyimide NF membrane due to its good thermal, mechanical and chemical stabilities as well as excellent rejections to multivalent cations (Cheng et al., 2012; Economy et al., 2009). However, the rejection of the highly positively charged membrane to multivalent anions is not so promising, which limits its application in the field of heavy metal removal. Thus, the purposes of the study are to (1) modify the surface charge of the NF membrane to neutral or slightly charged so that the membrane is capable of removing a wide range of heavy metals and (2) introduce the adsorption mechanism other than size exclusion and charge repulsion to improve the rejection efficiency of the membrane.

To our best knowledge, the concept of adsorbing polyelectrolyte chelating polymers onto NF membranes for heavy metal removal has not been proposed before. These polymers, such as poly (acrylic acid) (PAA), poly (acrylic acid-co-maleic acid) (PAM) and poly (dimethylamine-co-epichlorohydrin-co-ethylenediamine) (PDMED) (structures shown in Fig. S1 of the supporting material), are chosen because (1) the negatively charged functional groups on the polymers can enhance the adsorption of the polymers onto the oppositely charged membrane (Butt et al., 2003); (2) the induced negatively charged functional groups from these polymers can change the membrane surface charge, making it more negatively charged at high pH (Childress and Elimelech, 1996); (3) the adsorption of polyelectrolyte, such as PAA, has been reported to have the antifouling function in the previous literature (Ba et al., 2010); (4) chelating polymers are able to absorb heavy metal ions, which provides additional means to remove heavy metal ions (Van der Bruggen et al., 2004); (5) the polyelectrolyte coating may decrease the membrane pore size and enhance the rejection (Ba et al., 2010); and (6) the adsorbed coating is simple and can be customized according to different applications.

To effectively coat the polyelectrolytes and provide mechanically strong support under high pressure operations, a substrate with a macrovoid-free structure and finely tuned pore size was formed by P84 (copolyimide of 3,3',4,4'-benzophenone tetracarboxylic dianhydride with 80% toluenediisocynate and 20% methyl phenylene diisocyanate (BTDA-TDI/MDI)) because its excellent thermal and chemical stability (Toh et al., 2007). A hyperbranched PEI with a molecular weight of 60 K $gmol^{-1}$ was used for cross-linking with P84 before adsorption to induce more amine groups on the membrane surface and enhance the membrane performance after cross-linking (Albrecht et al., 2003; Sun et al., 2011). After all modifications, heavy metal salts, including $Pb(NO_3)_2$, $CuSO_4$, $NiCl_2$, $CdCl_2$, $ZnCl_2$, $Na_2Cr_2O_7$ and Na_2HAsO_4 were used to test the performance of the chelating polymer adsorbed membranes. The newly formed membranes may open opportunities of new NF membranes in wastewater treatment.

2. Experimental

2.1. Materials

P84 powders (molecular weight (MW) of 153 KDa, HP polymer GmbH, Australia) were used to form the hollow fiber substrates. The solvent and non-solvent to prepare the dope solution were n-methyl-2-pyrrolidine (NMP, 99.5%, Merck, Germany) and methanol (99.8%, Fisher Chemical, UK), respectively. The cross-linking agent, PEI (MW of 60 K $gmol^{-1}$, 50%), was purchased from Acro (USA). Isopropanol (99.98%, Fisher Chemical, UK) and deionized water were used to dissolve PEI. Chelating polymers, such as PAA 2K (MW of 2 K $gmol^{-1}$, 50%), PAA 100K (MW of 100K $gmol^{-1}$, 35%), PAA 250K (MW of 250 K $gmol^{-1}$, 35%), PAM (MW of 3 K $gmol^{-1}$, 50%) and PDMED (MW of 75 K $gmol^{-1}$, 50%), were acquired from Aldrich. To test the heavy metal ion rejections of the PEI cross-linked or polyelectrolyte adsorbed membranes, $Pb(NO_3)_2$ (99%), $CuSO_4 \cdot 5H_2O$ (>99%), $NiCl_2$ (98%), $CdCl_2$, $ZnCl_2$ (98.5%), $Na_2Cr_2O_7 \cdot 2H_2O$ (99%) and $Na_2HAsO_4 \cdot 7H_2O$ (>98%) were purchased from Acros. They were dissolved in DI water to form heavy metal solutions with 300 ppm or 1000 ppm concentrations. HCl (37%) and NaOH (>99%, Emsure®, Merck, Germany) were diluted and used to adjust the pH of salt solutions as well as to test the membrane stability.

2.2. Fabrication of the outer selective hollow fiber substrate

The spinning procedure is similar to our previous work (Gao et al., 2014). In short, the dope solution was prepared with vacuum dried P84 powders and was allowed to degas for 12 h after it was well-mixed. The bore fluid and the dope solution were purged by two different pumps at certain flow rates and met at the outlet of the spinneret. The mixture then passed through a certain air gap before entering the coagulant bath for phase separation and getting stretched by a take-up unit. The fibers were subsequently cut and transferred to a water basin to complete the phase inversion. After that, the fibers were immersed in a 50 wt% glycerol aqueous solution for 2 days and then air-dried. The formulations of the dope solution and the bore fluid, together with the spinning conditions, are summarized in Table 1. Hollow fiber modules consisting of 20 fibers with an effective length of 14 cm were prepared for all the experiments.

2.3. Modification of the as-spun membrane

A cross-flow set-up as described by Sun et al. (Sun et al., 2011) was used to achieve the cross-linking modification between PEI and the outer surface of P84 hollow fiber substrate. The cross-linking solution was formed by dissolving 1 wt% of PEI in a 50 wt% isopropanol aqueous solution. The solution was circulated in the shell side of the membrane substrate at 70 °C and 400 ml/min for 1 h. After that, the module was rinsed with DI water at 1 bar to remove the unreacted residuals. The rejection of the cross-linked membrane to $MgCl_2$ was then tested to ensure the cross-linking was efficient and consistent. The adsorptions of various polyelectrolytes were then