Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.23197

129 (2018) 304–308
October

Removal of lead ions using polyamide hollow fiber composite nanofiltration membrane containing crown ether

Xinyu Zhao, Baoxin Hu, Yao Shi, Yingbo Chen*, Dongqing Liu, Hong Chen, Yufeng Zhang

School of Materials Science and Engineering, State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, China, emails: chenyingbo@tjpu.edu.cn (Y. Chen), 445877006@qq.com (X. Zhao), 2811921345@qq.com (B. Hu), 2569308427@qq.com (Y. Shi), liudongqing@tjpu.edu.cn (D. Liu), 1424247992@qq.com (H. Chen), zyf9182@tjpu.edu.cn (Y. Zhang)

Received 7 August 2017; Accepted 16 May 2018

ABSTRACT

Hollow fiber composite nanofiltration membrane containing 4-aminobenzene 18-crown-6 was prepared through interfacial polymerization by using polysulfone hollow fiber ultrafiltration membrane as support, piperazine, triethylamine aqueous solution as aqueous phase, trimesoyl chloride/*n*-hexane solution as organic phase. The hollow fiber composite nanofiltration membrane was characterized by using scanning electron microscopy, infrared spectroscopy, and water contact angle measurement. Removal of lead ions of the composite nanofiltration membrane was discussed. The result showed that the hollow fiber composite nanofiltration membrane containing 4-aminobenzene 18-crown-6 has transmembrane flux of 3.87 ± 0.62 $L\cdot m^{-2}\cdot h^{-1}$, and lead rejection of 97.15% ± 0.41% by using 50 mg/L lead nitrate solution as feed and tested under 0.6 MPa. The lead rejection of the membrane without crown ether was 60.78% ± 6.34% and transmembrane flux was 4.24 ± 0.20 $L\cdot m^{-2}\cdot h^{-1}$. We found that the lead rejection of the membrane containing crown ether increased 59.8% and transmembrane flux declined slightly.

Keywords: Interfacial polymerization; Nanofiltration; Lead ions; 4-aminobenzene 18-crown-6

---

1. Introduction

Nanofiltration membrane, with a pore size around one nanometer, can be used to remove divalent or higher valent ions and low molecular weight organic pollutants, which made it widely apply to chemical engineering, electronics industry, food processing, and environmental protection [1]. Composite nanofiltration membrane prepared by interfacial polymerization has been the main trend of nanofiltration membrane due to its advantages of low operating pressure, high flux, high separation selectivity, and better antifouling property [2].

At present, treatment processes of lead ions in waste water included chemical precipitation, ion exchange, absorption, electrolysis, and liquid membrane [3]. Among which, chemical precipitation has effective treatment, although it is hard to deal with plenty of lead salt sludge, which is ease to cause secondary pollution. Furthermore, this method has disadvantages of large floor area, small handing capacity, and worse selectivity. Ion exchange method takes the advantages of small floor area, convenient manage, high rate of removal of lead ions, and no secondary pollution to environment. However, the investment is rather high; and regeneration of ion exchange resin is usually difficult. Absorption method has characteristic of high lead removal efficiency, moderate cost, without causing secondary pollution, thus has good use prospect, especially after modifying some adsorbents. Electrolytic process is restricted to high concentration of lead

---

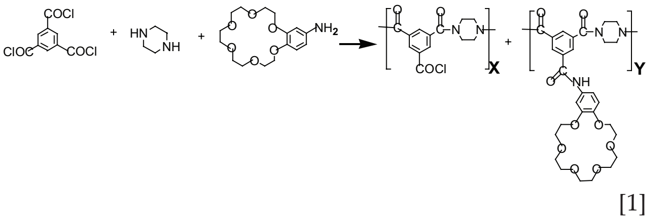
* Corresponding author.

Presented at 2017 Qingdao International Water Congress, June 27–30, 2017, Qingdao, China.

effluent. When electrolysis occurs in dilute solution, due to concentration polarization, the current efficiency is not high, thus difficult to realize purification deeply. Liquid membrane has double effects, both refining water and enriching and recycling metal ions. However, high difficulty in liquid membrane technology impedes its industrialization [4].

Crown ethers are compounds with cyclic structure of multiple ethoxy groups. They can complex with positive ions, especially alkali metal ions; and upon to the size of cycle and the difference of substituent groups on the cycle, they can selectively combine with metal ions with different diameters [5,6]. 18-crown-6 ether was proved to coordinate with lead ions perfectly, due to the specific interaction between 18-crown-6 and lead ions [7]. For example, Małgorzata and Longina [8] has prepared ionic recognition and separation membrane for lead ions by grafting 18-crown-6 ether groups to polymers.

In this study, crown ether groups were incorporated in PA composite nanofiltration membrane by the reaction of 4-aminobenzene 18-crown-6 ether with trimesoyl chloride (TMC) during interfacial polymerization (Reaction [1]). The composite nanofiltration membrane containing 4-aminobenzene 18-crown-6 ether showed higher rejection to lead nitrate due to the specific interaction between 18-crown-6 ether and lead ions.



[1]

2. Experiment part

2.1. Materials

Polysulfone hollow fiber ultrafiltration membrane (PSF, Tianjin Motimo Membrane Technology Ltd. Co.); epoxy resin (modified acrylate cementing compound) was purchased from Liaoning Fushun GOOD BROTHERS new material Ltd. Co. (Liaoning Province, China); piperazine (PIP) was purchased from Tianjin Kemiou Chemical Reagent Ltd. Co. (Tianjin, China); triethylamine was purchased from Tianjin Xingfu Fine Chemical Engineering Research Laboratory; TMC, *n*-hexane were purchased from Tianjin Fengchuan Chemical Reagent Ltd. Co. (Tianjin, China); 4-aminobenzene 18-crown-6 and lead nitrate were purchased from J&K Chemical Ltd. Co (Shanghai, China).

2.2. Preparation of the hollow fiber composite nanofiltration membrane

Polysulfone hollow fiber ultrafiltration membrane (15 cm) was immersed in pure water for 10 h. After air dried the membrane, it was sealed both ends with epoxy resin. Then it was put in aqueous phase (2 w/v % PIP, 1 w/v % triethylamine) for 5 min. Excess aqueous phase was removed by passing the hollow fiber membrane through filter paper with a pore smaller than the external diameter of the hollow fiber membrane. The hollow fiber membrane was then put into oil phase (0.15 w/v % TMC/*n*-hexane) for 1 min followed by drying at 60°C for 15 min. The prepared polyamide composite membrane was stored in pure water [9]. Preparation of hollow fiber composite nanofiltration membrane containing 4-aminobenzene 18-crown-6 adopts the similar way with add 0.1 w/v % 4-aminobenzene 18-crown-6 in aqueous phase.

2.3. Characterization of hollow fiber composite nanofiltration membrane

Infrared spectroscopy of the hollow fiber composite nanofiltration membrane was recorded by using Fourier transform infrared spectrometer (type Tensor37, Bruker Company, Germany) with scanning in the range of 400–4,000 cm^{-1}. Scanning electron microscope (SEM) was conducted by using field emission scanning electron microscope (Japan Hitachi FESEM S-4800). The samples were immersed in liquid nitrogen to obtain a sooth cross section and spraying with gold before the SEM observation. The hydrophilicity of the hollow fiber composite nanofiltration membrane was tested by contact angle measurement. The membrane pasted on a glass pane was placed on the platform of the contact angle measurement machine. 5 μL water was dropped on the surface of the membrane for testing the contact angle in sessile drop method (type DSA100, KRUSSA Company, Germany). It was tested for five times per sample to calculate an average value.

2.4. Performance of hollow fiber composite nanofiltration membrane

Water flux of the membranes was tested by a homemade membrane evaluation device (Fig. 1) [10] at 0.6 MPa. Water flux of the membrane was calculated by Eq. (1):

$$J = \frac{V}{S \cdot \Delta t} \tag{1}$$

where J stands for water flux ($L \cdot m^{-2} \cdot h^{-1}$); V stands for volume of the penetrated water through the membrane during the filtration time (L); S stands for the active area of membrane (m^2); Δt stands for the filtration time (h).

Rejection (R) of the membrane was calculated by using Eq. (2) as follows:

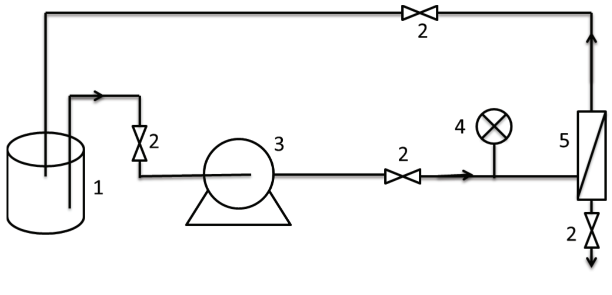


Fig. 1. Scheme of the set-up for membrane performance evaluation. (1) Store tank; (2) throttle; (3) pump; (4) pressure gage; and (5) membrane module.

$$R = \frac{1 - C_p}{C} \times 100\% \tag{2}$$

where C_p is the concentration of permeate, C is the concentration of the feed solution.

Lead nitrate solution was used as feed solution. The conductivity of permeate and feed was measured by conductivity meter. The concentration of feed is 50 mg/L.

3. Results and discussion

Figs. 2 and 3 show that a loose large pore structure is in the middle layer of the PSf support membrane, which is conducive to the transportation of water. After interfacial polymerization, an ultrathin polyamide (PA) function layer on the outside surface of membrane was formed with a nodular structure and a thickness ranging from about 0.2 to 2 μm (Fig. 2(d)). This was the typical granular structure of interfacial polymerization PA membrane. Addition of 4-aminobenzene 18-crown-6 (PA-crown membrane) affected little to the surface structure except for the decrease in the number and increase in size of the granules (Figs. 3(c) and (d)).

Fig. 4 shows the FTIR spectra of the support and composite membranes. PSf support membrane shows obvious benzene ring structure, and the peak at 1,580 cm^{-1} can be assigned to aromatic backbone vibration, while the absorption bands at 650–950 cm^{-1} are attributed to the aromatic C–H out-of-plane bending vibration. Compared with the support membrane, the peak at 3,430 cm^{-1} can be attributed to stretching vibration of N–H bond which comes from the amide group inside the composite membrane. The most typical C=O bond appears at 1,620 cm^{-1}, which is the most powerful evidence of the successful synthesis of amide structures. The peak of 1,054 cm^{-1} is ether bonding, while 1,468 cm^{-1} is the conjugate double bond stretching

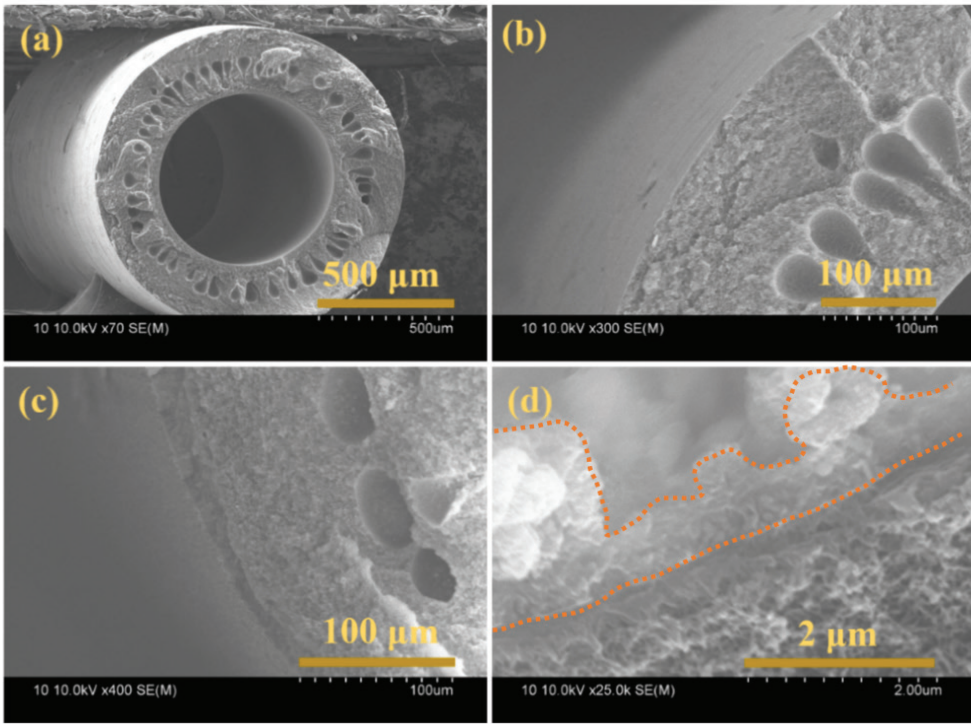


Fig. 2. SEM cross-section images of PSf support membrane ((a) and (b)) and PA membrane ((c) and (d)) and the outlined feature in (d) is the PA layer.

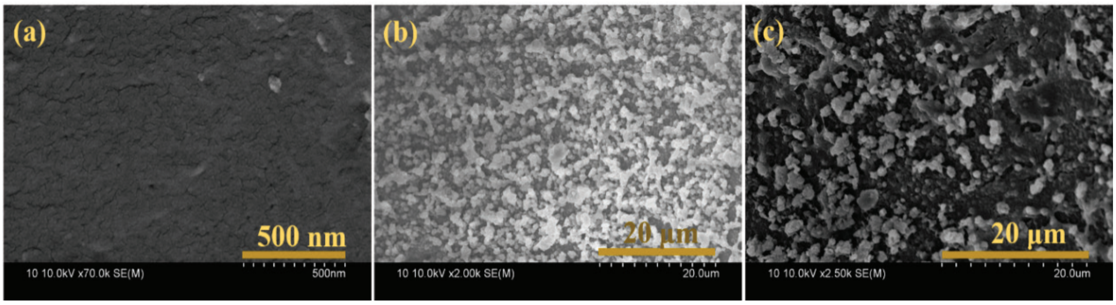


Fig. 3. SEM surface images PSf support membrane (a), PA membrane (b), and PA-crown membrane (c).

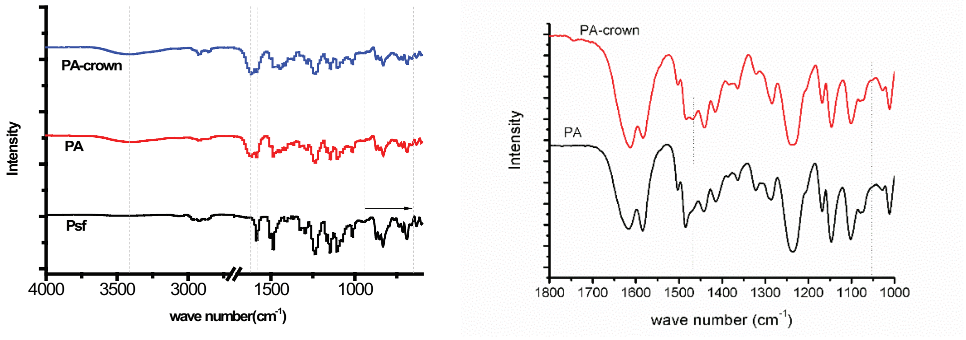


Fig. 4. FTIR spectra of PSf support, PA membrane and PA-crown membrane.

Table 1
Attribution of different groups in FTIR spectra and related references

Groups	Wave-number (cm^{-1})	Wave number in literature (cm^{-1})	Reference
Aromatic backbone vibration from PSf	1,580	1,580	[2]
C–H out-of-plane bending vibration from PSf	650–950	650–950	[2]
N–H from PA	3,430	3,450	[4]
C=O from PA	1,620	1,628	[4]
Ether bonding from PA-crown	1,054	890–1,150	[5]
Conjugate double bond stretching Vibration from PA-crown	1,468	1,450–1,550	[2]

Table 2
Water contact angle, water flux, and lead nitrate rejection of PSf support membrane, PA membrane, and PA-crown membrane

Membranous type	Water contact angle	Water flux $L\cdot m^{-2}\cdot h^{-1}$	Lead nitrate solution flux $L\cdot m^{-2}\cdot h^{-1}$	Lead nitrate rejection %
PSf support	80.1±2.1	69.10±4.6	68.01±3.5	2.33±0.46
PA membrane	31.2±1.6	4.24±0.20	3.89±0.18	60.78±6.34
PA-crown membrane	44.9±3.2	3.87±0.62	3.57±0.56	97.15±0.41

vibration of 4-aminobenzene 18-crown-6. The attribution of these groups is listed in Table 1 with the related references. The FTIR results proved that polyamide functional layer was formed successfully on the PSf support membrane by interfacial polymerization, and 4-aminobenzene 18-crown-6 ether was incorporated in the polyamide functional layer in PA-crown membrane.

The water contact angle of PSf support membrane was 80.1° ± 2.1°, which was much higher than that of PA composite nanofiltration membrane (31.2° ± 1.6°), suggesting enormous hydrophilicity of the composite nanofiltration membrane. This benefits the increase of permeate and antifouling property of the PA membrane. The water contact angle of PA-crown membrane was about 44.9° ± 3.2°. Compared with the support membrane, it still greatly improved the hydrophilicity.

The water flux of PSf support membrane was 69.10 ± 4.6 $L\cdot m^{-2}\cdot h^{-1}$ at 0.1 MPa; and the transmembrane flux for lead nitrate solution decreased to 68.01 ± 3.5 $L\cdot m^{-2}\cdot h^{-1}$ at 0.1 MPa. This was caused by the concentration polarization effect. Due to the formation of polyamide functional layer, transmembrane flux of PA membrane decreased to 4.24 ± 0.20–3.89 ± 0.18 $L\cdot m^{-2}\cdot h^{-1}$ at 0.6 MPa, while the rejection to lead nitrate was more than 60%. Because the improvement of hydrophilicity, transmembrane flux of pure water (4.24 ± 0.20 $L\cdot m^{-2}\cdot h^{-1}$) was slightly higher than that of lead nitrate solution (3.89 ± 0.18 $L\cdot m^{-2}\cdot h^{-1}$) for PA membrane. Especially, for PA-crown membrane, transmembrane flux of pure water (3.87 ± 0.62 $L\cdot m^{-2}\cdot h^{-1}$) was close to that of lead nitrate solution (3.57 ± 0.56 $L\cdot m^{-2}\cdot h^{-1}$) for its superior hydrophilicity and less concentration polarization effect. Moreover, due to the integration of 18-crown-6 ether, PA crown membrane has specific binding to lead ions, thus lead ions are absorbed and combined by crown ether. After absorbing lead ions on the surface of the membrane, because of Donnan effect and charge repulsion effect, the rejection to lead nitrate increased from 60.78% ± 6.34% of PA membrane to 97.15% ± 0.41% of PA crown membrane, suggesting the enhancement of lead nitrate rejection.

4. Conclusion

Hollow fiber composite nanofiltration membrane containing 4-aminobenzene 18-crown-6 ether was prepared via interfacial polymerization by using PSf ultrafiltration membrane as support and aqueous phase added with

4-aminobenzene 18-crown-6 ether. SEM and FTIR results proved that 4-aminobenzene 18-crown-6 ether was successfully incorporated in the polyamide layer. This improved the hydrophilicity of the composite nanofiltration membrane, and diminished the concentration polarization effect to stabilize membrane water flux. Meanwhile, the PA crown membrane showed higher rejection to lead nitrate for the specific interaction between 18-crown-6 ether and lead ions.

Acknowledgements

The authors acknowledge the financial support from the Science and Technology Plans of Tianjin (No. 16YFZCSF00330, 16PTSYJC00100), Tianjin Student's Platform for Innovation and Entrepreneurship Training Program (201610058083).

References

[1] Y.F. Zhang, E.H. Liu, Y. Wu, G.L. Huan, Q.Y. Du, C.F. Xiao, Preparation of polyamide nanofiltration hollow fiber composite membrane and its performance, J. Tianjin Polytech. Univ., 23 (2004) 8–10 (in Chinese).

[2] N.A. Fakhre, B.M. Ibrahim, The use of new chemically modified cellulose for heavy metal ion adsorption, J. Hazard. Mater., 343 (2018) 324–331.

[3] W. Qiao, Preparation of ZSM-5/PANI/PSS Electroactive Film by One-Step Co-deposition and Its Removal of Low-concentration Lead Ions in Water, Taiyuan University of Technology, 2017.

[4] F. Xiao, B. Wang, X.Y. Hu, Thin film nanocomposite membrane containing zeolitic imidazolate framework-8 via interfacial polymerization for highly permeable nanofiltration, J. Taiwan. Inst. Chem. Eng., 83 (2017) 1–9.

[5] C.D. Tran, S. Duri, A.L. Harkins, Recyclable synthesis, characterization, and antimicrobial activity of chitosan-based polysaccharide composite materials, J. Biomed. Mater. Res. Part A, 101 (2013) 2248–2257.

[6] X.L. Wang, C.H. Zhang, J. Zhao, Separation mechanism of nanofiltration membranes and its applications in food and pharmaceutical industries, Membr. Sci. Technol., 20 (2000) 29–36 (in Chinese).

[7] S.F. Zhang, X.E. Hu, The treatment Technology for waste water containing Pb^{2+} and its prospect, Techn. Equip. Environ. Pollut. Contr., 11 (2003) 68–71 (in Chinese).

[8] J. Małgorzata, M. Longina, Complex formation of crown ethers and cations in water–organic solvent mixtures: the thermodynamic functions of complex formation of benzo-15-crown-5 with Na+ in water + ethanol at 298.15 K, J. Chem. Eng. Data, 55 (2010) 1965–1970.

[9] X.Y. Zheng, X.Y. Wang, S.F. Yi, N.Q. Wang, Y.M. Peng, DFT study of the carbon-and nitrogen-pivot lariat crown ethers and their complexes with alkali metal cations: Na+, K+, J. Comput. Chem., 30 (2009) 2674–2683.

[10] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Thermodynamic and kinetic data for macrocycle interactions with cations and anions, Chem. Rev., 91 (1991) 1721–2085.

[11] X.J. Ju, W. Pi, R. Xie, L.Y. Chu, Comprehensive alcohol-/ion-responsive properties of poly(N-Isopropylacrylamide-co-benzo-18-crown-6-acrylamide) copolymers, Chin. J. Chem. Eng., 22 (2014) 1038–1045.

[12] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, 1996.

[13] X.P. Li, Y.B. Chen, X.Y. Hu, Y.F. Zhang, L.J. Hu, Desalination of dye solution utilizing PVA/PVDF hollow fiber composite membrane modified with TiO_2 nanoparticles, J. Membr. Sci., 471 (2014) 118–129.