Desalination performance of Al₂O₃ positively charged nanofiltration composite membrane

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Abstract. Al_2O_3 positively charged nanofiltration composite membrane was successfully prepared with aluminate coupling agent (ACA) as modifier, sodium bisulfite ($NaHSO_3$) and potassium persulfate ($K_2S_2O_8$) as initiator and methacryloyloxyethyl trimethylammonium chloride (DMC) as crosslinking monomer. The surface of the membrane before grafting and after polymerization were characterized by SEM and FT-IR. Three factor and three-level orthogonal experiments were designed to explore the optimal conditions for membrane preparation, and the optimal group was successfully prepared. The filtration experiments of different salt solutions were carried out, and the retention molecular weight was determined by polyethylene glycol (PEG). The results showed that the polymerization temperature had the greatest effect on the rejection rate, followed by the reaction time, and the concentration of DMC had the least effect on the rejection rate. The rejection rates of $CaCl_2$, $MgSO_4$, NaCl and Na_2SO_4 in the optimal group were 83.8%, 81.3%, 28.1% and 23.6% (average value), respectively. The molecule weight cut-off of 90% (MWCO) of the optimal group was about 460, which belongs to nanofiltration membrane.

Keywords: desalination; membrane; nanofiltration; orthogonal test; positively charged

1. Introduction

For a long time, the shortage of fresh water has forced mankind to constantly seek new water treatment methods. Membrane separation technologies were widely used in chemical industry, food biochemistry, water treatment and other fields because of its high rejection rate, environmental protection and easy operation (Jung *et al.* 2019, Abdel-Fatah *et al.* 2020, He *et al.* 2019, Moradi *et al.* 2018, Saleh *et al.* 2020). In recent years, nanofiltration membranes have attracted extensive attention because most of the membrane surfaces are charged and can achieve better separation effect under low pressure (Jung *et al.* 2019, Mohammad *et al.* 2015, Yu *et al.* 2001). Akbari *et al.* (2015) prepared positively charged PEI/ dichloro-p-xylene (XDC) nano-filtration membrane by interfacial poly-merization of iodomethane. The rejection rate of $CaCl_2$ solution was as high as 94%, and the permeation flux reached 54 $\cdot m^{-2} \cdot h^{-1} \cdot MPa^{-1}$, but the rejection rate of monovalent salt ions was relatively low. Ji *et al.* (2011) used hydroxyethyl acrylate (HEA) and DMC as raw materials, sodium bisulfite and potassium thiosulfate as initiators to prepare their polymers, and then crosslinked them on the membrane surface with glutaraldehyde as crosslinking agent under acidic conditions to prepare positively charged nanofiltration membrane. Chen *et al.* (2014) have studied $PDMC/Al_2O_3$ composite nanofiltration flat membrane. PDDA/GO multilayers were successfully fabricated by layer by layer self-assembly method (Wang *et al.* 2016). The flux of obtained membrane was 64.2 $kg \cdot m^{-2} \cdot h^{-1} \cdot MPa^{-1}$ and the methyl blue removal

retention rate was 99.2%. In addition, other papers (Wang and Ji 2012, Hu and Mi 2013, 2014, Zhang and Zhang 2015) have also reported the successful preparation of nanofiltration membranes using graphene oxide (GO).

At present, the research on the filtration technology of charged nanofiltration membrane mainly focuses on the polymer composite membrane. Most of them use polysulfone membrane as the support, and then the charged nanofiltration composite membrane is prepared by impregnation method, L-S phase conversion method, surface chemical treatment method, etc. However, the development and industrial application of this membrane are limited due to its low mechanical strength and short service life (Han *et al.* 2014, Wei *et al.* 2013, Joseph and Ahmadiannamini 2015, Lau and Ismail 2012). Due to the use of inorganic materials as support, organic-inorganic nanofiltration composite membrane has good mechanical properties. It is better than traditional polysulfone membrane support in pressure resistance, heat resistance and service life. In this paper, taking tubular alumina ceramic membrane as matrix, aluminate coupling agent (ACA) as modifie, sodium bisulfite ($NaHSO_3$) and potassium persulfate ($K_2S_2O_8$) as initiator and DMC as crosslinking monomer. Al_2O_3 positively charged nanofiltration composite membranes were prepared by grafting and polymerization.

2. Experimental procedures

2.1 Materials

Al_2O_3 ceramic membrane tube (Nanjing Jiuwu High Tech Co., Ltd, China, ϕ 12×2×15 mm, average pore diameter 0.5 μm), ACA (DL411, Dongguan Dinghai Plastic

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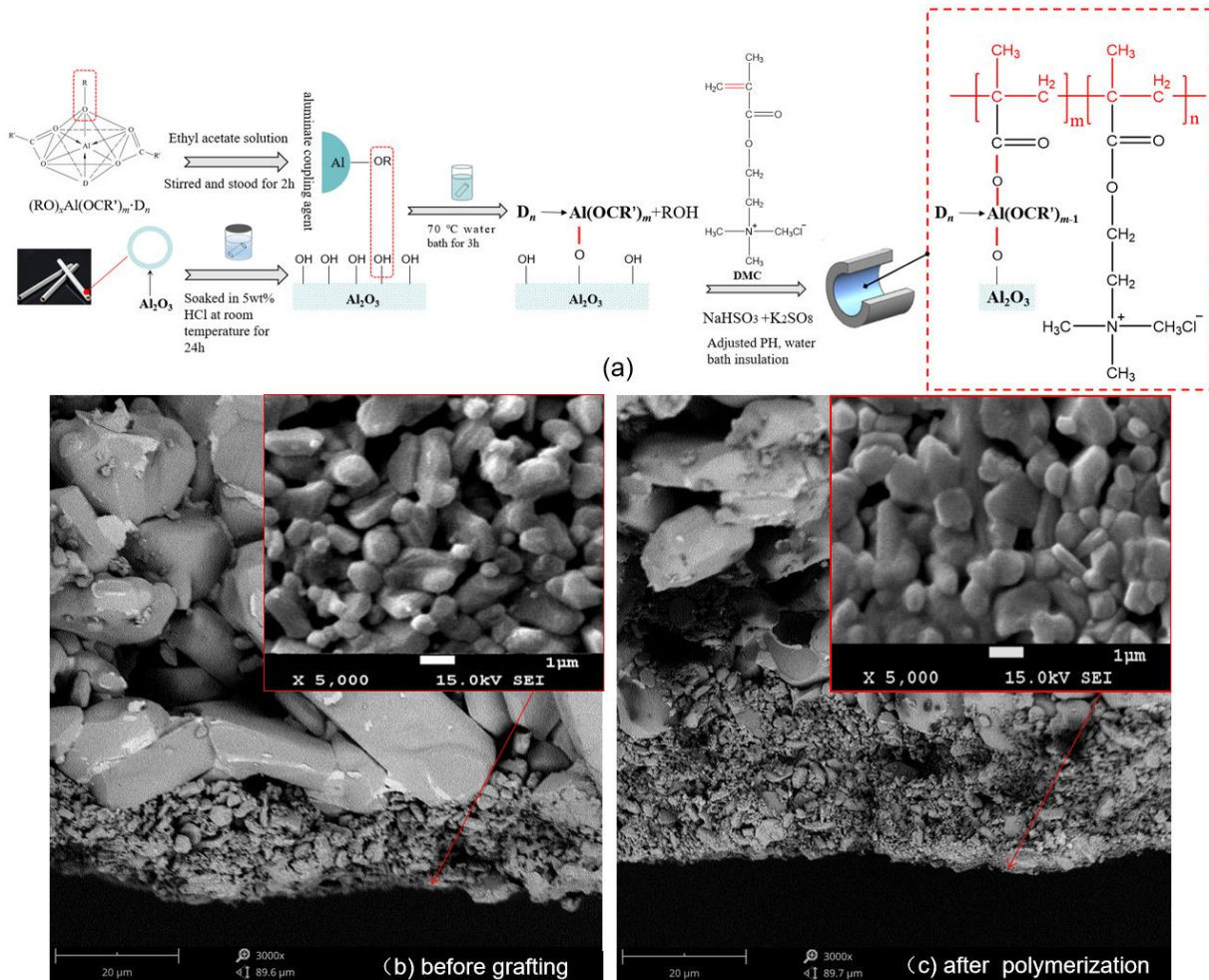*Corresponding author, M.Sc.,
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Fig. 1 (a) Schematic diagram of preparation process; (b) SEM and (c) SEM images of membrane before grafting and after polymerization

Chemical Co., Ltd., China), DMC (Aladdin reagent (Shanghai) Co., Ltd., China), other drugs (ethyl acetate, hydrochloric acid, anhydrous ethanol, PEG, $NaHSO_3$, $K_2S_2O_8$, NaCl, $MgSO_4$, all of them are from Chengdu Kelong Chemicals Co., Ltd., China, analytical pure), etc.

2.2 Instruments

The field emission scanning electron microscopy (TM 3030 plus), Fourier transform infrared spectroscopy (IRPrestige-21) were used to observe morphology and phase of composite membrane, respectively. Further, the conductivity of liquids were measured by conductivity meter (DDS-307). The absorbance of PEG solution were measured by UV-Vis spectrophotometer (721).

2.3 Methods

Firstly, soaked Al_2O_3 ceramic membrane tube in HCl (5.0 wt%) for 24 h, took it out, washed and dried. Secondly, prepared 1.0 wt% ACA-ethyl acetate solution, fully stirred and stand at room temperature for 2 h. Thirdly, put the membrane tube into the membrane reactor, added ACA-ethyl acetate solution, sealed and put it into a constant

temperature bath at 70°C for 3 h. and then tooks out the membrane tube, cleaned and dried it at 60°C for 4 h. Fourthly, prepared DMC aqueous solution with corresponding concentration, stirred evenly, added $NaHSO_3$ and $K_2S_2O_8$ (m($NaHSO_3$): m($K_2S_2O_8$) = 1:1, n($K_2S_2O_8$): n(DMC) = 0.01:1), and then continue stirred until it were completely dissolved. Fifthly, put the dried membrane tube into the membrane reactor, added the prepared DMC solution, sealed the cover, put it into the thermostatic bath, set the corresponding temperature and kept it for corresponding time. Finally, took out the membrane tube, cleaned and dried it at 30°C for 24 h. Al_2O_3 positively charged nanofiltration composite membrane was obtained after dried.

3. Results and discussion

3.1 Characterization

The SEM of the membrane before grafting and after polymerization were shown in Fig. 1. Obviously, the surface of the modified film became smoother than untreated. The film surface was covered by a layer of organic matter after
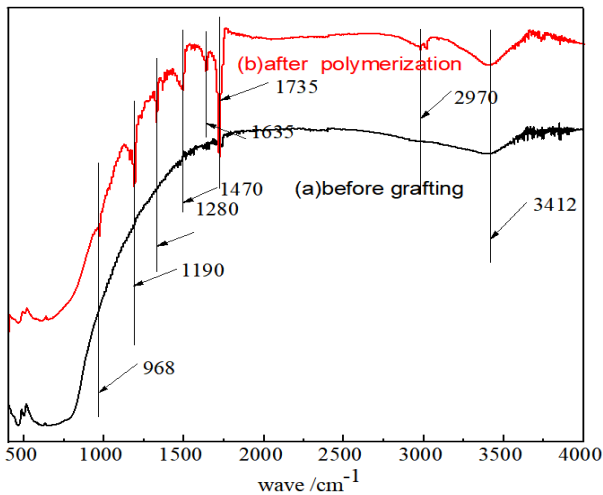
Fig. 2 FT-IR before and after grafting and polymerization

Table 1 Orthogonal experimental results

No.	Polymerization temperature A (°C)	DMC concentration B (mol·L⁻¹)	Reaction time C (h)	Rejection rate (%)
M1	30	0.5	1	28.7
M2	30	1.0	2	39.3
M3	30	1.5	3	36.7
M4	40	0.5	2	48.6
M5	40	1.0	3	76.0
M6	40	1.5	1	67.2
M7	50	0.5	3	70.1
M8	50	1.0	1	27.8
M9	50	1.5	2	62.6
k_1	34.9	49.1	41.2	
k_2	63.9	47.7	50.2	—
k_3	53.5	55.5	60.9	
R	29.0	7.80	19.7	

polymerization. Nevertheless, the peaks of FT-IR were different before and after modification (Fig. 2). The absorption peak at 3412 cm⁻¹ was the telescopic vibration absorption peak of O-H bond, indicating that the ceramic film treated with HCl (5.0 wt%) had O-H. The peak after polymerization with DMC was larger, mainly because ACA consumes some hydroxyl on the surface of ceramic membrane, but it brings more hydroxyl. The absorption peak at 2970 cm⁻¹ was the stretching vibration absorption peak of saturated C-H; the absorption peak at 1635 cm⁻¹ was the C=C absorption peak that were not involved in the reaction from the ACA; The absorption peak at 1735 cm⁻¹ was the stretching vibration absorption peak of C=O in ACA and DMC; The peak at 1470 cm⁻¹ was the bending vibration absorption peak of C-H; the peak at 1280 cm⁻¹ was the absorption peak of Al-O stretching vibration from ACA; The small absorption peaks around 1190 cm⁻¹ were the stretching vibration absorption peak of C-O and the skeleton vibration absorption peak of C-C; the peak at 968 cm⁻¹ was the stretching vibration absorption peak of C-N

from DMC. So far, it shows that grafting and polymerization had taken place and quaternary ammonia (C-N⁺(CH₃)₃) already existed on the surface of ceramic membrane (Chen *et al*. 2014).

3.2 Experimental results

In order to study the influence of the factors on the reaction effect and obtain the optimal scheme. In this paper, the polymerization temperature (30°C, 40°C, 50°C), DMC concentration (0.5 mol·L⁻¹, 1.0 mol·L⁻¹, 1.5 mol·L⁻¹) and reaction time (1 h, 2 h, 3 h) were selected as three factors, and the rejection rate of 2 g·L⁻¹ MgSO₄ solution were taken as the investigation index to design a three factor and three-level orthogonal experiment. The results are shown in Table 1 in which k_i (i = 1, 2, 3, 4) represents the average rejection rate at the level i, and R reflects the influence for each factor. The values of R_A, R_B and R_C are 29.0, 7.8 and 19.7 respectively, indicating that the polymerization temperature had the greatest effect on the rejection rate, followed by the reaction time, and the concentration of DMC had the least effect on the rejection rate. Moreover, it is not difficult to find that with the increase of temperature, the rejection rate increases first and then decreases. The main reasons can be considered that the temperature affects the activity of DMC and molecular weight of products. With the increase of temperature, the activity of DMC becomes higher, the reaction rate also increases, the density of cationic polymers on the membrane surface increases, and the rejection rate becomes higher. At the same time, the increase of temperature may reduce the molecular weight of the products, resulting in the decrease of rejection rate. The effect of reaction time on the rejection rate of the composite membrane should also be noted. With the extension of reaction time, the rejection rate increases gradually. This phenomenon is mainly due to the speed of the chemical reaction process and the time it takes for the reaction liquid to rise to the set temperature. DMC concentration has little effect on the experimental index, which is considered to be the comprehensive result of the collision probability of DMC monomer and the release of reaction system temperature. In conclusion, the best level combination of various factors were that reaction temperature was 40°C, the concentration of DMC was 1.5 mol·L⁻¹, and the time was 3 h, which was not included in the M1~M9.

The desalination capacity of the prepared positively charged nanofiltration composite membrane tube M10 (Optimal group) were observed. Test the desalination capacity of NaCl solution (0.5g·L⁻¹), MgSO₄ solution (2 g·L⁻¹), CaCl₂ solution (2g·L⁻¹) and Na₂SO₄ solution (0.5 g·L⁻¹) under the conditions of 0.25 MPa, 0.3 MPa, 0.35 Mpa and 0.4 MPa, respectively, and Fig. 3 for the results. It was found that the rejection rates of CaCl₂, MgSO₄, NaCl and Na₂SO₄ reached 83.8%, 81.3%, 28.1% and 23.6% (average value), respectively. The rejection rate of Mg²⁺ and Ca²⁺ by the composite membrane is much higher than Na⁺, because the positive charge density in the divalent ion solution is greater, the repulsion force to positive ions is stronger, and the rejection rate is higher.

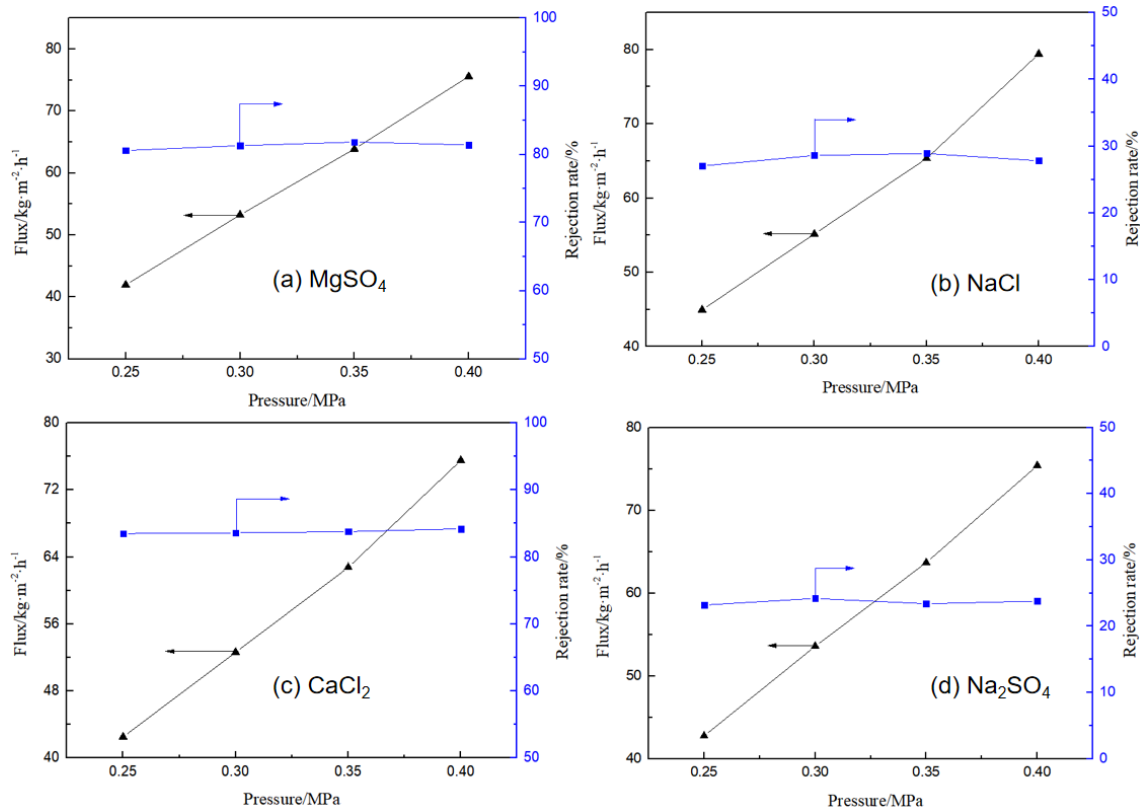Polyethylene glycol (PEG) solution with different

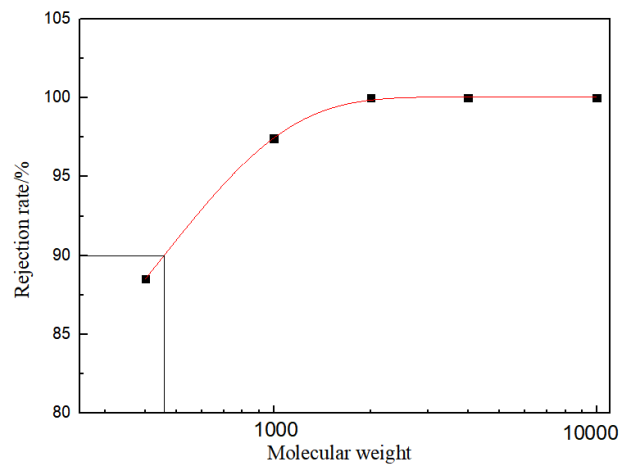Fig. 3 Experimental results of desalination for different salt solutions

Fig. 4 Cut-off performance of the composite nanofiltration membrane tube

molecular weight were used to measure the rejection rate of membrane tube to different PEG, and the molecular weight of PEG when the rejection rate was 90% was sought. The experimental results are shown in Fig. 4. It can be concluded that the molecular weight of PEG corresponding to the composite membrane tube at the rejection rate of 90% was about 460, which belongs to the category of nano-filtration membrane.

3.3 Performance comparison

Table 2 shows the comparison of performance of the membrane fabricated in this work with those of other works.

Obviously, compared with commercial nanofiltration membrane, the composite membrane still has a gap, but it has shown excellent performance compared with other similar studies. When the interception rate is approximately equal, the performance of permeation flux is significantly better than opponents. Moreover, it was prepared more easily than the other membranes in Table 2. Although the satisfactory membrane could be prepared by modification and polymerization, and its rejection rate is not high enough. Modification and polymerization conditions, such as modifier dosage, modification temperature, time, etc., should be further determined, this is an exciting future area of investigation for us.

Table 2 Comparison of desalination performance of nanofiltration membranes

References	Materials of membrane	Salt solution	Salt concentration	Permeability kg·m^{-2}·h^{-1}·MPa^{-1}	Rejection rate (%)
This paper	DMC/ACA/Al$_2$O$_3$	MgSO$_4$/NaCl/ CaCl$_2$	2 g·L^{-1}/0.5 g·L^{-1}/ 2 g·L^{-1}	188.9/198.5/ 188.8	81.8/27.8/ 84.2
Chen *et al.* 2014	PDMC/α-Al$_2$O$_3$	MgSO$_4$/NaCl	0.075 wt%/2.0 wt%	24.3/22.3	82.0/30.4
Wang *et al.* 2016	γ-AlOOH/γ-Al$_2$O$_3$/α-Al$_2$O$_3$	CaCl$_2$	2000 ppm	100	82
Fu *et al.* 2018	PSA/γ-AlOOH/γ-Al$_2$O$_3$/ α-Al$_2$O$_3$	MgSO$_4$/NaCl/ CaCl$_2$	2.0 g·L^{-1}/2.0 g·L^{-1}/ 2.0 g·L^{-1}	—	7.2/34.3/78.1
Zhao *et al.* 2021	PDA/PEI/GA/Al$_2$O$_3$	NaCl	1.0 g·L^{-1}	40	38
Qadir *et al.* 2021	commercial nanofiltration NFDK membrane	CaCl$_2$/NaCl	100 ppm	—	93.7/78.3

4. Conclusions

Al$_2$O$_3$ positively charged nanofiltration composite membrane was successfully prepared with ACA as modifier, NaHSO$_3$ and K$_2$S$_2$O$_8$ as initiator, DMC as crosslinking monomer. The best conditions for preparation of nanofiltration composite membrane were that reaction temperature was 40°C, the concentration of DMC was 1.5 mol·L^{-1}, and the time was 3h. The optimized composite nanofiltration membrane showed a high CaCl$_2$ rejection of 84.2% and pure water flux of 75.5 kg·m^{-2}·h^{-1} under 0.4 MPa. Under the optimum conditions, the exclusion of different inorganic salts followed the order of Na$_2$SO$_4$ < NaCl < MgSO$_4$ < CaCl$_2$. And the molecule weight cut-off of 90% (MWCO) was about 460 for composite membrane.

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