Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1189852

57 (2016) 28531–28536
December

Taylor & Francis
Taylor & Francis Group

Effect of electric field intensity on the performance of poly(piperazine amide) nanofiltration membranes

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Received 26 February 2016; Accepted 9 May 2016

ABSTRACT

Nanofiltration membrane has high flux and rejection to inorganic salts at relative low operation pressure, which is widely used in desalination and wastewater treatment. Negatively charged nanofiltration membrane prepared with interfacial polymerization method has high rejection to anion with high valence because of Donnan effect. In this work, negatively charged poly(piperazine amide) nanofiltration membranes with different rejections were used in separation of salt solution and low voltage direct current (LVDC) electric field was involved to increase the surface electric charge density to improve the membrane rejections to inorganic salts. When the forward electric field intensity was increased from 0 to 16 V/cm, the membrane rejections were all increased. The rejection to Na_2SO_4 of membrane (NO2) increased from 68 to 93%, while the membrane flux did not change obviously. At the same time, when the forward electric intensity is elevated, the membranes with low rejections show obvious elevation of permselectivity while the membranes with high rejections have limited elevation of performance. When reversed electric field was applied, the rejection to Na_2SO_4 of membrane (NO5) was decreased from 68 to 36%, while the flux changed little. It was demonstrated that the applied LVDC electric field can affect the surface charge density and change the permselectivity of negatively charged nanofiltration membranes, which is meaningful in desalination.

Keywords: Low voltage direct current (LVDC) electric field; Electric field intensity; Nanofiltration membrane; Desalination; Charged membrane

1. Introduction

Nanofiltration membrane has been widely used in desalination, removing heavy metal ions and wastewater treatment for its relative low operation pressure, low investment, low energy consumptions, high permeation flux, and high rejections of multivalent salts [1]. Negatively charged nanofiltration membrane has high rejection to multivalent salts by cooperating the sieve effect and Donnan effect because of the nano-sized pores and high charge density in the membrane surface [2]. In order to improve the performance of the nanofiltration membrane, a lot of efforts were made by changing the surface architectures and hydrophilicity. Membranes with different surface charge and polymer are prepared with interfacial polymerization or dip-coating methods [3,4]. Thin film

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nanocomposite membranes are also prepared via interfacial polymerization process while nanoparticles are incorporated in the polyamide dense layer to increase the hydrophilicity or surface charge density without sacrificing the separation efficiency of the composite membrane [5]. Electrochemical processing is an important part of the membrane industry. Dense ion exchange membranes are used in electrodialysis process for the separation of salts because high density of immobile ions within the membrane body will repulse the ions with the same charge sign. However, membrane fouling and concentration polarization cause the deterioration of the membrane performance, also the flux of the ion exchange membrane is low, and the voltage used is high which causes high energy cost [6,7]. Based on physicochemical and electrokinetic properties of the charged solutes in the feed solution, electric field was applied in the feed solution with an EDUF cell configuration (Anode-Ultrafiltration membrane-Cathode) which is useful for a variety of molecules [8,9]. Most of the results showed that solute flux was increased and membrane fouling was restrained by increasing the electric field intensity. As the nanofiltration membrane surface is often charged, membrane performance may be affected by the electric field intensity as ion exchange membrane. In this work, the negatively charged nanofiltration membrane with different rejections is prepared and used as one plate electrode while stainless steel plate with small pores is fixed in the permission side and used as the counter electrode. Forward or reversed electric field is applied for changing the electric charge density in the membrane surface to study the effect of electric field on the performance of the nanofiltration membrane. Polyether sulfone (PES) with excellent thermal resistance, mechanical strength, and chemical resistance is used to fabricate support layer of composite membrane. The functional layer of the composite nanofiltration membrane is prepared with interfacial polymerization of piperazine and trimesoyl chloride. The applied voltage is increased from 0 to 8 V with 0.5 cm between the two electrodes.

2. Experimental

2.1. Materials and instruments

PES supporting membrane is prepared in our laboratory with 15% PES and 2% polyvinyl pyrrolidone (PVP-K30) dissolved in *N*,*N*-dimethylacetamide. Trimesoyl chloride (TMC) is obtained from Benzo Chemicals in China. Other chemicals used in the experiments are of analytical purity grade without further purification. The membrane rejection is tested with conductivity meter (DDS-11A, Shanghai rex electric chemical instrument co., Ltd). A flat sheet dead-end filtration setup is used to evaluate the composite membrane performance, and a low voltage direct current (LVDC) electrical source is applied to study the effect of electric field intensity on the performance of the charged nanofiltration membrane. The sticky copper foil on the top surface of the membrane is connected with the cathode of the LVDC electrical source when forward electric field is applied. The effect of electric field intensity on the performance of the nanofiltration membrane is studied by changing the voltage of the electrical source and the electric charge density in the membrane surface. The testing equipment is shown as follows (Fig. 1).

2.2. Membrane preparation

The composite nanofiltration membranes are prepared by interfacial polymerization method. Piperazine is used for monomer in aqueous phase, and TMC is used as oil phase monomer in hexane solution. The membranes with different performance were prepared by adjusting the monomer concentration and reaction temperature [10] (Table 1).

2.3. Membrane characterization

The performances of the membrane are mainly described by product water flux, *F*, and rejection, *R*.

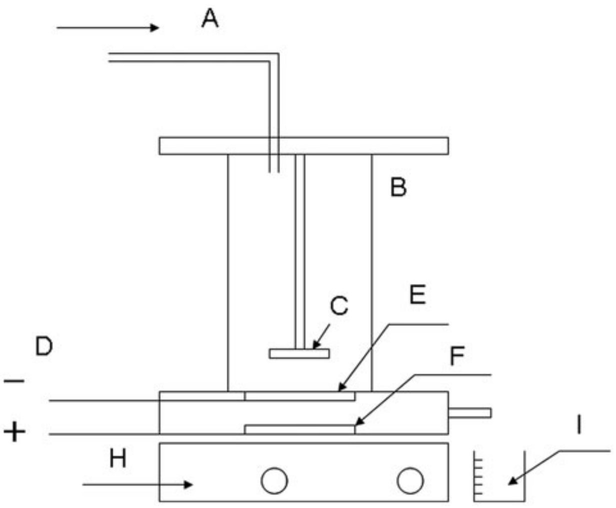

Fig. 1. The testing equipment with electric field.
Notes: (A) nitrogen gas, (B) nanofiltration membrane equipment, (C) stirrer with magnetic materials, (D) low voltage direct current source, (E) negatively charged membrane, (F) counter electrode, (H) magnetic stirring apparatus, and (I) measuring cylinder.

Table 1
The formulas of the nanofiltration membranes

NO	NO1	NO2	NO3	NO4	NO5	NO6
Piperazine concentration (%)	0.5	0.5	1	1	1	1
TMC concentration (%)	0.5	0.5	0.5	1	0.5	1
Reaction temperature (℃)	20	60	60	60	20	20

The membranes were characterized in the dead-end membrane module after they were pretreated under the pressure of 0.4 MPa for 30 min. The membrane performances including pure water flux and rejection ($NaSO_4$, 1 g/L) were measured under the pressure of 0.3 MPa at 20℃. The permeation flux, F, is calculated as follows [10]:

$$F = \frac{W}{At} \tag{1}$$

where W is the total weight of the water or solution permeated during the experiment, A is the membrane area, and t is the operation time. Rejection, R, is calculated using the following equation:

$$R = \left(1 - \frac{C_\mathrm{p}}{C_\mathrm{f}}\right)\% \tag{2}$$

where C_p and C_f are the concentration of the permeate solution and the feed solution, respectively. All the experiments on flux and rejection were repeated for three times. The relative standard deviation of the data was lower than 15%.

3. Results and discussion

3.1. Effect of forward electric field intensity on the membrane performance with different rejections

The membranes are tested at 20℃ under 0.3 MPa after the membrane is prepressed at 0.4 MPa for 30 min. Membranes with different rejections are used for demonstrating the effect of electric field intensity on the performance of membrane. The distance between the two electrodes is 0.5 cm, and the applied voltage is 0, 2, 4, 6, and 8 V, respectively. So the electric field intensity is 0, 4, 8, 12, and 16 V/cm. Poly (piperazine amide) nanofiltration is negatively charged in the membrane surface, so it is used as the cathode to test the forward voltage on the membrane performance. In this work, membranes with different rejections to Na_2SO_4 were studied.

As shown in Fig. 2, the membrane rejection of membrane NO1 increased from 29 to 63%, while the membrane flux did not decrease obviously when the applied electric field intensity was increased from 0 to 16 V/cm. The obvious rejection elevation occurred with the increased electric field intensity which demonstrated that the applied low voltage electric field is useful for the membrane rejection and affects the membrane flux little. This phenomenon is significant for decreasing the cost of desalination because nanofiltration membrane with low rejection to inorganic salts often has relative high flux.

In order to demonstrate the validity of the effect of electric field, membranes with different rejections were also tested. As shown in Fig. 3, when forward electric field was applied, the changes of membrane flux were unconspicuous. However, the rejection of membrane NO3 was improved remarkably from 68 to 93%. The membrane with increased rejection to inorganic salts at LVDC electric field may be used in desalination with low cost.

As shown in Fig. 4, when forward electric field was applied, the membrane flux was decreased from 8.8 to 7.6 L/m^2 h, while the membrane rejection was improved from 85 to 93%. As shown in Fig. 5,

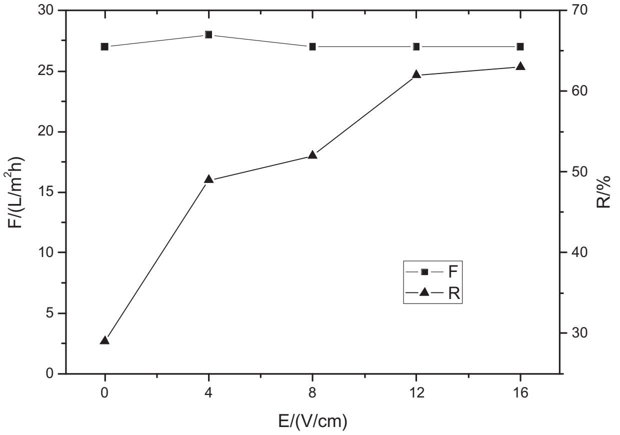

Fig. 2. Effect of forward electric field intensity on the performance of membrane (NO1).

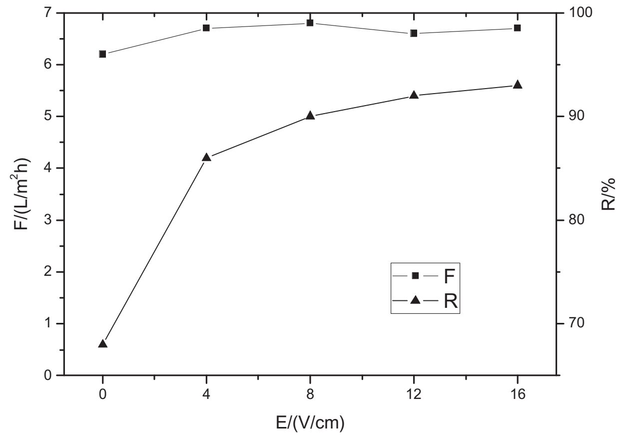

Fig. 3. Effect of forward electric field intensity on the performance of membrane (NO2).

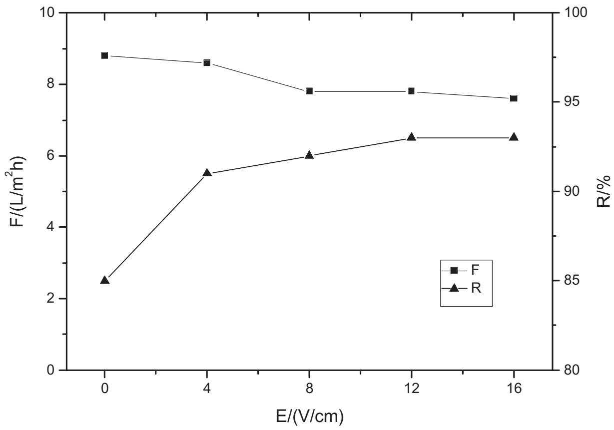

Fig. 4. Effect of forward electric field intensity on the performance of membrane (NO3).

the membrane flux changed from 7.1 to $7.9\,\mathrm{L/m^2\,h}$ while the rejection to Na_2SO_4 increased from 93.5 to 94.4% which did not change obviously with applied electric field. It means that the effect of applied electric field is not obvious on the membranes with high rejection. It may be caused by that the membranes NO3 and NO4 were prepared with high monomer concentration and reaction temperature has smaller pore size and high charge density in the membrane surface, so the applied electric field is not needful. The membrane with low rejection may have large membrane pores or low charge density, so applied electric field will increase the charge density and repulsion effect between the membrane surface and the inorganic ions with the same charge sign.

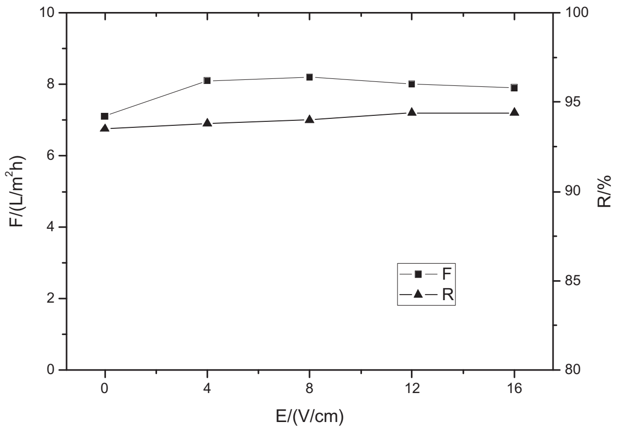

Fig. 5. Effect of forward electric field intensity on the performance of membrane (NO4).

3.2. Effect of reversed electric field intensity on the membrane performance with different rejections

In order to study the effect of electric field on the membrane surface charge and membrane rejection, reversed electric field was applied in the membrane testing apparatus and the negatively charged membrane was used as anode. As shown in Fig. 6, when reversed electric field intensity was increased from 0 to 16 V/cm, the flux of membrane NO5 changed little, while the membrane rejection decreased from 69 to 36%. The same phenomenon occurred on membrane (NO6) in Fig. 7; the membrane flux changed from 22 to $19\,\mathrm{L/m^2\,h}$ while membrane rejection to Na_2SO_4 decreased from 80 to 64%. This may be caused by that the membrane rejects salts by Donnan effect and sieve effect. When reversed electric field is applied, the partial negative charge is offset and the rejection of the membrane is decreased.

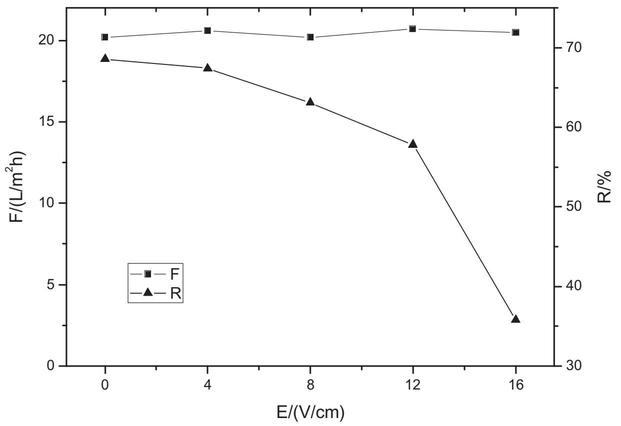

Fig. 6. Effect of reversed electric field intensity on the performance of membrane (NO5).

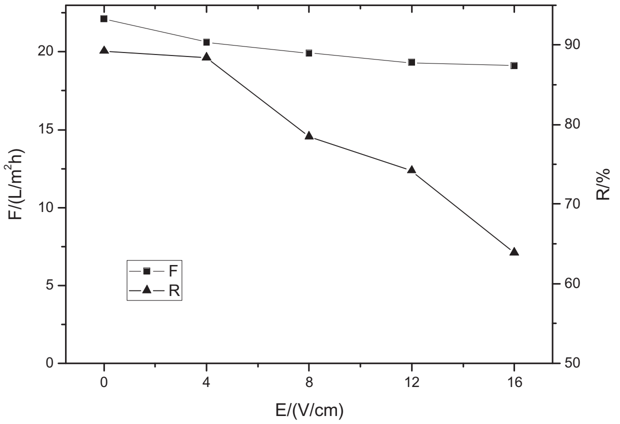

Fig. 7. Effect of reversed electric field intensity on the performance of membrane (NO6).

3.3. *The analysis of the electric field intensity on the membrane separation performance*

The rejection to salts by nanofiltration membrane depends on sieving and Donnan exclusion. For membrane with low charge, density may be not enough to retain ions. Negatively charged polyamide nanofiltration membrane often has the order of rejection to different salt solutions: $Na_2SO_4 > NaCl > MgCl_2$. It means that the Donnan exclusion effect plays a more important role in the permeation of inorganic salts [2]. The negatively charged membrane has a lot of charges in the membrane surface and pores. High valence anions also carry more negative charges and lead to a stronger repulsion between the anions and negatively charged membrane. If extra electric field is applied in the membrane surface, the surface charge density of the membrane will be changed. If the negatively charged membrane is used as cathode, with the increase in the electric field intensity, the surface charge density increased and the membrane rejection to Na_2SO_4 increased. When the negatively charged membrane is used as anode, with the involvement of the electric field intensity, the surface charge density is partially offset. The membrane rejection to Na_2SO_4 is decreased because of decreased repulsion between ions and membrane surface charge with the increase in electric field intensity.

4. Conclusions

LVDC electric field has obvious effect on the separation performance of negatively charged poly(piperazine amide) nanofiltration membrane. When the electric field intensity is increased from 0 to 16 V/cm with the membrane used as cathode, the membrane rejections all increased. The membrane with low rejection has obvious elevation in rejection, while the membrane with high rejection has limited elevation in rejection. It may be caused by that the membrane with low rejection may have large pore size and low surface charge density. Increasing the voltage of forward electric field will increase the surface charge density obviously. When forward electric field is applied, rejection to Na_2SO_4 of membrane NO2 can increase from 68 to 93% while the membrane flux does not change obviously. When the electric field intensity is increased from 0 to 16 V/cm with the membrane used as anode, the rejections to Na_2SO_4 of membrane NO5 and NO5 both decreased while the fluxes change little. It was demonstrated that the applied electric field can affect the surface charge density and change the membrane rejection which is very useful in desalination.

Acknowledgements

The authors wish to thank the support of Natural Science Foundation of China (No. 51503089), Jiangxi Province Natural Science Foundation (GJJ150916), the State Key Laboratory of Fine Chemicals (KF 1402).

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