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Effect of electric field intensity on the performance of positively charged quaternized chitosan nanofiltration membranes

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ABSTRACT

The positively charged nanofiltration membrane has a good anti-bacterial and anti-fouling performance. It often shows high rejection to multi-charged inorganic ions and great flux at relative low operation pressure which is meaningful for desalination and wastewater treatment. In this work, the performance of positively charged quaternized chitosan nanofiltration membranes is studied at low voltage direct current (LVDC) electric field. It is found that the involved electric charge in the membrane surface improved the rejection to inorganic salts. With the electric field intensity rising from 0 to 16 V/cm, the membrane rejections to $MgCl_2$ can increase from 54.1% to 81.2%. However, the membrane fluxes changes little and electric current is about 0 A which showed great energy efficiency at desalination process.

Keywords: Low voltage direct current (LVDC) electric field; Electric filed intensity; Nanofiltration membrane; Quaternized chitosan; Positively charged membrane

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1. Introduction

Nanofiltration (NF), an energy efficient, effective pressure-driven membrane process, is promisingly attractive for the removal of heavy metal ions and water desalination. It can be used in desalination, removing heavy metal ions and waste water treatment. The research on nanofiltration membranes prepared by interfacial polymerization and dip-coating method gains widespread attention and has been extensively applied for relative low operation pressure, high permselectivity to multivalent salts [1]. Nanofiltration membrane often has high rejection to multivalent salts by the corporate Donnan effect and sieve effect. The charged surface of the membrane endows the nanofiltration membrane with different rejections to salt ions with different valents [2]. However, the strict interfacial polymerization condition and low resistance to free chlorine limit the application of thin film composite membrane prepared with polyamide [3]. Moreover, the positively charged membrane is more suitable for the separation of cations, such as Mg^{2+}, Ca^{2+}, as well as many kinds of heavy metal cations according to Donnan exclusion theory [4]. A lot of efforts were made by changing the surface architectures and hydrophilicity including the use of nanomaterials in the functional layer. Because the nanoparticles provide additional permeation pathways for improved permselectivity [5]. However, the surface charge in the membrane may play a more important role in the separation of charged solute. In our previous work, based on physicochemical and electro-kinetic properties of the charged nanofiltration membrane, electric field was applied in the nanofiltration process because the membrane performance may be affected by the electric field intensity [6]. LVDC electric field was demonstrated with positive effect on the separation performance of negatively charged poly (piperazine amide) nanofiltration membrane when the membrane was used as cathode. The rejections of the poly(piperzaine amide) nanofiltration membrane were all increased especially the membranes with low rejection showed obvious elevation in rejection, while the membrane fluxes changed

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little. It was demonstrated that the applied electric field can affect the surface charge density of the negatively charged nanofiltration membrane and improve the membrane rejection. In this work, in order to demonstrate the effectiveness of electric field on the positively charged nanofiltration membrane, the positively charged chitosan nanofiltration membrane are prepared and used as anode while the other copper electrode is used as cathode in the permission side. Low voltage direct current (LVDC) electric field is applied for investigating the effect of electric charge density on the performance of the nanofiltration membrane. Polyether sulfone is used to fabricate support layer of composite membrane for its excellent thermal resistance, membrane forming ability and mechanical strength. The positively chagred chitosan nanofiltration membrane is prepared with dip-coating method. Quaternized chitosan (HACC) is used as the functional layer material of the composite nanofiltration membrane while glutaraldehyde is used as crosslingking agent [7]. The electric field intensity is changed from 0 to 16V/cm with 0.5 cm between the two electrodes.

2. Experimental

2.1. Materials and instruments

The PES (polyether sulfone) ultrafiltration (UF) membranes (tested with polyethylene glycol) are homemade with phase inversion method and used as support membrane of composite nanofiltration. 2-Hydroxypropyltrimethyl ammonium chloride chitosan (HACC) (Lvshen Bioengineering, China) is purified by polyester 200-mesh sieve under pressure. Glutaraldehyde (50%), NaCl, $MgCl_2$, Na_2SO_4 and other chemicals used in the experiments are all analytical purity grade without further purification. A flat sheet dead-end filtration set-up prepared with engineering plastics is used to evaluate the performance of the composite membrane under electric field, and the ionic concentration is analyzed with conductivity meter (DDS-11A, Shanghai Rex Electric Chemical Instrument Co. Ltd). A stirring bar is fixed above the membrane surface and a magnetic stirrer (Jiangsu Jiangyin Science Research Instrument Plant, China) is installed below the membrane set-up to alleviate concentration polarization.

2.2. Composite membrane preparation

1% and 2% (w/w) quaternized chitosan (HACC) solutions are dissolved in de-ionized water to prepare polymer solution. HACC solution is casted on the top surface of the PES ultrafiltration membrane. Then the excessive solution at the membrane surface is drained off by holding the membrane vertically. The membrane is dried in oven for forming a ultrathin layer in the membrane top surface. The functional layer of the formed composite membrane is then crosslinked with glutaraldehyde solution and cured at 50^{o}C for about 3 min [7]. The membranes prepared in this method are stored in de-ionized water before use.

2.3. Membrane characterization

FTIR-ATR spectrum obtained by Nicolet-20DXB is used to characterize the functional layer and support membrane surface. The morphology of the membrane is analyzed by SEM (FEI Nova NanoSEM). The samples are sputtered with gold after they were immersed in the ethanol solution to observe the structure of the membrane.

The performance of the membrane is mainly described by product water flux (F) and rejection (R). The performance of the membranes is characterized with the plastic dead-end membrane set-up under different electric intensity. The membranes are pressed under 0.4 MPa for 30 min in order to obtain stabilized membrane performance. The concentrations of testing solution include $MgCl_2$ solution are all fixed 1 g/L. The concentration of dye solution is 200 mg/L. The membrane performances including pure water flux and rejection are measured under the pressure of 0.3 MPa at 20°C [7]. The permeation flux (*F*) is calculated as follows:

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

where *W* is the total volume of the water or solution permeated during filtration process; *A* is the valid membrane area; and *t* is the operation time. Rejection, *R*, is calculated using the following equation:

$$R = (1 - \frac{Cp}{Cf})\% \tag{2}$$

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.

Quaternized chitosan nanofiltration membrane is positively charged in the membrane surface, so it is connected to the anode of the DC electrical source to test the forward voltage on the membrane performance. The multihole copper plate is connected to the negative plate of the DC current source. Membranes with different rejections are prepared with different ingredients to demonstrate the effectiveness of electric field intensity on the performance of positively charged nanofiltration membrane. The distance between the two electrodes is fixed 0.5 cm and the applied voltage between the electrodes is 0, 2, 4, 6, 8 V, respectively, therefore the electric field intensity is 0, 4, 8, 12, 16 V/cm. In this work, performance of membranes with different rejections to $MgCl_2$ is studied under different electric intensity. The different membranes prepared with different ingredients are listed in Table 1.

The testing equipment is shown in Fig. 1.

3. Results and discussion

3.1. Effect of electric field intensity on the performance of positively charged nanofiltration membranes

It can be observed from Fig. 2 that the rejections to $MgCl_2$ of membrane NO1 are elevated from 13.4% to 55.6%

Table 1
Membranes prepared with different ingredients

NO	NO1	NO2	NO3	NO4
Quaternized chitosan/(%)	1	1	2	2
Glutaraldehyde(%)	0.5	1	0.5	1

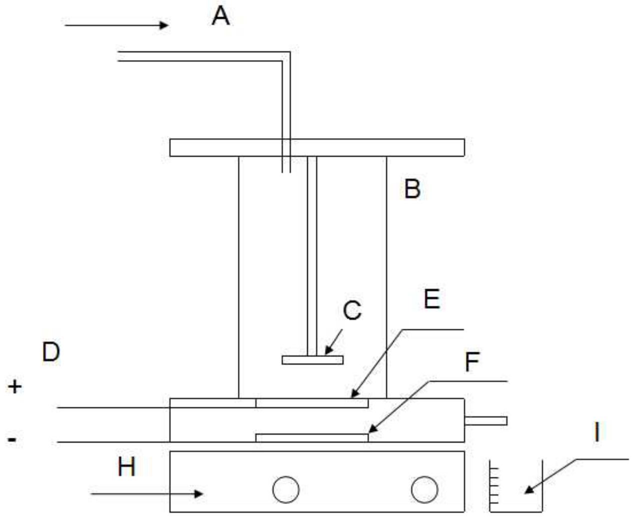

Fig. 1. The nanofiltration equipment with auxiliary electric field. (A, Nitrogen gas; B, Nanofiltration membrane testing equipment (Nylon); C, Stirrer with magnetic materials; D, Constant voltage direct current source; E, Positively charged membrane; F, Counter electrode; H, Magnetic stirring apparatus; I, Beaker or measuring cylinder).

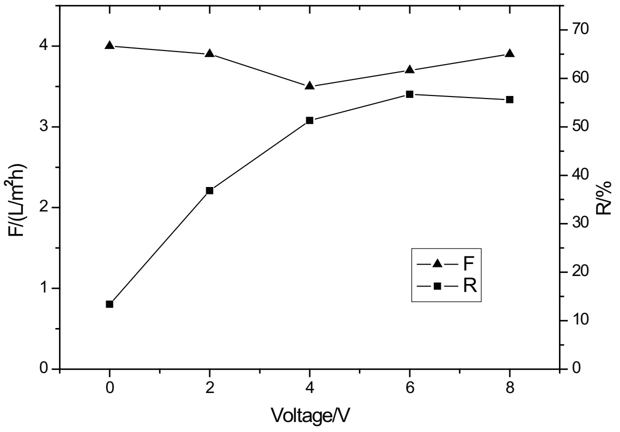

Fig. 2. Effect of electric field intensity on the performance of positively charged membrane NO1.

while the permeate flux changes little when the applied DC field intensity changes from 0 to 16 V/cm. The rejection elevation is about four-fold with the elevated electric field intensity added in the filtration process, which demonstrates the applied low voltage electric field is very useful for the improvement of membrane rejection while the membrane flux does not decline. At the same time, there is no electric current observed in the circuit which demonstrates the energy efficiency of the external electric field. This phenomenon has a great influence on the nanofiltration process for brackish water desalination and waste water treatment.

The membrane NO2 prepared with 1% HACC and 1% glutaraldehyde shows superior performance compared with NO1. It may be caused by that the high content of crosslinking agent endows membrane with high degree of crosslinking degree and high charge density. So the membrane has relative high rejection to $MgCl_2$. Membrane NO2 is also tested to demonstrate the effectiveness of the external electric field. Fig. 3 presents the similar phenomenon that the rejection is increased from 49.1% to 62.3% while the membrane flux is improved from 6.2 to 8.4 L/m^{2}h when the auxiliary electric field is imposed. It means that the involved electric filed has obvious effect on the performance of the positively charged nanofiltration. At the same time, the excessive crosslinking agent with low boiling temperature may be released during the curing step which caused the membrane has more rough structure which improves the membrane flux. The SEM image of the composite membrane has similar characteristic.

Fig. 4 also presents the validity of the electric field. As the forward electric field intensity increases from 0 to 16V/cm, the membrane flux increases about 10%, while the membrane rejections are improved from 54.1% to 81.2%. In Fig. 5, the same phenomenon is observed with

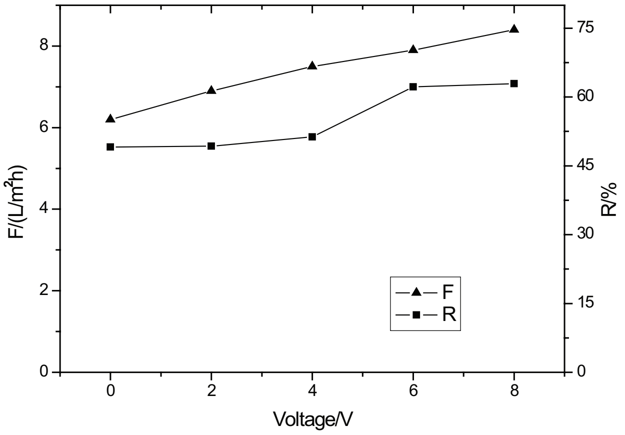

Fig. 3. Effect of electric field intensity on the performance of positively charged membrane NO2.

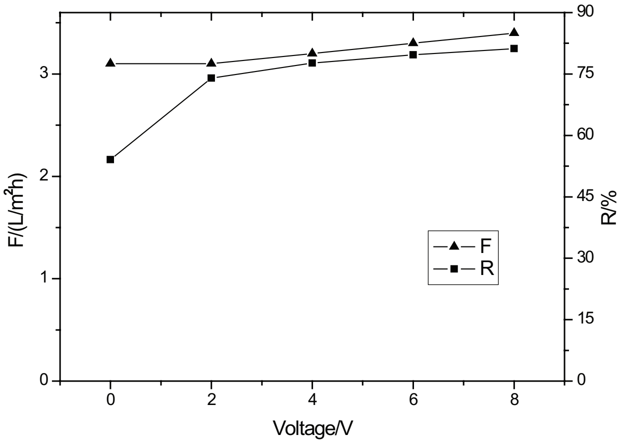

Fig. 4. Effect of electric field intensity on the performance of positively charged membrane NO3.

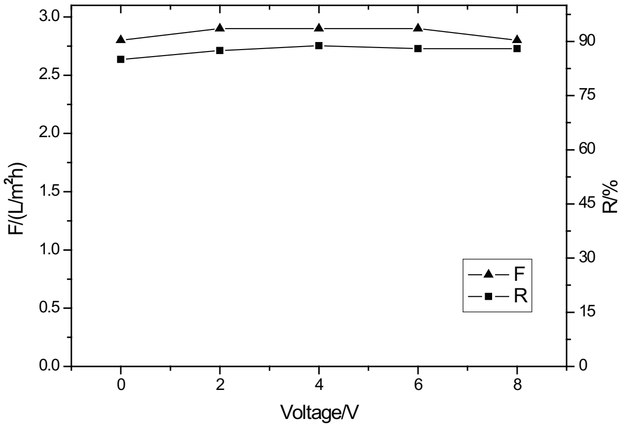

Fig. 5. Effect of electric field intensity on the performance of positively charged membrane NO4.

rejection increased from 85 to 88% at applied electric filed. It is also found that the effect of auxiliary electric field is not obvious when the membrane has high rejection itself. It may be summarized that the membrane with high rejection often has high charge density in the membrane surface, so the auxiliary electric field is not necessary. The membranes show low rejection often have large low charge density and membrane pores, so auxiliary electric filed will increase the electric charge density of the membrane surface and repulsion force between the membrane surface and the inorganic ions with the same charge type.

3.2. *Effect of the electric field intensity on the rejections to different salts*

The nanofiltration membrane has high rejection to multivalent salts because of Donnan exclusion. So nanofiiltration membrane with weak charge density in the membrane surface may show low rejection to ions. Positively charged nanofiltration membrane with or without electric field assistance has the same order of rejection to different salt solutions: $MgCl_2$ > NaCl > Na_2SO_4 as shown in Table 2. It means that the Donnan exclusion effect plays an important role in the filtration of ions and auxiliary electric field is useful for charged membrane. When the applied voltage is 4V, the membrane rejection still decrease with the elevated salt concentration, which is similar with the membrane separation without electric field. As shown in Fig. 6, positively charged nanofiltration membrane has high charge density in the membrane surface and pores. So high valence cations show high rejections because they possess high charge density which leads to a stronger repulsion between the cationic ions and positively charged membrane. The surface charge density of the membrane will be improved when extra electric field is imposed in the membrane surface. So the membrane rejection to $MgCl_2$ is increased. However, the rejections to NaCl and Na_2SO_4 did not change obviously. Maybe the opposite charges will attract on the membrane surface which offsets part of the Donnan effect.

Table 2
Effect of electric field intensity on the rejections to different salts (NO3, the applied voltage is 4 V)

Inorganic salts (1 g/L)	$MgCl_2$	NaCl	Na_2SO_4
R (%) – 0 V	54	18	10
F (L/m²·h) – 0 V	3.3	3.3	3.9
R (%) – 4 V	78	19	8
F (L/m²·h) – 4 V	3.2	3.3	3.5

Table 3
Effect of inorganic salts concentration on the performance of membrane (NO3, the applied voltage is 4 V)

Inorganic salt concentration (g/L)	0.5	1.0	1.5	2.0	2.5
F ($L\cdot m^{-2}\cdot h^{-1}$)	3.1	3.1	3	3.1	3.1
R (%)	83	78	72	64	64

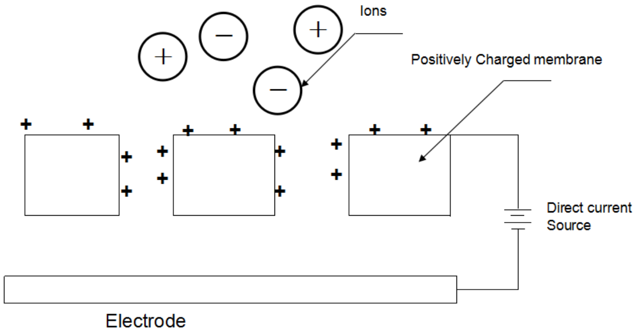

Fig. 6. The schematic diagram of the charge repulsion between ions and membrane.

In order to investigate the mechanism of electric field on the performance of nanofiltration, a neutral solute Gentian

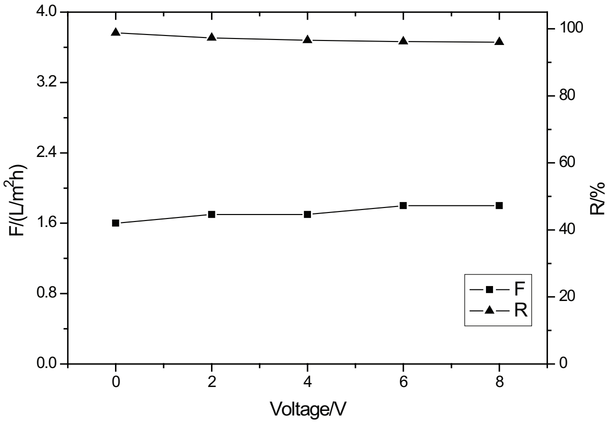

Fig. 7. Effect of electric field intensity on the performance of positively charged membrane NO2.

Violet (408Da) is used as shown in Fig. 7. With the increase of electric field intensity, the rejection of Gentian Violet declines a little from 98.8% to 96% while the membrane flux changes little, which may be caused by the concentration polarization and membrane fouling with the increase of operation time. At the same time, it further demonstrates the electric field improves the surface charge density of the positively charged nanofiltration membrane and increases the rejection of divalent ions.

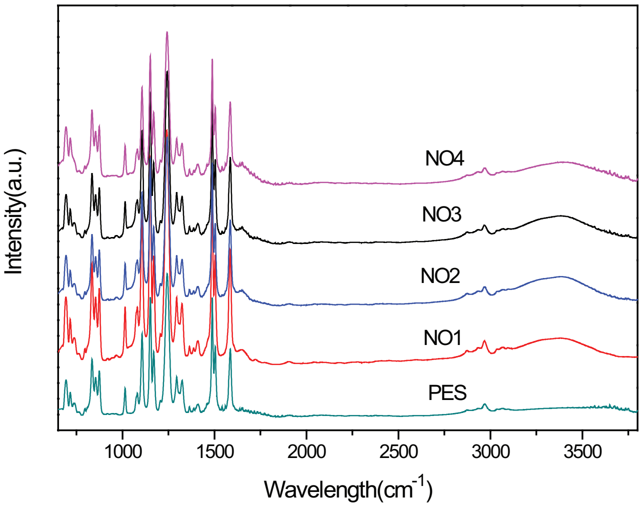

Fig. 8. Spectrum of the top surface of different membranes (From top to the bottom are PES support membrane, NO1, NO2, NO3 and NO4).

3.3. The spectrum and morphology of the composite NF membrane

The IR spectra of support membrane and composite membrane were measured in the range of 650–3800 cm^{-1}. As shown in Fig. 8, the absorption bands of different membrane are similar which can be ascribed that the detection depth of the infrared spectrometer is larger than the thickness of the functional layer. The absorption bands of 1487 cm^{-1} and 1585 cm^{-1} are the stretching vibration of benzene ring. The absorption bands of 1294 cm^{-1} and 1323 cm^{-1} are the antisymmetric stretching vibration of O = S = O. All the composite membranes show the -OH absorption peaks in the range of 3200–3400 cm^{-1}.

Fig. 9 shows the SEM images of the surface morphologies of the composite membrane. It is shown that the top surface of the membranes are all smoother compared composite membrane prepared with interfacial polymerization method. All the membranes do not show pores in the membrane surface and the membrane NO2 shows more dense surface.

4. Conclusions

It is found that the Low voltage direct current (LVDC) electric field can obviously improves the selectivity of positively charged quaternized chitosan nanofiltration membrane. When the imposed auxiliary electric field intensity is changed from 0 to 16 V/cm with the membrane used as anode, the membrane rejections to $MgCl_2$ are all elevated while the membrane fluxes changes little. The rejection to $MgCl_2$ of membrane NO3 increases from 54.1% to 81.2% and the membrane flux also increased about 10%. And the elec-

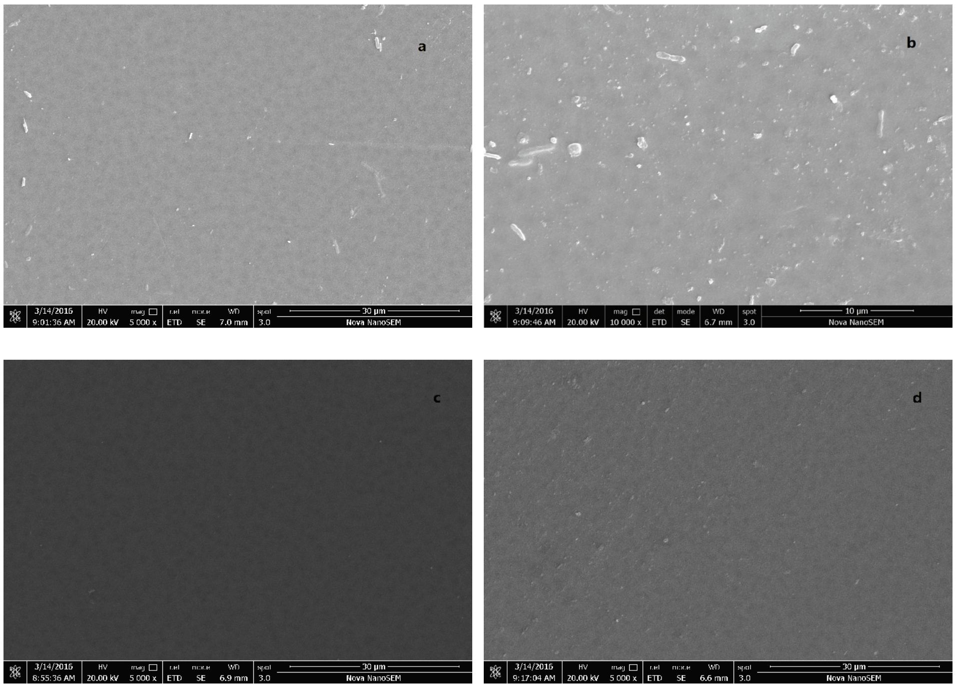

Fig. 9. The top surface morphology of composite NF membrane(a, NO1; b, NO2; c, NO3; d, NO4).

tric current of the circuit is not observed in all experiments which demonstrates the prominent low energy consumption of the auxiliary electric field. It is also found that the membrane with low rejection has more obvious elevation in rejection to $MgCl_2$ while the membrane with high rejection has small elevation in rejection with the increasing of forward electric field intensity which may be caused by that the electric field can improve the surface charge density of the membrane with low rejection. It is demonstrated that the auxiliary electric field can increase the surface charge density and improve the membrane rejection with little energy consumption. The membrane with high flux and charge characteristic can be efficiently used in desalination and waste water treatment process with auxiliary electric field.

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