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Abstract: A series of carboxymethyl cellulose sodium composite nanofiltration membranes were prepared through the method of coating and cross-linking. Effects of the preparation techniques and the operating conditions on the rejection performance of the resulting membranes were investigated, respectively. It suggested that the resulting composite NF membrane with excellent rejection performance should be prepared through a certain preparing technology. Attenuated total reflection infrared spectroscopy and atomic force microscopy were employed to characterize the

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resulting membrane. The rejection of this kind of negatively charged membrane to the electrolyte solutions decreased in the order of Na_2SO_4, NaCl, $MgSO_4$, and $MgCl_2$.

Keywords: Carboxymethyl cellulose sodium, composite nanofiltration membranes, rejection performance

INTRODUCTION

Nanofiltration (NF), a new type of membrane separation technology developed since the 1980's, lies between reverse osmosis (RO) and ultrafiltration (UF) (1). Nanofiltration can separate the low-molecular-weight organics due to the surface nano-sized pores. NF-membrane syntheses have been reviewed in the literature (2). Nanofiltration membrane process has been established as an important separation unit operation in environmental and pharmaceutical engineering processes (3–7).

Recently NF membranes based on natural polysaccharides gained more and more attention (7–10) due to their low cost and abundance. Polysaccharides can be easily modified into amphoteric, anionic, and cationic polymers. The problems related to the membranes prepared from polysaccharide and their derivatives are water solubility and excessive swelling, both of which could be solved by chemical cross-linking.

Cellulose, a linear polymer of β-(1→4)-D-glucopyranose units in $^4C_1$ conformation, is the most abundant and renewable natural polysaccharide on the earth. The cellulose-based membrane materials are traditional membrane materials and the most popular membrane materials for its abundance and re-usable characteristic. However, cellulose is a water-insoluble molecule because of its strong intra-molecular and intra-strand hydrogen bonds between polymer chains. So the dissolution of cellulose with chemical modification and derivatization is important for its further utilization in membrane materials. The hydroxyl groups on cellulose react similarly to simple substances such as alcohols. Thus, they may be readily oxidized, esterified, and etherified. The cellulose derivatives for membrane materials include regenerated cellulose (RCE), cellulose nitrate (CN), cellulose acetate (CA), cellulose triacetate (CTA), ethyl cellulose (EC)*s* etc. Many of the cellulose-based membranes were fabricated through the phase inversion method (11–13), and some were prepared using the method of coating and cross-linking (14).

Carboxymethyl cellulose (CMC), one of the important water-soluble cellulose ether derivatives, is synthesized by the alkali-catalyzed reaction of cellulose with chloroacetic acid. CMC is a negatively charged polymer, usually used in the form of sodium salt, i.e. carboxymethyl cellulose sodium (CMC-Na). In general CMC-Na is a water-soluble thickener, emulsifier and film-former often used in tablet coating. Owing to their low toxicity, CMC-Na has been frequently considered for various biomedical membrane materials (15–17). However, to our knowledge, there is no reported literature on using CMC-Na as the active layer material for composite NF membranes.

Epichlorohydrin (ECH) is a kind of generally used cross-linker. It is well known that the polysaccharides, including cellulose, are easily cross-linked with ECH. The earlier works (18–20) investigated the mechanisms of reaction of ECH with starch and cellulose, and physicochemical properties of modified carbohydrate polymers. The porous structure, forming from cellulose macromolecules cross-linking with ECH, forces the immobilization of oxygen groups of the polymer matrix. In this paper a novel kind of negatively charged composite NF membranes, CMC-Na/PVDF composite NF membranes, were fabricated through the method of coating and cross-linking. The rejection performance of inorganic electrolyte was also investigated. The objective of this study was to develop a novel kind of cellulose-based composite NF membrane and investigate systematically the effects of preparation and operation variables on the NF performances. The information will be useful for further improvement in the design of CMC-Na-based NF membranes.

EXPERIMENTAL

Materials and Apparatus

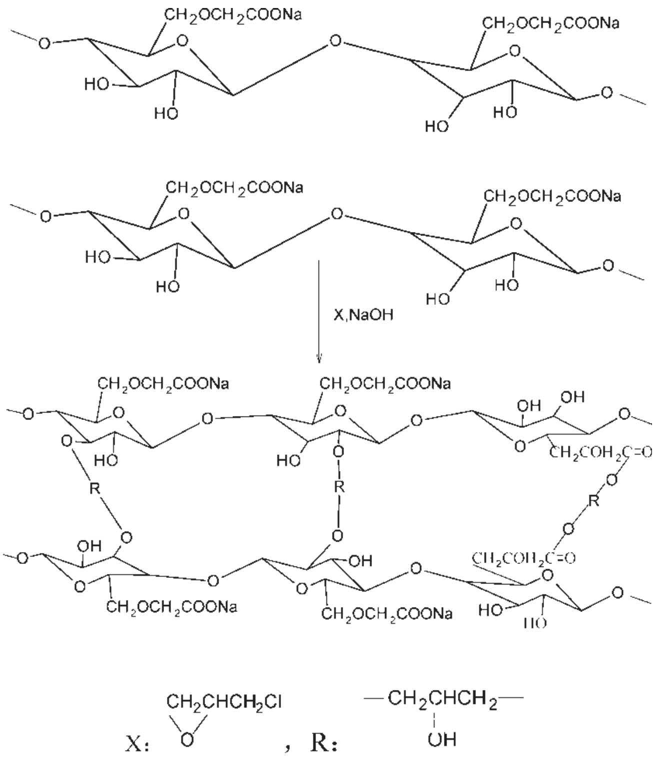
Poly (vinylidene fluoride) (PVDF) (FR904) resin and non-woven fiber were kindly supported by the Development Center of Water Treatment Technology, State Oceanic Administration, Hangzhou (China). Carboxymethyl Cellulose Sodium (CMC-Na) (degree of carboxymethylation (D.C.) $\approx$0.91) was provided by Shanghai Hengda Fine Chemical Co. (China). Analytical grade epichlorohydrin (ECH) was purchased from the Yixing Fandao Chemical Factory (China). Except for 1,4–Butanidol, which was of chemical grade, all the other reagents and solvents were of analytical grade and used without further purification. Deionized water with a conductivity of $2 \times 10^{-4}\,\mathrm{S \cdot m^{-1}}$ was used for membrane preparation and permeation experiments. G3 sand filter (4.5–9 um pore size; 25 mL volume) was purchased from Beijing Chemical Reagents Company (China).

Salt concentrations were determined with Model DDS-11A conductivity meter (Shanghai Lida Instrument Co., China). The ultrafiltration membrane evaluation apparatus was purchased from Development Center of Water Treatment Technology, State Oceanic Administration, Hangzhou (China). Infrared spectra (IR) and attenuated total reflection infrared spectra (ATR-IR) were measured with Avatar360 IR Spectrometer purchased from Nicolet Co. Contact atomic force microscopy (AFM) was performed using an SN-AF01 AFM system (Seiko Instruments Inc., Japan).

Preparation of CMC-Na/PVDF Composite Membranes

A PVDF UF membrane was cast from the PVDF solution in dimethyl formamide (DMF) at a weight ratio of 15:85 onto nonwoven fiber fixed on a glass plate with a glass blade at room temperature, immediately gelled in a water bath, and then rinsed for 24 h. The UF membrane had a pure water flux of 43.0 $\mathrm{kg \cdot m^{-2} \cdot h^{-1}}$ at 0.10 MPa pressure.

CMC-Na solutions were prepared by dissolving CMC-Na into deionized water at different weight ratios, stirring overnight, and being filtered with G3 sand filter. The degassed CMC-Na solution was coated onto the PVDF UF membrane taped to a glass plate with a finely polished glass rod. The thickness of the active layer was determined by 80 um-diameter brass wires attached to the two ends of the glass rod. Then they were cured in an oven at 50° for 1 h. After curing, the membranes were cross-linked under mild alkaline condition in a cross-linking bath composed of ethanol 96.7% and ECH with different concentration (0.067 M NaOH). Scheme 1 shows the cross-linking of CMC-Na with ECH. After cross-linking, the CMC-Na/



Scheme 1. Schematic representation of the cross-linking of CMC-Na with ECH.

PVDF composite membranes were washed with ethanol and acetone extensively, then immersed in deionized water before the permeation tests.

Characterization of the Resulting Composite NF Membrane

The chemical structure and the morphology of the resulting composite NF membrane were characterized with attenuated total reflection infrared spectroscopy (ATR-IR) and atomic force microscopy (AFM). The sample for characterization was prepared under the following conditions: CMC-Na concentration 2.2 wt%, curing time 1 h at 50°C, ECH concentration 7.0 wt%, and cross-linking time 3 h at 50°C.

ATR-IR characterization of the membrane surface was made with an ATR accessory of Nicolet Avatar360 IR Spectrometer. ZnSe crystal was used in the ATR accessory. Membrane samples were mounted flush to the ATR crystal. The ZnSe crystal was operated at a nominal angle of incidence of 45°, yielding 10 internal reflections at the membrane surface.

Contact mode AFM images in air were taken on an SN-AF01 AFM system (Seiko Instruments Inc., Japan) using the OLYMPUS Micro Cantilever with a specified spring constant of $0.09\ \mathrm{N \cdot m^{-1}}$. The tip on the end of the micro cantilever employed a sharpened pyramidal tip of silicon nitride.

Permeation Experiments

Without specification, the permeation tests were carried out using a UF membrane evaluation apparatus at a temperature, pressure, and concentration of inorganic electrolyte solution of room temperature, 0.40 MPa, and $1{,}000\ \mathrm{mg \cdot L^{-1}}$, respectively. The recirculation rate and fluid velocity in the channel were 40 L/h and $1.1\ \mathrm{m \cdot s^{-1}}$, respectively. The cycling flow of the feed solution was high-speed and cross-flow through the membrane test cell. Additionally, the operating pressure being lower, the concentration polarization could be minimized and ignored. The membranes were immersed in deionized water for 36 h and then pre-pressurized under 0.45 MPa for 0.5 h before testing. The concentrations of single inorganic electrolytes were determined conductometrically. The permeation flux of the membrane was determined by weighing the permeate penetrated through the membrane during a certain period of time.

Rejection was calculated with the following equation.

$$R = 1 - \frac{C_P}{C_f} \tag{1}$$

Where C_P and C_f are the concentrations of the permeate and the feed solution, respectively. The presented data are the averages of three measurements.

Molecular Weight Cut-off

Molecular weight cut-off (MWCO) of the resultant membrane for characterization was measured using 500 $\mathrm{mg \cdot L^{-1}}$ aq. solutions of polyethylene glycols (PEG) (M_W 200∼1,000 Da), respectively. The concentrations of the test solutes in the feed and the permeate were measured using Shimadzu TOC-V_{CPN} Total Organic Carbon (TOC) analyzer.

RESULTS AND DISCUSSION

Membrane Characterization

ATR-IR Spectra of CMC-Na/PVDF Composite NF Membrane

Figure 1 shows the ATR-IR spectra of a virgin PVDF UF membrane with just the CMC-Na coating (PVDF-CMC-Na), and with the cross-linked CMC-Na active layer (PVDF-CMC-Na-ECH). As for PVDF-CMC-Na-ECH, the bands at 1337.95 $\mathrm{cm^{-1}}$ and 1049.95 $\mathrm{cm^{-1}}$ became relatively intense and sharper, corresponding to the formation of the ether bonds synthesized by the etherization between ECH and -OH. The new band at 729.15 $\mathrm{cm^{-1}}$ represented the formation of the methylene present in the straight-chain aliphatic alcohol, which also confirmed the occurrence of the cross-linking reaction.

AFM Image of CMC-Na/PVDF Composite NF Membrane

Figure 2 shows the typical three-dimensional AFM image of CMC-Na/PVDF composite NF membrane in the scale of 1.25 μm. The AFM image gives the information that the surface of the resulting NF membrane is uneven and rough.

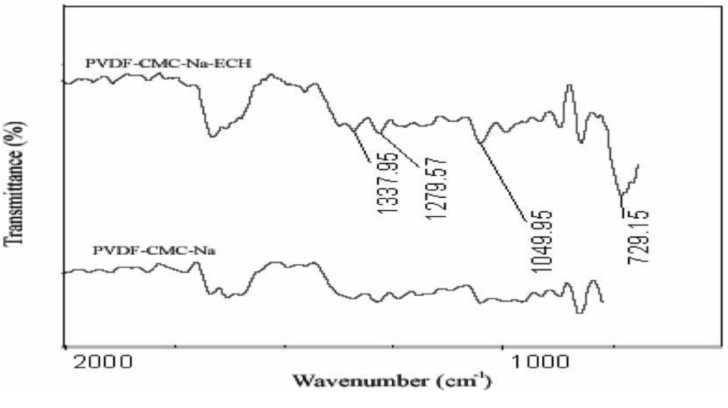


Figure 1. ATR-IR Spectra of CMC-Na/PVDF composite NF membrane.

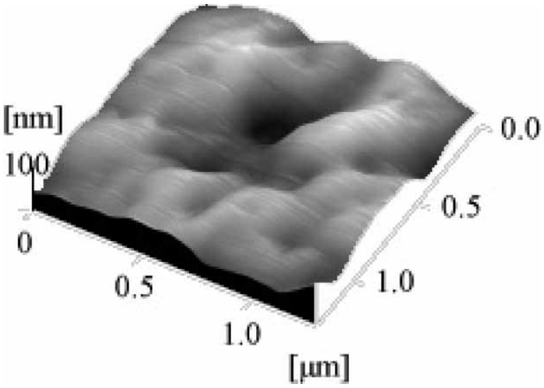


Figure 2. Three-dimensional AFM image of CMC-Na/PVDF composite NF membrane.

The color density shows the vertical profiles, where the bright regions are the high peaks and the dark regions are valleys. The roughness can be defined as Ra (the mean roughness of the surface), RMS (root-mean squared roughness), and P-V (the peak-to-valley distance). However, the other two definitions are less accurate than RMS (21), where RMS is 21.04 nm.

MWCO of the CMC-Na/PVDF Composite NF Membrane

MWCO was defined as the molecular weight of organic substance with retention of 90%. Figure 3 shows the rejections of the resultant NF membrane to polyethylene glycol (PEG) with different molecular weights. As shown in the figure, the observed rejections to PEG increased with the growth of their MWs under the operating pressure of 0.40 MPa. It can be concluded that the MWCO of the resultant NF membrane is ≈840 Da (corresponding to a rejection of 90%), which is in NF range. CMC-Na/PVDF composite NF membrane has a relatively high MWCO compared to many other polymer NF membranes.

Preparing Conditions on the Rejection Performance

Effect of CMC-Na Solution Concentration

A series of CMC-Na/PVDF composite membranes were prepared from CMC-Na solutions of different concentrations in the range of 0.5–2.2wt% following the same preparation technique as mentioned in 2.3. Figure 4 shows the effect of CMC-Na concentration on the rejection performance of the resulting composite membranes to 1,000 $\mathrm{mg \cdot L^{-1}}$ Na_2SO_4 solution. It can be seen

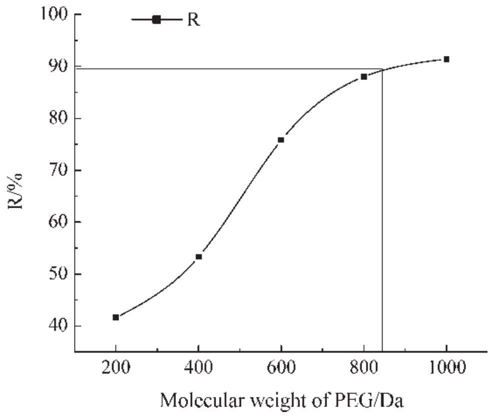


Figure 3. Rejections of CMC-Na/PVDF composite NF membrane to PEG with different molecular weights.

clearly that the rejection(R) was increased linearly while the permeate flux (F) decreased with the increase of CMC-Na concentration as it was in the range of 0.5–2.2 wt%. The low rejection and high flux at lower CMC-Na concentration might relate to defects, since smaller concentration ultimately means thinner layer and more defects. When the concentration of the casting solution increased, the density of the polymer network increased, resulting in a tighter skin layer and larger resistances to water flow. The resulting membrane prepared from CMC-Na solution concentration of 2.2 wt% has met an average rejection (88.5%) to Na_2SO_4 solution (1,000 mg · L^{-1}) as well as relatively low permeate flux compared to many other NF membranes.

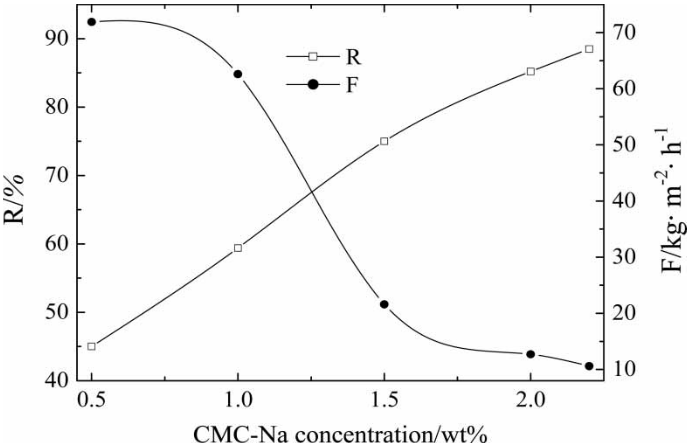


Figure 4. Effect of CMC-Na concentration on the rejection performance of CMC-Na/PVDF composite membranes.

Effect of ECH Concentration

Cross-linked with ECH solutions of different concentrations in the range of 4.0–8.0 wt%, a series of CMC-Na/PVDF composite membranes were prepared from 2.2 wt% CMC-Na solutions following the same preparation technique as mentioned in 2.3. Figure 5 shows the effect of ECH concentration on the rejection performance of the CMC-Na/PVDF composite membranes to 1,000 $\mathrm{mg \cdot L^{-1}}$ Na_2SO_4 solution. As can be seen from Fig. 5, the permeate flux decreased and the rejection to the electrolyte solution increased with the increase of ECH concentration until it was >7.0 wt%, which could be explained by the sieving effect. The increase of the cross-linking solution concentration would result in the reduction in pore size and water absorption, the increase in hydrophobicity and pore tortuosity, which would cause the decrease of the permeate flux and the increase of the rejection to inorganic electrolyte. Similar trends were also reported in the literatures (22, 23). However, the rejection began to decrease as ECH concentration >7.0 wt%, which could not be explained plausibly yet.

Effect of the Cross-linking Time

To investigate the effect of the cross-linking time, a series of CMC-Na/PVDF composite membranes prepared from 2.2 wt% CMC-Na solutions were cured in an oven at 50°C for 1 h, and then cross-linked with 7.0 wt% ECH solution for a period of time ranging from 1 h to 4 h. Figure 6 shows the effect of the cross-linking time on the rejection performance of CMC-Na/PVDF composite membranes to 1,000 $\mathrm{mg \cdot L^{-1}}$ Na_2SO_4 solution. As can be seen clearly from the figure, the cross-linking time had a remarkable effect on the rejection performance while it was $\leqq 3$ h. The rejection increased from 63.9

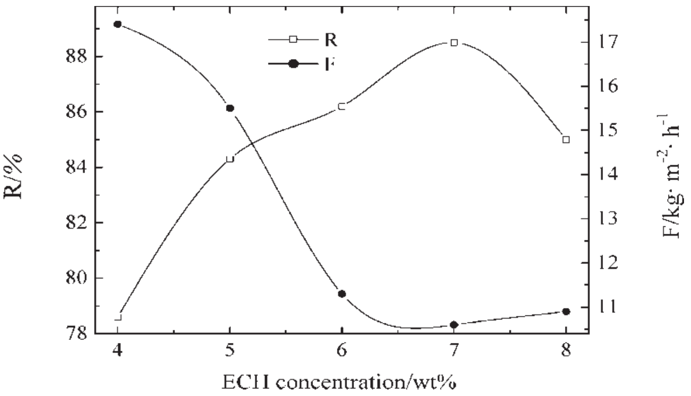


Figure 5. Effect of ECH concentration on the rejection performance of CMC-Na/PVDF composite membranes.

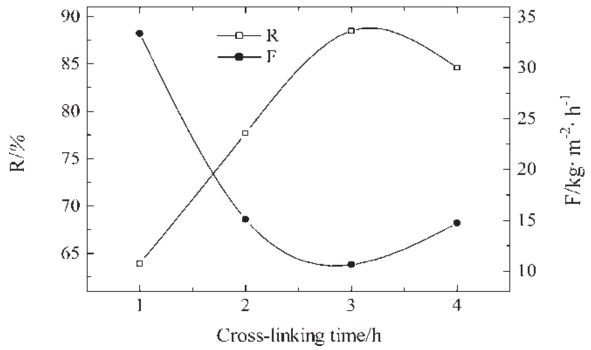


Figure 6. Effect of the cross-linking time on the rejection performance of CMC-Na/PVDF composite membranes.

to 88.5%, and the permeate flux decreased from 33.4 to 10.6 kg $\cdot$ m^{-2} $\cdot$ h^{-1} with the increase of the cross-linking time. However, the rejection began to decrease after ca. 3 h, for which there is no plausible explanation yet.

Effect of Low-Molecular-Weight Organic Additives in the Casting Solution

A low-molecular-weight organic substance can be employed as an additive to adjust the rejection properties of the membranes. CMC-Na/PVDF composite membranes were prepared from 2.2 wt% CMC-Na casting solution in the presence of four such kinds of low-molecular-weight organic additives by the same preparation technique described in 2.3, where the organic additives were each employed at 5.0 wt% concentration. It can be seen from Table 1 that the rejection to 1,000 mg $\cdot$ L^{-1} Na_2SO_4 solution decreased in the order of PEG200, glycerol, 1,4-butanediol, and PEG400, while the permeate flux increased in the order of PEG400, glycerol, 1,4-butanediol, and PEG200. Hence, PEG200 is an optional low-molecular-weight organic additive for CMC-Na/PVDF composite membranes.

Operating Conditions on the Rejection Performance

Operating Pressure

The Hagen-Poisuelle equation defines the relationship between solvent flux and trans-membrane pressure:

$$J_v = \frac{r_p^2}{8u_p(\Delta x/A_k)}\Delta P \tag{2}$$

where J_v is the solvent flux (kg $\cdot$ m^{-2} $\cdot$ h^{-1}), r_p the pore radius (m), ΔP the trans-membrane pressure (Pa), u$_p$ the solvent viscosity (Pa $\cdot$ s) in the

Table 1. Effect of low-molecular-weight organic additives into casting solution on the rejection performance of CMC-Na/PVDF composite membranes

Organic additives/ 5.0 wt%	R/%	$F/kg \cdot m^{-2} \cdot h^{-1}$
In the absence of organic additive	88.5	10.6
PEG400	76.5	8.7
Glycerol	83.5	9.3
1,4-Butanediol	83.1	12.9
PEG200	86.2	16.2

membrane pores, Δx the effective membrane thickness (m), and A_k the effective membrane porosity.

The effect of operating pressure on the rejection performance is shown in Figure 7. With the operating pressure increasing in the range of 0.10–0.45 MPa, both the flux and the rejection increased, and the curve of R became smooth after 0.40 MPa. The trans-membrane pressure is the difference of the operating pressure and the osmotic pressure. Compared with the operating pressure, the osmotic pressure could be neglected for NF of inorganic electrolytes of low concentration. The permeate flux presented a nearly linear relation with the operating pressure, in accordance with the Hagen-Poisuelle equation.

Feed Concentration

The effect of feed solution concentration on the permeate flux and the rejection to Na_2SO_4 solution by CMC-Na/PVDF composite NF

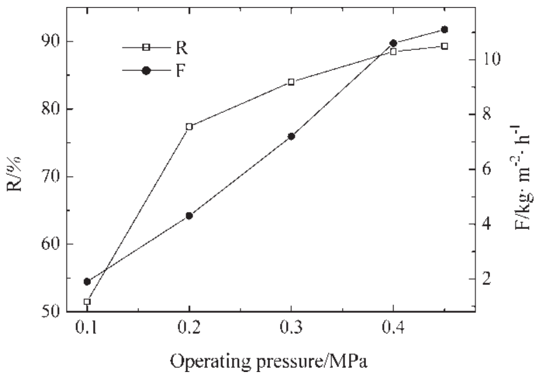


Figure 7. Effect of the operating pressure on the rejection performance of CMC-Na/PVDF composite membranes.

membrane is shown in Figure 8. Obviously both the rejection and the permeate flux decreased with the increase of the feed solution concentration. However, the feed solution concentration had a more marked effect on R than on F. As the feed solution concentration increased from 500 to 2,500 mg $\cdot$ L^{-1}, the rejection decreased from 92.1 to 65.1%, and the permeate flux decreased from 11.1 to 7.6 kg $\cdot$ m^{-2} $\cdot$ h^{-1}, which could be explained by Donnan exclusion theory. Because the active layer of the CMC-Na/PVDF composite NF membrane contains carboxymethyl groups, rejection to inorganic electrolyte mainly resulted from the repulsion between the membrane active layer and the anions. But the cations (Na$^+$) screening effect on the membrane negatively charged groups became stronger because of the increase of feed concentration, leading to the decrease of the membrane charge density and the repulsion forces on the anions (24). On the other hand, the trans-membrane pressure decreased because the osmotic pressure increased with the increase of the feed concentration, which resulted in the decrease of the permeate flux.

Rejection of Different Inorganic Electrolytes by CMC-Na/PVDF Composite NF Membrane

The rejection performances to different inorganic electrolytes by CMC-Na/PVDF composite NF membrane are shown in Table 2. It suggests that the rejection of this kind of membrane to the electrolyte solutions decrease in the order of Na_2SO_4, NaCl, $MgSO_4$, and $MgCl_2$, which is in accordance with most of the commercial NF membranes and agrees qualitatively with the Donnan exclusion principle. It is well-known that

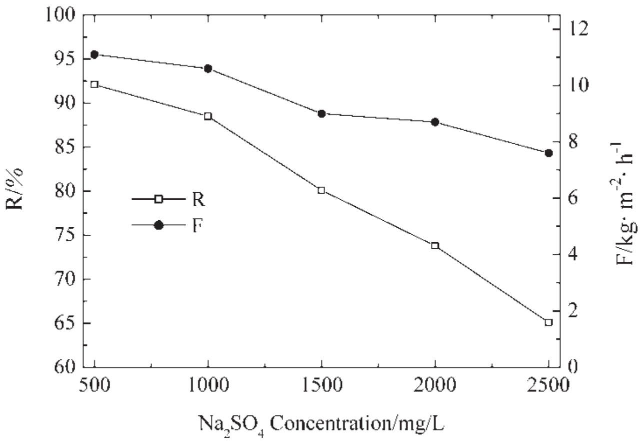


Figure 8. Effect of the feed concentration on the rejection performance of CMC-Na/PVDF composite NF membrane.

Table 2. Rejection to different inorganic electrolytes by CMC-Na/PVDF composite NF membrane

Feed solutions/ 1,000 mg · L^{-1}	F/kg · m^{-2} · h^{-1}	R/%
Na_2SO_4	10.6	88.5
NaCl	11.2	33.3
$MgSO_4$	7.2	30.0
$MgCl_2$	6.8	12.1

the charge effect of electrolyte-ions should be considered as a dominant factor for NF of inorganic electrolytes of low concentration (25). The active layer of CMC-Na/PVDF composite NF membrane contains carboxymethyl groups and had stronger repulsion to SO_4^{2-} than Cl^-. As for $R_{NaCl} > R_{MgSO4}$, it might be resulted from the combination between Mg^{2+} and the anions on the membrane surface, which would decrease the effective surface charge of membranes and then reduced the rejection performance. Lower salt rejections for divalent cations have also been reported in the literatures (26–28).

CONCLUSION

Novel negatively charged composite NF membranes were prepared through a method of coating and cross-linking using CMC-Na, PVDF UF membranes, and ECH as the active layer material, the base membranes, and the cross-linking agent, respectively.

The results suggest that the CMC-Na/PVDF composite NF membranes with excellent rejection performance could be prepared under the following conditions: CMC-Na concentration 2.2 wt%, curing time 1 h at 50°C, ECH concentration 7.0 wt%, and cross-linking time 3 h at 50°C in EtOH 96.7% (0.067 M NaOH) solution. At room temperature and 0.40 MPa the rejections of the resulting membrane to Na_2SO_4 and NaCl solutions (1000 mg · L^{-1}) were 88.5 and 33.3%, respectively, while the permeate fluxes were 10.6 and 11.2 kg · m^{-2} · h^{-1}, respectively. The MWCO of the resulting membrane was ≈840 Da. The resulting NF membrane had a relatively high MWCO, an average rejection to divalent anion, and a relatively low permeate flux compared to many other polymer NF membranes. The rejection order of this kind of membrane to the electrolyte solutions was in accordance with most of commercial NF membranes.

The preparation conditions, including CMC-Na concentration, ECH concentration, and cross-linking time, had effects on the rejection performance of the composite membranes. It suggested that the rejection increase linearly while the flux decrease with the increase of CMC-Na concentration as it was in the range of 0.5–2.2 wt%.

The rejection of this kind of negatively charged NF membrane to the inorganic electrolyte solutions decreased in the order of Na_2SO_4, NaCl, $MgSO_4$, and $MgCl_2$. The rejection and the permeate flux increased with the increase of the operating pressure in a certain range. The permeate flux presented a nearly linear increase, and the rejection curve became smooth after the operating pressure was >0.40 MPa. Because of the cations screening effect, both the rejection and the permeate flux decreased with the increase of the feed solution concentration.

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