Sulfated Chitosan (SCS)/Polysulfone (PS) Composite Nanofiltration Membrane Surface Cross-linked by Epichlorohydrin

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ABSTRACT

A series of composite nanofiltration membranes were prepared via a method of coating and cross-linking from sulfated chitosan (SCS) as the material of the active layer, Polysulfone (PS) UF membrane as the base membrane, and epichlorohydrin (ECH) as the cross-linker. Attenuated total reflection infrared spectroscopy (ATR-IR), scanning electron microscopy (SEM), and atomic force microscopy (AFM), were employed to characterize the resultant composite membrane. The effects of the operating conditions on the rejection performance of the composite membrane were investigated, respectively. The rejections of the resulting membrane to Na_2SO_4 and NaCl solutions (1000 $mg \cdot L^{-1}$) were 90.8 and 32.5% at 0.40 MPa and 15℃, while the permeate fluxes were 22.9 and 58.4 $kg \cdot m^{-2} \cdot h^{-1}$ respectively. The rejections of this kind of membrane to the electrolyte solutions decreased in the order of Na_2SO_4, NaCl, $MgSO_4$, and $MgCl_2$. It suggested that the membrane active layer acquires a negative surface charge distribution by the adsorption of anions from the electrolyte solution, and this charge distribution mainly determined the membrane performance.

***Keywords*:** sulfated chitosan (SCS), composite nanofiltration membranes, epichlorohydrin, rejection performance

1 INTRODUCTION

Most of NF membranes today are composite membranes, which consist of a UF membrane as the support for the very thin skin layer. Chitosan is easily modified and many derivatives have been prepared to meet different needs. Sulfated chitosan (SCS.) is the product of the chitosan sulfation, having sulfate groups on some of both the amino and primary hydroxyl sites of the glucosamine unites of the chitosan structure. ECH is a kind of generally used cross-linker. It is well known that the polysaccharides, including chitosan, are easily cross-linked with ECH.

In this paper, a novel kind of sulfated chitosan composite NF membranes surface cross-linked by ECH, were prepared through the method of coating and cross-linking. The rejection performance of inorganic electrolyte and the rejections of mono/oligosaccharides were also investigated. The objective of this study was to develop a novel kind of amphoteric composite NF membrane and investigate systematically the effects of preparation and operation variables on the NF performances. The results may provide a basis for further research on it.

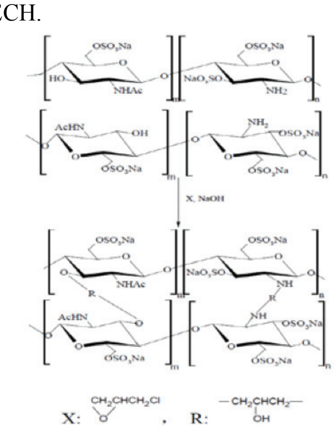
2 EXPERIMENTAL

2.1 Materials and apparatus

The Polysulfone (PS) UF membrane (MWCO= 10000 Da) and the ultrafiltration membrane evaluation apparatus were provided by the Development Centre of Water Treatment Technology, State Oceanic Administration, Hangzhou (China).

2.2 Synthesis of SCS and its cross-linking with ECH

Sulfated chitosan (SCS) was synthesized through a homogeneous method described in the literatures [1, 2]. The sulfate group content in SCS was determined to be 38.14wt% by the gravimetric analysis of hydrochloric and barium sulfate precipitation [3]. Scheme 1 shows the cross-linking of SCS with ECH.



Scheme 1 Schematic representation of the cross-linking of SCS with ECH

2.3 Preparation of SCS/PS composite NF membranes

SCS solutions were prepared by dissolving SCS into DI water at different weight ratios and were filtered with G4 sand filter.

SCS/PS composite membranes were prepared by coating the SCS solutions onto the PS UF membrane with a finely polished glass rod, followed by curing in an oven at 50℃ for 1h, then immersing the membranes in the ECH/EtOH 95% (0.067M NaOH) solution, and cross-linking at 50℃ for a period of time.

2.4 Characterization of the resulting composite NF membrane

The morphology and the chemical structure of the resulting composite NF membrane were characterized with attenuated total reflection infrared spectroscopy (ATR-IR), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

The sample for characterization and permeation experiments was prepared under the following conditions: SCS concentration 2.2 wt%, curing time 1h at 50℃, ECH concentration 2.0 wt%, and cross-linking time 2h at 50℃.

2.5 Permeation experiments

To test the rejection properties of the resulting composite membranes, Na2SO4, NaCl, MgSO4, and MgCl2 solutions were employed as the inorganic electrolytes. The concentrations of the single inorganic electrolytes were measured with the conductivity meter. The concentrations of the mono/oligosaccharides were determined using Shimadzu TOC-V_{CPN} Total Organic Carbon (TOC) analyser. The permeation flux of the membrane was determined by weighing the permeate penetrating through the membrane during a certain period of time.

2.6 Molecular weight cut-off (MWCO)

Molecular weight cut-off of the resulting membrane for characterization, was measured using 500 mg·L-1 aq. solutions of polyethylene glycols (PEG) (MW 200-1000Da), respectively. The concentrations of the test solutes in the feed and the permeate were also determined using the TOC analyser.

3 RESULTS and DISCUSSION

3.1. Membrane characterization

3.1.1. ATR-IR spectra of SCS/PS composite NF membrane

Fig.1 shows the ATR-IR spectra of a virgin PS. UF membrane with just the SCS coating (PS-SCS), and with the cross-linked SCS active layer (PS–SCS– ECH). As for PS–SCS– ECH, there is a distinct band at 1585.47 cm-1 attributed to the bending vibration of aliphatic secondary amine, which was synthesized by the reaction between -NH2 and ECH. The band at 1068.71cm^{-1} became relatively intense and sharper, corresponding to the formation of the ether bonds synthesized by the etherization between ECH and –OH. The sharper band at 1101.37cm^{-1}, corresponding to the stretching vibration of the chain aliphatic alcohol, confirmed the introduction of the hydroxyl groups into the straight chains. Another new band at 731.21 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.

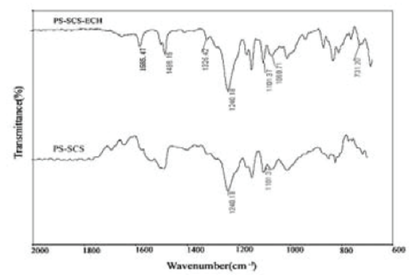


Fig. 1 ATR-IR spectra of SCS/PS composite NF membrane

3.2 Permeation characteristics

3.2.1 Molecular weight cut-off of SCS/PS composite NF membrane

Fig. 2 shows the rejections of the resulting 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 0.4MPa. The rejections to PEG200, PEG400, PEG600, PEG800, and PEG1000 are 24.1, 44.9, 73.4, 87.9, and 95.5%, respectively. Hence, the molecular weight cut off (MWCO) of the resulting NF membrane is 925Da (corresponding to a rejection of 90%).

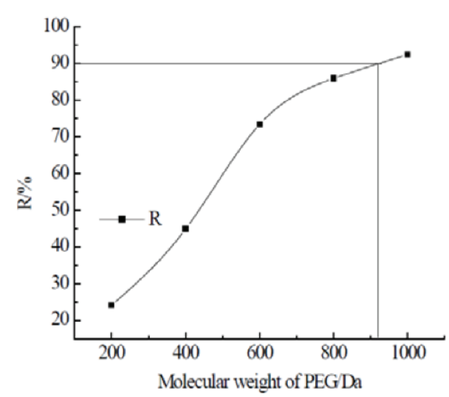


Fig. 2 Rejections of SCS/PS composite NF membrane to PEG with different molecular weights

3.2.2 Rejection of different inorganic electrolytes by SCS/PS. composite NF membrane

The rejection performances to different inorganic electrolytes by SCS/PS composite NF membrane are shown in Table 1. 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 agrees qualitatively with the 'Donnan' exclusion principle. With a MWCO of 925Da, it is obvious that sieving effects will be of no importance in the case of single inorganic electrolytes. Additionally, it is well known that the charge effect of electrolyte-ions should be considered as a dominant factor for NF of inorganic electrolytes of low concentration [4]. The active layer of SCS/PS composite NF membrane could acquire a negative surface charge distribution by the adsorption of anions from the solution, and this charge distribution mainly determines the NF performance [5]. On the other hand, the active layer of SCS/PS. composite membrane contained sulfate group 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.

Table 1 Rejections to different inorganic salts by SCS/PS composite NF membranes

Feed solution/1000 mg·L^{-1}	F/kg·m^{-2}·h^{-1}	R/%
Na_2SO_4	22.9	90.8
NaCl	58.4	32.5
$MgSO_4$	21.3	27.9
$MgCl_2$	58.2	8.6

3.3 Operating conditions on the rejection performance

3.3.1 Operating pressure

The effect of operating pressure on the rejection performance is shown in Fig. 8. With the operating pressure increasing in the range of 0.20-0.40 MPa, both the permeate flux and the rejection increased, and the curve of *R* became smooth after 0.35 MPa. The permeate flux presented a nearly linear relation with the operating pressure, which could be partly explained by the solution-diffusion model. The permeate flux is in direct proportion to the trans-membrane pressure, which 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. Thus the operating pressure is approximately lineally to the trans-membrane pressure.

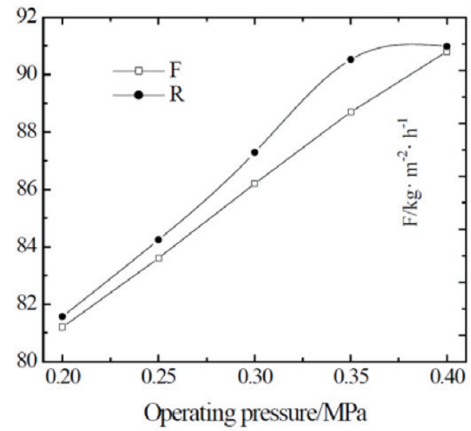


Fig. 3 Effect of the operating pressure on the rejection performance of SCS/PS composite NF membranes

3.3.2 Feed concentration

The effect of feed solution concentration on the permeate flux and the rejection to Na_2SO_4 solution by SCS/PS is shown in Fig.9. Obviously the feed solution concentration had a marked effect on the rejection. The rejection decreased with the increase of the feed solution concentration, and it was in the range of 86.3-98% as the feed solution concentration ranged from 500 to 2000 mg·L^{-1}, which could be explained by 'Donnan' exclusion theory. The rejection of SCS/PS composite membrane to inorganic electrolytes, mainly resulted from the repulsion between the membrane active layer and anions (SO_4^{2-}), and the rejection increases with the membrane charge density regardless of the kind of electrolyte and permeate volume flux, since fewer co-ions can enter the membrane pores [6]. But the cations (Na^+) shield 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 repulsion forces on the anions [5]. 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.

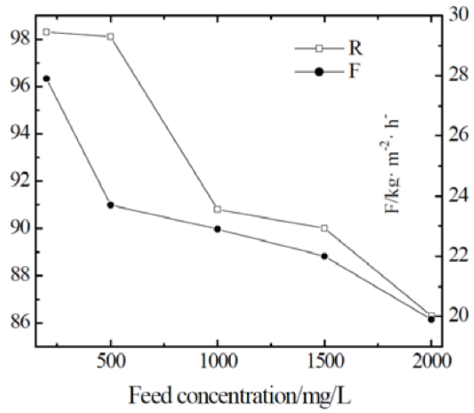


Fig. 4 Effect of the feed concentration on the rejection performance of SCS/PS composite NF membranes

4 CONLUSIONS

Novel amphoteric composite NF membranes were prepared through a method of coating and cross-linking using SCS, PS UF membranes, and ECH as the active layer material, the base membranes, and the cross-linking agent, respectively. Under the certain preparing conditions, the resulting NF membrane had moderate flux and excellent rejection to Na2SO4 solution (1000 mg·L-1). Based on the MWCO, the rejections of different inorganic electrolytes, and the rejections of mono/oligosaccharides, it can be concluded that the SCS/PS composite NF membranes cross-linked by ECH have a potential for the separation of mono/divalent inorganic electrolytes from low-molecular-weight organics.

In the ATR-IR spectrum of SCS/PS composite NF membrane surface cross-linked by ECH, there is a distinct band at $1585.47cm^{-1}$(due to the bending vibration of aliphatic secondary amine), and the intense and sharper band at $1068.71cm^{-1}$(due to the additional ether bonds). These two observations clearly revealed the cross-linking of hydroxyl groups and amino groups with ECH.

Both the rejection and the permeate flux increased with the increase of the operating pressure in a certain range. The permeate flux presented a linear increase, and the rejection curve became smooth after the operating pressure was ＞ 0.35MPa.

The resultant NF membrane was characterized with rejections of inorganic electrolytes including Na_2SO_4, NaCl, $MgSO_4$, and $MgCl_2$. The rejection of this kind of membrane to inorganic electrolyte solutions decreased in the order of Na_2SO_4, NaCl, $MgSO_4$, and $MgCl_2$. It can be seen clearly, from the results, that this kind of amphoteric composite NF membranes showed similar rejection performance to negatively charged composite NF membranes. It suggests that the membrane active layer acquire a negative surface charge distribution by the adsorption of anions from the electrolyte solution, and this charge distribution mainly determines the membrane performance.

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