

# Preparation and characterization of a novel emphatically charged strengthened chitosan composite nanofiltration membrane

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**Abstract.** In this paper, chitosan was grafted with acrylic acid and positively charged elements, and a series of reinforced nanofiltration membranes were prepared by coating modified chitosan polymer with polysulfone ultrafiltration membrane as support. The structure of chitosan derivatives and polymers was characterized by infrared spectrum, and the membrane structure was characterized by scanning electron microscope and atomic force microscope. The performance of composite nanofiltration membrane was closely related to the structure of polymer and the electrical properties of positively charged elements. The rejection rate of 50% molar ratio composite nanofiltration membrane to CaCl<sub>2</sub> reached 97.4%. The corresponding flux is 430.7 Lm<sup>2</sup>h<sup>-1</sup>. The retention order was: CaCl<sub>2</sub> > NaCl > Na<sub>2</sub>SO<sub>4</sub>. The tensile strength increased by 27.3%. Acid resistance (5%HCl) was improved by 50.5%. Alkali resistance (5%NaOH) increased by 42.2%. The results showed that the positive charge enhanced chitosan composite nanofiltration membrane had excellent performance. The charge effect had no effect on NaCl and Na<sub>2</sub>SO<sub>4</sub>, but had significant effect on CaCl<sub>2</sub>. The membrane is a typical positive charged nanofiltration membrane suitable for separating high-valent cations from weak acids or weak bases.

## 1. Introduction

Nowadays, Nanofiltration (NF) membrane, as a new type of separation membrane between reverse osmosis (RO) membrane and ultrafiltration (UF) membrane, has been developed actively [1]. Thanks to its special features like high separation efficiency and low energy consumption required in operation, NF has been connected solely or in combination with other division handle in numerous areas such as water softening treatment of squander water, oil industry, nourishment handling and so on[2,3].

In this paper, a composite NF membrane, based on multi-layer composite structure, was designed, with polysulfone UF membrane serving as the foundation to offer mechanical strength and the positively charged polymer of adjusted chitosan as the best layer to supply filtration work. In arrange to upgrade mechanical quality and electrical property of NF layer, crylic corrosive and emphatically charged compound were joined to chitosan through hydroxylation. At that point the polymer was gotten by free radical polymerization of adjusted chitosan. A arrangement of NF layer were arranged with this plan. The application prospect of the film will be overseas.

## 2. Experiment

### 2.1 Materials and approaches

A self-made device was utilized within the layer execution test. The conductivity of the arrangement was measured by DDS-307 conductivity meter (Shanghai Leici Instrument Production line). The chemical composition of the altered chitosan and polymer was measured by Range One infrared spectrometer (PerkinElmer). The morphology of NF film was watched by S4800 filtering electron microscopy (HITACHI) and Measurement Symbol transmission electron microscopy (Bruker company). LDS- 20KN ductile testing machine (Huikai Testing Instrument Co., Ltd.) was utilized for film malleable quality test.

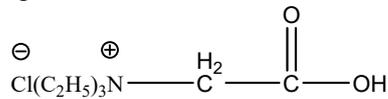
Chitosan [Mw≥20000 Da, degree of deacetylation (DD≥90%)]; N-methyl pyrrolidone, azodiisobutyronitrile (AIBN), methanesulfonic acid, acrylic acid, SOCl<sub>2</sub> and polyvinylpyrrolidone, gained from Sinopharm Chemical Reagent Co. Ltd, were all expository review acquired from Sinopharm Chemical Reagent Co. Ltd; acidic corrosive, acetone, glutaraldehyde and polyvinyl liquor were gotten from Shenyang Xinxin reagent Manufacturing plant; polysulfone was obtained from Shanghai Shuguang chemical plastics mechanical enterprise.

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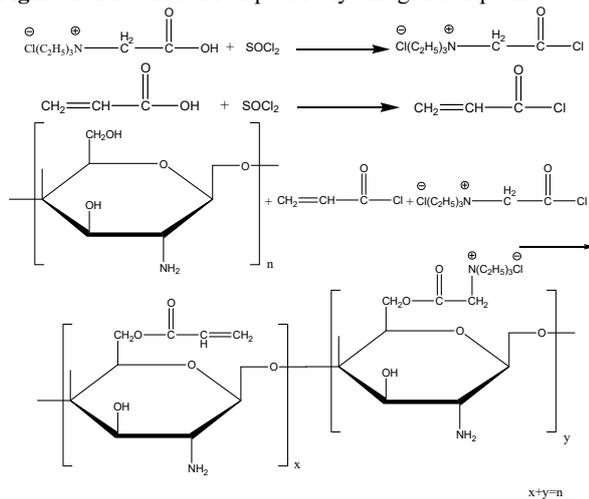
## 2.2 Preparation of modified chitosan

The structure of the positively charged compound (M<sub>1</sub>) was shown in Figure 1.

Chitosan was modified by acrylic acid and positively charged compound in different ratio. The schemes was shown in Figure 2.



**Figure 1.** The structure of positively charged compound



**Figure 2.** Scheme of modified chitosan synthesis Common forms to adjust chitosan preparation.

(1) Responding with SOCl<sub>2</sub> at 40°C for 3 hours, acrylic corrosive and emphatically charged compound chlorides were arranged. The items were decontaminated through distillation.

(2) Picked up from the final step, the acyl chlorides were broken down in chloroform, and is included to the chitosan methane sulfonic corrosive arrangement dropwise for more than 3.5 hours. Table 1 appears the proportion between emphatically charged compounds and acyl chloride. After the response, cool down the response blend to 4°C for 10 hours some time recently acetone precipitation treatment. Filt the items twice and dry beneath vaccuum condition.

**Table 1.** Esterification reaction feeding

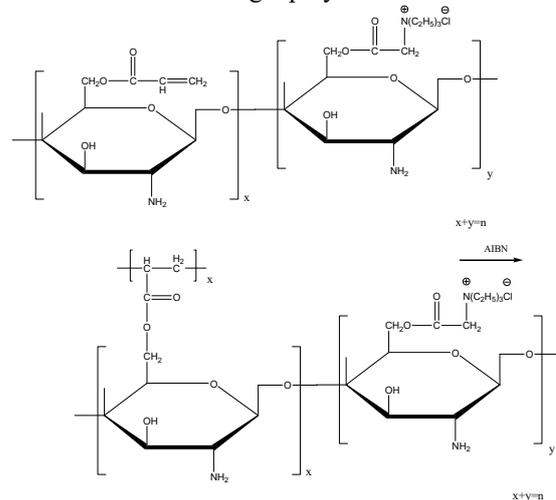
Chitosan derivatives	n <sub>cts</sub> /mol	n 丙烯酸氯 /mol	m <sub>M1</sub> /mol	A/%
D <sub>1-0</sub>	0.005	0.005	0	0
D <sub>1-1</sub>	0.005	0.0049	0.0001	2
D <sub>1-2</sub>	0.005	0.00475	0.00025	5
D <sub>1-3</sub>	0.005	0.0045	0.0005	10
D <sub>1-4</sub>	0.005	0.004	0.001	20
D <sub>1-5</sub>	0.005	0.0025	0.0025	50
D <sub>1-6</sub>	0.005	0.0015	0.0035	70
D <sub>1-7</sub>	0.005	0.0005	0.0045	90
D <sub>1-8</sub>	0.005	0	0.005	100

Note:A: molar ratio of positively charged compound and acyl chlorides.

## 2.3 Preparation of polymer

The general process of polymer preparation is shown in Figure 3.

The adjusted chitosan was broken down in dry tetrahydrofuran and AIBN was included as initiator. The polymerization was carried out beneath the assurance of nitrogen at 60 °C for 24 hours. The response blend was accelerated with methanol some time recently filtration. The item was washed once more with hot methanol and dried beneath vacuum to get polymer.



**Figure 3.** Scheme of polymer synthesis

## 2.4 Preparation of UF membranes

The polysulfone UF film was arranged by stage reversal, and the process was indicated as below[4]:

(1) 4.2g polysulfone was broken down in 25.7g N-methylpyrrolidone. 0.12g acetone and 0.075g polyvinylpyrrolidone (PVP) were included into the arrangement to create a casting arrangement, and the insoluble pollutions were evacuated by G2 sand channel. The arrangement was at that point permitted to stand for 10 hours.

(2) The casting arrangement was connected to a chunk of cloth (80 gap) dressing on the glass. To begin with, the dissolvable within the film was partially evaporated at room temperature for one diminutive, and after that the film was exchanged to a water shower for forming.

## 2.5 Preparation of composite NF membranes[5]

The polymer was broken down in 2.5ml 6% acidic corrosive arrangement with 0.06% polyvinyl liquor (porogen). The casting arrangement was gotten by deoxidizing the over solution.

The polysulfone ultrafiltration layer was settled on the glass. The pouring fluid was at that point coated on the ultrafiltration layer. The recently shaped layer was vaporized at room temperature for 60 seconds and after that crosslinked with 1% glutaraldehyde. The composite films were arranged after 16 hours at room temperature.

## 2.6 Permeation experiment

Flux and dismissal were calculated based on the conditions 1 and 2.

$$F = V / A t \quad (1)$$

Where: F is the flux; V is the volume of the penetrating liquid passing through the film; A is the compelling range of layer ( $0.93\text{cm}^2$ ); t is the time for saturation.

$$R = (1 - C_p / C_0) \times 100\% \quad (2)$$

Where: R is the dismissal;  $C_p$  and  $C_0$  are the concentrations of the penetrated liquid and bolster individually.

The concentration was supplanted by the conductivity of salt arrangements since the  $1000\text{mg/L}$  arrangements were exceptionally weakened arrangement in this research.

### 3. Results and discussions

#### 3.1 Infrared analysis

##### 3.1.1 Infrared examination of altered chitosan.

The assimilation band at  $1750\text{cm}^{-1}$  was related to the extending vibration of ester carbonyl; the assimilation band at  $1200\text{cm}^{-1}$  was related to the extending vibration of ether linkage; the assimilation band at  $1700\text{cm}^{-1}$ - $1600\text{cm}^{-1}$  was related to the extending vibration of carbon-carbon twofold bond; and the assimilation band at  $1039\text{cm}^{-1}$  was related to the extending vibration of C-N in quaternary ammonium gather.

##### 3.1.2 Infrared analysis of polymer.

The comes about appeared comparing with the adjusted chitosan, twofold bond assimilation top vanished at  $1600\text{cm}^{-1}$ - $1700\text{cm}^{-1}$ . The polymerization of altered chitosan was fruitful.

#### 3.2 Impact of molar proportion on the dismissal and flux of composite NF membrane

The test of composite nanofiltration layer was conducted after a pre-pressure at  $0.4\text{ Mpa}$  for  $0.5$  hour. The connections between molar proportion and film execution were appeared in Figure 4 and Figure 5. The dismissal for  $\text{CaCl}_2$  expanded as the expanding of molar proportion till  $50\%$ , which was from  $96.2\%$  to  $97.4\%$ . When molar proportion was higher than  $50\%$ , the dismissal dropped. Whereas the dismissal of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  diminished. The dismissal of  $\text{Na}_2\text{SO}_4$  was littler than  $\text{NaCl}$ . The flux expanded all the time as appeared in Figure 5. The information shown the structure of polymer, the charged characteristic of  $\text{M}_1$  and right rate was vital for the composite film execution. The acrylic corrosive made the polymer thickness expanded, which driven to thick structure in surface of NF film. So the dismissal of composite layer was tall for salt arrangement. The work of  $\text{M}_1$  was Donnon exclusion [6]. Since the dynamic layer had quaternary ammonium bunch dissemination and permitted a more grounded shock of  $\text{Ca}^{2+}$  than  $\text{Na}^+$ , the arrange of dismissal:  $\text{CaCl}_2 > \text{NaCl} > \text{Na}_2\text{SO}_4$ . The reason of  $\text{NaCl} > \text{Na}_2\text{SO}_4$  was that the fascination was more grounded for  $\text{SO}_4^{2-}$  than  $\text{Cl}^-$ . The drift of  $\text{CaCl}_2$  can be clarified as takes after: the electrostatic impact fortified with the increment of molar proportion, which driven to

the expanding of the dismissal. The dismissal started to diminish when molar proportion surpassed  $50\%$ , which was the result that the polymer consistency diminished. It was ordinary emphatically charged nanofiltration layer. The nanofiltration membrane of  $50\%$  molar proportion was the most excellent.

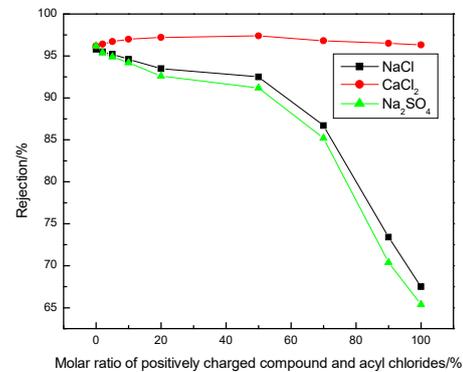


Figure 4. Effect of molar ratio on the rejection of the composite membrane

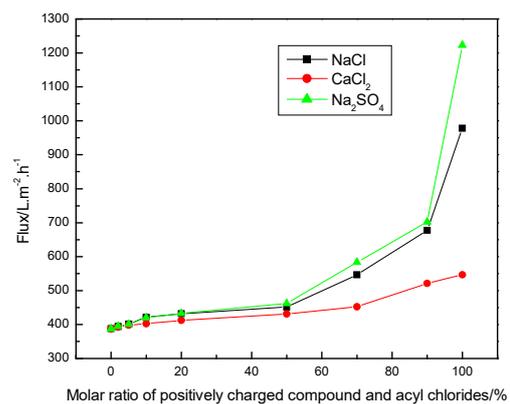


Figure 5. Effect of molar ratio on the flux of the composite membrane

#### 3.3 Investigation of mechanical quality

The tensile strength test was carried out on the film with a width of  $10\text{mm}$ . The tensile strength decreased from  $9.2\text{N}$  to  $6.6\text{N}$  with increasing molar ratio. The reason was that the viscosity of the polymer decreased with the increase of molar ratio. The tensile strength of  $50\%$  molar nanofiltration membrane was  $27.3\%$  higher than that of  $100\%$  molar nanofiltration membrane.

#### 3.4 Analysis of acid resistance

The acid resistance test was carried out with hydrochloric acid ( $5\%$ ) at  $0.4\text{ MPa}$ . When the molar ratio increased from  $36.8$  to  $20.2\text{ h}$ , the acid resistance decreased with the increase of the molar ratio. The reason was that the viscosity of the polymer decreased with the increase of the molar ratio, resulting in the decrease of the polymer density. Acid resistance of  $50\%$  molar ratio nanofiltration

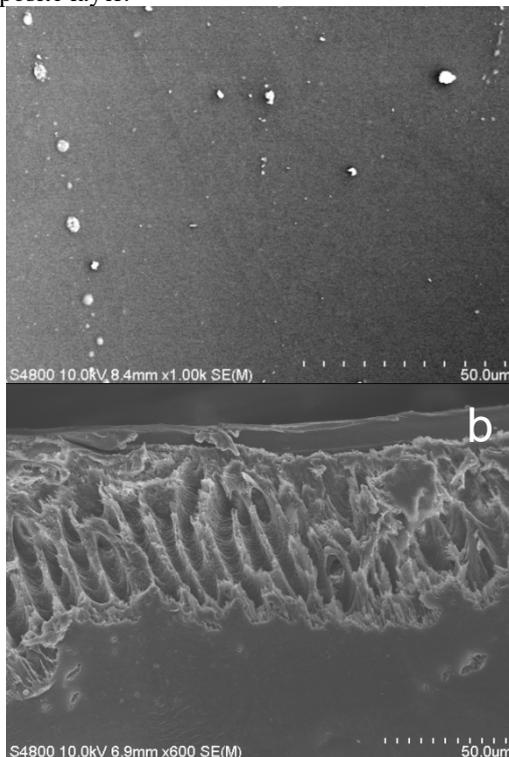
membrane increased 50.5% comparing with 100% molar ratio nanofiltration membrane.

#### Analysis of alkali resistance

Under the condition of 0.4 MPa, the alkali resistance test was carried out with 5% sodium hydroxide (NaOH). From 31.8 h to 18.7 h, the alkali resistance decreased with the increase of the molar ratio. The reason was consistent with acid resistance analysis. The alkali resistance of 50% mole ratio nanofiltration membrane was 42.2% higher than that of 100% mole ratio nanofiltration membrane.

### 3.5 Structure characteristic of composite membrane

The 50% molar proportion cross area and surface were characterized by S4800 filtering electron magnifying instrument, as appeared in Fig. 6. The surface of the composite layer was amplified by 1000 times, as appeared in Fig. 6 (a), and (b) the cross segment of the layer was amplified by 600 times. The surface of the composite layer was thick and there were a few arched zones, demonstrating that the surface of the composite layer was not totally smooth, but there were fine gel particles. They shaped the dynamic layer of the composite film. The cross area of the composite film comprised of two layers. The upper layer was a thick crosslinked layer. The lower portion was a light polysulfone back layer. The combination of the best thick useful layer and the free supporting layer kept the fabulous execution of the composite layer.



**Figure 6.** The surface and cross-section images of the composite membrane

### 4. Conclusion

The composite nanofiltration film detailed in this paper had two-layer structure: the upper one was the lean and

thick cross-linked layer, which played a key part in division; the lower layer was the polysulfone bolster layer, with a sponge-like permeable surface. The upper layer was arranged with polymers of acrylic corrosive and emphatically charged compound adjusted chitosan. The dismissal rate of 50% composite nanofiltration layer for  $\text{CaCl}_2$  was 97.4% for  $\text{CaCl}_2$  with 50% molar proportion composite nanofiltration film, comparing flux was  $430.7 \text{ Lm}^{-2}\text{h}^{-1}$ . the arrange of dismissal:  $\text{CaCl}_2 > \text{NaCl} > \text{Na}_2\text{SO}_4$ . Tensile quality of film expanded 27.3%. The HCl(5%) resistance expanded 50.5%. The NaOH(5%) resistance expanded 42.2%. This amazing execution was the comes about of the layer structure and electric property adjustment through the presentation of acrylic corrosive and emphatically charged compound. The coming about composite NF film was appropriate for isolating the multivalent cation solutes from pitifully acidic arrangement or pitifully soluble arrangement. The film had a wide application prospect.

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