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Study on Ce-doped Nonstoichiometric Nano-silica/PSF Composite Membrane for Separation of Chinese Yam Polysaccharide

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Abstract: In order to enhance the anti-fouling ability and separation efficiency of polysulfone (PSF) membrane during separating of Chinese yam polysaccharides, a novel composite membrane was prepared through a sol-gel process after adding Ce-doped nonstoichiometric nano-silica with higher activity and hydrophilic property to the porous matrix of PSF. Ce-doped nonstoichiometric nano-silica was synthesized by doping the rare earth Ce element. Novel composite membranes and ordinary membranes without doping Ce-doped nonstoichiometric nanosilica were used to separate Chinese yam polysaccharides while the content of polysaccharide was tested. The results designate that the content of polysaccharide separated by composite membrane which reached 78.3% was higher than that of polysaccharide separated by ordinary membrane which reached 46.7%. The flux of the composite membrane increased with increasing of operation pressure. With the temperature rising, the polysaccharide solution flux of composite membrane ascended from 289 L/(m^2h) to 312 L/(m^2h). The flux of the composite membrane was kept at a high value for 25 h before reaching a steady state (243 L/(m^2h)), which was higher than the stable flux of ordinary membrane (160 L/(m^2h)). After the composite membrane was washed for six times, its flux still reached 90% of initial value. The experiment data indicate that the anti-fouling ability and hydrophilic property of composite membrane were significantly enhanced. Therefore, Chinese yam polysaccharides can be efficiently separated by the novel composite membrane.

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Keywords: Ce-doped nonstoichiometric nano-silica, Chinese yam, composite membrane, polysaccharide, polysulfone, rare earth element

INTRODUCTION

Chinese yam polysaccharides are the main functional components in Chinese yams which belong to Dioscorea (1). It has been proved by modern medicine that Chinese yam polysaccharides are efficacious for anti-tumor, decreasing blood glucose, and modulating immune function (2,3). So it is significant to study the separation of polysaccharides from Chinese yams.

At present, there are numerous methods for extracting polysaccharides from Chinese yams, such as the impregnation method, the water-boiling method, and the alcohol sedimentation method (4,5). Besides, the technology of membrane is broadly applied in extraction and concentration of Chinese traditional herb drugs (6) while it is an effective method to separate polysaccharides from Chinese yams. But the membrane has a tendency to be contaminated for its hydrophobicity, which can result in the declining of the flux and the life of the membrane (7). So it is important to improve the hydrophilic property of the membrane without experiencing a marked decrease in permeability. Qiao et al. (8) studied the hydrophilic modification of ultrafiltration membranes for the separation of Chinese herbs and discovered that the hydrophilicity of these membranes was improved and their service lives were prolonged. What is more, it is a good method to improve the membrane property by adding inorganic oxide particles into the membrane (9–12). Zhang et al. (13) prepared a Nano-Al_2O_3-SiO_2 polysulfone composite membrane with the structure of phase interface and the flux of the composite membrane is higher than that of the ordinary membrane without doping inorganic oxide particles. However, further enhancement of the hydrophilic property of the polymer membranes by adding inorganic oxide particles mentioned above is limited for there are few Lewis acid sites and hydroxide radicals on the surface of the stoichiometric monocomponent inorganic oxide particles (14,15). Therefore, it is not well enough to separate Chinese yam polysaccharides efficiently for the adsorption of polysaccharide molecules on the surface and pores of the membrane (16).

Nonstoichiometric inorganic oxide nanoparticles have many point defects on the inside and lots of exposed hydroxide radicals on the surface, so these nanoparticles show stronger activity in the course of chemical bonding than stoichiometric monocomponent inorganic oxide particles (15,17), especially when nonstoichiometric inorganic oxide nanoparticles were filled in polymer membranes, the hydrophilic property of the membranes is evidently improved.

In order to enhance the membrane property further, a novel polysulfone composite membrane was prepared in this paper. First, nonstoichiometric nano-silica with higher activity and better hydrophilic property was synthesized by doping rare earth Ce element. Then, novel composite membrane was prepared by a process of adding Ce-doped nonstoichiometric nano-silica to the porous matrix of PSF, and an ordinary membrane was obtained under the same process without doping Ce-doped nonstoichiometric nano-silica to PSF. Composite membrane and ordinary membrane were applied to the separation of Chinese yam polysaccharides. The research indicates that the composite membrane fitted separation of Chinese yam polysaccharides.

EXPERIMENTAL

Materials and Reagents

Chinese yam (polysaccharide wt. about 20%) was supplied by Hunan Jinnong Biotic Resources Corporation, China. Papain and trypsase were purchased from Beijing Aobo Xing Biotech Co. Ltd, China. Chloroform and isoamyl alcohol were obtained from Tianjin Tiantai Fine Chemical Co. Ltd, China. Polysulfone was purchased from Dalian Plastics Co. Ltd, China. N, N-dimethylacetamide (DMAC) was Purchased from Tianjin Damao Chemical Factory, China.

Ordinary membranes (A and B) and composite membranes (C and D) were prepared by our lab (18,19).

Preparation of Membranes

First, DMAC in a 500 mL flask was heated to 40–50°C in a water bath. PSF was then added and dissolved with stirring. And then, PEG 400 with a mass ratio of 1:10 to PSF was added as porogen to promote the yield of pores in the gelation process. After that, Ce-doped nonstoichiometric nanosilica with a mass ratio of 1:10 to PSF was added into the casting solutions. They were mixed with vigorous stirring by using ultrasounds until a homogenous solution was obtained. And then the solution was kept undisturbed for 24 hours. Then the solution was poured onto a dense glass plate and cast as thin films (thickness *ca.* 300 μm) that after a 10 s exposure period in air (20°C and 60% relatively humidity) were immersed into a water bath at 20°C. Membranes were leached under running water for at least 2 d prior to being soaked in 30 wt.% glycerin aqueous solution. Finally, membranes were stored in deionized water containing 1 wt.% formaldehyde to avoid bacteria growth at ambient condition.

Ordinary membranes were prepared by using the same procedure mentioned above without adding Ce-doped nonstoichiometric nano-silica to casting solutions. According to the method above, ordinary membranes (A and B) and composite membranes (C and D) were obtained, respectively. The molecular weight cut-off (MWCO) of A and C was 50 thousand and the MWCO of B and D was 60 thousand.

Pore Size Measurement

The pore size of the membrane was determined by the calorimetry. The liquid-solid heating effect of water in membrane was measured by the DSC. It was supposed that all the pores were columned. The pore size was calculated by

$$r_p = 0.68 - \frac{32.33}{\Delta T} \qquad (2)$$

$$w = -0.155\Delta T^2 - 11.39\Delta T - 332 \qquad (3)$$

where r_p is the pore radius (nm), ΔT is the degree of super cooling (°C), w is the liquid-solid heating effect (J/g).

Hydrophilic Property Measurement

Contact angles of membrane samples were measured to specify the hydrophilic property with a DCAT21 dynamic contact angle measuring instrument supplied by Data Physics Corporation from Germany. The accuracy of measurements is ±0.1°.

MWCO Measurement

The MWCO measurement is the same as reference (20).

Crude Extraction of Chinese Yam Polysaccharide and Removing of Protein

The crude extraction process of Chinese yam polysaccharide is the same as literature (21).

The distilled water with a mass ratio of 10:1 was added to the crude Chinese yam polysaccharide to form the polysaccharide solution with stirring. And then, papains and trypsases were added to polysaccharide solution for hydrolyzing. One hour later, chloroform and isoamyl alcohol (chloroform:isoamyl alcohol 5:1 volume ratios) were added into this solution to form a gelatinous deposit. After discarding the deposit the albumen in the crude Chinese yam polysaccharide was removed.

Polysaccharide Content Measurement

Phenol-vitriol method (22) would be used to determine the polysaccharide content. A standard curve was made with dextrose in good merchantable quality. The polysaccharide content was calculated by

$$c = \frac{\rho \times n \times v}{m} \times 100\% \tag{1}$$

where c is the content of polysaccharide (%), ρ is the mass concentration (Kg/m^3), n is the dilute multiple, v is the volume of reaction solution (m^3), m is the mass of Chinese yam sample (Kg).

Separation of Chinese Yam Polysaccharide

Figure 1 shows a schematic diagram of the experimental set-up used in this study. The feed was pumped to the membrane module by using a centrifuge pump. The flow was regulated using value V1 while the pressure on the membrane was adjusted by valve V2. The feed stream splits in two streams; one, the concentrate which contains non-passing components is returned to the feed tank. The other one, the permeate, contains components passing through the membrane and it is measured by a measuring cylinder. The permeate after measurement was returned to the feed tank in order to have a feed with constant concentration.

The mass concentration of the solution acquired according to section 2.6 was 73 Kg/m^3. The total polysaccharide content of Chinese yams was 17.3 g/100 g. At the condition of 0.1 MPa and 20°C, the polysaccharide solution was filtrated by composite membrane and ordinary membrane, respectively. The operation type of membrane process was cross flow and the membrane area was 0.51 m^2. As shown in Fig. 2, the polysaccharide solution was treated by ordinary membrane B primarily. Then the permeate was treated by ordinary membrane A. Similarly, the polysaccharide solution was treated by the composite membrane D primarily. Then the permeate was treated by the composite membrane C. The feed

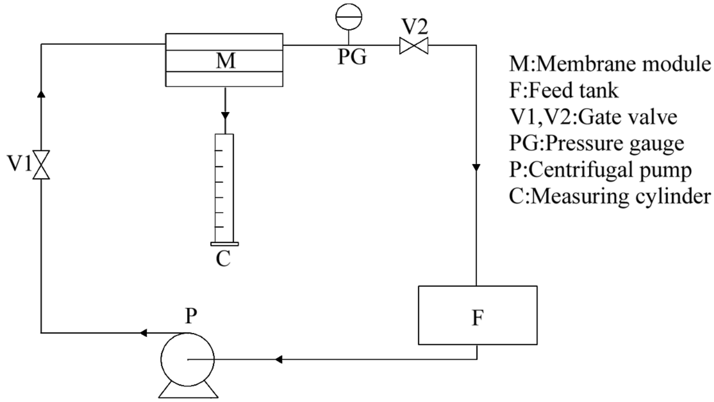

Figure 1. Schematic diagram of the experimental equipment.

volume was 0.3 m^3 while the permeate volume was 0.21 m^3. The flux, temperature, time, and operation pressure were recorded in the process of treatment.

Cleaning of Membranes

After using membranes for two weeks fluxes of membranes decreased, so the membranes need to be cleaned to regain its original permeability.

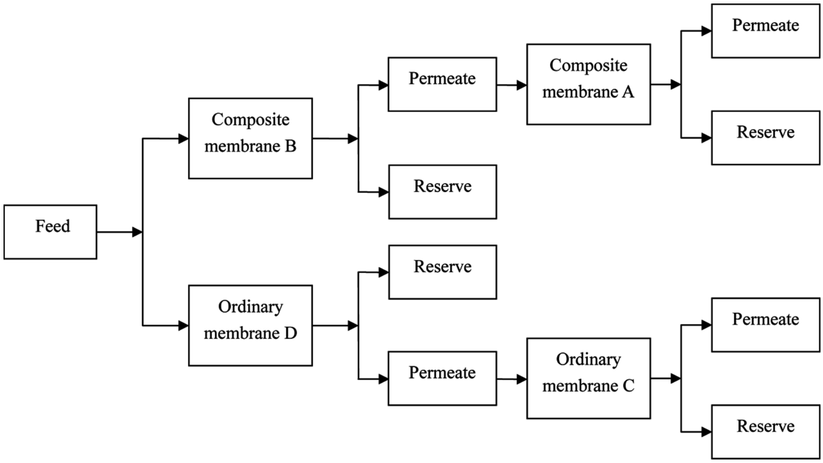

Figure 2. Schematic diagram of the separation for Chinese yam polysaccharide solution.

First, membranes were rinsed by using 3% Na_2CO_3 solution, and then they were cleaned by using deionized water and 3% citric acid. The 3% citric acid was used to adjust pH value. The total of the cleaning time was 30 min (23). Finally, membranes were cleaned to pH = 7 by deionized water and the fluxes of the membranes were measured again until the fluxes regained to 95% of its original permeability.

RESULTS AND DISCUSSION

Properties of Membranes

It can be seen from the Table 1 that the contact angles of the composite membranes were smaller than those of ordinary membranes. Thus, the composite membrane is more hydrophilic than the ordinary membrane obviously; the pore radius of membranes A, B, C and D is 6.3, 7.2, 6.6, and 7.8 nm, respectively. The MWCO of the membrane A and the membrane C was 50 thousand and the MWCO of the membrane B and the membrane D was 60 thousand.

Separation of Chinese Yam Polysaccharide

The content of polysaccharide separated by the composite membrane is higher than that of polysaccharide separated by ordinary membrane (Fig. 3). For example, the mass of polysaccharide (molecular weight above 60 000) separated by composite membrane is 11.75 g while the mass of polysaccharide separated by the ordinary membrane is only 7.9 g. By the calculation, the yield of polysaccharide was gained. The yield of polysaccharide separated by the composite membrane which is 78.3% is higher than that separated by the ordinary membrane which is 46.7%. These

Table 1. Contact angle, pore radius and MWCO of membranes

Membrane	Contact angle/°	Pore radius/nm	MWCO
A	78.6	6.3	50000
B	77.9	7.2	60000
C	41.7	6.6	50000
D	41.3	7.8	60000

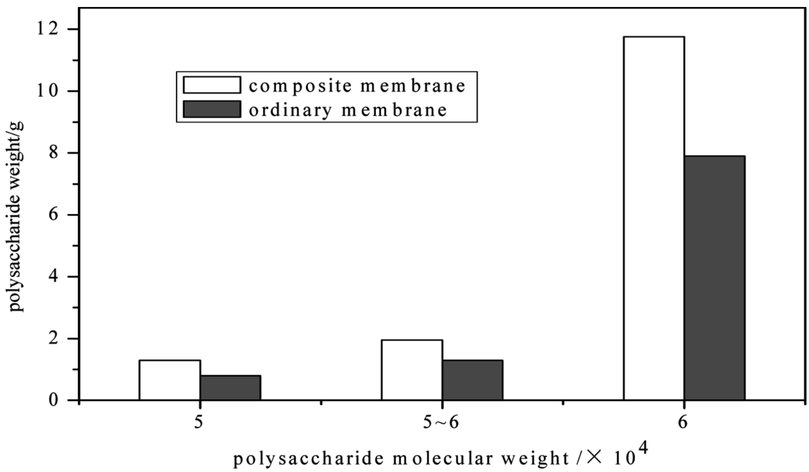

Figure 3. Results of separation by composite membrane and ordinary membrane.

results show that the composite membrane is more effective than the ordinary membrane for the separation of Chinese yam polysaccharides.

Relationship Between Membrane Flux and Operation Pressure

As shown in Fig. 4, the relationship between fluxes of these membranes and operation pressure were observed. The fluxes of two kinds of membranes increased with increasing operation pressure. But the composite membrane flux was higher than the ordinary membrane flux at the same operation pressure. For example, at 0.1 MPa the composite membrane flux reached 289 L/(m^2h) while the ordinary membrane flux was 204 L/(m^2h). The reason is that hydrophilic Ce-doped nonstoichiometric nano-silica is dispersed uniformly in the composite membrane, which makes the composite membrane more hydrophilic. Therefore, it is difficult that the composite membrane combine with organics to form a gel layer on the surface and pores of the membrane. To sum up, compared with the ordinary membrane the composite membrane owns a better property of anti-fouling and higher permeate flux.

Relationship Between Membrane Flux and Operation Temperature

The Chinese yam polysaccharide solution was treated by composite membrane at 0.1 MPa and 20 ~ 30°C. The flux of the composite

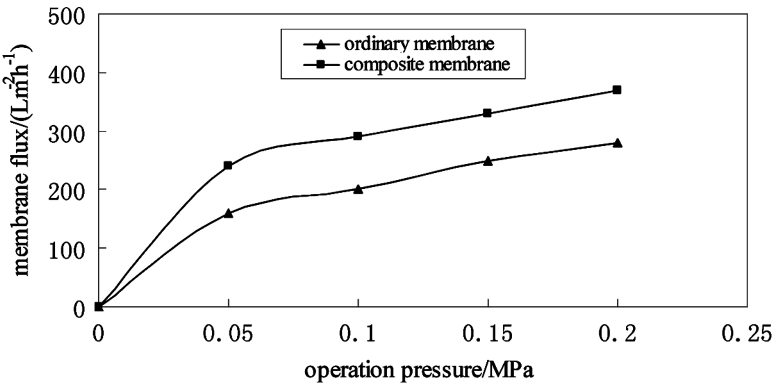

Figure 4. Relationship between membrane flux and operation pressure.

membrane increased from 289 L/(m^2h) to 312 L/(m^2h) with increasing operation temperature (Fig. 5). This is because the solution viscosity reduced with increasing temperature. The lower viscosity enhanced the solution fluidity and accelerated the transmission process, thus the membrane flux was increased.

Relationship Between Membrane Flux and Operation Time

The Chinese yam polysaccharide solution was treated by the composite membrane and the ordinary membrane under the same condition of

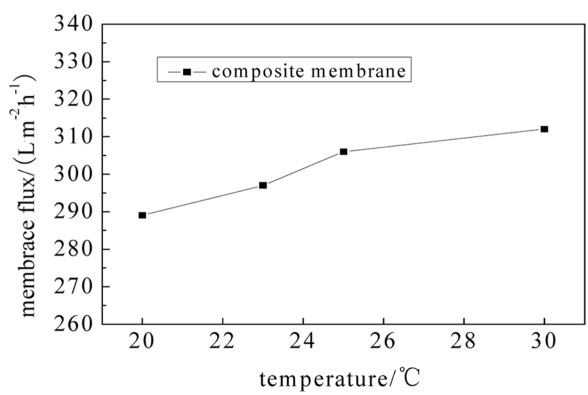

Figure 5. Relationship between membrane flux and operation temperature.

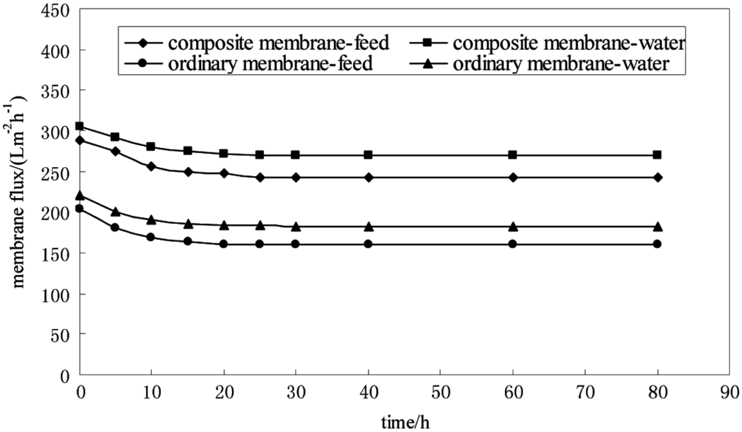

Figure 6. Relationship between membrane flux and operation time.

0.1 MPa and 20°C respectively. The pure water fluxes were investigated as the control experiment. The fluxes of these membranes were observed as shown in Fig. 6. The initial flux of the composite membrane and the ordinary membrane for the polysaccharide solution were 289 L/(m^{2}h) and 204 L/(m^{2}h), respectively. The fluxes of these two sorts of membranes decreased with the passage of time, and the composite membrane flux became steady state after 25 h, while the ordinary membrane flux needed 20 h to become steady state. Besides, average fluxes of the two sorts of membranes were 243 L/(m^{2}h) and 160 L/(m^{2}h), respectively. It can be seen that the ordinary membrane flux decreased quickly in initial 20 h. The reason is that the gel layer was formed on the membrane surface and membranes were impacted. However, the flux of the composite membrane decreased slowly in initial 25 h. In addition, the average flux of the composite membrane was higher than that of the ordinary membrane. The reason is that Ce-doped nonstoichiometric nano-silica was added into the composite membrane uniformly which improved its hydrophilic performance. A thin hydrophilic layer (water film) can be engendered on the composite membrane surface and this hydrophilic layer can prevent gel layer from being formed. Even if the gel layer was formed, it had been easy to slip under the scouring of the feed and clean the composite membrane. Also it can be seen from Fig. 6 that the composite membrane had a higher pure water flux and a lower flux reduction compared with the ordinary membrane. The polysaccharide solution flux for both the composite membrane and the ordinary membrane was lower than pure water flux due to the slight contamination of polysaccharide.

Table 2. Cleaning experiments of composite membranes and ordinary membranes

Number of cleaning	The flux resuming rates %	
	Composite membrane	Ordinary membrane
1	100	100
2	100	98
3	98	95
4	94	91
5	92	87
6	90	82

Cleaning of Membranes

After a membrane was used for some time, the membrane flux would decrease because of the formation of the gel layer and fouling on the membrane surface. In order to continue using the membrane once more, it must be cleaned after some time to regain the original permeability of the membrane. The composite membrane and the ordinary membrane were cleaned according to the requirement of section titled cleaning of membranes and the fluxes of the membranes were observed. The flux resuming rate was calculated with results listed in Table 2. After cleaning for six times, the flux resuming rate of the composite membrane reached 90% while that of the ordinary membrane was 82%, which indicates that the composite membrane can be easily cleaned and reused. With continuing of the use, the composite membrane performance is obviously superior to the ordinary membrane performance with a longer service life.

CONCLUSIONS

1. The content and the yield of the polysaccharide separated by composite membrane are obviously higher than that of the polysaccharide separated by ordinary membrane. The composite membrane is more effective than the ordinary membrane in the separation of Chinese yam polysaccharides.
2. The flux of the composite membrane increases with increasing operation pressure. At the same operation pressure, the flux of the composite membrane is higher than that of the ordinary membrane.

3. The composite membrane flux increases with increasing operation temperature.
4. The flux of the composite membrane, which is higher than that of ordinary membrane, can keep at high value for 25 h before reaching stable value.
5. The flux of the composite membrane can be resumed well with proper cleaning method and the service life of the composite membrane is prolonged.

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