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Application of integrated membrane technology in purification of chlorogenic acid

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ABSTRACT

Integrated membrane technology is a membrane separation system, which can overcome the disadvantage of single membrane, save the cost, and improve the product quality. Chlorogenic acid, which is an effective component of Chinese medicine and a heat-sensitive substance, is not stable at high operation temperature. Chlorogenic acid with molecular weight of 354 Da and good solubility in water can be treated by nanofiltration (NF) membrane. In this work, polyetherimide (PEI) ultrafiltration (UF) membrane with good chemical and thermal stability is used in the purification of chlorogenic acid solution. Positively charged HACC/PEI NF membrane with good antibacterial performance and hydrophilicity is used to concentrate chlorogenic acid solution. It is found that, the PEI UF membrane can separate chlorogenic acid with other components and improve the purity of chlorogenic acid. At the same time, the rejection to chlorogenic acid of the positively charged NF membrane is about 92% which is suitable for the concentration of chlorogenic acid solution. The integrated membrane technology is very useful in the production of chlorogenic acid.

Keywords: Chlorogenic acid; Ultrafiltration membrane; Nanofiltration membrane; Integrated membrane technology; Chinese medicine

1. Introduction

Membrane technology has recently gained increasing worldwide research interest because of its advantages, such as low operation pressure, low investment, low energy consumptions, and high permeation flux [1]. It is widely used in many separations and treatment processes, such as sea water desalination, water softening, and wastewater treatment [2,3]. Ultrafiltration (UF) membrane is widely used in separating water and small molecules from macromolecules and colloids by size exclusion. The average pore diameter of the membrane is in the 1–100 nm range [4]. Polyetherimide (PEI) with excellent thermal stability, chemical stability, and mechanical stability is a suitable material to prepare UF membrane because it can be used at harsh conditions, such as high temperature

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wastewater treatment, recycling of hot water, and soybean oil separation [5–7]. The separation of nanofiltration (NF) membrane is dominated by both size exclusion and the Donnan effect. Rejection by NF membranes to various salts will change with their surface chemical composition and charge character [8,9]. NF membrane with quaternary ammonium group endows membrane with excellent antibacteria performance and chlorine resistance, which may expand the utilization area of membrane especially in food industry and traditional Chinese medicine industry. HACC/PEI composite NF membrane with excellent antibacterial performance and hydrophilicity was successfully prepared in our laboratory [10]. It is suitable in the separation and purification of Chinese medicine. Chlorogenic acid is an important biologically active substance, which is used as antibacterial, antiviral, has other important performances in health [11,12]. Application of chlorogenic acid is very extensive in medicine, daily chemical, and food industry. Traditional methods of extraction and purification of chlorogenic acid showed low rate of extraction, destruction of chlorogenic acid, low product purity, and poor safe sanitation [13]. Chlorogenic acid, which is the active ingredients of traditional Chinese medicine, is a heat-sensitive material with molecular weight of 354 Da as shown in Fig. 1. NF has been recognized having the properties in between UF and reverse osmosis (RO), and high retention of molecular weight compounds (>300) [14]. It is very suitable in the treatment of heat-sensitive materials such as Chinese medicine without secondary pollution. PEI UF membrane and positively charged HACC/PEI NF membrane are integrated firstly in purification and concentration of chlorogenic acid. Effects of operation parameters on the treatment of chlorogenic acid with membrane technology are investigated for the production of chlorogenic acid, which is useful for environmental protection.

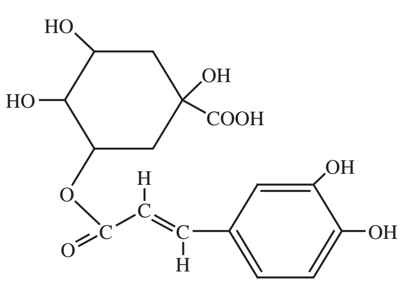

Fig. 1. The chemical structure of chlorogenic acid.

2. Experimental

2.1. Materials and instruments

The PEI UF membranes (tested with polyethylene glycol, PEG1000) are prepared in our laboratory with phase inversion method. 2-Hydroxypropyltrimethyl ammonium chloride chitosan (HACC, DS of quaternization is above 90%) purchased from Lvshen Bioengineering is purified by filter paper under reduced pressure. Glutaraldehyde (50%), *N*,*N*-dimethylacetylamide, NaCl, $MgCl_2$, Na_2SO_4, and other chemicals used in the experiments are all analytical purity grade without further purification. Chlorogenic acid (25% HPLC), extracted from eucommia ulmoides, is used to prepare simulated solution. A stainless flat sheet dead-end filtration setup is used to evaluate the composite membrane performance. Magnetic stirrer was installed in the membrane feed side to reduce concentration polarization. Electrical conductivity meter (DDS-11A, Shanghai Youke Instrument Works, China) is used to measure the concentration of salt in the feed and permeated solutions. Spectrophotometer 752 PC (Shanghai Spectrum Instrument Co. Ltd., Shanghai, China) is used to determine the concentration of chlorogenic acid and PEG1000.

2.2. Membrane preparation

The PEI UF membranes prepared with phase inversion method were cast from PEI solution in solvent (*N*,*N*-dimethylacetylamide) on a horizontal glass plate with a glass blade [15]. After evaporation in the air, the membranes were precipitated by immersing them in a water bath at certain temperature. Positively charged HACC/PEI NF membrane is prepared with dip-coating method on the PEI UF membrane [10]. The skin side of the PEI UF membrane was brought in contact with the HACC solution. The solution at the membrane surface was drained by holding the membrane vertically, leaving a thin layer of the HACC solution. The coated layer was then cured at 50℃ for a certain time after its contact with a cross-linking agent, glutaraldehyde. The membranes, so prepared, were stored in deionized water until ready to be used.

2.3. Membrane characterization

The performances of NF membranes and UF membrane are mainly described by product water flux, *J*, and rejection, *R*, which was described before [10,15]. The membranes were characterized in the dead-end membrane module after they were pretreated under the pressure of 0.5 MPa for 30 min. The performance of UF membrane is tested at 0.1 MPa and the performance of NF membrane is tested at 0.4 MPa. The permeation flux, J is calculated as follows:

$$J = \frac{W}{At} \quad (1)$$

where W is the total volume of the water or solution permeated during the experiment; A is the membrane area and the effective membrane area is 41 cm^2; and t is the operation time. Rejection, R, is calculated using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \quad (2)$$

where C_p and C_f are the concentrations of the permeate solution and the feed solution, respectively. All the experiments on flux and rejection were repeated for three times. The Relation Standard Deviation of the data was lower than 15%.

The morphologies of the top surface of the asymmetric membranes were observed with a scanning electron microscope (SEM; JSM-6700F, JEOL, Japan). The samples were fractured in liquid nitrogen and sputtered with gold after they were immersed with ethanol and hexane to observe the structure of the membranes.

3. Results and discussion

3.1. Effect of PEI concentration on the membrane performance

The chlorogenic acid solution is prepared by chlorogenic acid dissolved in deionized water. Then it is diluted with different ratio to acquire concentration, such as 0.2, 0.4, 0.6, 0.8, and 1 g/L. In order to determine the performances of different membranes, the concentration of chlorogenic acid is tested with UV–Vis. The absorbance maximum of chlorogenic solution in water is 325 nm, according to the experimental result. It can be found from Fig. 2 that there is a good linear relationship between the absorbance of the solution and the chlorogenic acid concentration. So, it is suitable for the utilization of UV–Vis method to analyze the concentration of the chlorogenic acid solution.

The performances of the PEI UF membranes prepared with different PEI concentrations are shown in Table 1. The PEI UF membrane performances are greatly affected by the polymer concentration of the casting solution, because the increased polymer concentration and viscosity will induce smaller pore sizes. In this work, the PEI UF membranes are prepared

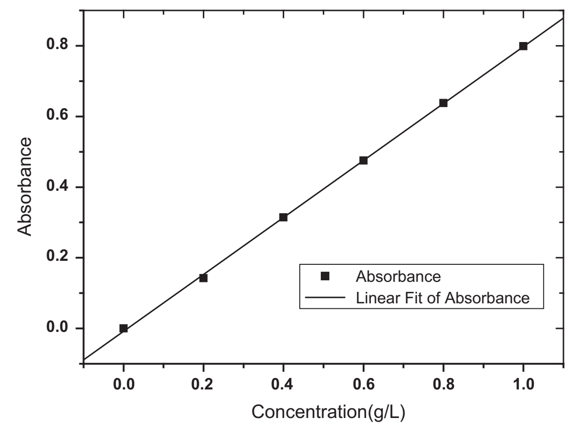

Fig. 2. The relationship between absorbance and chlorogenic concentration.

with different PEI concentrations to acquire membranes with different rejections. As shown in Table 1, with the increase of PEI concentration, the rejection to PEG1000 is increased obviously, while the membrane flux declines. It demonstrates that the functional layer of UF membrane becomes denser and the membrane pore is smaller. When the membranes are used in the purification of chlorogenic acid solution, as shown in Table 1, all the membranes have high fluxes and low rejections to chlorogenic acid. The partial rejection to chlorogenic acid may be caused by the rejection of impurities where chlorogenic acid is encapsulated. All the membranes have obvious decoloration effect on the chlorogenic solution. The UF2 membrane has relative high flux (129 (L/m^2 h)) and low rejection to chlorogenic acid (3.4%) at 0.1 MPa and 20℃, which is suitable for the purification of chlorogenic acid.

3.2. Decoloration effect of the PEI UF membrane

There are a lot of impurities in the rough chlorogenic acid solution when it is produced with water extraction. It can be found from Fig. 3 that the membrane has obvious effect in decoloration of chlorogenic acid solution. The feed solution with impurities is black–brown. After filtration with PEI UF membrane, the solution becomes clear and transparent which demonstrated the good purification effect of the UF membrane. So, the PEI UF membrane with high flux and low rejection to chlorogenic acid can be used in the purification of chlorogenic acid solution.

3.3. Effect of operation pressure and feed concentration on the performance of the PEI UF membrane

The membrane flux can be improved by the elevation of transmembrane pressure as shown in Fig. 4.

Table 1
Effect of different PEI UF membranes on the performance of chlorogenic acid treatment

		PEG1000 solution		Chlorogenic acid solution	
Membrane type	PEI concentration	R/%	F/(L/m^2 h)	R/%	F/(L/m^2 h)
UF1	14%	18.6	192	5.3	138
UF2	16%	45.7	133	3.4	129
UF3	18%	73.2	87	6.5	76
UF4	20%	86.8	55	8.7	55

Fig. 3. The decoloration effect of the PEI UF membrane.

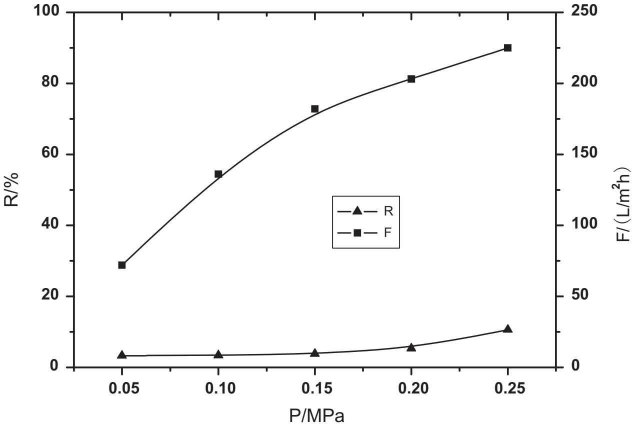

Fig. 4. Effect of operation pressure on the PEI UF membrane performance.

However, because of the increase in the operation pressure, membrane fouling and concentration polarization became obvious because of the consolidation of the polarized layer of solute and impurities. At the same time, high pressure will induce the formation of "polarization layer" and improve the rejection of chlorogenic acid. So, the operation pressure of the UF membrane is fixed below 0.15 MPa for high flux and low fouling.

Feed concentration affects the membrane flux greatly, which is similar with many cases. As the feed concentration increases, the viscosity, density, and diffusivity of the feed solution will increase [16]. So, the membrane flux will decrease as shown in Fig. 5. Moreover, high feed concentration will induce the partial precipitation of chlorogenic acid on the membrane surface and pores.

3.4. *Performance of the positively charged HACC/PEI NF membrane on the treatment of chlorogenic acid*

There are some papers about the concentration of Chinese medicine with RO membrane and UF membrane [17,18]. However, the fluxes of the membranes are low because of dense functional layer of RO membrane. Positively charged HACC NF membrane is utilized in this work, because HACC is a cheap and available positively charged membrane material. The positively charged NF membrane also has high hydrophilicity and good antibacterial performance which is suitable to be used in Chinese medicine treatment. The performances of different positively charged NF

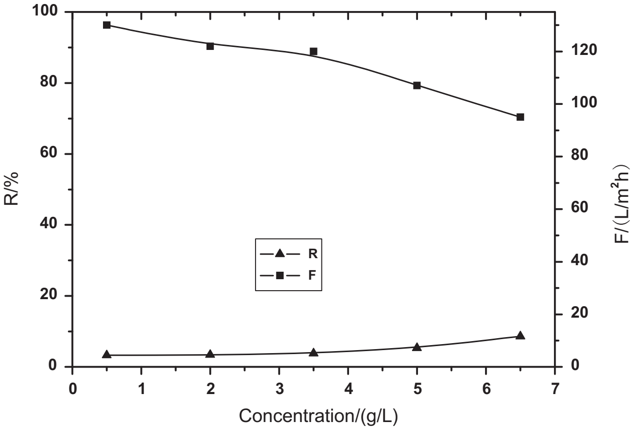

Fig. 5. Effect of feed concentration on the PEI UF membrane performance.

Table 2
The treatment of chlorogenic acid by positively charged NF membrane

Membrane type	$MgCl_2$ solution		Chlorogenic solution	
	F/(L/m^2 h)	R/%	F/(L/m^2 h)	R
NF5	19.4	70	16.1	83
NF6	16.3	88	15.7	92

membranes are listed in Table 2. As shown in Table 2, the membrane with high rejection to $MgCl_2$ also has high rejection to chlorogenic acid. NF6 has high rejection to chlorogenic acid as 92% and relatively high flux 15.7 L/m^2 h, when the concentration of chlorogenic is fixed at 0.5 g/L, operation pressure is fixed at 0.4 MPa, and operation temperature is fixed at 20°C. The positively charged NF membrane showed excellent performance in chlorogenic acid concentration because of its good hydrophilicity and dense functional layer.

3.5. *Effect of operating pressure and feed concentration on the NF membrane performance*

The flux of the NF membrane increased about 2.5 times with the increase of operation pressure while the rejection did not change obviously as shown in Fig. 6. Because of good antifouling performance, the membrane flux increased linearly with the pressure. As the feed concentration increases, the viscosity, density, and diffusivity of the feed solution will also increase, which is similar with the UF treatment process. So the membrane flux and rejection to chlorogenic acid will decline because of concentration polymerization (see Fig. 7) [19].

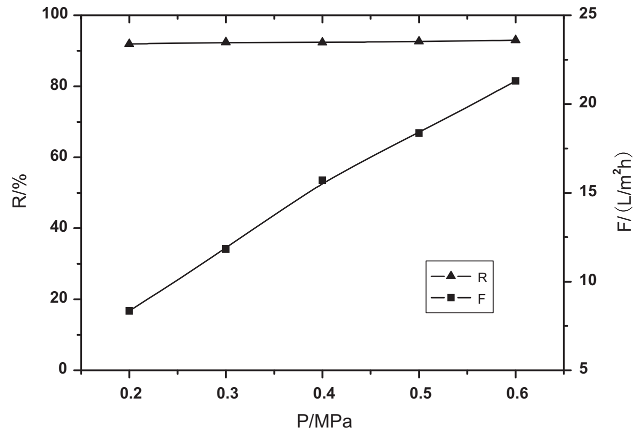

Fig. 6. Effect of operation pressure on the NF membrane performance.

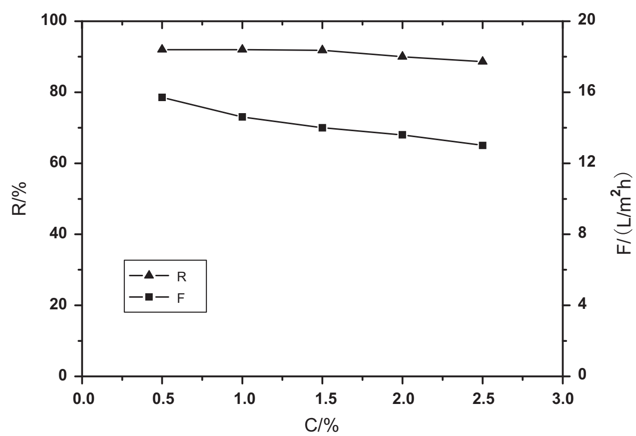

Fig. 7. Effect of feed concentration on the NF membrane performance.

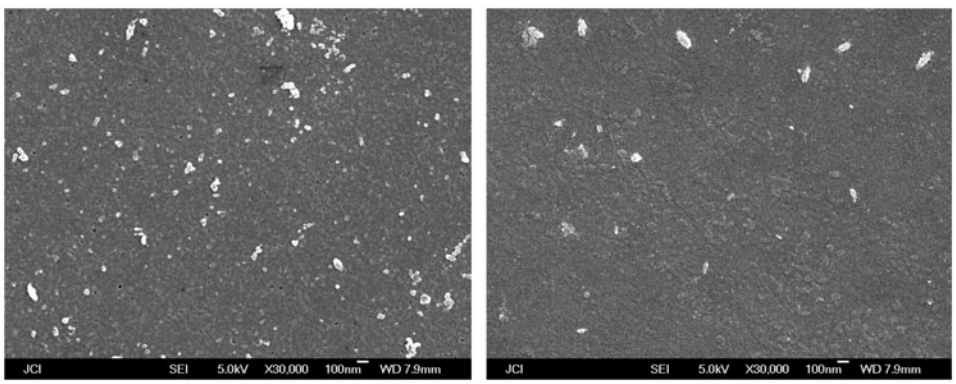

Fig. 8. The SEM images of the UF membrane and NF membrane (left, UF; right, NF).

3.6. The morphologies of the membranes

After the picture is magnified 30,000 times, the differences between two membranes are shown clearly in Fig. 8. There are a lot of small nano-sized pores at the top layer of the UF membrane while no obvious pores are observed in the top layer of NF membrane. At the same time, the top surface of the PEI UF membrane is very smooth while there are some small protuberances in the surface of the HACC/PEI NF membrane. This phenomenon is similar with other works which indicates the excellent performance of the membranes used.

4. Conclusions

PEI UF membrane and positively charged HACC/PEI composite NF membranes were utilized in purification and concentration of chlorogenic acid solution. The PEI UF membrane showed good purification effect on the chlorogenic acid and high permeation flux. After filtration, the solution became clear and transparent. The UF membrane flux reaches up to 129 L/m^2 h at 0.1 MPa and 20℃. It is very useful for preparing chlorogenic acid with high quality. High feed concentration and high pressure will result in heavier pollution. The HACC/PEI composite NF membrane with high rejection to $MgCl_2$ also has high rejection (92%) to chlorogenic acid and high flux (15.7 L/m^2 h) at 0.4 MPa and 20℃ which can be used in concentration of chlorogenic acid. The composite NF membrane showed high flux and rejection to chlorogenic acid even at high feed concentration, because the positively charged NF membrane has good antifouling performance.

Acknowledgments

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