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The characterization of polysulfone–Fe_3O_4 composite ultrafiltration membrane and its application

Ya-Hui He[a,b,c], Li Zhou[c], Bei Gao[b], Feng Feng[b], Xiao-Jing Fan[a], Can-Ping Pan[c], Qing-Jun Liu[a], Xiao-Gang Chu[b,*]

[a]*Beijing Center For Physical & Chemical Analysis (Beijing Food Safety Test Engineering Research Center), Beijing 100089, China*
[b]*Chinese Academy of Inspection and Quarantine, Beijing 100123, China*
Email: xgchu@vip.sina.com
[c]*Department of Applied Chemistry, College of Science, China Agricultural University, Beijing 100193, China*

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ABSTRACT

In this paper, a novel polysulfone (PSF)–Fe_3O_4 composite ultrafiltration membrane was prepared and employed to purify the flavonoids from the ginkgo biloba extraction (GBE). The mass susceptibility (χ) of the ginkgo flavonoids with 98% purity was tested to be greater than 0, so they showed paramagnetism. Hysteresis curve indicated that the composite membrane have superparamagnetism for the addition of nano-sized Fe_3O_4 particles. The process of ultrafiltration was performed without and in the magnetic field with different intensities, respectively. The flavonoids content in the products is much superior when performed in the magnetic field than that without magnetic field. In the absence of magnetic field, the flavonoids content in the products was purified to 30.16% from 15.60% in crude GBE. Once the magnetic field with 0.2 T was added in the process, the purity was enhanced to 35.24%. Furthermore, the purity was persistently increasing with the incremental magnetic intensity. When the magnetic intensity was strengthened to 1.0 T, the purity approaches saturation, with being up to 52.87%.

Keywords: Polysulfone (PSF)–Fe_3O_4 composite ultrafiltration membrane; Ginkgo flavonoids; Mass susceptibility; Superparamagnetism; Magnetic field

1. Introduction

Ginkgo biloba extraction (GBE) has attracted an increasing exploration due to a large number of amazing active components among which flavonol glycosides (flavonoids) and terpenoids are the most important ones. They have been shown to exhibit a variety of pharmacological actions [1,2]. It was reported to antagonize the action of platelet-activating factor [3], provide protection in myocardial and brain ischemia-reperfusion injury [4,5], and prevent ischemia-induced oxidation [6], and so on.

*Corresponding author.

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There have been various separation methods to purify flavonoids from the crude GBE products, such as organic solvent extraction [7], macroporous-resin adsorption [8], and supercritical fluid extraction (SFE) [9,10]. Compared with the above-mentioned methods, ultrafiltration separation may be more efficient and promising due to its advantages of high selectivity, no contamination, and ease of operation.

In the previous paper [11], we reported the preparation of polysulfone (PSF)–Fe_3O_4 magnetic ultrafiltration membrane. Subsequently, the membrane was attempted to purify the flavonoids from GBE.

Fe_3O_4 nanoparticles have been used in the magnetic liquid, magnetic memorizing material, magnetic polymer microspheres, and so on for its superparamagnetism [12–17]. PSF–Fe_3O_4 composite membrane was prepared using the phase-inversion method by adding nano-sized Fe_3O_4 particles to the casting solution. So, the composite membrane has magnetism and is performed in a magnetic field.

All matter has magnetism. According to the magnetism they possess, they can be classified to diamagnet ($\chi < 0$), paramagnet ($\chi > 0$), ferrimagnetics ($\chi \gg 0$, 100–10^3), and ferromagnet ($\chi \gg 0$, 10–10^6) [17]. In a magnetic field, the diamagnet gets repulsion force while the paramagnet, the ferrimagnetics, and the ferromagnet get attraction [18]. As we know, almost all organic compounds are diamagnetic, while in the recent years, some organic compounds are found be paramagnetic or ferromagnetic for their radicals [19–21].

2. Experimental process

2.1. Materials

The GBE crude products and the ginkgo flavonoids with the purity of 98% were supplied by Heifei TuoFeng Biotechnology Company, China. Mohr's salt ($FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$), polyethylene glycol (PEG) with average molecular weight of 400, and dimethylformamide (DMF) were purchased from Shanghai Chemical Regents Company. The PSF ($[\eta] = 0.62$) was purchased from ShuGuang chemical plant in Shanghai. Fe_3O_4 nanoparticles enwrapped in the oleic acid (8–12 nm in size) were purchased from Anhui Jinke Magnetic Liquid Com. Ltd.

2.2. Preparation of aqueous solution of GBE crude product

Ethanol aqueous solution (30 vol.%) was used to dissolve a certain amount of GBE crude product. Then the GBE solution was prefiltered.

2.3. Mass susceptibility (χ) of the ginkgo flavonoids measurement

The mass susceptibility (χ) of the ginkgo flavonoids with the purity of 98% was measured using Gouy magnetic balance (KY-TP-A). The principle of the Gouy measure is as follows: In a magnetic field, paramagnet will get attraction while diamagnet will get repulsion force. So their weights in a magnetic field will be different from that in the absence of the magnetic field. The weight of the paramagnet will be increasing in the magnetic field while that of the diamagnet will be opposite.

With the mass susceptibility of the Mohr's salt (χ_s) being a standard, the experimental condition of the ginkgo flavonoids was controlled. It was calculated as follows [22]:

$$\chi_s = \frac{9,500}{T+1} \times 4\pi \times 10^{-9} \quad (1)$$

where T is thermodynamics temperature.

The susceptibility (χ) of the ginkgo flavonoids was calculated as follows:

$$\frac{\chi}{\chi s} = \frac{\Delta m}{\Delta ms} \times \frac{ms}{m} \quad (2)$$

where m_s and m are the weights of the Mohr's salt and ginkgo flavonoids with the same height in the test tube, Δm_s and Δm denote the change of the weight of the Mohr's salt and ginkgo flavonoids inside and outside the magnetic field.

2.4. Preparation of the composite membrane

PSF–Fe_3O_4 composite membrane was prepared by the phase-inversion method. Polymer dope consisting of PSF (15%, by weight of the solution), PEG (2%, by weight of the solution), and DMF (83%, by weight of the solution) was dissolved at about 60°C for 3 h with vigorous stirring. After the uniform polymer dope was formed, nano-sized Fe_3O_4 particles were added to the dope with vigorous stirring for 3 h. Fe_3O_4/PSF ratio (w/w) of casting solution was 0.27. Then the casting solutions were kept in the dark for at least 12 h to remove air bubbles. Casting solutions were casted with 100 μm casting knife onto the polyester nonwoven fabric. The membrane evaporated at 20 ± 1°C, 60 ± 5% relative humidity for 1 min before it was immersed in 15 ± 1°C deionized water coagulation bath.

2.5. The morphology of the composite membrane

The morphology of the surface and cross-section of PSF membrane, and the composite membrane were observed by scanning electron microscope (TSM-6700F). Cross-section of membrane was prepared by being fractured in liquid nitrogen. Samples were coated with a thin layer of gold before analysis.

2.6. The magnetism of the Fe_3O_4 nanoparticles and the composite membrane

Hysteresis loops of the Fe_3O_4 nanoparticles and the composite membrane were carried out using Quantum design MPMS (XL-7) to research their magnetism in the magnetic field. The temperature of the operation process was controlled at 26.5°C. The magnetic field intensity was increased from 0 to 1.0 T, then decreased from 1.0 to −1.0 T, and finally increased to 1.0 T. Moments of the Fe_3O_4 nanoparticles and the composite membrane were recording with the change of the magnetic intensity. The weights of the Fe_3O_4 nanoparticles and the composite membrane used in the experiment are 89.65 and 13.07 mg, respectively.

2.7. Molecular weight cut-off measurement

The objective molecular weight cut-off of the membrane was determined by a common ultrafiltration process using aqueous solution of proteins with various molecular weights. The proteins used are lysozyme (MW = 14,700), chymotrypsin (MW = 24,500), α-amylase (MW = 45,000), and bovine serum albumin (MW = 67,000). The ultrafiltration process was performed at 20°C and 0.15 MPa. Both the retentate and the permeation were recirculated to the feed bank. After the process reached a steady state, the samples from feed side and permeate side were both taken and determined by using a UV-spectrophotometer (UV-1600) at a wavelength of 280 nm.

The rejection rate of proteins through the membrane was calculated according to Eq. (3).

$$R(\%) = (1 - C_{\text{per}}/C_{\text{feed}}) \times 100 \quad (3)$$

where R is defined as the rejection rate, C_{per} denotes the concentration of the permeation, and C_{feed} is the concentration of the feed.

The objective molecular weight cut-off of the membrane was equal to the certain molecular weight, the rejection rate of protein through which the membrane reached 90%.

2.8. Separation process in and out the magnetic field

Ultrafiltration experiments for the purification of GBE were performed using a continuous resting device as shown in Fig. 1. The effective membrane area fixed in membrane cell was 0.0201 m^2. The upstream pressure and the feed flow rate were adjusted with a throttle valve. The magnetic field is produced by silicon steel encompassed by loops galvanized. Membrane cell is placed in a shelf and is just over the silicon steel encompassed where the distance between the membrane in the cell and the silicon steel was 2.5 cm. Magnetic line of force passes through the membrane close to upright. The distribution of magnetic intensity along the membrane surface can be considered close to uniform because the weakening of the intensity from the center to the rim of the membrane is so little that it can be neglected. Magnetic intensity can be modulated by changing the electric current in the loops. Magnetometer (MPMS XL) was used to detect the external magnetic intensity (B_e). In the set, the external intensity can be controlled at 0–1.0 T.

The separation process was carried out under the condition of 0.15 Mpa at 20±1°C. When the flux is almost stable without magnetic field, the content of flavonoids and the flux of GBE solution were examined. Initially, the investigation was performed in the absence of magnetic field for 30 min and then in the magnetic field with B_e of about 0.2, 0.4, 0.6, 0.8, 1.0 T for 30 min, respectively. Finally, the magnetic field was withdrawn and the ultrafiltration was continued for 30 min.

The content of flavonoids were analyzed with a Waters 510 HPLC pump, equipped with a 10 μL sample loop. Flavonol glycosides was determined on a reversed column packed with Agilent C18 (5 μm) with a 360 refractive index detector by using methanol–water–phosphoric acid (50:49.5:0.5) as the eluents at a flow rate of 0.8 mL/min.

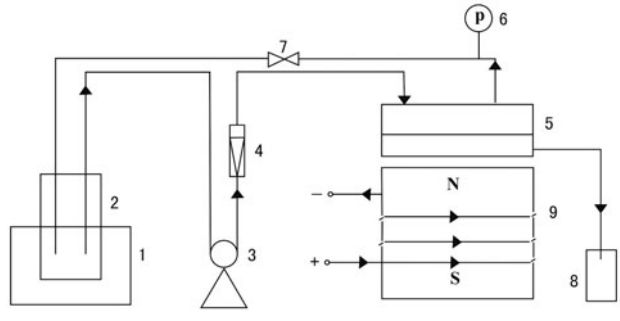

Fig. 1. Schematic diagram of the crossflow filtration system. (1) Constant temperature trough; (2) feed tank; (3) pump; (4) flowmeter; (5) membrane cell; (6) pressure gauge; (7) throttle; (8) collect tank; and (9) galvanized magnet.

The permeation flux (J) was calculated with the following equation:

$$J = \frac{V}{A \times t} \tag{4}$$

where V is the permeate volume (L), A is the effective membrane area (m^2), and t is the experimental time (h).

3. Results

3.1. Mass susceptibility (χ) of the ginkgo flavonoids

The mass susceptibility of the ginkgo flavonoids with the purity of 98% is calculated from formula (2). It shows paramagnetism with the mass susceptibility being 3.99×10^{-4} under 24.5°C. The difference of the magnetism between ginkgo flavonoids and impurities may avail to the process of ultrafiltration with composite magnetic membrane in the magnetic field.

3.2. Microstructure of the membrane

Fig. 2 shows micrographs of the surface and cross-section structures of PSF membrane and the composite membrane. It can be seen that most particles were distributed uniformly in the surface, inner pores, and walls except for a few large clusters. The membrane showed typical asymmetric morphology with spongy-like pores. The association of Fe_3O_4 particles with PSF membrane may attribute to some ways as follows [11]. Firstly, the oleic acid combined with PSF forms

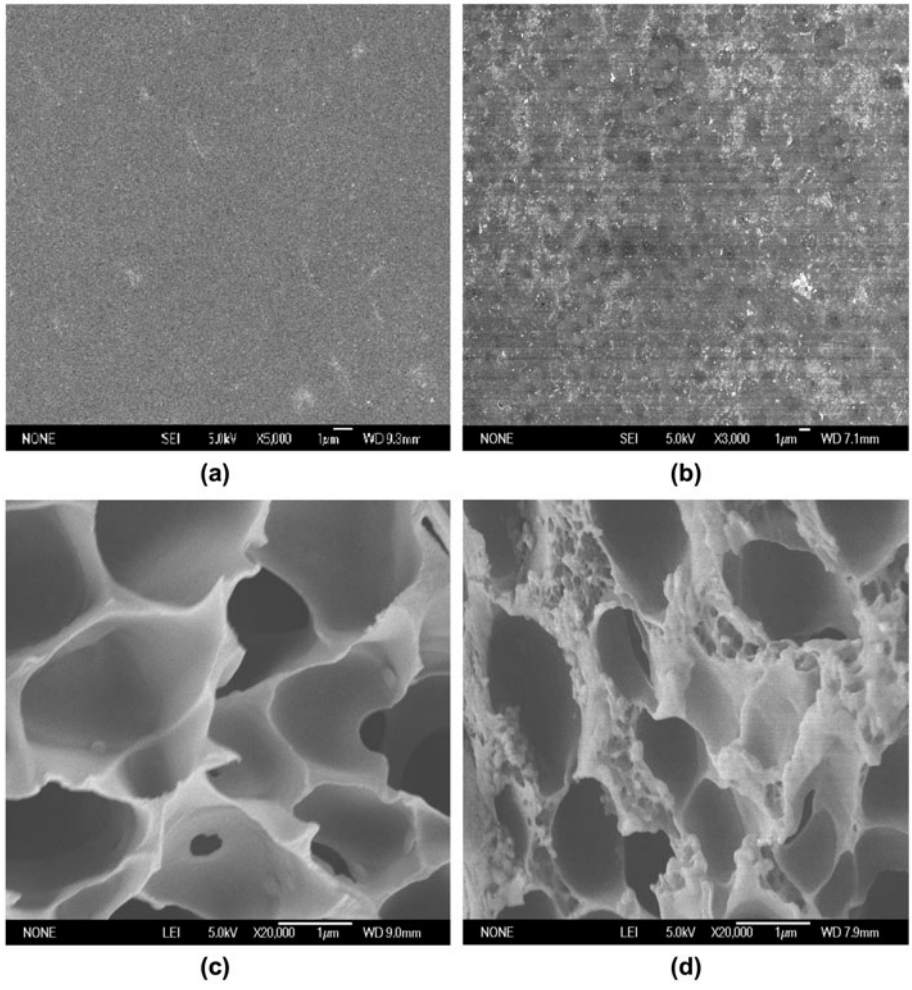

Fig. 2. SEM micrographs of the surface, cross-section structures of the PSF membrane, and PSF–Fe_3O_4 composite membrane. (a) The surface of PSF membrane; (b) the surface of the PSF–Fe_3O_4 composite membrane; (c) the cross-section of PSF membrane; and (d) the cross-section of the PSF–Fe_3O_4 composite membrane.

strong chemical bond. Thus, these Fe_3O_4 particles are fixed in membrane. Secondly, some oleic acid fell off from Fe_3O_4 particles and got into DMF during dispersion of particles in the casting solution because DMF is a strong protonic solvent. Then these particles were aggregated to clusters and associated with PSF. When performing in magnetic field, the particles will produce a strong induced magnetic field and so, the membrane is magnetic.

3.3. Magnetism of Fe_3O_4 nanoparticles and the composite membrane

To observe the magnetism of Fe_3O_4 nanoparticles and the composite membrane in a magnetic field, their hysteresis curves are shown in Figs. 3 and 4. It can be seen that the movement of the Fe_3O_4 nanoparticles and the size of the composite membrane increased when the magnetic intensity was enhanced gradually. Their movements increase acutely with the enhancement of magnetic intensity initially and then approach to saturation when the intensity of the magnetic field is about 1.0 T. The movements decrease to 0 emu when the intensity reduces to 0 T, so their coercive force is zero. This indicates their superparamagnetism. That is to say, the Fe_3O_4 nanoparticles and composite membrane shows magnetism when placed in magnetic field and their magnetism will disappear when the magnetic field is withdrawn.

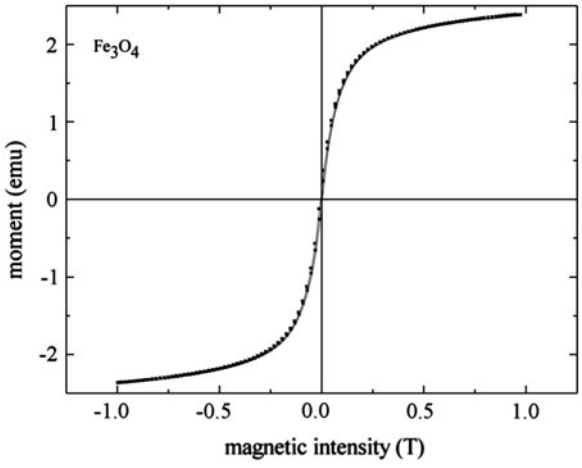

Fig. 3. Hysteresis curve of the Fe_3O_4 nanoparticles.

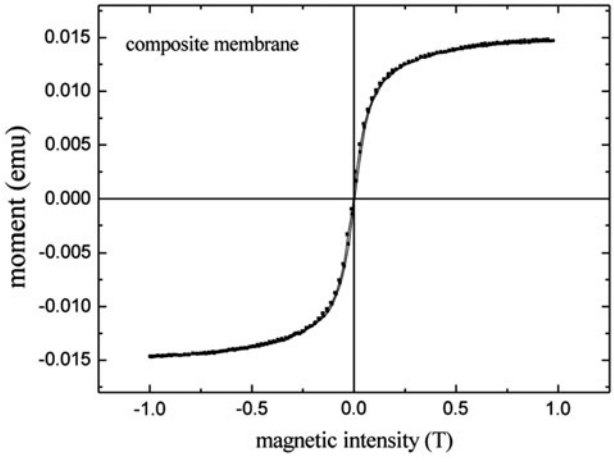

Fig. 4. Hysteresis curve of the composite membrane.

3.4. Molecular weight cut-off

It can be seen from Fig. 5 that the molecular weight cut-off of the composite membrane is about 20,000. The composite membrane with the MWCO is fit to the separate flavonoids from the GBE.

3.5. Effect of magnetic field on the separation process

Fig. 6 shows the effect of magnetic field on the content of ginkgo flavonoids in the product and flux of the GBE solution.

The graph shows the effect of magnetic field on the content of ginkgo flavonoids in the product. It can be seen from the graph that the products formed in the magnetic field have higher content of ginkgo flavonoids than that formed without the field. The content of ginkgo flavonoids increase acutely with the increase of the magnetic intensity initially and then approach to stable and finally decrease sharply to the initial value

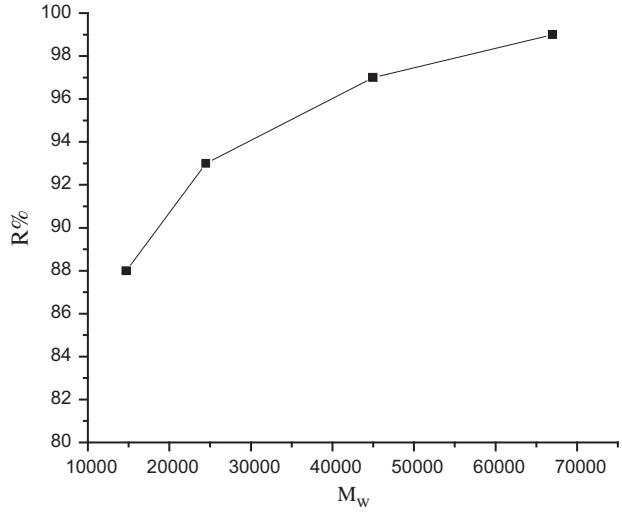

Fig. 5. Observed retention of the composite membrane.

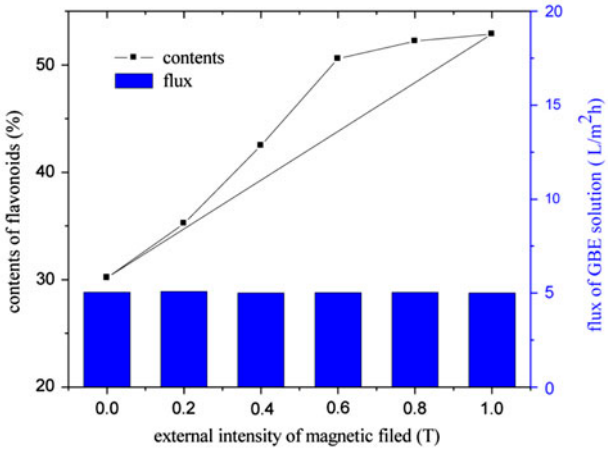

Fig. 6. Diagram of the effect of magnetic field on the content of flavonoids and flux of GBE solution.

when the field is withdrawn from 1.0 T. The contents of flavonoids in the products were 30.16 wt.% formed in the absence of magnetic field, 35.24 wt.% in the magnetic field of about 0.2 T, 42.5 wt.% in 0.4 T, 50.58 wt.% in 0.6 T, 52.20 wt.% in 0.8 T, 52.87 wt.% in 1.0 T, and 30.20 wt.% when the magnetic field is withdrawn. The current content shown in Fig. 6 is consistent with that shown in Figs. 3 and 4.

The common purities of GBE are 24, 50, and 90% in the market. The price difference of GBE with the purity of 24 and 50% is very large. A product of GBE with the purity of 50.58% in 0.6 T.

The composite membrane shows magnetism in the magnetic field. The paramagnetic ginkgo flavonoids will get attraction when they get across the membrane. So, fine GBE products of higher flavonoids content can be obtained in the magnetic field. The magnetism of the composite membrane increases acutely with the increase of magnetic intensity initially, then increases slowly, and approaches to saturation when B_e is about 1.0 T; so is the current content of flavonoids. Finally, the content of flavonoids decreased sharply to the initial value of 30.20 from 52.87 wt.% because the magnetism, superparamagnetism, of the composite membrane disappeared when the magnetic field is withdrawn from 1.0 T.

The histogram shows the effect of magnetic field on the GBE solution flux. It can be seen that the magnetic field has no effect on the flux. Though the nano-sized Fe_3O_4 particles may bring deformation of the skin layer and membrane pore structure in the magnetic field, the porosity of the membrane does not change [11].

4. Conclusions

In this paper, PSF–Fe_3O_4 composite ultrafiltration membrane was attempted to refine the flavonoids from GBE. Micrographs show most particles were distributed uniformly in the membrane. Hysteresis curve indicates that the composite membrane has superparamagnetism for the addition of nano-sized Fe_3O_4 particles. The ginkgo flavonoid with the purity of 98% was tested to be paramagnetic. So we can obtain fine GBE products of higher flavonoids content with the composite membrane in the magnetic field. The content of flavonoids increase acutely with the increase of the magnetic intensity initially, then approach to be stable. In the magnetic field with its intensity of about 1.0 T, the flavonoids were purified to 52.87 from 15.60 wt.% in the crude GBE and purified to 30.16 wt.% without magnetic field. The magnetic field has no effect on the flux.

Symbols

χ — mass susceptibility (cm^3/g)
J — GBE solution flux (L/m^2h)
R — rejection (%)
B_e — magnetic intensity of the external magnetic field (T)

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