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A convenient method for the determination of molecular weight cut-off of ultrafiltration membranes☆

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ABSTRACT

With the rapid increase of water contamination, membrane separation technology and their corresponding molecular weight cut-off (MWCO) evaluation method become more necessary. In this study, *Panax notoginseng saponins* was used as a new standard marker to determine ultrafiltration (UF) membrane MWCOs, series of Millipore membranes were selected as control group to analyze and calculate the relationship between retention rate and MWCOs with exponential or logarithmic equation. A new and convenient method was provided for determining the membrane MWCO by modeling analysis retention rate with MWCOs, and the regression coefficients ≥0.990. The feasibility and practicability of established method was verified by different manufactures' membrane and dextrans. In the detection progress, as the main ingredient of *Panax notoginseng saponins*, *Notoginsenoside* R_1, *Ginsenoside* Rg_1, *Ginsenoside* $Rb_1$and *Ginsenoside Rd* with different surface activity, the MWCO range of UF membranes can be divided into two zones mainly due to the retention rate difference among *Notoginsenoside* R_1, *Ginsenoside* Rg_1, *Ginsenoside* Rb_1 and *Ginsenoside Rd*. Zone I, 1000–10000; and Zone II, 10000–100000. Thus, the new method would be helpful to improve the applicability of UF membrane in separation technology.

1. Introduction

Ultrafiltration (UF) has been applied in various types of industries such as sewage treatment, seawater desalinization, biology and medicine. For example, Harmen J. Zwijnenberg used a UF membrane to produce a higher quality protein from potato fruit juice [1]. Akon Higuchi investigated the use of immobilized DNA membranes for chiral separation of phenylalanine [2]. Wang *et al.* [3] developed a membrane-based cost-effective process for the separation and purification of superoxide dismutase (SOD) from garlic. The membrane molecular weight cut-off (MWCO) and its distribution are very important parameters for membrane quality and membrane transport mechanisms. The pore size distribution dominates the separation characteristics of asymmetric membranes, which can be used to predict the MWCO of porous membranes and the rejection for different solute molecules or particles.

Different experimental methods can be employed to evaluate membrane pore size, such as microscopic, bubbling test, liquid displacement and thermoporometry [4–6], these methods mentioned above all have certain advantages. Furthermore, existing detection techniques for the MWCO of UF membranes calls for the use of standard solutes with known molecular weight such as dextran, protein or polyethylene glycol (PEG) [7,8]. These methods mentioned above have their specific characteristics for various membranes with different pore sizes, and also exhibits some limitations in membrane type and pore size. One of the obvious defects was membrane fouling, for example, dextran fouling was visualized using atomic force microscopy (AFM) and quantified by ATR-IR spectroscopy and by the mass balance in simultaneous diffusion–adsorption measurements (SDAM) [9]. The fouling mechanisms of PEG involved in the UF were investigated by Vela *et al.* [10], and the membrane pollution characters of BSA were detected by dye tests [11], electron spin resonance (ESR) spectroscopy [12], *etc.*

The MWCO of UF membranes is defined as the molecular weight of a solute that has a rejection value of 0.9, which might be used as selection parameters in mixture separation [13]. In the progress of membrane MWCO testing, the membrane retention rate can be critically affected by the standard solutes molecular weight distribution. But the molecular weight distribution of standard solutes varies with different factories, in other words, the same molecular weight of dextran, BSA and

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PEG had different molecular weight distribution, respectively. And eventually the quality of standard solutes had an impact on the accuracy of membrane MWCO, and the above method was complicated in operation, detection and analysis. Therefore, a convenient and accurate method was urgently needed for the determination of UF membranes MWCO.

After abundant experiments based on UF separation of compounds, *Panax notoginseng saponins*, a low-cost and accessible water extract was from *Panax notoginseng* or American *ginseng*, was selected as standard substance, which had four representative elements: *Notoginsenoside* R_1, *Ginsenoside* Rg_1, *Ginsenoside* Rb_1 and *Ginsenoside Rd*. The four solutes had similar molecular weight 932–1108 with different surface activity and existential state in aqueous solution and showed different retention rate with series of MWCO UF membranes. In this paper, the membrane operating condition and concentration polarization were discussed, and the relationship between solutes retention rate and membrane MWCO was analyzed by the "three-step" method. The method was developed to predict the MWCO of different manufacturer UF membrane. In addition, the measuring accuracy and convenience of this method were also measured and compared.

2. Materials and Methods

2.1. Materials

In order to determine the MWCO of UF membranes, series of regenerated cellulose membranes were selected as standard MWCO membranes in this paper, which manufactured by Millipore Co. in USA, and these membranes had the same properties, such as morphology, except pore sizes. The detail membrane properties are listed in Table 1. The UF apparatus is shown in Fig. 1.

Masterflex® L/S™ peristaltic pump (pump head: easy-load ® Model 7017-21, Millipore Corporation, USA) was used to circulate the feed solution, which can provide the constant flux at different feed pressure. *Notoginsenoside* R_1 ($C_{47}H_{80}O_{18}$, CAS: #80418-24-2), *Ginsenoside* Rg_1 ($C_{42}H_{72}O_{14}$, CAS: # 22,427–39-0), *Ginsenoside* Rb_1 ($C_{54}H_{92}O_{23}$, CAS: #41,753–43-9) and *Ginsenoside Rd.* ($C_{48}H_{82}O_{18}$, CAS: # 52,705–93-8) were purchased from National Institute for the Control of Pharmaceutical and Biological Products in China, *Panax notoginseng saponins* (Cat. No.: 090701, from Yunnan Yuxi Wanfang natural medicines Co., Ltd. in China) was used to characterize the rejection coefficient of the hollow fiber membranes in salt-free Milli-Q water. Six untested commercial UF membranes and series of molecular weight dextrans were selected to verify the feasibility and superiority of this method and the detail membrane properties are listed in Tables 2 and 3.

2.2. Membrane characterization

The size of the pores as well as pore size distribution is an important parameter deciding the separation performance [14]. We obtained volumetric permeation flux and solute retention rate during solute separation experiments with filtration membranes. Both the flux and retention rate are strongly dependent on the structure of the membrane. Therefore, if the relationship between the flux and retention rate and the membrane structure is known, we can characterize the membrane structure, such as pore size, pore size distribution, pore density, and so on. The relationship is founded on the molecular transport through the membrane. We can also interpret diffusion and sieving measurements in terms of the pore size distribution.

2.2.1. The influence of operating pressure

All UF experiments were performed in a thin channel module described in Fig. 1 with an effective membrane area of 0.5 m^2, adjustable feed flow, and pressure. Prior to a UF experiment, deionized water was circulated in the test loop until steady state.

Pressure influence measurements were carried out with *Panax notoginseng saponins*. The test solutions were prepared by dissolving reweighed amounts of *Panax notoginseng saponins* in deionized water at a concentration of 10 $g \cdot L^{-1}$. Test conditions were pressures of 0.01, 0.05, 0.1, 0.15, 0.2 and 0.25 MPa, circulation velocity was regulated by

Table 1
The properties of the standard membranes

Properties①	Membrane parameter						
MWCO	1000	3000	5000	10000	30000	50000	100000
Membrane Material	Regenerated cellulose	Regenerated cellulose	Regenerated cellulose	Regenerated cellulose	Regenerated cellulose	Regenerated cellulose	Regenerated cellulose
Dextran Retention	90% at 1000	90% at 3000	90% at 5000	90% at 10000	90% at 30000	90% at 50000	90% at 100000
Filter mode	Plain	Plain	Plain	Plain	Plain	Spiral	Plain
Wettability	Hydrophilic	Hydrophilic	Hydrophilic	Hydrophilic	Hydrophilic	Hydrophilic	Hydrophilic

① Provided by Millipore Co.

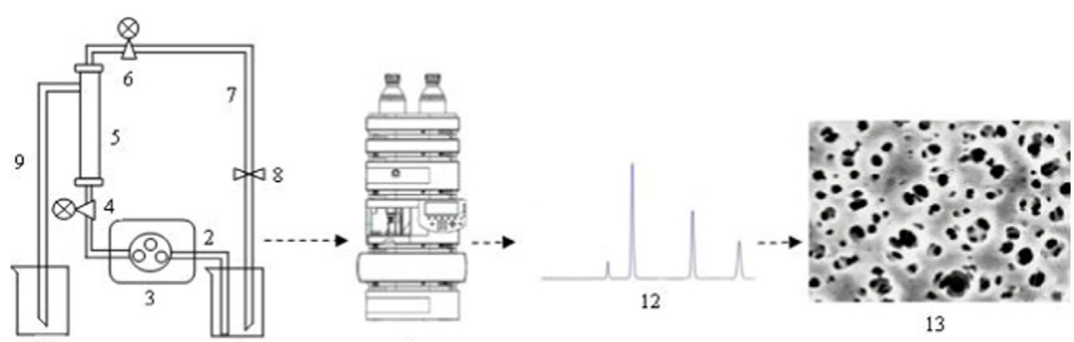

Fig. 1. UF process diagram. 1. Stock solution tank; 2. inlet pipe; 3. peristaltic pump; 4. pressure gage; 5. UF membrane; 6. pressure gage; 7. rejected solution; 8. speed regulator valve; 9. ultrafiltrate; 10. ultrafiltrate tank; 11. HPLC; 12. chromatogram; 13. membrane pores.