

## PREPARATION AND CHARACTERISTICS OF A PAPER-BASED ULTRAFILTRATION MEMBRANE

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A novel process involving a paper-based ultrafiltration (UF) membrane was developed via paper coating technology. The membrane employed a paper sheet as support layer and a coated thin film layer of adhesive. The proper selection of paper sheet support layer was crucial to the performance of the ultrafiltration membrane. A paper sheet with beating degree of 85°SR and basis weight of 50g/m<sup>2</sup> was chosen as the support. PVA was chosen as the adhesive. The paper-based ultrafiltration membrane achieved high retention performance while using a simple production process and keeping the production cost low. Disadvantages of the membrane included low porosity and low pure water flux. So further investigation is still needed to produce a fully satisfactory paper-based ultrafiltration membrane.

*Keywords:* UF membrane; Coating; Porous support layer; Retention rate

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### INTRODUCTION

Membrane separation technology, which uses natural, artificial, and selective membranes, can isolate, grade, and enrich gas or water by means of two-component or multicomponent systems (Zheng 1999). Compared with traditional separation technologies, membrane separation technology has the advantages of high separation efficiency, low energy consumption, and simple operation (Shi et al. 2001). Membrane separation processes can be classified as follows: (1) using pressure difference as its driving force: MF, UF, NF, RO, pressure dialysis, etc.; (2) using concentration or activity difference as its driving force: gas separation, steam dialysis, etc.; (3) using temperature difference as its driving force: heat penetration, membrane distillation; and (4) using potential difference as its driving force: electrodialysis, electroosmosis, membrane electrolysis, etc. (Wang et al. 2007).

The pore diameter of an ultrafiltration (UF) membrane ranges from 1 nm to 100 nm, which is between that of a microfiltration (MF) and a nanofiltration (NF) membrane. UF membranes include inorganic and organic types, the latter of which usually have polysulfone as a porous support layer because of its good mechanical strength, thermal stability, and chemical stability (Mulder 1996). There are many methods of making ultra-thin layers of UF membranes, such as interfacial polymerization, monomer catalyst polymerization, and plasma polymerization. The production method of inorganic UF membranes usually includes pigment particles, as well as a great investment in production facilities. With such as method, however, it is difficult to control the membrane pore size distribution (Wang 2008).

The present research aims to develop a new asymmetric UF composite membrane. The new membrane was produced by combining the methods of a paper-making process, production of an organic UF composite membrane, and fabrication of an inorganic UF membrane. The first step involved selecting the paper to be used as the porous support layer of membrane. The second step involved adopting a coating process of paper-making to form a thin cortex, which simplified the production process of the UF membrane. This method is similar to the inorganic ceramic ultrafiltration membrane manufacturing methods, but it doesn't require high temperature. In principle, if the process can be properly controlled, an ideal pore size can be obtained. This method is easy to operate, it also greatly reduces the cost of production, and the equipment investment is less. There are multiple influencing factors in membrane forming process, such as selection of support layer, selection of adhesive, dosage of adhesive, coating weight, coating times, drying temperature, drying time, and so on. Only the influence of the support layer on the membrane qualities is considered in this paper.

## EXPERIMENTAL

### Materials

A coniferous fiber handsheet ( $50\text{g/m}^2$ ) made from bleached kraft pulp was used as a porous support layer (self-made). Polyvinyl alcohol (PVA) was provided by Sinopharm Chemical Additives Co., Ltd. Bovine serum albumin (MW 67,000) was provided by Shanghai Health Research Biochemical Reagent Co., Ltd. The protein  $\gamma$ -globulin (MW 160,000) was provided by Shanghai Hui Xing Biochemical Reagent Co., Ltd. Polyamide polyamine epichlorohydrin resin of high purity (PAE) was provided by Jingzhou Chemical Reagent Co., Ltd. Poly vinylidene fluoride (PVDF) commercial UF membrane was provided by Shenzhen Jia Quan membrane filtration Equipment Co., Ltd.

### Methods

#### *Preparation of the paper-based ultrafiltration membrane*

Using a PFI mill (ZQS<sub>7</sub> Machinery Plant, Shaanxi University of Science and Technology) to process the pulp, bleached softwood pulp was chosen as the raw material. The beating degree targets for the pulp were 50°SR, 60°SR, 70°SR, 75°SR, 80°SR, and 90°SR. The pulp samples of different beating degree were treated with wet-strength agent (at a relative amount of 1% based on dry pulp) before preparing handsheets (weight  $50\text{g/m}^2$ ). Then the maximum pore size, porosity, average pore size, pure water flow, and retention rate of handsheets were evaluated. A cup plate ultrafilter (MSC300, Shanghai Morocco Speed Technology Co., Ltd.) was used to pre-stress the supporter under 0.1 MPa of pressure for 20 minutes for the determination of pure water flow. A retention rate of  $200\mu\text{g/mL}$  of bovine serum albumin was determined using the UV spectrophotometer (Shanghai Precision Scientific Instrument Co., Ltd.) at room temperature. Retention (%) of BSA and pure water flow were calculated using formulas (1) and (2), respectively,

$$R(\%)=(1-A_t/A_0)\times 100 \quad (1)$$

where  $R$  is the percentage rejection,  $A_0$  the absorbance of the feed solution and  $A_t$  the absorbance of permeate at time ' $t$ '. The pure water flow is given by,

$$J=Q/At \quad (2)$$

where  $J$  is the pure water flow,  $Q$  the permeate liquid volume,  $A$  the membrane area, and  $t$  time. The average radius and maximum pore of supporter were determined by mercury porosimetry and a bubble method.

As it has the characteristics of a linear molecular structure, a high chemical stability, and suitable mechanical strength, PVA was chosen as the adhesive and was coated on the surface of the support using a k-type coating method. After drying, the pure water flow and retention rate were determined (coating weight  $10\text{g/m}^2$ , adhesive concentration 10%, drying temperature  $105^\circ\text{C}$ , and drying time 60 s). Then, the membrane was crosslinked with glutaraldehyde (concentration was 1%) for 10 minutes, because PVA membrane could be swelled by water, and that could affect the membrane's structure.

#### *Physical and chemical properties of the membrane*

The combined membrane was immersed in a water bath of  $80^\circ\text{C}$  for three hours, then water resistance and temperature resistance were determined. The combined membrane was soaked in 0.5 mol/L solutions of NaOH and HCl for 72 h, and then chemical stability was determined.

#### *Membrane structural analysis*

The paper-based ultrafiltration membrane was treated by desiccation, brittle fracture, and sputter-coating with gold. Scanning electron microscopy was conducted with an FEI Quanta 200 device (Japan).

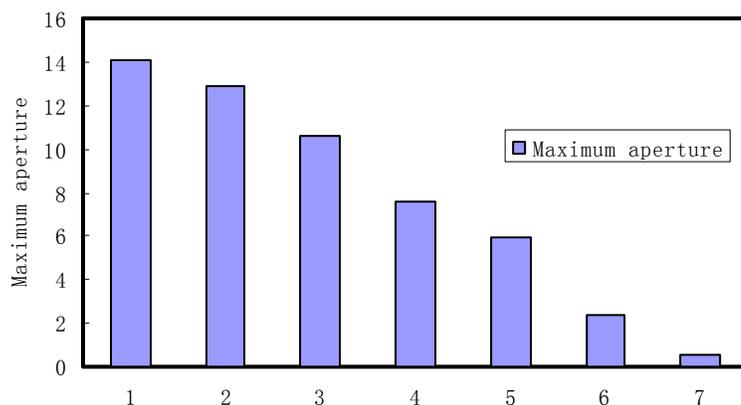
## RESULTS AND DISCUSSION

### Preparation of the Paper-Based Ultrafiltration Membrane

#### *Maximum aperture of paper of different beating degree*

An ultrafiltration membrane must have a miniscule pore diameter. For this reason, the pore diameter of the paper sheet used as a support layer has to be suitably low. Usually, a paper sheet would achieve smaller pore diameters with a high beating degree than with a low beating degree. So, pulp with beating degrees ranging from  $50^\circ\text{SR}$  to  $90^\circ\text{SR}$  were chosen as material for the paper sheet while keeping the basis weight at  $50\text{g/m}^2$ . Maximum pore diameter of the paper was determined in this part.

Figure 1 shows a comparison between paper sheets prepared from fibers with different beating degree. It is apparent that maximum pore diameter decreased with increasing beating degree. This decrease can be explained by improvement of tightness of paper sheet and filling of pores with fines derived from the beating process. Maximum pore diameter was down to  $5.98\ \mu\text{m}$  when the beating degree exceeded  $80^\circ\text{SR}$  and even  $0.52\ \mu\text{m}$  at  $90^\circ\text{SR}$ . If a paper sheet still could exhibit high porosity when its beating degree exceeded  $80^\circ\text{SR}$ , it could be accepted as the support for a UF membrane.



**Fig. 1.** Maximum aperture in  $\mu\text{m}$  of paper of different beating degree (1- Beating degree 50°SR, 2-Beating degree 60°SR, 3-Beating degree 70°SR, 4-Beating degree 75°SR, 5-Beating degree 80°SR, 6-Beating degree 85°SR, 7-Beating degree 90°SR)

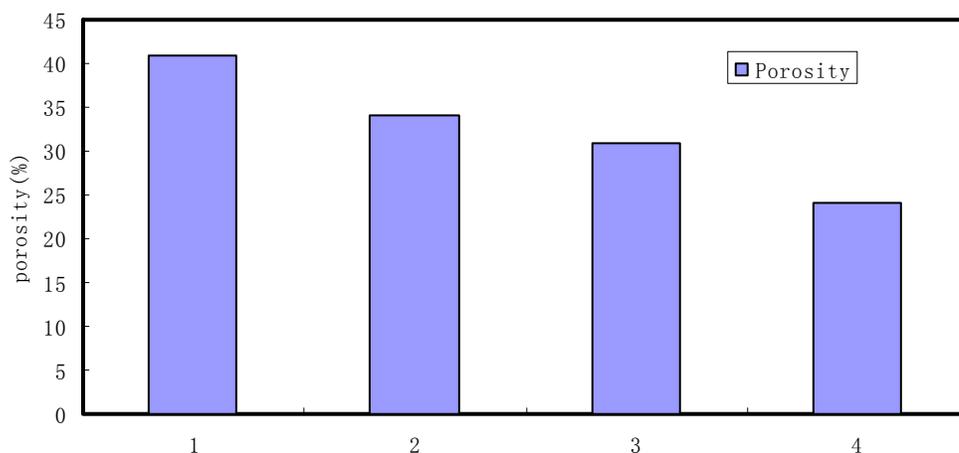
#### *Porosity of paper of different beating degree*

In addition to the requirement of having a very small pore diameter, an ultrafiltration membrane also demands high porosity. In this part, paper sheets, with quantity of  $50\text{g}/\text{m}^2$  and beating degrees of 75°SR, 80°SR, 85°SR, and 90°SR, were measured to search for the most suitable porosity.

Figure 2 shows that the porosity of the paper sheets declined in an orderly manner with the increasing beating degree. Raising tightness of paper sheet caused the decline of porosity. According to micro-pore shape, a microfiltration membrane can be divided into two kinds: bending pore membranes and cylindrical pore membranes (Peng 2009). The micropore structure of a bending pore membrane is a network of tortuous pore channels that are interdigitally connected, while that of a cylindrical pore membrane is a cylindrical capillary structure penetrating the membrane in parallel fashion. The pore structure of a paper sheet belongs to the bending pore category, for which porosity is mostly between 35% and 70%. As can be seen from Fig. 2, the porosities of paper sheets with beating degree under 85°SR exceeded 30%, and this could in principle meet the needs of a support for an ultrafiltration membrane. The average pore diameter of a paper sheet with beating degree of 90°SR possibly reached the ultrafiltration level because of its extremely low maximum pore diameter, though its porosity was a bit lower than the others'. Based on these considerations, paper sheets with beating degrees of 80°SR, 85°SR, and 90°SR were selected for further testing.

#### *Average pore diameter of paper of different beating degree*

The average pore diameter of paper sheets with beating degree of 80°SR and 85°SR met the standard for a high filtering precision microfiltration membrane, while that of 90°SR achieved the level of UF membrane (2nm~100nm) (Tab. 1). In order to make a better choice, pure water flux and retention effect of bovine serum albumin will be measured in next part.



**Fig. 2.** Porosity of paper of different beating degree (1- Beating degree 75°SR, 2-Beating degree 80°SR, 3-Beating degree 85°SR, 4-Beating degree 90°SR)

**Table 1.** Average Pore Diameter with Supports of Different Beating Degree

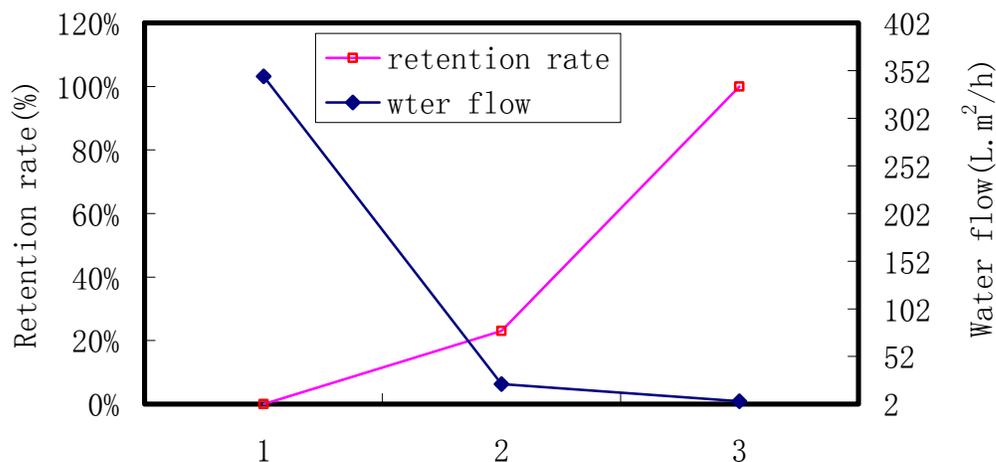
Beating degree	80°SR	85°SR	90°SR
Average pore diameter	1.87 $\mu\text{m}$	0.37 $\mu\text{m}$	0.088 $\mu\text{m}$

#### *The retention rate and pure water flux of paper of different beating degree*

The pure water flux and the retention rate of bovine serum albumin would reflect the performance of the membrane much more directly than maximum pore diameter and average pore diameter. The samples in this part were paper sheets with beating degree of 80°SR, 85°SR, and 90°SR (weight 50g/m<sup>2</sup>).

As shown in Fig. 2, the pure water flux dropped continuously with increasing beating degree, while the retention rate increased progressively. According to the former analyses, paper sheets with higher beating degree would lead to lower maximum pore diameter and average pore diameter, and this could be expected to favor good retention performance, but it also meant the loss of pure water flux due to smaller pore diameter and lower porosity. It should be noticed that the retention rate of a paper sheet prepared from fibers with a beating degree of 80°SR was nearly zero, but that with 90°SR it was up to 100%. The average pore diameter of a paper sheet with 80°SR was bigger than the requirement of pore diameter of a UF membrane.

If there is a sufficiently large gap between the support and an UF membrane layer, this circumstance may induce poor support strength, and the surface layer would be crushed under the applied pressure. So, the paper sheet prepared with fibers of beating degree 80°SR had to be abandoned. A paper sheet with 90°SR should also be abandoned due to its poor pure water flux (2.8L/m<sup>2</sup>·h), although its retention rate for the protein was perfect. The paper sheet with 85°SR was chosen as the support for the membrane, though further improvements are needed to fully meet the requirements.



**Fig. 3.** The retention rate and pure water flux of paper of different beating degree (1- Beating degree 80 °SR, 2-Beating degree 85°SR, 3-Beating degree 90°SR)

## Physical and Chemical Properties of the Membrane

### *The mechanical strength of membrane*

In this part, mechanical strengths of composite membranes were evaluated and compared with those of commercial membranes.

From Table 1 it is apparent that the paper-based compound film membrane exhibited much better dry/wet tension strength and dry/wet bursting strength than the commercial one. In practical applications, it could be expected to bear higher pressure and as a result achieve higher flow speed.

**Table 1.** The Mechanical Strength of Membranes

Film categories	Dry tensile strength	Dry bursting strength	Wet tensile strength	Wet bursting strength
	kN/m	kPa	kN/m	kPa
Paper-based compound film	4.346	262	1.452	138
Commodity UF	0.505	69	0.388	65

### *Film temperature resistance*

For comparison with composite membrane without treatment, the membrane was soaked in a water bath at 80 °C for 3 h, and was tested to find out its retention rate and water flow. Results are shown in Table 2.

**Table 2.** The Heat Resistance of Membrane

	Retention rate (%)	Water flow (g/min)
Membrane without heat treatment	78.6%	0.79
Membrane with heat treatment	75.8%	0.82

As shown in Table 2, heating of the membrane while wet had little or no effect on the retention rate and water flow. These results show that the composite membrane had good heat resistance.

#### *Membrane chemical stability*

To estimate its chemical stability, the membrane was exposed to strong acid and alkaline solutions, respectively. Results are shown in Table 3.

**Table 3.** Chemical Stability of the Membrane

	Retention rate (%)	Water flow (mL/min)
Membrane without chemical treatment	78.6%	0.79
Membrane with acid treatment	69.3%	0.88
Membrane with alkali treatment	81.2%	0.74

According to Table 3, owing to damage to pores of the base membrane, the retention rate of membrane exposed to acid solution dropped significantly, while its water flow was increased. However, the retention rate of the membrane exposed to alkaline solution rose, while its water flow was similar to the untreated one. Thus, the membrane had better stability under alkaline than that under acid conditions.

#### *Water flux recovery of membrane contaminated after cleaning*

When bovine serum albumin was used as a test solution to evaluate the retention rate of a membrane, some of it was adsorbed on the surface of the membrane or jammed in the membrane pores, and this caused loss of pure water flux. After being washed with distilled water 10 times, the pure water flux of polluted membrane was measured to determine whether or not the adsorbed bovine serum albumin could be cleaned easily.

**Table 4.** Water Flux Recovery of Contaminated Membrane after Cleaning

	Water flow(g/min)	Recovery ratio (%)
Uncontaminated membrane	0.79	
After contaminated membrane cleaning	0.73	92%

As shown, the pure water flux of a contaminated membrane, after cleaning, was only 8% lower than the new one (Table 4.). The membrane was judged to have good antifouling ability, since its recovery rate was much higher than 90%.

#### *Retention rate of membrane*

The retention rate of a membrane was evaluated with bovine serum albumin and  $\gamma$ -globulin (Li 2008). Results are shown in Table 5.

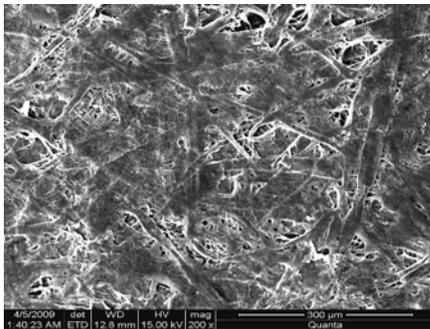
**Table 5.** Retention Rate of Membrane for Bovine Serum Albumin and  $\gamma$ -Globulin

	Bovine serum albumin (200 ug/mL)	$\gamma$ -globulin (200 ug/mL)
Rejection	65%	82%

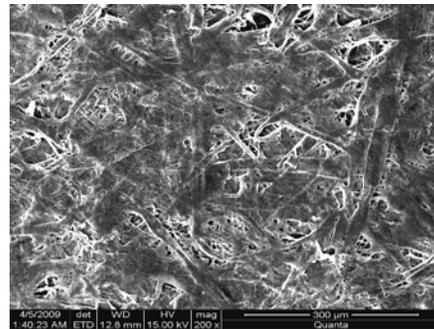
Table 5 shows that the retention rate for bovine serum albumin and  $\gamma$ -globulin was 65% and 82%, respectively. It also shows that this membrane had a good retention rate for materials with MW more than 160,000, but poor for that less than 67,000.

### Membrane Structural Analysis

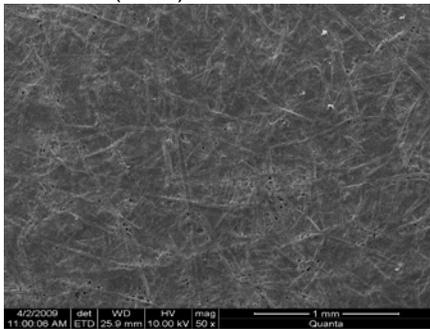
*SEM images of the porous support layer and surface structure of the ultrafiltration membrane*



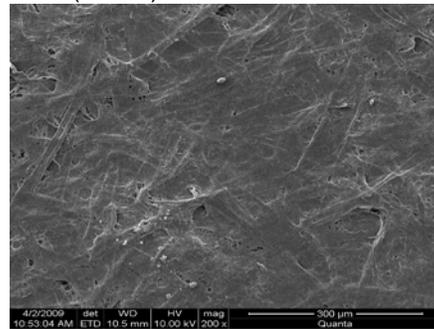
**Fig. 4(a).** SEM image of porous support layer ( $\times 50$ )



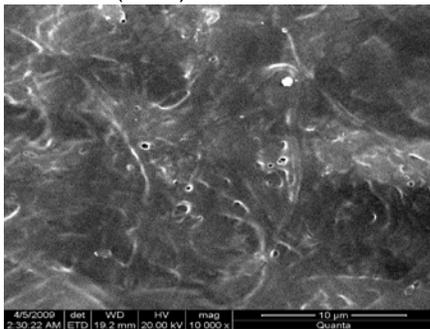
**Fig. 4(b).** SEM image of porous support layer ( $\times 200$ )



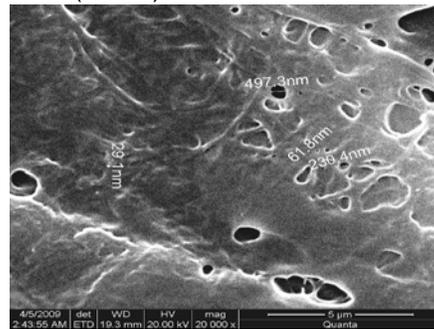
**Fig. 4(c).** SEM image of UF membrane ( $\times 50$ )



**Fig. 4(d).** SEM image of UF membrane ( $\times 200$ )



**Fig. 4(e).** SEM image of UF membrane ( $\times 10000$ )



**Fig. 4(f).** SEM image of UF membrane ( $\times 20000$ )

The surface of porous support [Figs. 4(a) and 4(b)] and PVA composed membrane [Figs. 4(c) and 4(d)] were compared at the same magnification. Film-forming reagent was coated on the surface of porous support, and a layer of homogeneous membrane structure was formed. But the existence of large pore size defects was readily apparent. This may be explained by film breakage occurring during the drying process. During this process, the membrane shrunk non-uniformly. On the other hand, microbubbles in the film-forming reagent ruptured during the drying process. This rupture, caused by the occurrence of stomata, would also form large pore size defects. These were the most important reasons for rejection rate of membrane failing to reach 90%.

Figures 4(e) and 4(f) are local enlargements of the membrane. In these images the micropore structure can be seen clearly. Generally, the pore diameter of ultrafiltration membranes should be in the range of 2 to 100 nm. In Fig. 4(f) the pore diameter of minor micropores was about 29 nm, and that of large micropores was about 500 nm. The existence of large micropores has an unfavorable effect on rejection rate. Also, micropores appearing in the Fig. 4(f) are limited. These features contributed to low porosity, accounting for the observed low pure water flux and filtration rate.

## CONCLUSIONS

1. The paper-based compound membrane studied consisted of a 85°SR coniferous handsheet as a porous support layer, together with latex PVA as an adhesive.
2. The compound membrane was found to have good physical strength, heat resistance, alkali resistance, and anti-fouling performance.
3. Analysis by scanning electron microscopy revealed that the composite membrane had a wide pore size distribution and relatively low porosity.

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