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Large pore size polyacrylonitrile membrane for ultrafiltration

WU Kai-fen, QIU Ping, WANG Zheng-jun, WANG Jing-rong

(Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China)

Abstract: The effects of the components of solution for membrane casting and preparation conditions on the membrane performances are studied in this paper. Polyacrylonitrile(PAN) was used as polymer and DMAC as solvent. The ultrafiltration (UF) membranes whose cut-off of molecular weight is 150000 and flux of pure water reaches 150—200 ml/($cm^2 \cdot h$) were prepared by selecting proper components of solution for membrane casting and membrane preparation conditions.

Key words: PAN; ultrafiltration membrane; large pore size

Introduction

In recent years, the technique for ultrafiltration has gained rapid development. More and more kinds of membranes are studied and manufactured, and a large-scale industrial application has been grown.

PAN polymer is extensively used to prepare UF membranes(Stoiko, 1991). Its hydrophilicity and resistance to fouling are quite good, so it has found favor with people increasingly. This paper introduces how to enhance the separation properties of PAN UF membrane for industrial application. PAN UF membranes with high pure water permeability were prepared as flat sheets by selecting proper components of casting solution and preparation conditions.

1 Experimental

1.1 Materials

γ-globulin($M_w \approx 150000$ g/mol) was obtained from TCI(USA), polyvinyl pyrolidone(PVP) from SIGMA(USA), PAN from Shanghai Jinshan Chemical Industrial Factory, DMAC from Shanghai Shuguang Chemical Industrial Factory, PEG from Shanghai Pudong Gaonan Chemical Industrial Factory, egg albumin ($M_w \approx 43000$ g/mol) from Beijing Market and bovine serum albumin(BSA, $M_w \approx 67000$ g/mol) from Shanghai Biological Products Institute.

1.2 Apparatus

Permeability of UF membranes was measured on a permeability apparatus constructed in this lab. UV-260 spectrophotometer is from Shimadzu, Japan. Membrane casting machine is from Amicon, USA.

1.3 Membranes

Membranes were prepared as flat sheets by Loeb-Sourirajan technique(liquid-solid)(Loeb, 1964). PAN was used as polymer and DMAC as solvent.

1.4 Measurement

Permeability of UF membranes was measured at operating pressure of 0.1 MPa and temperature of 20℃. Flux of pure water(f) was obtained from Equation(1):

$$f(\mathrm{ml}/(\mathrm{cm}^2 \cdot \mathrm{h})) = \frac{V(\mathrm{ml})}{S(\mathrm{cm}^2) \times t(\mathrm{h})}, \tag{1}$$

where, V(ml) is the volume of pure water permeating through the membrane; S(cm^2) the effective area of membrane; t(h) the time of ultrafiltration.

Retention(R) of membrane was obtained from Equation(2) by using a certain concentration of albulin solutions. Relation between optical density value and concentration accords with Bill Role (Zhu, 1995):

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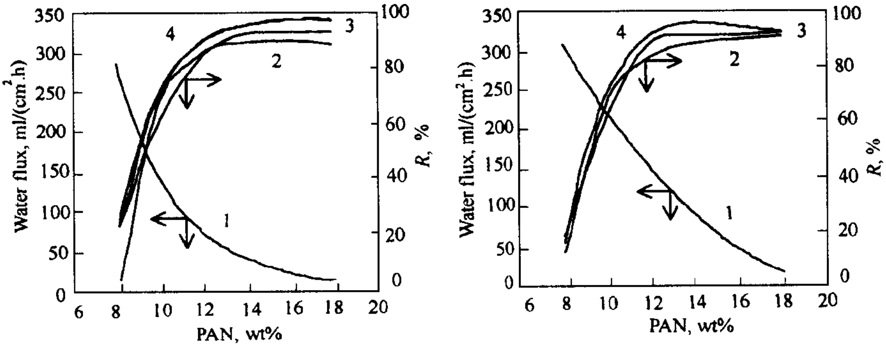
$$R\% = \left(\frac{C_0 - C}{C_0}\right) \times 100\% , \tag{2}$$

where, C is the optical density value of the permeate solution; C_0 the optical density value of the solution before ultrafiltration. The optical density value of albumin solution was determined by UV-260 spectrophotometer.

2 Results and discussions

2.1 Effect of polymer concentration

In the casting solution, polymer concentration is the main factor that affects membrane performances, and the effects of which are shown in Fig. 1.



a no additive

b Dioxide as an additive

Fig. 1 Effect of PAN concentration

1. water flux; 2. egg albumin; 3. BSA; 4. γ-globulin

Fig. 1 shows that the flux obviously decreased with increasing PAN polymer concentration, but it decreased relatively slowly if dioxane was added. When PAN concentration ranged from 8% to 12%, the retention increased rapidly with slight increasing of PAN polymer content. But when the polymer concentration was 14% to 18%, the retention did not change so much with increasing content of PAN polymer.

2.2 Effect of different kinds of additive reagents

Table 1 shows the effects of different kinds of additive reagents on membrane performances.

Table 1 Effects of additive reagents

Additive	f, ml/(cm²·h)	R, %	
		BSA	γ-globulin
EGME	108	78.3	90.5
Butanone	213	79.5	88.9
PEG-400	138	71.4	92.1
PVP	162	76.0	89.2
Dioxane	252	74.1	89.3
LiCl	57	80.2	93.1
H_2O, 3% (wt.)	63	80.2	86.7
None	86	84.6	89.7

Notes: PAN: 12% (wt); additive: 8% (wt.)

It is seen from Table 1 that flux of membrane was affected remarkably by changing additive reagents. When dioxane or butanone was used as additive, the flux is quite large; while with LiCl or H_2O as additive, the flux is small, but the effect of additive reagents on retention is fairly small.

2.3 Effect of the contents of additive reagents

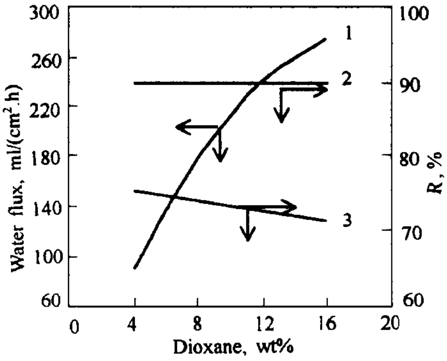


Fig.2 Effect of contents of additive reagents
1. water flux; 2. γ-globulin; 3. BSA

The effect of the content of dioxane on PAN membrane performances is shown in Fig. 2.

It is apparent from Fig. 2 that water flux increased with increasing the contents of additives, and retention did not change too much with increasing contents of dioxane.

2.4 Effect of gelation medium

Table 2 shows if some other solutes were added to pure water which acts a gelation medium, flux of membrane is relatively small, but retention of γ-globulin is quite large; while when pure water was used as gelation medium, the flux is much larger, but retention of γ-globulin is comparatively petty.

Table 2 Effects of gelation medium

Gelation medium	f, ml/(cm^2·h)	R, %	
		γ-globulin	BSA
30% glycerine(wt.)	117	95.50	66.25
3% SOS(wt.)	112	95.56	71.61
3% meek agent(wt.)	108	93.49	74.27
3% NaCl(wt.)	122	94.50	49.53
0.1 mol/L NaOH	128	95.40	62.62
H_2O	252	89.3	74.1

Notes: PAN:12%(wt.); dioxane: 8%(wt.)

2.5 Effect of gelation temperature

The flux and retention irregularly changed with increasing of gelation temperature(Table 3). This may be due to strong hydrophilicity of PAN polymer, so the membrane performances are not very susceptible to water temperature.

Table 3 Effect of gelation temperature(water as gelation medium)

Gelation temperature, ℃	f, ml/(cm^2·h)	R, %	
		γ-globulin	BSA
80	266	90.26	49.45
65	257	90.0	57.18
50	221	92.93	56.91
20	288	91.62	74.03
8	238	91.48	59.81

Notes: PAN:12%(wt.); dioxane: 8%(wt.)

2.6 Effect of evaporation time

It is can made out from Table 4 that the flux and retention are slightly affected by evaporation time. In order to prevent the dilute casting solution from soaking into that bottom of non-woven fabrics, the non-woven fabrics covered with casting solution should be steeped in gelation medium rapidly.

Table 4 Effect of evaporation time

Evaporation time, s	f, ml/(cm^2·h)	R,%	
		γ-globulin	BSA
3—5	238	95.44	75.14
30	198	91.33	59.81
60	196	95.10	70.17
90	234	93.50	68.09

Notes: PAN:12%(wt.); dioxane: 8%(wt.)

3 Conclusions

From the experimental results, the following conclusions are made.

The UF membranes which cut off of macromolecular weight is 150000, retention is 90%—95% and flux reaches 150—200 ml/(cm^2 · h) can be made by selecting appropriate polymer concentration and type and content of additive reagent.

Because PAN is a kind of strong hydrophilic material, the membrane performances are slightly affected by evaporation time and gelation temperature.

Flux of PAN UF membrane increases obviously with increasing of additive reagents, but retention not too changes.

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