

聚偏氟乙烯大孔超滤膜的研究*

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摘要 以国产聚偏氟乙烯(PVDF)为原料,选择不同种类的单一溶剂、混合溶剂和添加剂为铸膜液组成,研究了若干制膜因素对膜性能的影响,采用混合溶剂 DMAC/AC 之比控制 AC 含量在 40%—60%,添加剂含量在 10%—20%,制膜的气氛温度为 25—30℃,铸膜液温度为 50℃左右,可制得截留分子量为 15 万和 24 万,透水速度达 30—70ml/(cm²·h),截留率为 90%以上的大孔超滤膜。

关键词 聚偏氟乙烯,大孔径超滤膜,超滤技术。

聚偏氟乙烯(PVDF)工程塑料具有良好的化学稳定性和热稳定性,耐酸碱,耐生物侵蚀,机械强度高,是良好的制膜材料。笔者等曾以 PVDF 为原料,制成了截留分子量为 6.7 万、透水速度为 30—50ml/(cm²·h)的超滤膜^[1,2]。本文仍以 PVDF 为原料,研究了不同铸膜液组成和不同制膜条件对膜性能的影响。制膜中均采用无纺布为支撑层,为连续机械生产大孔径超滤膜和器件奠定了基础。

1 实验部分

1.1 主要原料、药品、仪器

聚偏氟乙烯(PVDF):上海氟材料研究所生产;二甲基乙酰胺(DMAC),上海化工厂(聚合级); γ -球蛋白,MW=150 000,德国进口;过氧化氢酶,MW=240 000,德国进口;有机玻璃杯型超滤器,不锈钢评价器,本单位研制;紫外分光光度计,日本岛津 UV-260。

1.2 制膜及膜评价方法

制膜采用 L-S 方法,在无纺布上刮膜,蒸馏水中凝胶。将膜在 0.3MPa 压力下预压 2h,用杯型超滤器在 0.1MPa 压力下测定膜的透水速度(f)并按下式计算:

$$f[\text{ml}/(\text{cm}^2 \cdot \text{h})] = \frac{\text{透水量}(\text{ml})}{\text{膜面积}(\text{cm}^2) \times \text{透水时间}(\text{h})}$$

膜截留率($R\%$)是对 0.1%蛋白水溶液进行超滤,用紫外分光光度计测定并按下式计算:

$$R(\%) = \frac{\text{原液光密值} - \text{透过液光密值}}{\text{原液光密值}} \times 100\%$$

2 结果与讨论

2.1 铸膜液组成对膜性能的影响

2.1.1 单一溶剂和混合溶剂的影响

表 1 列出采用不同溶剂对膜性能的影响。可看出,采用混合溶剂 NMP/AC 和 DMF/THF、DMAC/THF、DMAC/AC 分别可得到对过氧化氢酶或 γ -球蛋白截留率大于 90%的超滤膜。

表 1 溶剂对膜性能的影响

溶剂 ¹⁾	f [ml/(cm ² ·h)]	$R(\%)$		
		过氧化氢酶	γ -球蛋白	牛血清蛋白
DMF	70.5	82.80	15.50	44.90
DMF/AC	22.5	90.91	91.00	78.30
DMAC	45.0	26.43	23.24	2.70
DMAC/THF	19.5	93.19	90.08	22.95
DMAC/AC	40.1		93.70	75.58
NMP	63.0	71.55	52.03	56.70
NMP/AC	21.0	91.44	42.20	65.40
DMSO	114.0	9.26	12.75	9.80
DMSO/THF	20.0	91.98	89.28	80.80

1) 混合溶剂比均为 1:1

2.1.2 丙酮(AC)含量对膜性能的影响

采用不同的 DMAC/AC 比例,在相同的条件下制膜,可得到性能不同的超滤膜。结果列于表 2。表 2 结果说明,铸膜液中随丙酮含量的增加,透水量逐渐下降,截留率升高,这是因为丙酮含量的增加,导致易挥发组分的挥发量增加,造成

膜的孔径减小,孔隙率下降。此外随着丙酮含量的增加,聚合物的溶解性逐渐降低,膜液的粘度增大,成膜不易均匀。一般丙酮的比例可控制在 40%—60% 为宜。对制备更大孔径的超滤膜,丙酮用量应低于 30%。

表 2 不同 DMAC/AC 对膜性能的影响

DMAC/AC	f [ml/(cm ² ·h)]	$R(\%)$ γ -球蛋白
100/0	103.19	47.14
90/10	89.81	75.40
80/20	71.66	80.96
70/30	64.97	81.74
60/40	49.94	91.10
50/50	38.22	93.70
40/60	22.20	96.90
30/70	17.50	89.40
20/80	18.00	90.90
10/90	10.00	95.80

2.1.3 添加剂含量对膜性能的影响

固定 PVDF、溶剂用量,改变添加剂用量在相同的条件下制膜。结果列于表 3。结果表明,随着添加剂含量的增加,透水量逐渐升高而截留率变化不大,但是,添加剂含量的增加导致膜液的粘度增大,孔径增大。添加剂含量控制在 10%—20% 为宜。

表 3 添加剂含量对膜性能的影响¹⁾

添加剂 含量(%)	f [ml/(cm ² ·h)]	$R(\%)$	
		γ -球蛋白	牛血清蛋白
0	4.50	93.84	84.41
5	16.02	95.17	80.98
10	36.31	92.76	80.27
15	50.12	92.94	79.01
20	63.06	90.95	84.65
25	76.43	86.68	83.54

1) 采用混合溶剂 DMAC/AC, 比例为 1 : 1

2.2 制膜条件对膜性能的影响

2.2.1 气氛温度的影响

制膜的气氛温度直接影响溶剂的蒸发速度和挥发量,由于采用的溶剂体系是 DMAC/AC, 含易挥发的丙酮,控制适当的气氛温度可得到性能较好的膜(表 4)。结果表明,随着气氛温度的升高,透水量逐渐增加,截留率下降。对制备截留分子量为 15 万以上的大孔膜,气氛温度控制在 25—30℃ 为宜。

表 4 气氛温度对膜性能的影响

气氛温度(℃)	f [ml/(cm ² ·h)]	$R(\%)$ γ -球蛋白
25	51.59	94.55
30	42.99	89.59
35	59.24	85.76
40	76.43	68.62
45	118.47	44.61

2.2.2 铸膜液温度的影响

铸膜液温度与制膜的气氛温度对膜性能有相类似的影响,结果列于表 5。从表 5 中可以看出,透水量随铸膜液温度升高有所增加,截留率稍有下降。由于采用的溶剂体系是 DMA/AC,铸膜液在较低的温度下容易凝结,不利于制膜,故铸膜液温度选择在 30—40℃ 为宜。

表 5 铸膜液温度对膜性能的影响

铸膜液温度 (℃)	f [ml/(cm ² ·h)]	$R(\%)$ γ -球蛋白
25	49.68	94.55
30	45.86	90.34
35	48.22	90.24
40	46.00	90.60
45	68.79	89.49
58	59.24	81.58

3 结论

(1) 用 NMP/AC、DMSO/THF、DMF/THF、DMAC/AC、DMAC/THF 做混合溶剂,混合比为 1 : 1,PEG-600 做添加剂分别可制得截留分子量为 24 万和 15 万的大孔径超滤膜,其透水量可达 30—70ml/(cm²·h),截留率在 90% 以上。

(2) 经过对部分影响膜性能参数的考察,适宜的制膜条件为:混合溶剂 DMAC/AC 之比控制 AC 在 40%—60%,添加剂含量在 10%—20%,制膜的气氛温度为 25—30℃,铸膜液温度为 30—40℃ 左右。

(3) 适当改变制膜条件,可得到更大孔径超滤膜。

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Abstracts

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of 146.8—351.4 ml/(L · d), a hydrogen content of above 60% in the gas, and a COD removal of 62.3%—78.2%. When the concentrations of wastewater ranged from 1260 to 5040 mgCOD/L, the IPSB could maintain stable hydrogen production for 93 hours, with an average gas production rate of 120.7—140.0 ml/(L · d), a hydrogen content of above 75% in the gas, and a COD removal of 41%—61.3%.

Key words: hydrogen production, photosynthetic bacteria, soybean wastewater.

Pilot Study on the Capacity of Coarse Sediments to Purify Wastewater. Zhang Mingquan et al. (Research Division of Water Resource & the Environ., Lanzhou Univ., Lanzhou 210024); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 45—47

The capacity of coarse sediments to purify waste water was determined in laboratory by both continuous and intermittent infiltration tests. It was found that more than 50 percent of bacteria, synthetic detergent and total chromium can be removed from the municipal waste water after its infiltrating through a 1.5m thick gravel soil. The removal of Mn(II) may be up to 76.2% in the intermittent infiltration test, but only 24.7% in the continuous infiltration test. There is an aeration condition in coarse sediments when waste water is infiltrating through it, that is advantageous for nitrification.

Key words: purifying of waste water, coarse sediments, continuous infiltration, intermittent infiltration.

A New Method for Assessing Environment Quality: Twice-slope classification. Ding Jinbao (Zhuzhou Research Institute of Environmental Science, Zhuzhou 412000); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 48—51

Based on the principles of the white function construction in the grey system theory and the grey classification, and the weight thought from fuzzy comprehensive assessment, a new method for assessing environment quality, i. e., the twice-slope classification, was suggested. A successful example of using the new method to assess air environment quality was given in this paper. A function based on the twice-slope method was established, and the value range of pollutants in the function was expanded with a full use of information. Compared with other methods, the new method made the use of information much fuller and gave the conclusion more reasonable and credible. It could also overcome the defects of both fuzzy comprehensive assessment

and grey classification and have more practical use in environment quality assessment.

Key words: twice-slope classification, fuzzy comprehensive assessment, grey classification, environment quality assessment.

Study on Large Pore Size Ultrafiltration Membrane of Polyvinylidene fluoride (PVDF). Wang Jingrong (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 52—53

A study on the preparation of large pore size ultrafiltration membrane of PVDF was reported in this paper. The effect of main parameters, such as solvents, additives and temperature, on the membrane properties was discussed. The membranes with a weight cut-off of 240000 and 150000 were prepared. The flux of 30—70 ml/(cm² · h) and the rejection rate above 90% can be achieved.

Key words: polyvinylidene fluoride, large pore size, ultrafiltration membrane.

Meteorological Characteristics of the Surface Dust Storm Bearing Yellow Sands Occurred on 8 April 1994 in the Hexi (Gansu) corridor and the Determination of Atmospheric Aerosol. Quan Hao et al. (Sino-Japanese Friendship Center of Environmental Protection, Beijing 100029); *Chin. J. Environ. Sci.*, **16**(1), 1995, pp. 54—57

The process of forming the weather characterized by the surface dust storm bearing yellow sands occurred on 7—8 April 1994 in the Hexi Corridor of Gansu Province, and the results from both the meteorological observation and the determination of atmospheric total suspended particulates (TSP) were reported, along with describing the meteorology and the characteristics of a atmospheric aerosol while a weather of surface dust storm bearing yellow sands being occurred in northwest China. This surface dust storm was centred on the area of Jiayuguan and Jiuquan, where it was found to have a TSP concentration of up to 38.00mg/m³, an indoor TSP level of 8.63 mg/m³, a natural dust deposition intensity of 296.22 t/(km² · month), a cloud of yellow sands raising up to an altitude of about 2000 to 3000 m, and an increase in the levels of main constituting elements such as Si, Al, Ca, Fe, Mg, Mn and Ti. The atmospheric contents of yellow sands were being progressively decreased along the line from Jiayuguan, Jiuquan, Jincang, Lanzhou to Beijing as the distance increased. Then, at 2 AM on 11 April, the Haboob phenomenon occurred in most parts of the Gansu Province. It was suggested that in a future study on the dust storm bearing yellow