

高渗透聚砒中空纤维超滤膜制备*

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摘要 介绍了采用独创制膜液三元体系添加剂(水-盐-表面活性剂), 以及相应发展的干喷-湿纺制膜工艺条件, 研制出具有高透水性能, 无大孔缺陷, 孔分布狭窄, 截留性能优异的聚砒中空纤维超滤膜。膜结构为双排指状孔结构, 膜内外表面具有相近的孔分布皮层, 可用于内压或外压超滤操作。已研制出切割分子量为1万、3万、5万和10万4种超滤膜。在环境保护领域具有广泛的应用前景。

关键词 聚砒, 中空纤维, 超滤膜, 制备。

1 原理

超滤膜的制备是超滤膜技术的核心。所研制的高渗透性聚砒中空纤维超滤膜系采用干喷-湿纺技术。其原理基于高分子溶液在沉淀剂的作用下发生相转化过程, 最终形成非对称中空纤维超滤膜。膜的分离性能取决于膜结构, 膜结构的形成主要取决于2方面的效应: ① 制膜溶液和沉淀剂体系的热力学平衡性质; ② 在膜形成过程中溶剂逸出和沉淀剂浸入制膜液界面的相对交换速率对成膜动力学影响^[1, 2]。

非对称膜的形成过程中产生2类不同相转化: ① 在聚合物浓度较高区域, 发生凝胶或结晶过程; ② 在聚合物浓度较低区域, 发生液-液相分离过程, 多用于制造多孔非对称膜。制膜过程中, 决定究竟发生哪种类型转化过程, 主要因素取决于发生相转化瞬间该区域聚合物的实际浓度。该浓度不仅与初始制膜液配制的高聚物浓度有关, 也与成膜过程中, 沉淀剂的浸入和溶剂逸出制膜液界面的速率有关。另一方面, 该浓度也与在同一聚合物初始浓度时, 制膜液里组成“偏离”该体系热力学平衡相转化曲线距离相关。若越靠近相转化平衡曲线, 实现相转化时所需浸入沉淀剂量越少, 实现相转化越快, 实现相转化时聚合物浓度较低, 易于产生皮层薄, 高孔容非对称多孔膜。

2 技术关键

(1) 添加剂的选择 溶液的选择应使其溶解参数与聚合的溶解参数相近, 使制膜液可形成均匀的溶液。二甲基乙酰胺, N-甲基吡咯烷酮等溶剂均是聚砒的良溶剂, 可形成均匀的溶液。聚合物与良溶剂之间强的相互作用使相转化延迟, 往往造成非对称皮层增厚, 渗透性下降。通常采用加入适当添加剂, 改变制膜体系属性, 从而调整所形成膜的结构。实际上, 有实用价值的膜均系加入合适的添加剂而制成的。因而制膜中关键技术问题之一是合适添加剂的选择, 即制膜液的配方组成。

国内外诸多文献和专利皆以发明不同制膜液添加剂和发展相应工艺来制造中空纤维超滤膜。其中, Cabasso 等人采用水溶性高分子(如 PEG, PVP)为添加剂以增加膜粘度, 改善体系亲水性, 来制备聚砒中空纤维超滤膜^[3]。这一方法 80 年代曾被广泛采用, 我国一些单位也采用类似体系生产聚砒中空纤维超滤膜, 其膜通常水渗透较低。美国 Amicon 公司采用聚砒-溶剂-盐三元体系来制造单层结构聚砒中空纤维超滤膜^[4]。采用加盐的还有日本电气工业株式会

* 获 1995 年国家发明奖三等奖

收稿日期: 1996-04-20

社^[5]. 日本旭化成工业株式会社采用加入三乙二醇等各种多元醇为添加剂来制造双层皮层结构聚砜中空纤维超滤膜^[6]. 笔者等相继开展了下述几方面研究: ① 系统测定了聚砜制膜体系在各溶剂体系的相分离数据, ② 从所测数据计算了聚砜制膜体系其化学位与组分函数关系, 并讨论了 Flory-Huggins 相互分子作用参数对成膜体系影响, ③ 发展出以测定体系相分离数据为依据, 选择制膜体系实用方法. 然后采用独创的水-盐-表面活性剂三元体系作为制膜液的添加剂, 通过改变制膜液中聚砜的含量, 调整添加剂用量, 以及相应的纺丝制膜工艺可以制得具有不同孔分布的中空纤维超滤膜. 它们具有如下优点: ① 由于实现相转化快, 制备出皮层薄、高孔容的超滤膜, 它具有高的水渗透性, ② 由于可制得相容性好的均匀制膜液, 使所研制的膜具有孔分布狭窄并消除了针孔和缺陷, ③ 发展出相应的制膜工艺, 制造出内外皮层孔分布相近的中空纤维超滤膜, 用于内、外压超滤操作均可(见图 1), ④ 水-盐-表面活性剂制膜液的添加剂是最易制备, 最价廉的增粘制膜添加剂.

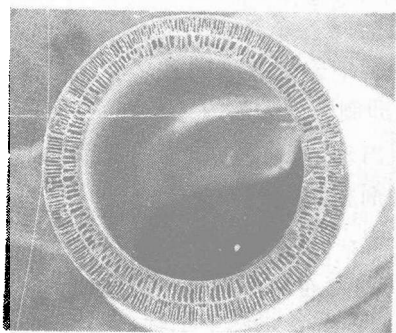


图 1 中空纤维超滤膜横断面照片

(2) 制膜浆液的配制、所研制的超滤膜所用聚砜(Psf)可采用特性粘度为 $\eta_{0.5}$ —0.7 的产品, 溶剂可采用二甲基乙酰胺(DMAC), 二甲基甲酰胺(DMF), 二甲基亚砜(DMSO)或者 N-甲基吡咯烷酮(NMP), 非溶剂为去离子水, 盐可为硝酸锂, 氯化锂或高氯酸镁, 表面活性剂可采用 TritonX-100, 吐温 T-80 或者其它乳化

剂.

(3) 制膜工艺 高渗透性聚砜中空纤维超滤膜制备工艺除了制膜浆液配制外, 另一制备要点就是采用适当的制膜工艺条件. 本发明中滤膜就是采用干喷-湿纺法纺丝技术而制成的. 其工艺流程如图 2 所示. 在图 2 中: 喷头 4 具有同心圆环式结构, 料罐 1 中制膜液经过滤器 2 过滤后, 由泵 3 打入喷头 4, 从圆环间隙中喷出, 而内管注入内凝介质, 使初生态纤维形成中空, 然后注入外凝槽 5 的凝固浴中凝固成膜. 根据制膜液的不同配比, 适当地调节纺丝操作条件: 喷头结构与尺寸, 喷头温度, 内外凝介质和温度, 喷头至凝固浴间的距离, 泵喂料, 内凝供给和拉伸速度等, 可在一定范围内改变膜的孔径大小和结构形态, 从而获得具有不同分子切割性能的中空纤维超滤膜.

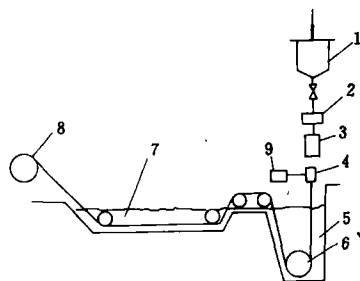


图 2 纺丝工艺流程图

1. 料罐 2. 过滤器 3. 泵 4. 喷头
5. 外凝槽 6. 8. 滚筒 9. 内凝剂罐

为了使所研制的超滤膜可以在干燥状态下保存, 还必须对膜进行保护处理. 本发明中采用的保护处理是利用甘油和表面活性剂的水溶液一次浸润纤维膜的方法. 经这样处理后, 制得的中空纤维超滤膜在干燥保存中完全保持其高渗透性能, 并在组装中空纤维过滤器时保证中空纤维丝与环氧树脂粘接材料良好粘接性能.

3 BS 系列中空纤维超滤膜截留率与纯水渗透性

按照上述技术方法, 制造出聚砜中空纤维超滤膜命名为 BS 系列中空纤维超滤膜, 其截留率与纯水渗透性与美国 Amicon 的 P 系列超滤

膜相近,其测定结果如表 1 和表 2 所示.

所研制的高渗透性聚砜中空纤维超滤膜,它具有高透水性、无大孔缺陷、孔径分布狭窄、截留性能优异、现已实现规模生产,并在全国

约 60 家厂家、单位实际生产应用^[7-9],已和两家合作办厂批量生产中空纤维超滤膜组件. 它将为环境保护等领域提供了有效分离手段,可取得显著的经济效益和社会效益.

表 1 BS 系列膜与 Amicon P 系列膜典型的溶质截留特性对比¹⁾

溶质	分子量	BS1	BS3	BS5	BS10	P10	P20	P100
枯草杆菌肽	1400					25		
细胞色素 C	12400	95				85	45	
核糖核酸酶	13700		61	16	0			
糜蛋白酶	25000		85	67	0	95	75	20
卵蛋白酶	45000	98	98					
牛血清蛋白	67000	98	98	98	77	98	98	30
γ -球蛋白	156000				96	98	98	98

1) P 系列数据取自 Amicon Operating Instruction Publication 1-25813(1985)

表 2 BS 系列与 Amicon P 系列膜纯水渗透性能对比¹⁾

膜型号	切割分子量	组件型号	膜面积 /m ²	纯水渗透率 /L · (m ² · h) ⁻¹
BS1	10000	ZBS1	2.2	60—80
BS3	30000	ZBS3	2.2	160—210
BS5	50000	ZBS5	2.2	250—300
BS10	100000	ZBS10	2.2	560—600
P10	10000	H26P10-43	2.4	56—74
P30	30000	H26P30-43	2.4	194—217
P100	100000	H26P100-43	2.4	560—740

1) 压力 0.1 MPa, 温度 25℃, P 系列数据取自 Amicon Instructions Publication 1-258139(1985)

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Assessment of Critical Loads for Acid Deposition in Liuzhou Area. Xie Shaodong, Hao Jiming et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 1—4

In order to provide a quantitative evidence for establishing the target load, acidification processes of soils in Liuzhou area under different acid depositions levels were simulated using a revised MAGIC model on the basis of data about the physic-chemical properties of red earth, the surface water, and the background and present situation of precipitation, which were obtained by field investigations and experiments. The results showed that the soils in Liuzhou area have been already acidified and the acidification trend of the soils will become more serious with time. The upper soil layer is more sensitive to acid deposition while the bottom layer and surface water have larger buffer capacity. Critical loads of potential acidity for different red earth in this area are determined as $0.6—3.8 \text{ keq} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$, and that of sulfur deposition $0.7—3.2 \text{ g} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$. In order to protect 95% of soil area from acidic deposition, sulfur deposition should be cut down by 70% of the present level at least.

Key words: critical load, acid deposition, red earth.

Preparation of Polysulfone Hollow Fiber Ultrafiltration Membrane with High Permeability. Jiang Chengzhang et al. (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 5—7

A kind of originally created unique ternary additive of spinning solution and corresponding dry-jet wet-spinning membrane fabricating conditions were invented. The hollow fiber ultrafiltration membrane developed has high permeability, no defect, narrow differential pore size distribution and excellent retentivity. The membrane have double-row finger-like pore support layer structure and have skins both on the inner surface and on the outer surface, so the hollow fiber membrane can be operated under inside pressure or outside pressure. A series of hollow fiber ultrafiltration membranes with molecular weight cut-off of 10000; 30000; 50000 and 100000 respectively.

Key words: polysulfone, hollow fiber, ultrafiltration membrane, preparation.

Study on Biodegradability of Benzene Homolog Compounds by Mixed Bacteria from petrochemical Wastewater Treatment Plant. Wang Jusi, Zhao Lihui et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Envi-*

ron. Sci., 17(5), 1996, pp. 8—12

This paper reported the biodegradability of benzene, toluene, ethylbenzene, o-, m- and p-xylene by mixed bacteria, which were enriched from activated sludge of petrochemical wastewater treatment plant, under aerobic condition. When the concentration of the tested compounds were 50—140 mg/L, the six tested compounds can be biodegrade. Seventeen bacteria strains were sifted from the mixed bacteria, they can biodegrade toluene, ethylbenzene, trimethylbenzene, o-, m- and p-xylene. The ratio of o- and m-xylene were 100% by sifting bacteria. The results indicated that the biodegradability of the compounds strongly depends on its chemical component and structure. At the test system, the biodegradable order of the six tested compounds was: toluene, p-xylene, m-xylene, ethylbenzene, benzene and o-xylene. The intermediates of toluene degraded were detected and was pathway for toluene degraded at aerobic condition.

Key words: biodegradability, benzene, toluene, ethylbenzene, activaty sludge, wastewater treatment.

Development of Simple and Dry Gas Desulfurization Process. Dixin Shen and Guangbin Liu. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 13—15

A simple and economical control technology of sulfur dioxide from the coal-fired boilers using activation calcium hydroxide injection has been developed. The activation calcium hydroxide as a sorbent was prepared by hydrolytic method. The specific surface area of sorbent was $41 \text{ m}^2 \cdot \text{g}^{-1}$, while particles size distribution region 0—10 μm accounted for 24.0%, 10—20 μm for 20.1%, 20—40 μm for 29.0%, 40—60 μm for 16.6% and 60—90 μm for 10.3%. Factors influencing the reaction of sorbent with SO_2 were studied by using a sand-bed reactor in a bench-scale. Preliminary pilot scale test results showed that flow rate gas was $1000 \text{ m}^3 \cdot \text{h}^{-1}$, the concentration of SO_2 was $1430 \text{ mg} \cdot \text{m}^{-3}$ — $4290 \text{ mg} \cdot \text{m}^{-3}$, Ca/S was 1.5—1.8 and SO_2 removal was 60%—70%. The purpose was to develop a FGD technology of low capital and low operating costs to control the SO_2 emission in China.

Key words: sorbents, flue gas desulfurization, pilot scale test.

Experimental Study on Flue Gas Desulfurization with Duct Slurry Injection. Lu Yongqi and Hao Jiming (Dept. of Eviron. Eng., Tsinghua Univ., Beijing 100084), Hou Dongqi and Yu Ronghua (Harbin Power