

超滤法处理乳化油废水的研究

王静荣 吴光夏 王正军 刘捷

(中国科学院生态环境研究中心, 北京 100085)

摘要 采用 CMPS、PS、PS/CMPS 共混、PAN、PS 和 PS/PDC 共混材料的中空纤维超滤膜, 对乳化油废水进行了超滤实验和比较, 探讨了料液流速, 操作温度, 操作压力, 运行时间对膜性能的影响, 研究了清洗方法对膜性能的恢复效果。试验表明, 采用 CMPS、PS/CMPS 中空纤维膜处理乳化油废水效果较好, 透过液含油量符合生产回用标准 (300mg/L), 适宜的操作温度为 50℃, 进口压力为 0.12MPa, 出口压力为 0.10MPa, 采用 0.1mol/L HCl 作为清洗剂, 膜性能恢复效果最佳。

关键词 CMPS, 乳化油废水, 超滤, 中空纤维膜, 膜清洗。

乳化油废水是一种常见的工业废水, 水中含有非离子表面活性剂、NaOH、Na₂CO₃、Na₂B₄O₇ 和 NaN₂O₂, 不能直接排放。目前, 乳化油废水的处理方法很多, 常见的有机械分离、加凝聚剂、重力分离、粗粒化法、过滤法和空气上浮法等。但是, 机械分离法效果不理想, 若加入凝聚剂, 会产生含油污泥, 此外, 该方法处理周期长, 占地面积大。而重力分离法、粗粒化法、过滤法和空气上浮法等也收不到满意的效果^[1,2]。膜分离技术近几年发展很快, 其优点是物质在分离过程中无相变, 耗能少, 设备简单, 操作容易, 分离效果好。

本研究对北京吉普车有限公司脱脂工段乳化油废水进行超滤实验, 用不同膜材料处理乳化油水, 对一些影响因素和膜清洗条件进行了探讨。

1 实验部分

1.1 材料及仪器

氯甲基化聚砜和聚砜共混中空纤维膜 (chloromethylated polysulfone and polysulfone, CMPS/PS), 自制;

聚丙烯腈中空纤维膜 (polyacrylonitrile, PAN), 自制;

聚砜中空纤维膜 (polysulfone, PS), 自制;

聚砜和圈型聚砜共混中空纤维膜 (polysul-

fone and condensation-polymerized product of phenolphthalein and dichlorodiphenylsulfone, PS/PDC), 自制;

氯甲基化聚砜中空纤维膜 (chloromethylated polysulfone, CMPS), 自制;

NaOH、HCl 和 KMnO₄, 分析纯, 北京化工厂产;

牛血清白蛋白, 北京百泰生化公司;

紫外分光光度计, 日本岛津 UV-260;

中空纤维膜评价装置, 自制。

1.2 实验方法

采用外壳长 60cm, 内径 2.5cm 耐温较好的材料制成中空纤维组件, 运行中自动控温, 蠕动泵循环料液, 实验装置见图 1。

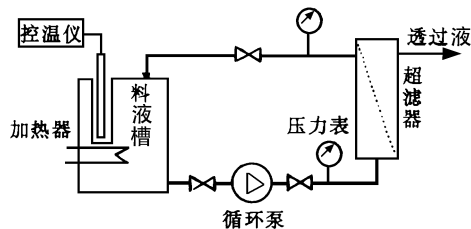


图 1 超滤流程示意图

2 结果和讨论

2.1 膜材料的选择

选择 5 种膜材质的中空纤维膜组件,对乳化油水进行超滤实验,结果列于表 1.

表 1 不同中空纤维膜性能比较

膜材料	纯水通量	乳化油水通量 ¹⁾	含油量
	/ml·cm ⁻² ·h ⁻¹	/ml·cm ⁻² ·h ⁻¹	/mg·L ⁻¹
PS/PDC	9.6	1.5—0.3	12.6
CMPS	41.3	3.3—2.5	18.0
PAN	18.6	3.7—0.01	11.7
PS	16.5	2.4—0.4	12.0
PS/CMPS	12.4	1.1—0.6	60.0

1) 运行 8h 起始和终止的数据

由表 1 数据可知,不同膜材料的透水通量衰减速度为 PAN> PS> PS/PDC> PS/CMPS> CMPS,其中 CMPS 和 PS/CMPS 2 种膜的透水通量衰减较小,说明膜被污染程度较轻,适用于乳化油水的处理.

2.2 料液温度对透水通量*f* 的影响

试验中固定进口压力为 0.12MPa,出口压力为 0.10MPa,改变料液温度,考察温度对透水速度的影响.实验表明,随着料液温度的升高,透水速度增加,其结果见图 2.一般在 50 左右时用超滤法处理乳化油水较有利.

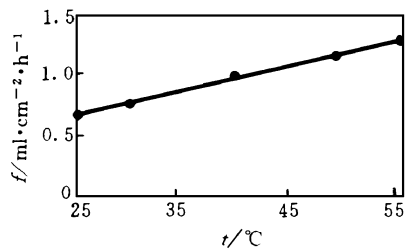


图 2 温度与透水通量*f* 的关系

2.3 压力对透水通量的影响

试验中操作压力高低直接影响膜的透过性能.由图 3 可以看出,在料液温度为 50 时,操作压力对膜的透水速度影响十分显著.适当增加操作压力,可大幅度提高膜的透水量.一般固定进出口压差为 0.03MPa,进口压力控制在 0.10—0.13MPa 之间即可.操作压力过高时,动力消耗较大,并影响膜的使用寿命.

2.4 压差对透水通量的影响

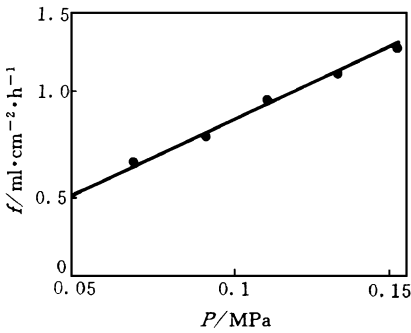


图 3 压力与透水通量的关系

固定料液温度为 50 ,改变组件进出口压差,比较透水通量的变化(见图 4).提高料液进出口压差有利于提高料液流速,有利于减小浓差极化和延缓透水速度的衰减.但它的能耗大,对于特定的超滤组件,采用一定的压差即可.

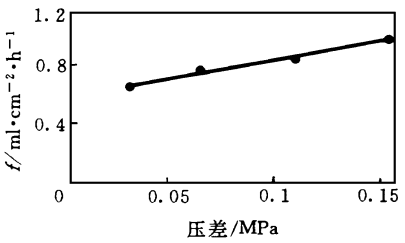


图 4 压差与透水通量的关系

2.5 浓缩倍数对透水速度的影响

料液浓缩倍数与透水通量的关系如图 5 所示.在运行中料液保持 50 ,进出口压力分别为 0.12MPa、0.10MPa.料液浓缩倍数增大,原液浓度也随之增大,即溶质量增加,随着浓缩倍数的增加,透水速度逐渐下降,含油量变化不大,这是因为料液在中空纤维内孔的浓差极化愈加重,造成透水通量下降.

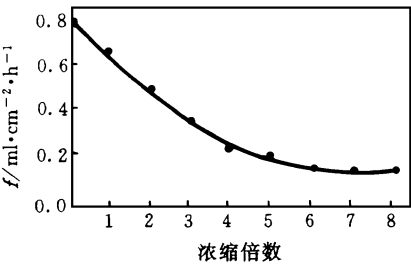


图 5 浓缩倍数与透水通量关系

2.6 运行时间与透水通量的关系

试验操作条件: 料液温度 50℃, 组件入口、出口压力 0.12MPa、0.10MPa. 每天运行 8h 后, 用 0.1mol/L HCl 清洗 20min, 再用纯水洗 10min, 如此往复.

运行时间与透水通量的关系如图 6 所示, 每天膜经清洗后, 透水通量基本得到恢复.

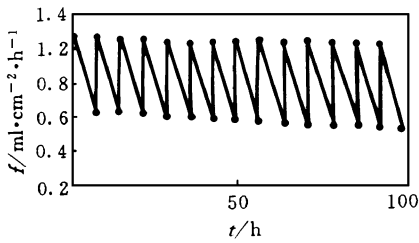


图 6 运行时间与透水通量关系

2.7 膜清洗实验

采用 0.1mol/L HCl、2%NaOH、2%KMnO₄和透过液 4 种清洗剂, 清洗前用乳化油水超滤运行 8h. 每种清洗剂均洗 20min, 再用纯水洗 10min.

表 2 不同清洗剂效果比较($f/\text{ml} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$)

清洗剂	清洗前 f	清洗后 f
0.1mol/L HCl	0.97—0.51	0.97
2%NaOH	0.97—0.51	0.53
2%KMnO ₄	0.97—0.51	0.76
透过液	0.97—0.51	0.51

从表 2 数据可知, 清洗效果为: 0.1mol/L HCl> 2% KMnO₄> 2% NaOH> 透过液. HCl 清洗效果最好, 透水量可得到较好恢复.

3 结 论

(1) 经过对膜材料的选择, 采用 CMPS、PS/CMPS 中空纤维膜, 膜污染轻, 处理乳化油水效果较好.

(2) 用 CMPS、PS/CMPS 中空纤维膜透水通量分别为 2.5—3.3 和 0.6—1.1ml·cm⁻²·h⁻¹. 透液中的含油量分别为 18 和 60mg/L, 符合生产回用标准(回用标准 300mg/L). 由于 PS 原料价格便宜且易得, 采用 PS/CMPS 共混比为 1:1 的中空纤维膜, 可降低膜材料的成本.

(3) 适宜的操作条件是温度 50℃, 进口压力 0.12MPa、出口压力 0.10MPa.

(4) 通过用不同清洗剂进行实验, 采用 0.1mol/L HCl 作清洗剂清洗 20min, 透水通量可完全恢复.

(5) 采用超滤法处理乳化油水, 可除去溶液中的大部分油. 透过液中含有少量油和表面活性剂、盐及小分子物质. 再补充适量的表面活性剂和盐即可返回脱脂槽回用.

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1 刘廷惠, 吴光夏等. 超滤法处理喷漆工段含油废水. 环境化学, 1990, 9(2): 41
2 刘廷惠等. 超滤法处理原油污水的研究. 环境科学学报, 1986, 6(4): 455

NO formation are discussed. The defects of De Soete fuel NO model are shown out through numerical calculation and theoretical analysis. Furthermore, after introducing the concept of "native oxygen concentration", the fuel NO formation rate is obtained by multi-component regression method.

Key words fuel NO, global reaction, native oxygen concentration, reaction pathway, multi-component regression.

Study on Treatment of Emulsified Oil Wastewater by Ultrafiltration Method. Wang Jingrong, Wu Guangxia et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 53—55

In this paper, treatment of emulsified oil wastewater using chloromethylated polysulfone (CMPS), polysulfone and chloromethylated polysulfone (PS/CMPS), polyacrylonitril (PAN), polysulfone and condensation-polymerized product of phenolphthalein and dichlorodiphenylsulfone (PS/PDC), polysulfone (PS) hollow fiber ultrafiltration membranes was studied. The influence of different factors, such as feed temperature, operating pressure and operating time on ultrafiltration performance, as well as recovery of the membrane property by cleaning procedure were investigated. The effect CMPS, PS/CMPS hollow fiber membranes treating emulsified oil wastewater is better. The oil content in the permeating liquid met the standard of production recycling water. The proper operating conditions were: temperature 50 °C, inlet pressure 0.12 MPa, exit pressure 0.10 MPa and cleaning agent 0.1 mol/L HCl.

Key words: emulsified oil wastewater, ultrafiltration, membrane, hollow fiber.

Study on Treatment of Textile Printing and Dying Wastewater with Facultative Aerobic Process. Guo Maoxin, Yu Ganshen et al. (Zhejiang Industrial Environmental Protection Design Institute, Hangzhou 310005): *Chin. J. En-*

viron. Sci., **18**(4), 1997, pp. 56—58

The trial's conclusion showed that the process has the advantage of lower electricity consumption, bearing high pH value, degrading some part of organic material and increasing the ability of biochemistry treatment. The result of pilot project showed that the pH value achieved 7.6—10.1 and COD concentration reached 894.0 mg/L in the effluent when the pH value was 8.8—12.5 and COD concentration was 1266.9 mg/L in influent. The removal rate of COD was 29.4%. The effluent quality was up to the GB8978-88 National Two-Grade Effluent Standard after the continued aerobic treatment.

Key words: facultative aerobic, textile printing and dying wastewater, treatment.

The Primary Study on Treatment of Amino-Acid from Waste Water Using Emulsified Liquid Membrane. Pan Luting, Zhu Yiren (Dept. of Chemistry, Fuyang Normal College, Fuyang 236032), Den Chuan Yun (College of Chemical Engineering, Hefei University of Technology, Hefei 230009): *Chin. J. Environ. Sci.*, **18**(4), 1997, pp. 59—61

In this article, emulsified liquid membrane separating was applied for purifying the waste water from production of amino-acid. Influences of separation efficiency such as kinds and concentration of surfactant and carrier, the internal reagent NaOH concentration, the pH of external phase were studied. The results indicated that the separation efficiency is over 60% when the liquid membrane of LMA-1 (3 g/100 ml kerosene oil), TOA (2 ml/100 ml kerosene oil) and 10% NaOH was used. The separation efficiency do not change as the oil phase was reused for many times.

Key words: emulsified liquid membrane, amino-acid, waste water treatment.

Study on Conversion of Two Monitoring Concentration of Atmospheric SO₂. Zhang Deqiang, Yu Mengde, Kong Guohui et al. (South China Institute of Botany, Chinese Academy of