摘 要

水环境中硝酸盐氮污染来源广，分布多，不仅造成河流水质退化，还会对人类健康造成严重威胁，目前已成为水污染关注的重点。纳滤膜分离技术因应用方便、不易造成二次污染，在硝酸盐处理中具有很好的应用前景，但目前市面上纳滤膜对于 NO_3^-类一价离子截留性能偏低。为满足市场需求与工业发展，研发制备高通量、高截留纳滤膜，应用于硝酸盐处理中，是当前的研究热点之一。本研究选用聚醚砜（PES）超滤膜为基膜，以间苯二胺（MPD）、单宁酸（TA）、2,4-二氨基苯磺酸（MPDASA）、纳米二氧化硅颗粒（SiO_2）等为主要水相单体材料，均苯三甲酰氯（TMC）、对苯二甲酰氯（TPC）为有机相单体材料，通过界面聚合法制备不同聚酰胺复合纳滤膜，以期能够应用于硝酸盐处理中。

分别以 MPD 为水相，TMC、TPC 为有机相，制备 MPD-TMC 复合纳滤膜、MPD-TMC/TPC 复合纳滤膜；以 MPD、TA、MPDASA 为水相，TMC 为有机相，制备 TA/MPD-TMC 复合纳滤膜、磺化 TA/MPD-TMC 复合纳滤膜；以纳米二氧化硅颗粒（SiO_2）、TA、MPD 为水相，TMC 为有机相，制备 TA/SiO_2-TMC 复合膜、MPD/TA/SiO_2-TMC 复合膜。采用 ATR-FTIR、SEM、接触角测量仪、固体 Zeta 电位仪等仪器设备，对复合纳滤膜结构表征并与基膜对比，探究复合膜的结构、形貌及化学组分等性质与膜性能的关系；通过实验室错流过滤装置对制膜参数、最优膜性能进行探究。研究结果如下：

（1）MPD-TMC 复合膜在 MPD 浓度 1.5wt%，TMC 浓度 0.2wt%，热处理时间 10 min 时性能最佳，在 0.9 MPa 操作压力下，处理 1 $g\cdot L^{-1}$ 的 $NaNO_3$ 溶液，膜通量为 3.43 $L\cdot m^{-2}\cdot h^{-1}$，截留率为 81.26%。MPD-TMC/TPC 复合膜在酰氯浓度 0.2wt%，TMC/TPC 比例为 4:1 时性能最佳，在 0.9 MPa 操作压力下，处理 1 $g\cdot L^{-1}$ 的 $NaNO_3$ 溶液，截留率达到 90.75%，但膜通量较低，为 2.73 $L\cdot m^{-2}\cdot h^{-1}$。MPD-TMC 复合膜截留分子量约 532 Da；对不同无机盐截留率分别为 Na_2SO_4（92.77%）>$MgSO_4$（88.36%）>NaCl（88.34%）>$MgCl_2$（83.02%），BSA 截留率高达 100%，葡萄糖截留率为 94.21%。

（2）TA/MPD-TMC 复合膜在 TA 浓度 0.2wt%，MPD 浓度 1.5wt%时性能最佳，在 0.9 MPa 操作压力下，处理 1 $g\cdot L^{-1}$ 的 $NaNO_3$ 溶液，膜通量为 6.23 $L\cdot m^{-2}\cdot h^{-1}$，截留

率为 72.48%。磺化 TA/MPD-TMC 复合膜在 MPD 浓度 1.5%，TA 浓度 0.2wt%，MPDASA 浓度 0.1wt%时性能最佳，在 0.9 MPa 操作压力下，处理 1 $g·L^{-1}$ 的 $NaNO_3$ 溶液，膜通量为 7.8 $L·m^{-2}·h^{-1}$，截留率为 84.22%。磺化 TA/MPD-TMC 复合膜截留分子量约 766 Da；对不同无机盐截留效果分别为 Na_2SO_4（91.06%）>$MgSO_4$（88.29%）>NaCl（86.7%）>$MgCl_2$（86.52%），BSA 截留率为 100%，葡萄糖截留率为 88.92%。

（3）TA/SiO_2-TMC 复合膜在 TA 浓度 0.2wt%，SiO_2 浓度 0.04wt%时性能最佳，在 0.9MPa 操作压力下，处理 1 $g·L^{-1}$ 的 $NaNO_3$ 溶液，膜通量为 21.1 $L·m^{-2}·h^{-1}$，截留率为 70.54%。MPD/TA/SiO_2-TMC 复合膜在 MPD 浓度 1.0wt%，TA 浓度 0.2wt%，SiO_2 浓度 0.04wt%时性能最佳，在 0.9 MPa 操作压力下，处理 1 $g·L^{-1}$ 的 $NaNO_3$ 溶液，膜通量为 7.02 $L·m^{-2}·h^{-1}$，截留率为 90.24%。MPD/TA/SiO_2-TMC 复合膜截留分子量约 688 Da，对于不同无机盐、有机物均具有较好的截留效果，无机盐截留效果分别为 Na_2SO_4（93.04%）>$MgSO_4$（92.75%）>$MgCl_2$（90.63%）>NaCl（90.59%）；BSA 截留率为 100%，葡萄糖截留率为 90.82%。

本研究制备的复合纳滤膜对于硝酸盐有较高的截留率和较好的渗透性能，且制备方法简单、容易操作，可为制备不同纳滤膜应用于硝酸盐处理中提供思路。

关键词：纳滤膜；硝酸盐；间苯二胺；单宁酸；纳米二氧化硅颗粒

ABSTRACT

Nitrate nitrogen pollution in water environment is widely distributed, which not only causes river water quality degradation, but also poses a serious threat to human health. Therefore, it has become the focus of water pollution. Nanofiltration membrane separation technology has a good application prospect in nitrate treatment due to its convenience in application and no secondary pollution. However, nanofiltration membrane on the market currently has a low retention performance for NO_3^- monovalent ions. In order to meet the market demand and industrial development, the development and preparation of high flux and retention nanofiltration membranes for nitrate treatment is one of the current research hotspots. In this study, polyether sulfone (PES) ultrafiltration membrane was selected as the base membrane, with m-phenylenediamine (MPD), tannic acid (TA), 2,4-diaminobenzenesulfonic acid (MPDASA), nano-silica particles (SiO_2) as the main aqueous monomer materials, and homophenyl chloride (TMC) and p-phenylxylchloride (TPC) as the organic monomer materials. The nanofiltration membranes of different polyamides were prepared by interfacial polymerization to be used in nitrate treatment.

MPD-TMC composite nanofiltration membrane and MPD-TMC/TPC composite nanofiltration membrane were prepared using MPD as water phase and TMC, TPC as organic phase. TA/MPD-TMC composite nanofiltration membrane and sulfonated TA/MPD-TMC composite nanofiltration membrane were prepared by using MPD, TA and MPDASA as aqueous phase and TMC as organic phase. TA/SiO_2-TMC composite membrane and MPD/TA/SiO_2-TMC composite membrane were prepared by using nano silica particles (SiO_2), TA and MPD as aqueous phase and TMC as organic phase. By using ATR-FTIR, SEM, contact angle measuring instrument and solid zeta potentiometer, the structure of the composite nanofiltration membranes was characterized and compared with the base membrane, and the relationship between the structure, morphology, chemical composition and properties of the composite membrane was explored. The parameters of membrane making and the optimum membrane performance were investigated by the laboratory cross-flow filtration device. The results are as follows:

(1) MPD-TMC composite membrane has the best performance when MPD concentration is 1.5wt%, TMC concentration is 0.2wt% and heat treatment time is 10 min. Under the operating pressure of 0.9 MPa, the membrane flux is 3.43 $L \cdot m^{-2} \cdot h^{-1}$, and the retention rate is 81.26% when treating 1 $g \cdot L^{-1}$ $NaNO_3$ solution. MPD-TMC/TPC composite membrane has the best performance when the acyl chloride concentration is 0.2wt% and the TMC/TPC ratio is 4:1. Under the operating pressure of 0.9 MPa, the retention rate reaches 90.75% when treating 1 $g \cdot L^{-1}$$NaNO_3$ solution. Howevere, the membrane flux is relatively low, which is 2.73 $L \cdot m^{-2} \cdot h^{-1}$. The molecular weight of MPD-TMC composite membrane is about 532 Da. The retention rates of different inorganic salts were Na_2SO_4 (92.77%) >$MgSO_4$ (88.36%) >NaCl (88.34%) >$MgCl_2$ (83.02%), the retention rate of BSA was as high as 100%, and the retention rate of glucose was 94.21%.

(2) TA/MPD-TMC composite membrane has the best performance at TA concentration of 0.2wt% and MPD concentration of 1.5wt%. Under the operating pressure of 0.9 MPa, 1 $g \cdot L^{-1}$ $NaNO_3$ solution is treated with membrane flux of 6.23 $L \cdot m^{-2} \cdot h^{-1}$and retention rate of 72.48%. The sulfonated TA/MPD-TMC composite membrane has the best performance at the MPD concentration of 1.5%, TA concentration of 0.2wt% and MPDASA concentration of 0.1wt%. Under the operating pressure of 0.9 MPa, 1 $g \cdot L^{-1}$ $NaNO_3$ solution is treated with the membrane flux of 7.8 $L \cdot m^{-2} \cdot h^{-1}$and the retention rate of 84.22%. The molecular weight of the sulfonated TA/MPD-TMC composite membrane is about 766 Da. For different inorganic salts and organic compounds, the retention effect of inorganic salts was Na_2SO_4 (91.06%) >$MgSO_4$ (88.29%) >NaCl (86.7%) >$MgCl_2$ (86.52%), the retention rate of BSA was 100%, and the retention rate of glucose was 88.92%.

(3) TA/SiO_2-TMC composite membrane has the best performance when TA concentration is 0.2wt% and SiO_2 concentration is 0.04wt%. Under the operating pressure of 0.9 MPa, 1 $g \cdot L^{-1}$ $NaNO_3$ solution is treated with a membrane flux of 21.1 $L \cdot m^{-2} \cdot h^{-1}$ and the retention rate of 70.54%. MPD/TA/SiO_2-TMC composite membrane has the best performance when MPD concentration is 1.0wt%, TA concentration is 0.2wt% and SiO_2 concentration is 0.04wt%. Under the operating pressure of 0.9 MPa, the membrane flux rreached 7.02 $L \cdot m^{-2} \cdot h^{-1}$, and the retention rate was 90.24% when treating 1 $g \cdot L^{-1}$ $NaNO_3$ solution. The molecular weight of MPD/TA/SiO_2-TMC composite film is about 688 Da, and

the retention effect for different inorganic salts is Na_2SO_4 (93.04%) >$MgSO_4$ (92.75%) >$MgCl_2$ (90.63%) >NaCl (90.59%). The retention rate of BSA was 100%, and the retention rate of glucose was 90.82%.

The composite nanofiltration membranes prepared in this study has high retention rate for nitrate and good permeability, and the preparation method is simple and easy to operate, which can provide ideas for the preparation of nanofiltration membranes for nitrate treatment.

Key words: Nanofiltration membrane; Nitrate; M-phenylenediamine; Tannic acid; Nano silica particles

目 录

Contents