Available online at www.sciencedirect.com
SCIENCE DIRECT
Separation and Purification Technology 51 (2006) 80–84
Separation Purification Technology
www.elsevier.com/locate/seppur

Preparation of coal-based microfiltration carbon membrane and application in oily wastewater treatment

Chengwen Song, Tonghua Wang *, Yanqiu Pan, Jieshan Qiu **

Carbon Research Laboratory and State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China

Received 10 October 2005; received in revised form 26 December 2005; accepted 28 December 2005

Abstract

The coal-based microfiltration carbon membrane with low cost for the treatment of oily wastewater was prepared by carbonization of tubular carbonaceous precursor obtained by extrusion method. The pore size of carbon membrane was controlled by adjusting the particle size of coal. Effects of pore size of carbon membrane, transmembrane pressure and crossflow velocity on the filtration flux were investigated in the treatment of oily wastewater. The results indicate it is feasible to treat oily wastewater by coal-base microfiltration carbon membrane. The carbon membrane with pore size of 1.0 μm and the operation conditions of 0.10 MPa transmembrane pressure and 0.1 m/s crossflow velocity are recommended. After treated by coal-based microfiltration carbon membrane, the oil rejection coefficients of oily wastewater are up to 97%, and the oil concentrations of the permeate are less than 10 mg/L, which can meet the National Discharge Standard of China for wastewater.

Keywords: Microfiltration; Carbon membrane; Coal; Application; Oily wastewater

1. Introduction

Oily wastewater generated by various industries is the main pollutant to environment. The conventional treatment methods such as gravity separation and skimming, dissolved air flotation, demulsyfing, coagulation and flocculation are frequently not efficient enough to solve the problem, especially when the oil droplets are finely dispersed and their diameters are less than 20 μm [1]. Therefore, some new technologies have been developed. Among them, membrane separation has been found to be an effective method for the treatment of oily effluents because of high oil removal efficiency, low energy cost, no chemical additives and small space occupancy. In past years, many membrane processes such as microfiltration [2,3], ultrafiltration [4], nanofiltration [5] and reverse osmosis [6], are applied for treatment of oily wastewater. The membranes used in these processes mainly focused on polymeric membrane [7] and ceramic membrane [8,9].

Carbon membrane, as a new type of porous inorganic membranes prepared by carbonization of various carbonaceous materials, is a good membrane material for treatment of oily wastewater owing to their stability in aggressive (vapor or solvents, and nonoxidizing acids or bases) and adverse (high temperature and pressure operation) environments [10–12]. The objectives of this paper are to prepare microfiltration carbon membrane by coal, which is a cheap carbonaceous material and has an abundant deposit in China, and to apply for treatment of oily wastewater.

2. Experimental

2.1. Materials

The coal used for preparing carbon membrane is Ningxia coal from China, whose properties are listed in Table 1.

It can be seen from Table 1 that the Ningxia coal is an anthracite with high carbon content, moderate volatile matter and low ash content, which is a good material for preparation of coal-based carbon membrane.

The process employed for preparing coal-based carbon membrane is shown in Fig. 1. The coal is ground into fine particles first, and then mixed with binder into a dough, which is extruded into a tube of 10 mm external diameter by a hydraulic extruder

* Corresponding author. Fax: +86 411 88993968.
** Corresponding author. Fax: +86 411 88993991.
E-mail addresses: wangth@chem.dlut.edu.cn (T. Wang), jqiu@dlut.edu.cn (J. Qiu).

1383-5866/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2005.12.026

Table 1
Analysis of coal sample

Sample	Proximate analysis (%)			Ultimate analysis (%)		
	Moisture	Ash	Volatile matter	Carbon	Hydrogen	Nitrogen
Ningxia coal	2.34	3.13	15.70	87.25	1.06	3.54

at 2.5–3.0 MPa. After drying at ambient atmosphere, the tubular membrane is carbonized in Ar up to 900 °C at the rate of 3 °C/min and held for 1 h. The final product is cooled to room temperature naturally.

2.2. Characterization of carbon membranes

The pore structure characteristics of coal-based carbon membranes are measured by bubble-pressure method with wetting liquid of isopropanol and porometry gas of nitrogen at room temperature. The average pore size and pore size distribution are calculated with the recommended method [13]. The porosity is measured by the criterion method of China National Standards. The surface morphology of carbon membrane is observed by scanning electron microscopy (JSM-5600).

2.3. Treatment of oily wastewater with microfiltration carbon membranes

The oily wastewater was obtained by mixing crude oil with tap water for 10 min at a speed of 5500 rpm using a homogenizer. The experimental apparatus is schematically shown in Fig. 2. The oily wastewater is fed into the module by screw pump. Inlet flow rate is measured by the flow meter. The transmembrane pressure and the crossflow velocity are adjusted by means of valves.

The rejection coefficient (R) for microfiltration separation is calculated as a percentage according to the Eq. (1):

$$R = (1 - C_p/C_f) \times 100\% \quad (1)$$

where C_f is the oil concentration in the feed and C_p is the oil concentration in the permeate.

The oil concentration of the feed and the permeate is analyzed by UV spectrophotometry (UV7500). The size of oil droplets is observed by XSP-2XC optical microscope.

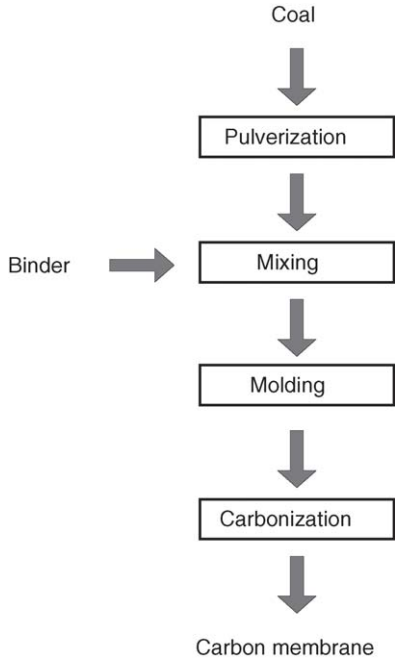

Fig. 1. Preparation process of coal-based carbon membranes.

3. Results and discussion

3.1. Preparation of coal-based microfiltration carbon membranes

In the treatment of oily wastewater, the pore size of carbon membrane has a great effect on separation performance. Therefore, the choice of pore sizes of membrane is very important for getting high oil removal efficiency. In the preparation of carbon membrane, the pore structure of carbon membrane is formed by evolution of small molecular gas produced by decomposition of binder filled in the space among coal particles and volatile in the coal during carbonization. The size of coal particle will determine the pore structure and pore size of carbon membrane. Therefore, the microfiltration carbon membranes with different pore sizes can be prepared by controlling the coal particle size in this work.

The samples with different particle sizes (4, 11 and 20 μm) are used to prepare coal-based microfiltration carbon membranes. The properties of resulting carbon membrane are listed in Table 2 and Fig. 3. It can be seen that with the increase of coal particle sizes, the average pore sizes of carbon membrane increase, pore size distributions become broad and their pure water flux increase, but their porosities decrease. SEM micrographs of the three carbon membranes (shown in Fig. 4) indicate that carbon membranes have homogenous and smooth surface structure, and with the decrease of coal particle sizes, the pore structure of carbon membrane is richer. Results obtained above also show that coal-based microfiltration carbon membranes have uniform pore structure with high porosity.

Table 2
the properties of three membrane modules prepared by different particle coal

Coal average particle size (μm)	Membrane properties			
	Pore size (μm)	Porosity (%)	Area (m^2)	Water flux[a] (L/m^2 h)
4	0.6	45.63	0.0275	230.1
11	1.0	42.15	0.0275	450.7
20	1.4	39.94	0.0275	530.6

[a] At 0.10 MPa.