Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–10

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Preparation and characterization of a diatomite hybrid microfiltration carbon membrane for oily wastewater treatment

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ARTICLE INFO

Article history:
Received 1 January 2018
Revised 9 April 2018
Accepted 29 April 2018
Available online xxx

Keywords:
Oily wastewater
Carbon membrane
Diatomite
Modification
Incorporation

ABSTRACT

High performance diatomite hybrid microfiltration carbon membranes (MFCMs) were developed for oil removal from oily wastewater. The thermal stability, functional groups, microstructure, morphology of the membranes were analyzed by thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscope, respectively. The effects of diatomite amount, oil concentration, operation time and regeneration on the removal efficiency of MFCMs were investigated. Results show that the addition of diatomite can effectively adjust the microstructure and property of MFCMs. The oil rejection elevates by increasing the diatomite amount in starting materials or the oil concentration in feed stream. The maximum oil rejection is achieved at 98.2% for 200 mg/L oily wastewater using MFCMs prepared from the precursors with diatomite content of 15 wt%, together with all the oil concentration beneath 10 mg/L in the penetrating stream within the scope of this work. After regeneration of MFCMs by simple water backwashing, the permeation flux could be almost completely recovered.

1. Introduction

Oily wastewater is usually produced from various fields, such as petroleum refineries, petrochemical industries, food processing, textile plants, steel working, and so on, which would do great harm to the ecological environment of humanity, flora and fauna without strict treatment before discharge [1–3]. At present, there are numerous techniques for oily wastewater treatment, including air flotation [4,5], adsorption [6,7], skimming, photocatalysis [8,9], electrochemistry, coagulation [10], flocculation [11] and membrane separation process [12,13]. Among them, membrane separation process is regarded as one of the most promising technologies for the advantages of superior oil removal efficiency, simple operation process, low energy consumption, and no chemical addition with an acceptable emission level [14–16].

To date, related studies have been undertaken by using membrane for oily wastewater treatment [17,18]. Singh et al. [19]. diminished the oil of oily wastewater by an organic polyamide membrane, resulting an oil concentration of 4.5 mg/L in permeate stream. Zhang et al. [18]. fabricated graphene oxide/polyacrylonitrile fiber membrane that showed ultra-high permeation flux and preferable oil rejection ratio. Hua et al. [20]. obtained a good TOC (Total Organic Carbon) removal efficiency for oily wastewater by a ceramic membrane. Abadi et al. [21]. found that the oil and grease content in permeate side reduced to 4 mg/L for oily wastewater after filtration of ceramic membranes. Nevertheless, the frequently used polymeric membranes are short of stable separation performance especially in chemical or thermal working medium due to their swelling property in aqueous liquor. In addition, ceramic membranes are usually suffered from the drawbacks of lower permeation flux and higher preparation cost [17]. Therefore, it is imperative to develop novel membrane materials with more promising potential for the application of oily wastewater treatment, *e.g.*, microfiltration carbon membranes (MFCMs).

MFCMs are excellent in chemical stability, thermal and mechanical resistance, controllable porous structure and economically feasible precursors, apart from excellent separation performance [22–24]. In general, MFCMs are prepared by the carbonization of carbonaceous precursors, such as coal, phenolic resin, etc. [25,26] Previously, our group developed phenolic resin-based MFCMs, of which the oil rejection coefficient was remarkably increased from 71.7% to 95.3% by addition of demulsifier ethanol for 200 mg/L oily wastewater [27]. However, the use of ethanol tends to cause a secondary pollution to environment during application. Thus, it should be replaced by other potential protocols in the preparation of MFCMs, *e.g.*, incorporation of porous fillers [28–31]. Unfor-

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https://doi.org/10.1016/j.jtice.2018.04.035
1876-1070/

tunately, most of the fillers (including zeolite, silica, carbon, etc.) in reports are merely effective for adjusting the gas permeation of carbon membranes, rather than liquid permeation (*e.g.*, oil–water mixture) due to the limitation of their narrow pore dimension.

Therefore, it is of great significance to develop suitable fillers for MFCMs. Here, an attempt was made to modify the MFCMs by incorporating diatomite in order to improve the treatment efficiency for oily wastewater. The motivation for us to select diatomite as fillers of MFCMs lies in the following points: (1) Diatomite is an outstanding adsorbent for wastewater treatment due to their characteristics of large surface area, high adsorption capacity, strong chemical and thermal resistance, as well as the advantages of light and available in large deposits around the world [32,33]; (2) In particular, the honeycomb structure of diatomite with high porosity might be beneficial for the rejection of oil in wastewater by size exclusion [34].

2. Experimental section

2.1. Raw materials

All the materials were technical grade and used as commercially received, including phenolic resin (PR), hexamethylenetetramine (HMTA), sodium carboxymethyl cellulose (NaCMC) and diatomite (Beichen Fangzheng Reagent Factory in Tianjin, purity > 98.5%, $SiO_2 \bullet nH_2O$, 80–90% in porosity, 300–500 nm in pore size, 20–40 μm in particle diameter [33,35,36]), without further treatment.

2.2. Fabrication of MFCMs

The raw material thermoplastic PR was first mixed with HMTA in a mass ratio of 10:1.2 and then partially cured at 150 °C for 1 h. Next, the cured PR was ground and screened through a sieve with 100 mesh numbers. After that, NaCMC was added and evenly blended into the sieved PR at a mass fraction of 20 wt%. Furthermore, diatomite powder was scattered into the as-obtained PR mixture in a mass fraction of 0–15 wt%, together with appropriate double-distillated water by agitation to form a plasticine-like paste. After aged for 80 min, the paste was pressed into dozens of circular plates with a diameter of 3 cm and thickness of 5 mm by a tablet machine at 4 MPa. Then, the plates were naturally dried at room temperature with keeping away from sunlight irradiation. Finally, precursor membranes were obtained and denoted with PM-t%, where the letter t refers to the diatomite contents in the starting mixture.

The carbonization was conducted in a horizontal furnace with an automatic temperature controller under the atmosphere of 100 mL/min flowing nitrogen. The precursor membranes were first heated at 2 °C/min from room temperature to 400 °C with dwelling for 2 h, then ramped at 1 °C/min to 600 °C with dwelling for 2 h, next at 0.5 °C/min to 650 °C with dwelling for 2 h before naturally cooling down to room temperature. The as-obtained MFCMs made from PM-t% were labeled as CM-t%.

2.3. Characterization

The thermal stability of precursor membranes was monitored by a TGA-4000 thermogravimetric analyzer (Perkin Elmer) at a heating rate of 20 °C /min from room temperature to 800 °C in an atmosphere of 20 mL/min flowing nitrogen.

The functional groups of precursors and MFCMs were examined by a TENSOR II Platinum ATR-FTIR (Bruker) in a wavenumber range of 4000–400cm^{-1}.

The pore size distributions of MFCMs were detected by a bubble pressure method using isopropyl alcohol as a wetting agent on the basis of famous Laplace equation [37]. The macroporosity of MFCMs was measured by a boiling point method according to the National Standard of China GB/T 1966–1996 [38]. Besides, the adsorption isotherms and BET specific surface areas of samples were also measured by an ASAP2420 nitrogen adsorption analyzer (Micro-meritics, USA) at −196 °C.

The microstructure of samples was analyzed by an Ultima IV (185 mm) X-ray powder diffractometer (Rigaku, operated at 40 kV and 40 mA) in a 2θ range of 10–60°. Based on the diffraction angle, the microstructural parameter d-spacing can be calculated by the famous Bragg equation.

The morphology of MFCMs was observed by a Hitachi TM-3000 scanning electron microscope (SEM) at an accelerating voltage of 15 kV in a standard mode.

2.4. Treatment of oily wastewater

First of all, a series of standard solutions and feed solutions of oily wastewater were made by fully smashing and uniformly mixing the crude oil droplets into double-distillated water through ultrasonic concussion for at least 1 h. During the preparation of solutions, no additional dispersant was used to avoid any side effects. The characteristic of the crude oil was given in our previous report [27]. The size distribution of oil droplets in the feed solution was measured by a laser diffraction particle size analyzer, Zetasizer Nano ZS90, manufactured by Malvern Co. (UK).

The optical magnification images of the oily wastewater solutions are shown in Fig. 1. In Fig. 1(d), it demonstrates that all the feed solutions are emulsified oil–water mixture because of the dispersed oil droplet size falling in the range of 0.1–10 μm, along with the average size of 284.2 nm for 50 mg/L solution, 384.5 nm for 200 mg/L solution and 534.9 nm for 100 mg/L solution.

A standard equation was ultimately acquired by correlating the oil concentrations of standard oil–water solutions with their absorbance, which was measured by a UV1800 PC UV-spectrophotometer at a wavelength of 222 nm.

During measurement, the feed stream was varied in a four-stage mode, in order to evaluate the comprehensive separation performance of MFCMs for oily wastewater. Namely, the feed was first pumped with double-distillated water for 60 min, and then quickly switched to oily wastewater with oil concentration of 50 mg/L for 60 min, 100 mg/L for 60 min, and 200 mg/L for 60 min, respectively. The feed side of the membrane cell was kept at 0.01 MPa for the 1st stage and the 2nd stage, 0.02 MPa for the 3rd stage and 0.03 MPa for the 4th stage by a pressure regulator. The permeate side was maintained at atmospheric pressure throughout the permeation process. Seen from Fig. 1(d), it shows that the initially turbid oily wastewater turns to quite clear after the membrane filtration treatment of present MFCMs.

The permeation flux of MFCMs was calculated according to the following Eq. (1):

$$J = \frac{W \times 600}{t \times S \times \Delta P} \tag{1}$$

Where, J, W, t, S and ΔP refer the permeation flux (Kg m^{-2} h^{-1} MPa^{-1}), the collected weight of penetrating fluid (g), the operation time (min), the effective area of MFCMs (cm^2) and the trans-membrane pressure (MPa), respectively.

The oil rejection of MFCMs was determined by Eq. (2):

$$R(\%) = \left(1 - C_p/C_f\right) \times 100\% \tag{2}$$

Where, R, C_p and C_f are oil rejection, oil concentrations (mg/L) at permeate side and feed side, respectively. The oil concentration in the penetrating stream was detected in real time by UV-spectrophotometer correlating the absorbance with the standard equation.

Please cite this article as: X. Zhang et al., Preparation and characterization of a diatomite hybrid microfiltration carbon membrane for oily wastewater treatment, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.04.035