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Carbon–silica composite nanofiber membrane for high flux separation of water-in-oil emulsion – Performance study and fouling mechanism

Ming Hang Tai [a], Jermyn Juay [a], Darren D. Sun [a,*], James O. Leckie [b]

[a] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore
[b] Department of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305-4020, United States

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ABSTRACT

A flexible, hydrophobic and oleophilic carbon nanofiber membrane was prepared from electrospinning for cross-flow filtration of water-in-oil emulsion under various operating conditions. Experimental results show that the membrane has a high throughput of clean oil at low pressure. Furthermore, the membrane performance in terms of permeate flux was governed by the operating pressure and cross-flow velocity. The membrane has a water breakthrough pressure of 0.206 bar under constant cross-flow velocity. The investigation of membrane fouling mechanisms using pore blocking models and resistance model reveals that the membrane experiences either of external or internal fouling or a combination of both under different operating conditions. Using the contour plot analysis, it was suggested that the optimum operating conditions for the membrane to perform efficiently shall be at high cross-flow velocity and at low pressure (between 0.07 and 0.206 bar).

1. Introduction

Oil is a hydrophobic liquid that is rich with hydrogen and carbon. It serves as an important energy resource and raw materials for various synthetic polymers and chemicals. There is a wide variety of oils that can be categorized based on the viscosity, volatility, toxicity, etc. For commercial use, oil needs to be processed to meet certain requirements such as high purity. This involves selective removal of unwanted components while concentrating the desired substances. One of the contaminants likely found in oil is water. Water can exist in oil in three states, namely free water, emulsified water and dissolved water. In some industries such as oil refinery and recovery industries, the existence of water in oil poses adverse effect to the oil performance and even to the machine component longevity. Therefore, purification of oil is important prior to further processing.

Traditional techniques used in oil–water separation involves chemical coalescence followed by gravity settling [1,2], air flotation [3,4] or flow through packed beds [5,6]. More advanced methodologies employ hierarchically micro and nano-structured materials such as zinc oxide rods [7], copper nanowires [8] and silica nanoparticles [9] to induce super selective wettability for high flux separation of oil–water emulsion. However, further study is required to examine their applicability at industrial scale. Recent development of membrane technology has opened up a new avenue for efficient processing of oil–water emulsion [10–15]. In theory, under pressurized condition, the wetting phase of the emulsion is driven through the membrane while retaining the non-wetting phase on the membrane surface.

The rejection efficiency is primarily dependent of the membrane pore size. A membrane with small pore size is able to reject smaller size of liquid droplets and vice versa. Generally, microfiltration and ultrafiltration membranes are two common types of membrane used for separation of oil and water [16–22]. Microfiltration membrane offers high flux but suffers from lower breakthrough pressure. In contrast, ultrafiltration membrane has tighter pore size and hence guarantees production of higher quality permeate. However, a higher operating pressure is required. Another factor affecting the rejection efficiency is the transmembrane pressure. When the applied pressure exceeds the liquid breakthrough pressure, they can be squeezed into and permeate through the membrane pore despite having larger size. Hence, the rejection efficiency is reduced. Taking these factors into consideration, a membrane that can produce a large quantity of high quality permeate at low operating pressure is highly favorable.

Electrospun fibrous membrane has been used as a free-standing filter media [23–25] or supporting substrate [26,27] to improve the permeate flux. Due to its interconnected open pore structure, the pores in the membrane are less likely to be entirely blocked by

* Corresponding author.
E-mail address: ddsun@ntu.edu.sg (D.D. Sun).

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the particulates that have penetrated into the membrane. Hence, it is suitable to be used in liquid filtration under hydraulic pressure. When used as an independent filter media, the electrospun fibrous membrane has shown excellent liquid permeability at low applied pressure. This is advantageous because it is less prone to be membrane fouling under low pressure and the membrane life span can be extended.

While majority of the research focuses on treatment of oily water using hydrophilic polymeric membrane, less attention has been paid to the hydrophobic electrospun membrane for oil purification. Hence, the basic of this study objective is to evaluate the potential of electrospun carbon-based nanofibrous membrane as energy efficient and high flux oil–water separator. In this paper, the membrane performance and its fouling mechanisms will be discussed based on the fouling and resistance models. Lastly, an optimum operating condition is suggested.

2. Membrane fouling theory and models

To identify the fouling mechanism, the resistance model derived from Darcy's law has been developed. The resistance model is expressed as:

$$J = \frac{\Delta P}{\mu_o(R_t)} = \frac{\Delta P}{\mu_o(R_m + R_c)} \tag{1}$$

which can be rearranged into

$$R_t = \frac{\Delta P}{\mu_o J} \tag{2}$$

where J is the permeate flux, ΔP transmembrane pressure, μ_o the solution viscosity, R_t total resistance to flow, R_m the inherent membrane resistance and R_c the cake fouling. As seen, R_t is a total of R_m and R_c. The increase in R_m over time is due to the internal fouling that occurs in the internal pore structure of the membrane whereas the formation of cake layer is responsible for the increase in R_c. Both standard blocking and complete blocking account for the internal fouling. On the other hand, external fouling is due to the formation of cake layer on membrane surface.

For standard blocking model, it is assumed that the foulants deposited evenly along the pore wall such that the pore diameter is reduced due to constriction in pore diameter while the number of pores is remained constant [28]. These assumptions yield the following expressions

$$\frac{t}{V} = K_1 t + \frac{1}{Q_o} \tag{3}$$

where t is operation time, V the accumulated permeate volume, K_1 the standard blocking constant, Q_o the initial permeate flow rate. The value of initial flow rate and the constant, K_1 can be determined by plotting t/V versus t using experimental data. The standard blocking model can also be written in terms of membrane resistance as a function of time:

$$R_m = R_{mo}(1 + K_1 Q_o t)^2 \tag{4}$$

where R_{mo} is initial membrane resistance. From Eq. (4), one can see that the resistance increases over time with an increasing slope and the curve produced from plotting the resistance versus time is concave up.

Assuming that the pore diameter is constant and the number of clogged pores increases with the permeation volume, the flow rate described by pore blocking model can be estimated using the following equation [28]:

$$Q = Q_o - K_2 V \tag{5}$$

where K_2 is the pore blocking constant. The value of Q_o and K_2 can be determined by plotting Q versus V. The expression in term of membrane resistance for pore blocking model is as follow:

$$R_m = R_{mo} e^{(K_3 t)} \tag{6}$$

The membrane resistance increases exponentially over time with an increasing slope. The plot of resistance against time produces a curve that is concave up.

The resistance to flow can also be contributed by the formation of cake due to the accumulation of rejected foulants on membrane surface. The membrane is fouled externally in this case. For external fouling, the membrane resistance is constant whereas the cake resistance increases with the time due to the accumulation of rejected foulants. This yields the following equation [28]:

$$\frac{t}{V} = K_3 V + \frac{1}{Q_o} \tag{7}$$

where K_3 is cake filtration constant. In terms of total resistance, the cake filtration model can be expressed as:

$$R_{tot} = R_{mo}(1 + 4tK_3 Q_o^2)^{0.5} \tag{8}$$

Like internal fouling model, the resistance increases with time. However, the changing pattern is a decreasing slope and the curve is concave down. In short, internal fouling model is characterized by an increasing slope while external fouling model has a decreasing slope. Therefore, by looking at the characteristic slope (concave up and down, increasing or decreasing slope) in a total resistance curve, one can readily identify the fouling mechanism.

3. Experimental

3.1. Preparation of electrospun SiO_2–carbon composite nanofibers

The SiO_2–carbon composite nanofibers was prepared according to Tai et al. [29]. Briefly, polyacrylonitrile (PAN, M.W. = 150,000 g/mol, 7 wt.%) and tetraethyl orthosilicate (TEOS, 0.5 wt.%) was mixed with a mixture solvent of dimethylformamide (DMF)/acetic acid (volume ratio of 15/1). The precursor solution was then heated in water bath at 60 °C for 30 min before it was used for electrospinning. The electrospinning was performed at room temperature in a closed chamber where the electric field strength was sustained at approximately 0.6–0.8 kV/cm. The tip-collector distance was kept at 20 cm. To retard the hydrolysis of precursor, N_2 was purged from the side of spinneret during the electrospinning. At a solution feeding rate of 9–10 μl/min, 11–15 h were required to electrospin the membrane. Subsequently, the collected non-woven fibrous assembly was oxidatively stabilized at 280 °C for 2 h followed by carbonization at 900 °C in N_2 for another 2 h.

3.2. Membrane pore size determination

The pore size of the as-fabricated membrane was determined by a capillary flow porometer (CFP 1500A, Porous Material. Inc. (PMI), Singapore). The method used is bubble point analysis which is based on the fact that the pressure required to force an air bubble through the pore is inversely proportionally to the pore size. Hence, under wetting condition, the pore size can be determined from the pressure necessary to push water out of the pore.

Prior to analysis, the membrane was pre-wetted with Galwick fluid (surface tension = 15.9 dynes/cm). The measurement was performed in a dead-end cell where the wetted membrane was placed onto a filter holder that was connected to a source of regulated pressure. The pressure on the membrane was then increased stepwise while giving a 10 min stabilization time after each 14 kPa