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Electrospun Polyacrylonitrile Fibrous Membranes as Pre-filters: A Case Study of Carbon Black Removal from Lubricating Oil

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Abstract: *Electrospun polyacrylonitrile (PAN) fibrous membranes with fiber diameters in the range of 120-250 nm were prepared and employed as a membrane material for lubricating oil filtration due to their excellent chemical and thermal resistance as well as high oil wettability. They separated different types of carbon black with varied separation performances, depending on the size of carbon black. The smaller the particle size, the higher was the average flux. As the content of particles were extremely high, they were able to pack closely together on the membrane surface giving a so called "layer effect" and thus reducing the effective pore-size of the electrospun membrane significantly at the surface. This dense "cake" acted as the separating layer for the electrospun membrane, resulting in unusually high recovery flux for high amount of particles. The fouling mainly occurred within the surface of the electrospun membrane since particles were mostly retained on the surface and only slightly within and at the bottom of the membrane.*

Keywords: *Electrospinning; Fibrous membrane; Polyacrylonitrile; Carbon black; Lubricating oil*

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1. INTRODUCTION

Clean oil is vital to engine performance and durability. Oil must lubricate, cool, and clean the engine as it circulates. In order to remain effective, it must be filtered as it cycles. The function of the oil filter is to remove the contaminants introduced into the lubricating oil and prevent them from reaching sensitive engine parts without restricting normal oil flow to the various points requiring lubrication. Internal sources of contamination include wear products from the rubbing surfaces of the engine, blow-by gases leaking past the rings of the pistons and degradation of the oil itself. In principle, a filter must perform well in the areas of efficiency, capacity, flow, and life. Efficiency is the ability of filter to capture contaminants. The more efficient a filter is, the more contaminants it will remove from the oil. To make a filter more efficient the spaces between the fibers in the media are made smaller, creating more resistance and limiting the ability of oil to flow through the filter. Achieving maximum efficiency along with limited resistance is critical to good filtration. In addition, capacity is an important factor to be concerned, which is the amount of contaminants a filter can hold and still remain effective. When a filter reaches maximum capacity the oil continues to flow through unfiltered, leaving harmful contaminants circulating in the oil.

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If a pre-filter is used to remove coarser particles, the performance of the down stream filter unit can be maintained for much longer times before cleaning and/ or replacement. There are various forms of pre-filters currently available such as packed sand beds, woven and non-woven fibrous meshes, etc. [1, 2] for the separation of two distinct phases. The choice of pre-filter is usually governed by its properties, performance, and durability. The pre-filter should have an extremely large surface area, relating to high dirt-loading capacity. The smaller the fiber diameter used in the pre-filter, the greater the surface area for particle adsorption and the better the retention of small particles. Previously, asbestos fibers were well known as the best pre-filter media. The individual fibrils were smaller than 0.01 μm and they had a positive zeta potential. However, when it was proved that asbestos fibers caused a health hazard, fine diameter glass and polymeric fibers were used as substitutes [3]. Unfortunately, these replacement materials give inferior performance compared to asbestos since current techniques are unable to produce sub-micron fibers with large surface areas.

The electrospining technique is a well-known process for making continuous sub-micron to nano-size fibers in the non-woven mat form. In this process, a high voltage is applied to the anode, immersed in the spinning solution. When the electrical force is higher than the surface tension of the solution, a charged jet of fluid is produced [4-6]. Electrospun nanofibers have a variety of potential uses as sensors [7], tissue engineering scaffolds [8], wound dressings [9, 10], high performance air filter [11, 12], nano-filler materials [13, 14], and as membranes [15-19] due to their large specific surface area, high fiber aspect ratio and high degree of interconnection. In separation technology, electrospun nanofibrous membranes have been used in a number of commercial air filtration applications over the last 20 years, and hold promise for technical benefits in an expanding field of these applications [20]. For example, a recognized industry, Donaldson Company Inc., commercially produces nanofibrous membrane incorporated in air filter products [21, 22]. Recently, Gopal and *et al.* [18, 19] have explored the viability of developing polyvinylidene fluoride and polysulfone membranes via the electrospinning process with heat treatment to increase the structural integrity of the as-spun nanofibrous membrane before particle-water separation. Their applicability in particulate removal has been demonstrated. Later, Aussawasathien *et al.* [23] proposed the use of electrospun Nylon-6 as a pre-filter without any treatment for sub-micron and micron size of particulate-water separation. Taking advantage of the ability to produce submicron fibers with relative ease and low cost, it is anticipated that a highly efficient fibrous pre-filter for fluid separation can be produced via the electrospinning technique.

Generally, the membrane performance is defined by two key parameters: flux and selectivity. Flux indicates the rate at which liquid is transported across the membrane whereas selectivity is governed by the surface properties of membrane that allows the specific type of species to pass through. The structural and morphological properties of the membrane such as porosity, pore size and distribution, wettability, pressure drop across membrane and membrane thickness influence these two factors.

In this study, the development of a pre-filter based on electrospun fibers is proposed for the removal of carbon black as a contaminant from the lubricating oil. Electrospun polyacrylonitrile fibrous membrane was prepared and employed as a membrane material without any treatment due to its excellent chemical and thermal resistance and high oil wettability. Furthermore, characterization and separation evaluation of as-spun fibrous membranes were carried out to relate its structural properties to membrane separation performance.

2. MATERIALS AND METHODS

2.1 Preparation of Electrospun Fibers

A predetermined amount of PAN (weight average molecular weight of 150,000 from Aldrich, USA) was dissolved in N,N-dimethylformamide (DMF) purchased from Aldrich (USA) to yield a 6.5 wt% PAN solution. The solution was heated at 60°C and stirred for 1 h until a light yellow clear solution was obtained [24]. The electrospinning technique was employed to prepare non-woven fibrous membranes from aforementioned solution. The fiber spinning was performed at room temperature under atmosphere. A copper wire as an anode was immersed in the spinning solution contained in a glass pipette. The as-prepared PAN solution was subsequently electrospun under 15 kV applied voltage with 20 cm gap distance between the tip of the pipette and the collector. The diameter of the stretched pipette tip was approximately 0.1 mm. PAN fibers were collected on a grounded 12×6 cm^2 substrate covered with aluminum foil.

2.2 Fiber Characterization

The thickness of as-spun membranes was measured using a digital micrometer thickness gage (Mitutoyo absolute, Japan). The morphology of as-spun fibers before and after the separation process were observed using a scanning electron microscope (SEM, JEOL, JSM-5410 Scann) and a digital camera (Sony Handycam, DCR-DVD405, Japan), respectively. Prior to SEM characterization, a fiber sample was attached onto an SEM stub using conducting tape and then sputter coated with a thin layer of gold using JEOL JEC-1200 Fine Coater at 15 mA for 120 sec. The surface area, total pore volume, and average pore diameter were determined by using a N_2 adsorption technique and BET method (Autosorb-1C, Quantachrome Instrument, USA). The static contact angle of the electrospun membrane was measured using a contact angle analysis system (Ramehart, USA). A 0.5 μl droplet of distilled water was dispensed onto the membrane using a sessile drop method and the measured angle was recorded.

2.3. Flux and Permeability

Circular electrospun membranes, 20 mm in diameter and approximately 0.15 ± 0.05 mm in thickness, were selectively cut from non-woven fiber mat. Without further treatment, three specimens were used for the testing of carbon black-lubricating oil separation in the simple opened-end filtration set-up shown in Fig. 1. A dried membrane was placed on an aluminum rectangular sieve substrate with 0.2 mm x 0.5 mm sieve size and 0.2 mm thickness. Both components were put inside the membrane holder, screwed into the bottom part of the separation column. The small hole at the end of the column for water outlet was 4.6 mm in diameter. The amount of starting oil was 40 ml. The N_2

pressure was set-up at 10 psi using a regulator and then N_2 flow rate of 4.5 L/min at such pressure was controlled at the beginning of the oil flux measurement by a flow meter. The N_2 gas was applied to the system to distribute carbon black in oil and increase the flow rate of oil throughout the membrane. The N_2 flow rate kept decreasing throughout the separation process without any adjustment due to the fouling phenomenon.

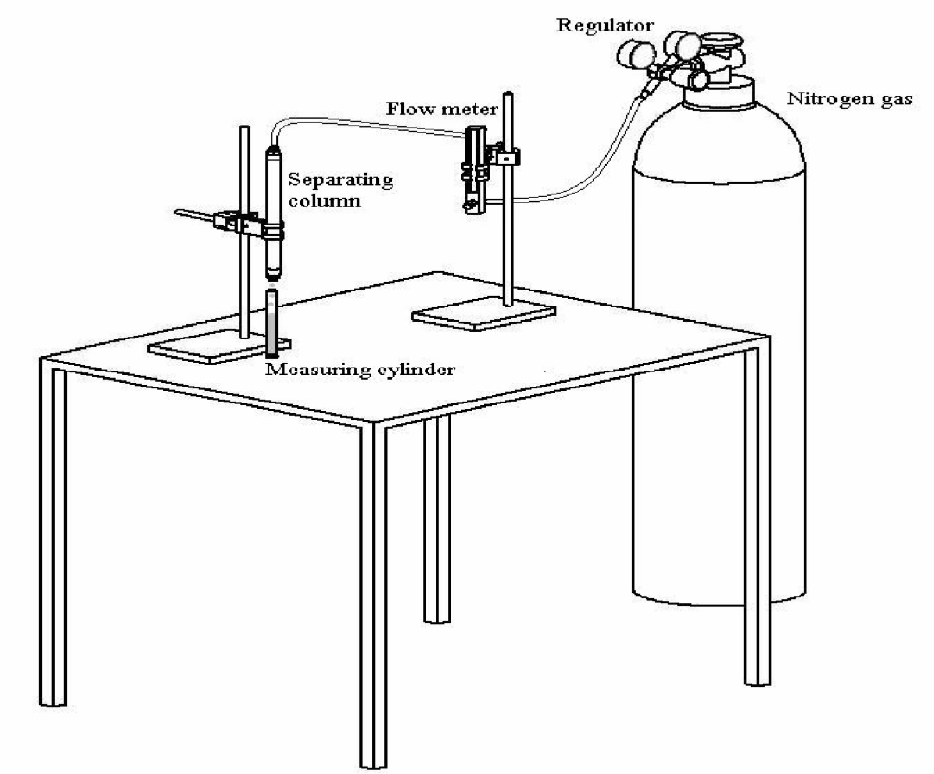

Figure 1: Fluid Separation Apparatus and its Components

Three types of carbon black, N220, N660 from Thai carbon black (Thailand), and XE-2B from Degussa (Germany) were added in the lubricating oil (V120B, viscosity of 0.304 Pa-s at room temperature) supplied from PTT, Thailand. These carbon blacks were reconstituted in lubricating oil using a measured volumetric flask to prepare different concentrations of carbon blacks. The prepared concentration of N220 and N660 was 20 ppm and of XE-2B were 5, 10, 15, and 20 ppm in lubricating oil. The separation process was performed three times for each carbon black-lubricating oil mixture at a pre-set pressure using electrospun fibrous membranes. A new membrane was used for each separation experiment. The flux of pure oil was firstly determined, followed by the separation of carbon black-oil suspension. The separation flux was measured for every 5 ml of permeate collected. The separation experiment was continued until no permeate was collected. The first permeate flux was calculated from the collecting time of the first

5 ml of oil collection whereas the last permeate flux was derived from the collecting time of the last set of oil collection at the end of the separation cycle. In addition, the flux before separations is defined as the average flux of first cycle of each carbon black-oil separation. The average flux after separation was obtained from the separation of the permeate collected from the first cycle of separation. Additionally, the flux recovery after each separation was also determined using Eq. (1), which is the ratio of pure oil flux after separation, W_A, and before separation, W_B, of carbon black.

$$Flux\ recovery = \frac{W_A}{W_B} \times 100\% \tag{1}$$

3. RESULTS AND DISCUSSION

3.1 Electrospun PAN Nanofibers

Electrospun PAN fiber mat was used as prepared without any treatment. The fiber diameter of as-spun fibers was approximately 120-250 mm as shown in Fig. 2. A small amount of beaded fibers was also observed in the electrospun material. Table 1 outlines PAN fibrous membrane properties.

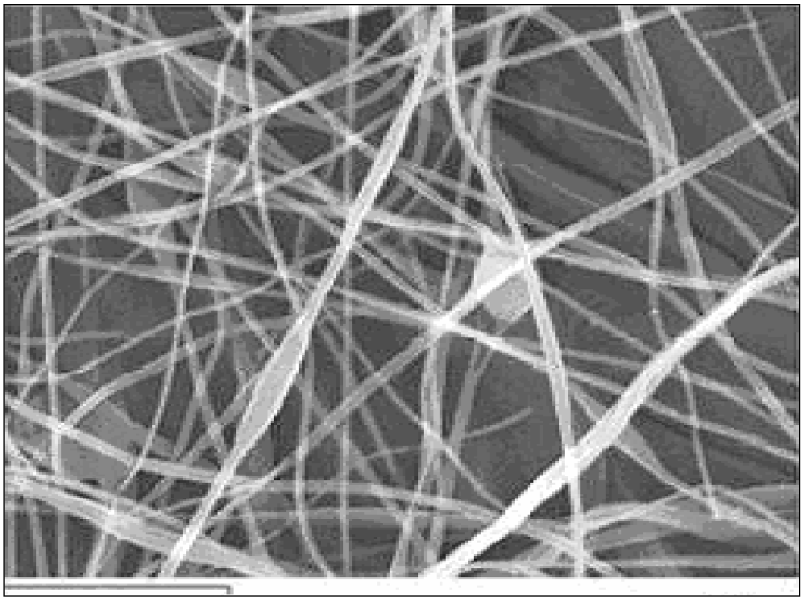

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Figure 2: SEM Image of Electrospun PAN Fibers

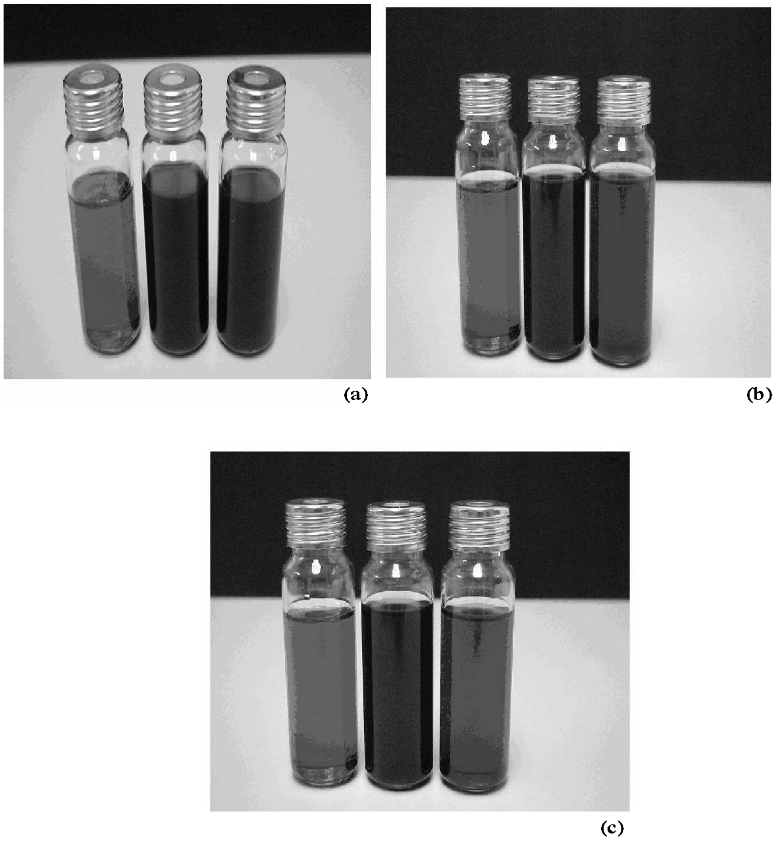
3.2 Carbon Black-lubricating Oil Separation

It should be noted that electrospun PAN fibrous membrane exhibited hydrophobic behavior, implying that there was no resistance to oil flow through an absolutely dry electrospun membrane. Once the electrospun membrane was completely wetted, the

Table 1
Properties of Electrospun Fibrous Membranes

Membrane properties	
Fiber diameter (nm)	120-250
Membrane thickness (mm)	0.15±0.05
Average pore diameter (nm)	101.9
Average total pore volume (cm^3/g)	42.97
Average surface area, BET method (m^2/g)	1.69×10^2
Contact angle (°)	117 (distilled water)

high porosity contributed to relatively large flow rates. Different carbon blacks were used in this study to measure the filtering efficiency of electrospun nylon-6 fibrous membranes. The results of the experiments are presented in Fig. 3 and 4. It is obviously seen from Fig. 3 and 4 that as-prepared PAN fiber membrane could mostly separate XE-2B particles, while poorly filtering N-660 and N-220 particles. This indicated that


(a) (b)

(c)

Figure 3: Photographs of Lubricating Oil before and after Carbon Black Separation for Different Types of Carbon Black at the same Content (from Left to Right: Oil without Carbon Black, Oil with Carbon Black before Separation, and Oil after 1st Separation, Respectively): (a) N-220, (b) N-660, and (c) XE-2B

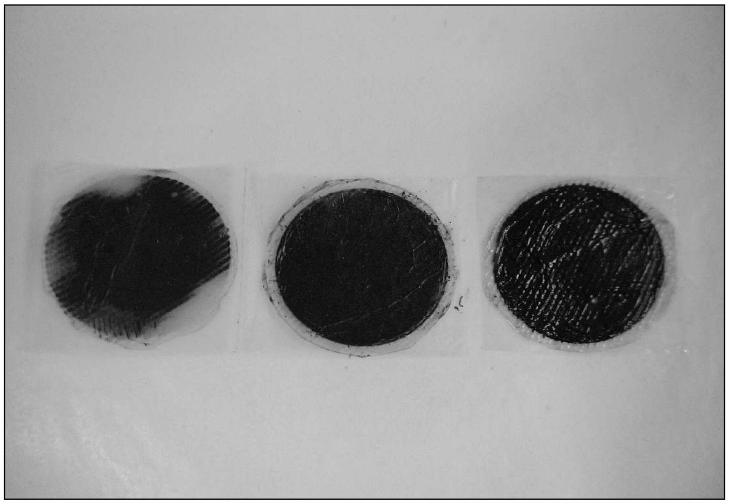


Figure 4: Photograph of Carbon Black on Electrospun PAN Fibers after 1st Separation for Different Types of Carbon Black at the Same Content (from Left to Right: N-220, N-660, and XE-2B, Respectively)

the size of carbon black from small to large would be in the order of N220, N660, and XE-2B, respectively. However, the average flux of XE-2B separation was somewhat low compared to those of N-660 and N-220, respectively, (Table 3) due to the thick layer of XE-2B particles on the membrane surface (fouling effect). An average flux after separation of each XE-2B content (5, 10, 15, 20 ppm) increased compared with an average flux before separation (see Table 4). In addition, XE-2B yielded high flux recovery at high particle concentration. As the amount of carbon black particles was high, particles were able to pack closely together, reducing the effective pore-size of the electrospun membrane significantly at the surface. This dense "cake" acted as the separating layer for the electrospun membrane, resulting in unusually high separation factor for high amount of carbon black particles. Fig. 5 shows top surfaces of the electrospun membrane at different concentrations after 1st and 2nd separations. The membrane surface was completely covered by a dense cake-layer of carbon black particles for the 1st separation. After 2nd filtration, a thin layer of carbon black particles was accumulated on the top surface of the filtering membrane for each carbon black concentration. It appeared that the electrospun membrane had a potential use as a screen filter in this instance.

Table 4
Different Types of Carbon Black-lubricating Oil Separation using Electrospun PAN Fibrous Membranes

Compositions	*Average flux (L/h m²)*	*Average first permeate flux(L/h m²)*	*Average last permeate flux(L/h m²)*
Oil	115.66±10.3	127.39±12.7	95.54±7.1
Oil + 20 ppm N-220	91.72±5.4	95.54±5.9	76.43±3.6
Oil + 20 ppm N-660	42.20±2.2	76.43±4.7	19.11±1.4
Oil + 20 ppm XE-2B	15.24±1.5	95.54±5.2	9.55±0.8

Table 5
Carbon Black (XE-2B)-Lubricating Oil Separation at Different Carbon Black Contents using Electrospun PAN Fibrous Membranes

XE-2B (ppm)	*Average flux before separation (L/h m^2)*	*Average first permeate flux (L/h m^2)*	*Average last permeate flux (L/h m^2)*	*Average flux after separation (L/h m^2)*	*Average flux recovery (%)*
5	40.68±2.0	114.65±9.4	4.78±0.34	122.29±10.7	300.61±1.0
10	26.23±1.9	133.76±10.7	9.55±0.67	164.81±12.4	628.33±2.18
15	24.81±1.7	95.54±6.1	8.39±0.51	161.57±11.7	651.23±2.89
20	15.24±1.4	95.54±5.8	9.55±0.76	157.64±11.4	1034.38±3.74

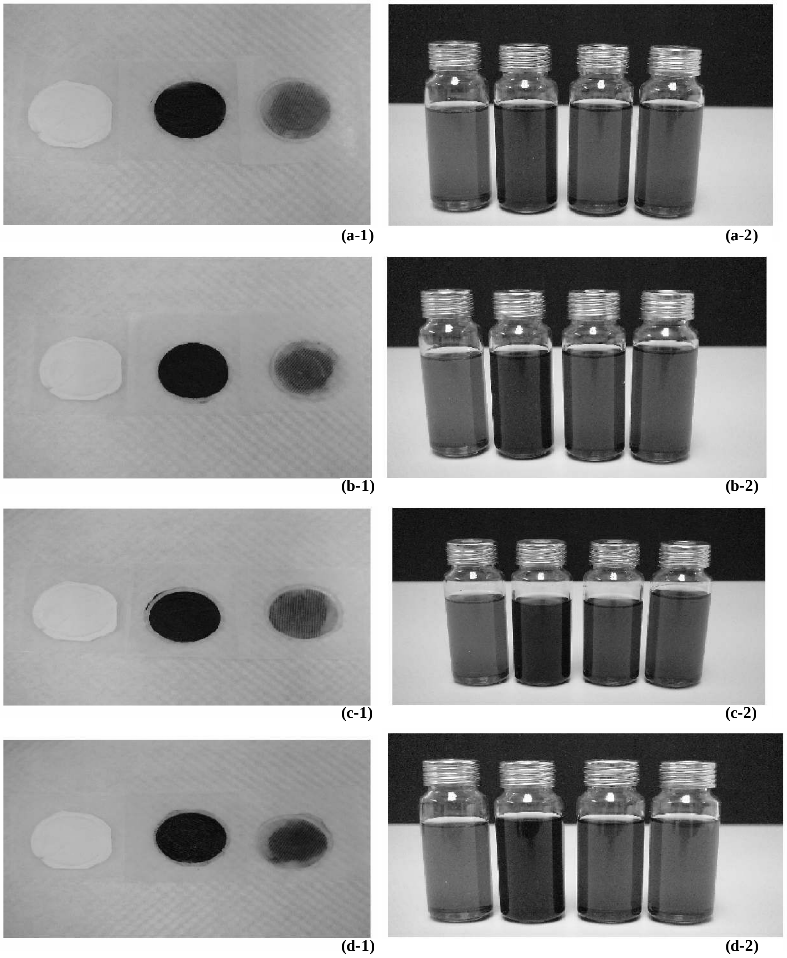


Figure 5: Photographs of PAN fiber membrane before (left), after 1st separation (middle), and after 2nd separation (right) for carbon black (XE-2B)-lubricating oil separation at different concentrations together with photographs of lube oil at different conditions (oil without carbon black, oil with carbon black before separation, oil after 1st separation, and oil after 2nd separation from left to right, respectively) on the side of each set: (a) 5 ppm, (b) 10 ppm, (c) 15 ppm, and (d) 20 ppm.

4. CONCLUSIONS

Electrospun PAN membranes could be utilized effectively as pre-filters for the removal of carbon black as a contaminant above the membrane average pore-size without severe fouling. In addition, the "layer effect", particulate accumulation on the membrane surface, was also observed when small particle size of carbon black were separated, especially at high concentration. This phenomenon significantly affected the filtering performance and extent of fouling. The present study has shown the possibility of using membranes of electrospun nanofibers as pre-filters prior to ultrafiltration or nanofiltration to increase the filtration efficiency and prolong the life of downstream membranes. To improve understanding of separation behavior, the method used for separation factor determination, effect of flow patterns, and cross-flow versus through-flow should be investigated to further design and develop an efficient pre-filter.

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