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Preparation and Application of Functional Carbon Whisker Membrane for Separation Process

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Abstract

Membrane separation is extensively used for water/wastewater treatment because of its efficiency separation processes. However, particles in the feed water can deposit and accumulate on the membrane surface to created cake layer. As a consequence, the selectivity of the membrane and flux through the membrane are decreased, which is called fouling/blocking phenomenon. In order to solve fouling problem, we developed a novel membrane named Carbon Whisker Membrane (CWM) which contains vapor-grown carbon fibers/whiskers on the surface of the membrane and a layer of carbon film coated on the ceramic substrate. We firstly employed polymethyl methacrylate (PMMA) as a testing material to investigate the fouling mechanism. The results suggested that Carbon Whiskers on the surface of the membrane can prevent the directly contact between the membrane body and particles so that the fouling/blocking could not occurred easily compared to the membrane without carbon whiskers. We also researched the relationship with the diameter, density of carbon whisker on the membrane surface and total flux of solutions. Finally, we will be able to control the diameter and density of carbon whiskers on the membrane and existence of carbon whiskers on the membrane, it is important factor, might be prevent fouling/blocking in the water treatment.

Key Words : Carbon Whisker Membrane, Carbon Membrane, Drinking Water Treatment, Preventing Fouling/ Blocking

1. Introduction

During the past years, membrane separation has become more widely used in separation processes. It is also an important tool for the treatment of oil/water emulsions and waste sludge. The efficiency of membrane technology is, however, hindered by fouling. Membrane fouling usually result from plugging the pores of membrane by foulant and/or agglomeration of foulant and eventual blockage of membrane pores[1]. The foulant can be adsorbed very strongly on the membrane surface and it is therefore that the permeate flux and selectivity decreased. Although several membrane materials such as polymeric, metal, and ceramic are present, fouling is still a critical problem in membrane processes[2]. It is necessary needed a frequent cleaning processes to regenerate the membrane. A promising technique for fouling reduction is called backflushing. Backflushing is a process of reverse filtration followed by forward filtration. The forward flow during each backflushing removes the particles deposited on or in membrane[3]. This study reports an investigation of CWM on cross-flow filtration performance. We expect that use of the CWMs could prevent particles to attach on the membrane so that flux could be improved. Further, it might be easier to clean

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the membrane after use. A concept of anti-attachment of particle on CWM and cleaning process of CWM are shown in Fig. 1.

2. Material and Methods

2.1. Materials

CWM contains vapor-grown carbon fibers/whiskers with hydrocarbon source on the surface of the membrane and a layer of carbon film on the ceramic substrate. Membrane has been made by CVD using nitrogen as carrier gas at a flow rate of 60ml/min purge, mixture gas (methane : nitrogen = 20 : 80) as the precursor, ferric sulfate ($Fe_2(SO_4)_3 \cdot nH_2O$) as the catalytic precursor (0.1-1M) and porous ceramics as membrane support at 100-1000ml/min flow rate of mixture gas, 1000-1100℃ and 5-40 minutes of hydrocarbon deposition time. The experiments began by increasing the temperature to 1000-1100℃ at the rate of 10℃ per min prior to introduction the mixture gas into the reactor. When the stage increasing the temperature was completed, the mixture gas was introduced into the quartz reactor and was reacted by thermal pyrolysis.

Ceramic substrates are produced by molding and sintering of mullite ($SiO_2 \cdot Al_2O_3$) particles from Kubota Ltd. Substrates are 13 mm O.D. with 9 mm I.D. and nominal pore is 2.3 μm, and another one has a skin layer of 0.1 μm on the outer surface[4]. PMMA (Poly Methyl Methacrylate) particles were supplied from Souken Kagaku Ltd. They are spheric particles with 0.15, 0.8 and 3.0 μm in diameter respectively.

2.2. Methods

It observed the outside structure of carbon membrane and CWM with SEM, the inside of the membranes was observed with the liquid and gas permeation.

Gas permeation measurement was carried out seven gases, hydrogen, helium, methane, nitrogen, oxygen, argon, and carbon dioxide. Membranes were set in glass module with 15 mm O.D. and 2 mm thickness. Gas was introduced to the module and permeation flux was measured under 100 mmHg pressure drop by a bubble flow meter at room temperature. The measurement of gas flux as a function of transmembrane pressure can be used to determine a mean pore radius of polymer membrane. However, more recent studied suggest that the value of the mean free path might depend on the type of gas used. So we carried out nitrogen permeation with membrane that we made and Millipore filters that we known its pore size 0.025 μm.

Liquid circulation type apparatus for membrane filtration shown in Fig. 2 was used. Experiments were carried out using a 15 cm long membrane in a cross-flow apparatus, which consists of a feed reservoir, a membrane module, a backflushing reservoir and a regeneration reservoir. We firstly used pure water for the permeability experiments on CWM. For comparison reason, we employed Carbon Membrane (CM) which has the similar water permeability for the PMMA filtration experiments. 1000 mg/l PMMA was prepared for the experiment. The membrane was placed in the module and then evacuated by a magnet

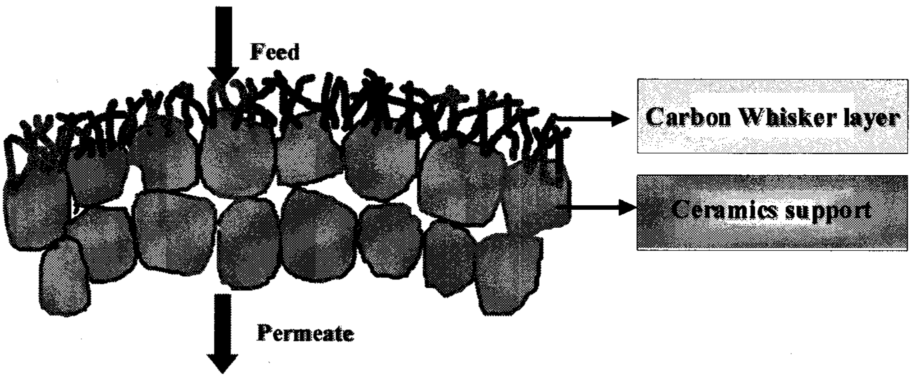

Fig. 1. A conception figure of carbon whisker membrane.

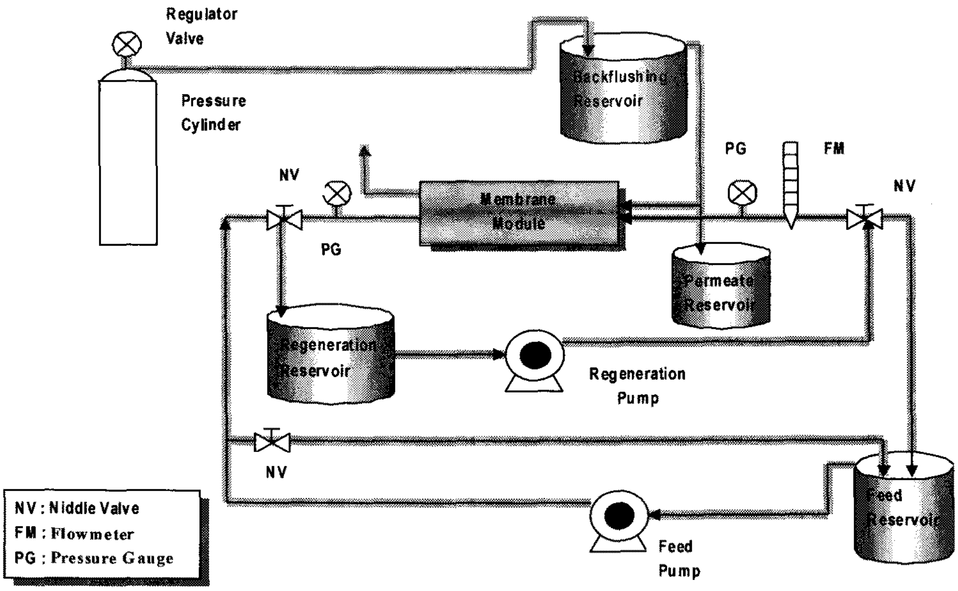

Fig. 2. Schematic of the experimental apparatus of liquid permeability.

gear pump while the cross-filtration experiment was carried out. The membranes were cleaned by back-flushing technique for 1 minute using pure water with a pressure of 2 kg/cm^2.

3. Results and Discussion

3.1. Membrane structures

Fig. 3 shows the SEM of manufactured membranes used in this study. They are Ceramic membrane (A),

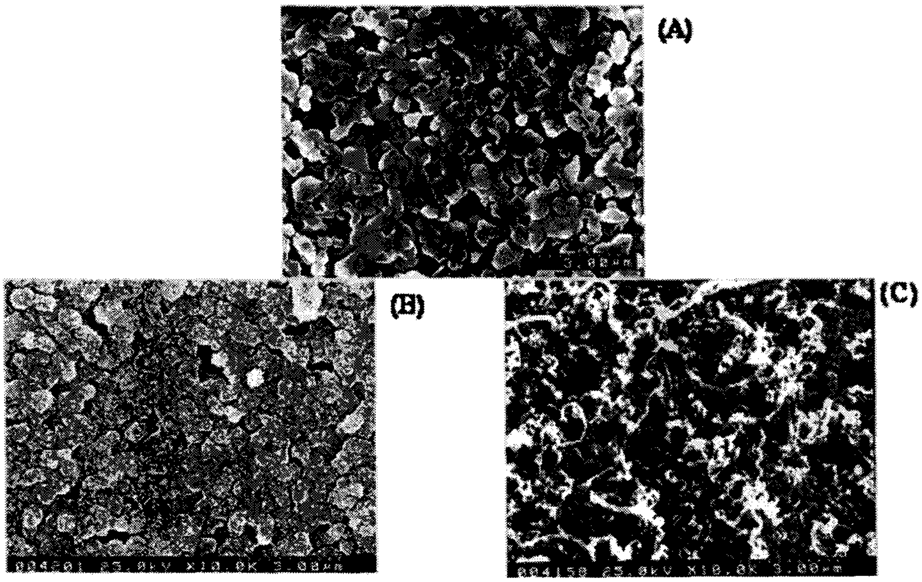

Fig. 3. SEM pictures of three membranes used in this study.
(A) Ceramic membrane, (B) Carbon Membrane, (C) Carbon Whisker Membrane.

Carbon Membrane (B), Carbon Whisker Membrane (C). Ceramic membrane was used as a substrate for fabrication of CM[5] and CWM[6]. It is tubular membrane with 13 mm O.D. and 9 mm I.D. The pore size is about 0.1 μm supplied from Kubota Ltd. Japan. This is the SEM picture that changed diameter and surface density of the carbon whiskers due to the concentration of the catalyst and deposition time (Fig. 4, 5). In case of changed concentration of catalyst, it shows remarkable change of surface density on the membrane. Meaning of concentration of catalyst change is meaning of change of the numbers of reacting catalyst particles. It seems to be recording where the catalyst concentration will be high it gets high surface density. Another case of changed deposition time with hydrocarbon source, it shows change of diameter of carbon whisker and surface density on the membrane. If the time of the deposition will be longer the diameter of carbon whisker is bigger than before. Because the amount of carbon is increase more and more. Fig. 4 shows the differences of the diameter and density of CM and CWM with the same/similar pore size that determined by gas and liquid permeability was used for

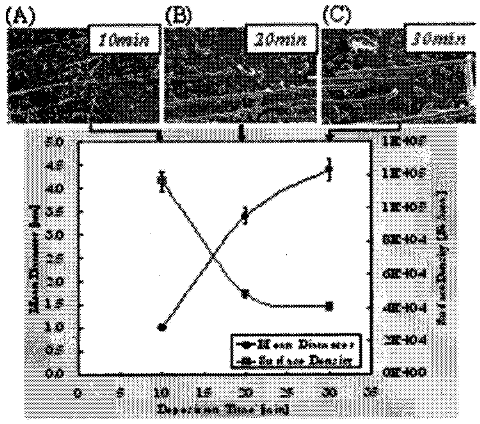

Fig. 5. Change of the Carbon Whisker to deposition time with hydrocarbon source (A) 10 min (B) 20 min (C) 30 min Ceramic 0.1 μm, Catalyst 0.5 M, dipping 1 min.

the PMMA filtration experiments as a compassion reason. We also carried out the PMMA permeability experiments as different membrane surface of carbon whiskers with concentration of catalyst and deposition time of the hydrocarbon source. (Fig. 4, 5)

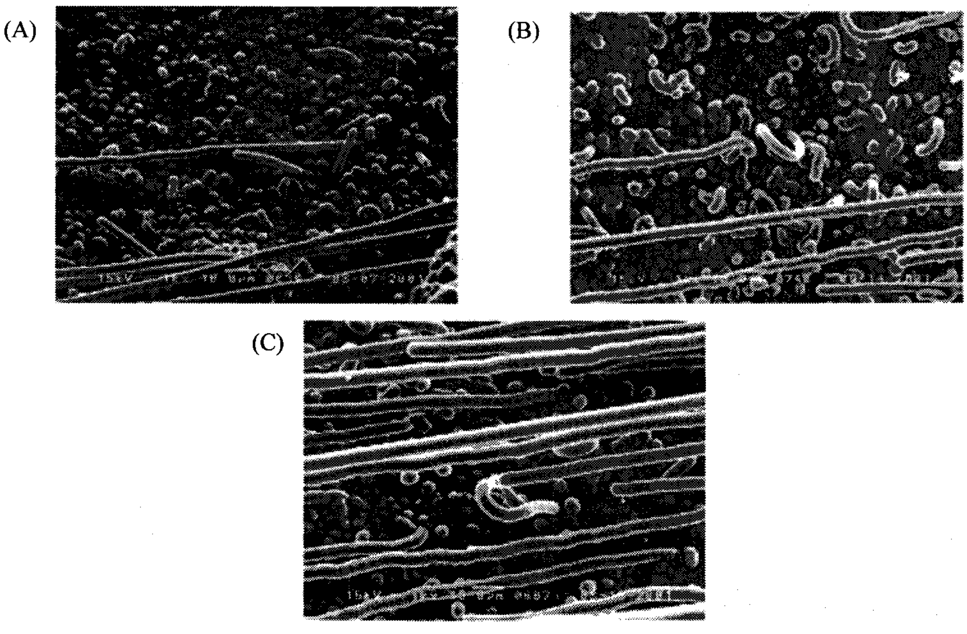

Fig. 4. Change of the Carbon Whisker Membrane due to the concentration of the catalyst (A)0.1 M (B)0.5 M (C)1 M Ceramic 0.1 μm, dipping 1 min, deposition 20 min.

3.2. Gas permeation and Pure Water Flux (PWF)

Fig. 6 shows the results of hydrogen, helium, methane, nitrogen, oxygen, argon, and carbon dioxide permeation under pressure of 100 mmHg with ceramic membrane, CM, and CWM. All of samples, permeation flux becomes proportional to -0.5 power of molecular weight. This means for membrane samples, flow in the pore becomes Knudsen flow type[7].

Fig. 7 show the pure water flux of ceramic membrane, CM, CWM. As can be seen, the flux of CM and CWM drop distinctly in comparison of ceramic membrane. This is because the results suggest that the CWM and the CM process similar poses so that both membranes can be used for PMMA filtration experiment as a comparison reason. The fabrication process of membrane by CVD technique narrowed the pore size.

3.3. PMMA solution filtration

Fig. 8 (A) shows that the membrane was firstly purged with water for 10 minutes and then introduced PMMA solution for the experiments. As expected, the flux declined because of the generation of cake layer or/and fouling. Comparing with the flux through CWM and CM, the performance of CWM in terms of water permeability seems better than that of the CM. When the flux declined to a certain level, the backflushing processes was employed for 1 minute for the regeneration. As we can see that the flux recovered to a certainly level by backflushing technique. We found that a higher recovery rate can be obtained in the case of using CWM. This suggests that CWM can be cleaned easier and more efficient than CM by the backflushing technique.

The experiment continued after cleaning proceeds for a second cycle and third cycle of the filtration-cleaning process. It shows similar results as the first cycle. The same experiments were carried out with 0.8 μm PMMA solution as show in Fig. 8 (B). Because of the use of smaller PMMA particles, the flux drop rapidly after the solution introduced. This might be because of the dense packing of the small particles. The flux patterns are similar to the Fig. 8 (A) and the performance of CWM on the Cross-filtration was better than that of CM with the 0.8 μm PMMA solution. However, it 0.15 μm PMMA solution was used for the experiments, it was found that both the CM and the CWM can not be clean/regeneration easily by backflusing technique so that the flux continue to decline. In addition, the CWM performed a worse flux in comparison of CM. This might be because the diameters of the PMMA particles were smaller than diameter of the CWs on the membrane. (in this case, we used the CWM with 0.8 μm on the surface). Particles were trapped in the whiskers network so that they were difficult to be cleaned out.

The backflushing efficiencies were analyzed and shown in Fig. 9. Cleaning recovery rate of CWM and CM for the 3 μm, 0.8 μm, 0.15 μm PMMA particles are shown in Fig. 9. (A), (B) and (C), respectively. The

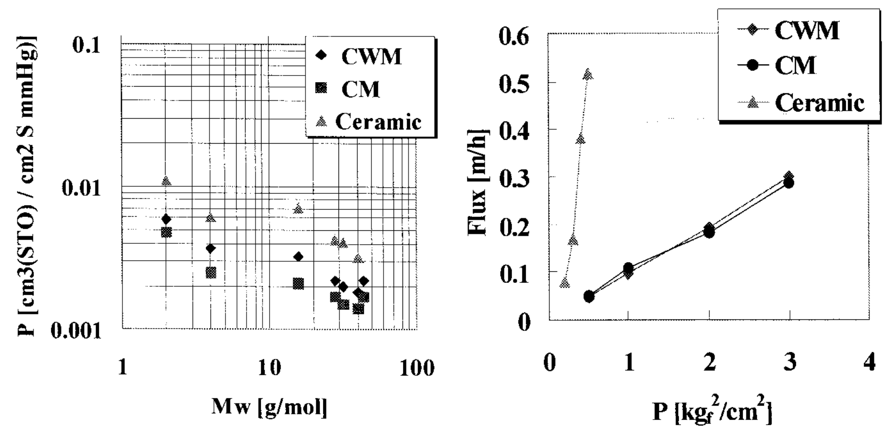

Fig. 6, 7. Comparison of gases and liquid permeability with CWM, CM and Ceramic.

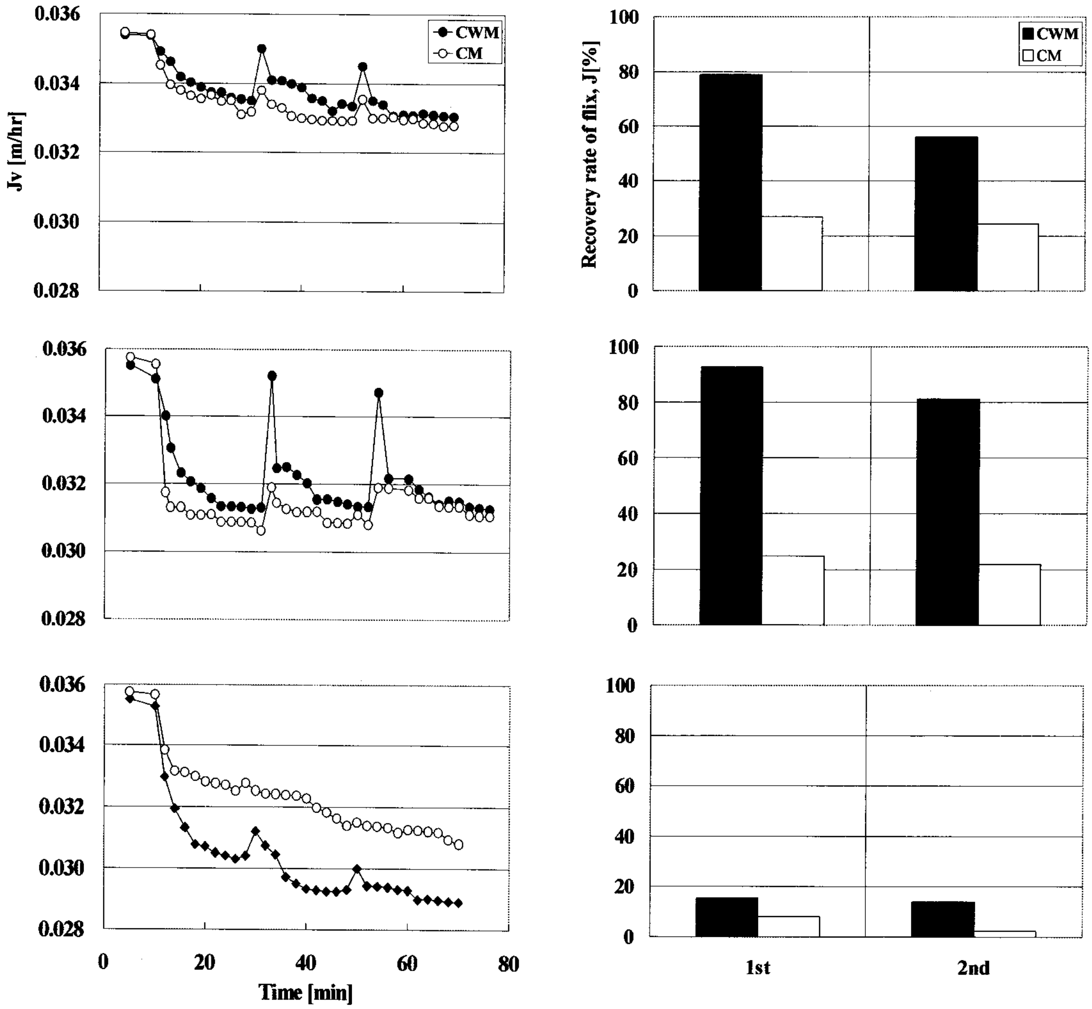

Fig. 8, 9. The permeability of PMMA solution and its recovery rate of flux with backflushing. (A) PMMA size 3 μm, (B) 0.8 μm, (C) 0.15 μm.

results clearly demonstrate cleaning recovery rates of the CWM are better than that of the CM, in the case of using 3 μm and 0.8 μm PMMA solution. Moreover, in all the cases, first cleaning processes have a higher recovery rate than that of second cleaning process. A maximum of 92.9% recovery rate can be obtained if 0.8 μm PMMA solution was employed.

4. Conclusions

We have found that the novel membrane, Carbon Whisker Membrane (CWM), is a promising membrane for cross-flow filtration. Because of its unique feature, carbon whiskers on the surface of the membrane can prevent the directly contact between the membrane body and particles so that the fouling/blocking could not occur easily compared to the membrane without carbon whiskers. In addition, it offers an advantage of easy cleaning for the regeneration of the membrane. However, the restriction of CWMs is that the size of the foulants should be bigger than the diameter of the whisker and the population density of carbon whiskers.

The results suggested that Carbon Whiskers on the surface of the membrane can prevent the directly contact between the membrane body and particles so that the fouling/blocking could not occur easily compared to the membrane without carbon whiskers. We also researched the relationship with the diameter, density of carbon whisker on the membrane surface and total flux of solutions. Finally, we will be able to control the diameter and density of carbon whiskers on the membrane and existence of carbon whiskers on the membrane, it is important factor, might be prevent fouling/blocking in the water treatment.

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