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Powdered Activated Carbon Coated Hollow Fiber Membrane: Preliminary Studies on its Ability to Limit Membrane Fouling and to Remove Organic Materials

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Abstract−A new approach to a membrane hybrid system by pre-coating the hollow fiber membrane with powdered activated carbons (PAC) was evaluated for its ability to minimize the fouling of the membrane and to remove organic material from wastewater. This preliminary study evaluates the performance of a microfiltration membrane coated with three kinds of PACs: wood based (WB), charcoal based (CB) and coconut based (HA). Broadly, two scenarios were evaluated: one with low amounts of PAC coated on the membrane and another at higher amounts of PAC coating. The results indicate that the pre-coated membrane can effectively arrest the fouling agents in the wastewater in reaching the membrane pores and thereby limit membrane fouling. Interestingly, it was also found that, without any pre-treatment or addition of PAC in the tank, the pre-coated membrane also had the ability to retain organic materials. For the hollow fiber microfilter membrane used in the study having surface area of 2.58×10^{-03} m^2 surface area, pre-coating the membrane individually with 458 mg of HA-PAC, 497 mg of WB-PAC and 906 mg CB-PAC, the reduction in permeate flux was as little as 14-20% after 8 hours of each operation and the maximum organic removals was about 76%, for all the three kinds of PAC coatings. The type of PAC coated on the membrane and the amount coated could be the key factors in deciding the performance of the system. Although further studies are required, it is evident that the PAC pre-coated membrane system has great potential in successfully reducing membrane fouling, which could improve membrane life, enhance process performance and reduce membrane cleaning time.

Key words: PAC, Coated Membrane, Hybrid Process

INTRODUCTION

In the field of water and wastewater treatment, the application of activated carbon in combination with microfiltration (MF)/ultrafiltration (UF) as a hybrid system is a promising and rapidly emerging technology, mainly for the removal of organic material. Studies have long been carried out by using PAC as a pretreatment before membrane operation or by adding PAC in the same tank where separation by MF/UF membrane takes place [Adham et al., 1991; Crozes et al., 1993; Jacangelo, 1995; Lebeau et al., 1998; Konieczny and Klomfas, 2002; Vigneswaran et al., 2003]. Although there has been some variation in the amount of organic removal depending on the type of membrane used, feed water characteristics and difference in operating conditions, one common problem faced is the rapid flux decline due to membrane fouling. In fact, membrane fouling is the major obstacle that hinders widespread application of the membrane process [AWWA Committee Report, 1992]. Causes of fouling are varied [Wakeman and Williams, 2002; Kaiya et al., 1996] and researchers are trying to deal with this issue in a multifaceted approach by designing new membranes, efficient pre-treatment, modifying membrane surface, modifying the system design, altering the hydrodynamics of the solution and developing a effective cleaning regime [Brink et al., 1993; Jacangelo et al., 1995; Lim and Bai, 2003; Ma et al., 2000]. Simpler and effective prospects are constantly sought after in this area.

This study investigates the ability of a PAC-coated microfiltration hollow fiber membrane to minimize membrane fouling and its possibility for organic removal from secondary treated domestic wastewater. Three kinds of PACs--Wood based (WB), Charcoal based (CB) and coconut based (HA) PACs–were individually coated on the membrane before the start of the study, and their performances were evaluated based on the permeate flux decline, turbidity removal and organic removal in terms of absorbance UV_{254} measurements.

EXPERIMENTAL

1. PAC, Influent Wastewater, and Membrane Characteristics

The characteristics of three kinds of PACs used and the secondary treated wastewater are given in Tables 1 and 2, respectively. The physical and chemical properties of the microfiltration hollow fiber membrane are given in Table 3.

2. PAC Coating

The membrane coating procedure employed in this study is only rudimentary and ways to make it more efficient and simpler are being evaluated. Without going into the exact procedure involved, a brief description of the coating operation involves the initial step of cleaning and drying of the membrane surface to remove trace organics, inorganics and moisture. Three kinds of PAC concentrate solutions were prepared by adding three different PACs (WB, CB and HA). Only one type of PAC was coated on the membrane at a time. For this laboratory scale study, a thick paste of PAC concen-

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Table 1. Characteristics of PACs

Specifications	Wood based PAC (WB)	Coal based PAC (CB)	Coconut based PAC (HA)
Bulk density (kg·m^3)	290-390	100-300	350-500
Surface area (m^2/g)	882	915.2	1,198.6
Mean pore dia (Å)	30.61	24.2	30.41
Micropore vol (cc/g)	0.34	0.192	0.067
Mean diameter (μm)	19.72	10.9	34.15
Nominal size	80% finer than 75 micron	55-65% finer than 45 micron	75% finer than 75 micron
Iodine number (mg/g min)	900	800	900

Table 2. Characteristics of wastewater

Parameters	Average values
pH	8.0
Turbidity (NTU)	1.0
Suspended solids (mg/L)	14.2
Conductivity (μS/cm)	611
Absorbance UV_{254}	0.085
TOC (mg/L)	4.7
BOD (mg/L)	12.4
COD (mg/L)	21.2
T-N (mg/L)	18.24
T-P (mg/L)	1.21

Table 3. Properties of MF hollow fiber membrane

Properties	Description/Value
Material	Polyethylene
Type	Hydrophilic
Total surface area (m^2) (10 modules 0.2 m length each)	0.00258
Pore size (μm)	0.4
Internal diameter (μm)	0.27
External diameter (μm)	0.41

trate solution was prepared by adding 6-7 g of PAC to 50 ml distilled water. At this PAC concentration, the PAC concentrate is almost like a paste instead of solution. However, the optimum amount of PAC required to make the coating solution is being investigated. Membrane was then dipped in the PAC concentrate solution until the entire membrane surface was covered with PAC. The PAC-coated membrane was then dried overnight at 50 °C. The coated membrane was then dipped in clean water to remove un-adhered PACs. The membrane was then immersed into the influent wastewater tank before the start of the study. The amount of PAC coated was evaluated by measuring the weight of carbon on the membrane. This was determined by removing the PAC deposit on the membrane, after the experimental run, by first physically washing the membrane surface and them by using ultrasonication (Branson- B-52H, Smith-Kline Company, USA). The washwater was then filtered through 150 mm filter paper (ADVANTEC, Japan). The filter paper was then dried and the weight of carbon on the filter paper was determined. The surface of the membrane with and without PAC coating was examined with a scanning electron microscope (SEM) (HITACHI, Japan, Model S-4700).

Table 4. Amounts of PACs pre-coated on the hollow fiber membrane

PAC type	PAC Pre-coating amounts (mg)/ 2.58×10^{-3} m^2 membrane surface area	
	Lower range	Higher range
Wood based (WB)	57	497
Coal based (CB)	80	906
Coconut based (HA)	33	458

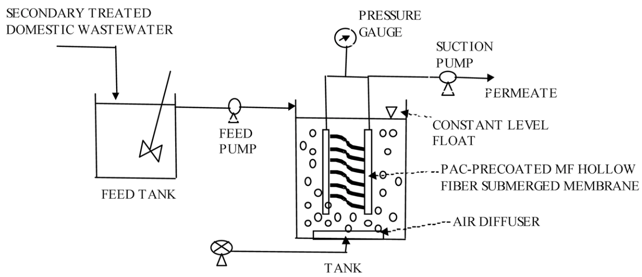

Fig. 1. Schematic of membrane hybrid system with pre-coated membrane.

At this stage, the amount of PAC to be coated on the membrane could not be controlled precisely. Making the PAC solution thicker or thinner was one way to approximately control the amount coated, when the membrane is immersed in the PAC solution. In this study, in order to demonstrate the effectiveness of pre-coating, the coating amounts on the membrane were broadly distinguished as low coating and high coating, as given in Table 4.

3. Hybrid System

The schematic of the PAC coated membrane hybrid system is shown in Fig. 1. The membrane hybrid system was operated as a continuous stirred tank reactor (CSTR). The wastewater was continuously fed from the feed tank so as to maintain a constant level in the influent tank. No additional PAC was added into the influent tank during the experiment. The permeate was not recirculated. The system was operated at a constant negative pressure.

The organic content was determined by measuring the absorbance at 254 nm by using a UV Spectrophotometer (SHIMADZU, Japan, Model UV-1700). Turbidity was measured with the turbidity meter (HACH 2100P). The permeate volume was monitored in order to calculate the permeate flux. UV_{254} and turbidity were measured constantly both in the influent tank as well as in the permeate. Before the samples for UV_{254} were collected, they were filtered through

150 mm filter paper. All samples were analyzed as per the standard procedures [APHA, 1998].

RESULTS AND DISCUSSION

The performances of each of the three PACs pre-coated membrane based on permeate flux, with low and high amounts of PAC coating are shown in Figs. 2 and 3, respectively. Coating low amounts of PACs (HA=33 mg, WB=57 mg and CB=80 mg) was not effective in minimizing the rate of permeate flux decline. However, for the membrane with higher PAC pre-coating (HA=458 mg, WB=497 mg and CB=906 mg) the flux decline was effective prevented. The maximum flux decline after 8 hours of experimental run for WB, CB and HA coated membranes was 14, 17 and 20%, respectively. Among the three PACs, the performance of WB coated membrane was found to be the best, both under and low and high coating amounts. Generally, greater part of flux decline occurs during the initial period of the membrane operation due to membrane pore blocking. But, in the case of pre-coated membrane, this was effectively prevented. The amount of coating and the nature of the particles coated on the membrane appear to control the passage of the fouling material in the wastewater in reaching the membrane. It was difficult to predetermine the exact amount of PAC coated on the membrane. However, the nature of PAC solution prepared and the physical properties of the carbon determined the amount able to coat.

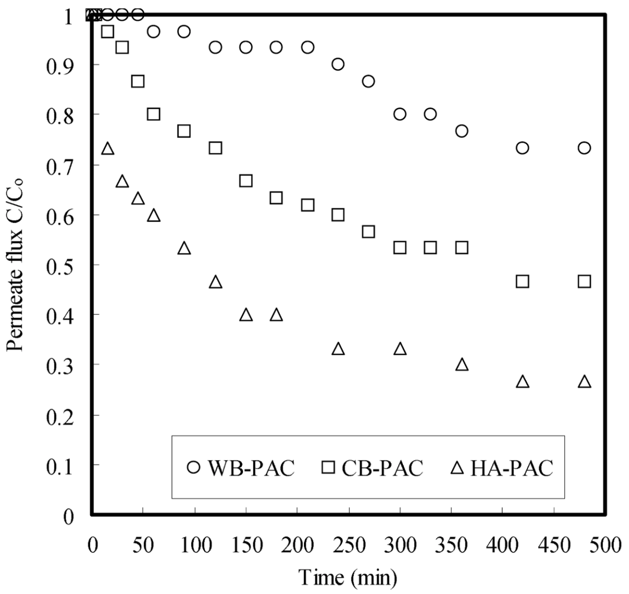

Fig. 2. Performance of the pre-coated membrane for three different PACs in terms of permeate flux (Amounts of PAC pre-coated: HA-33 mg, WB-57 mg and CB-80 mg; Initial flux: 348.8 L/m^{2}h).

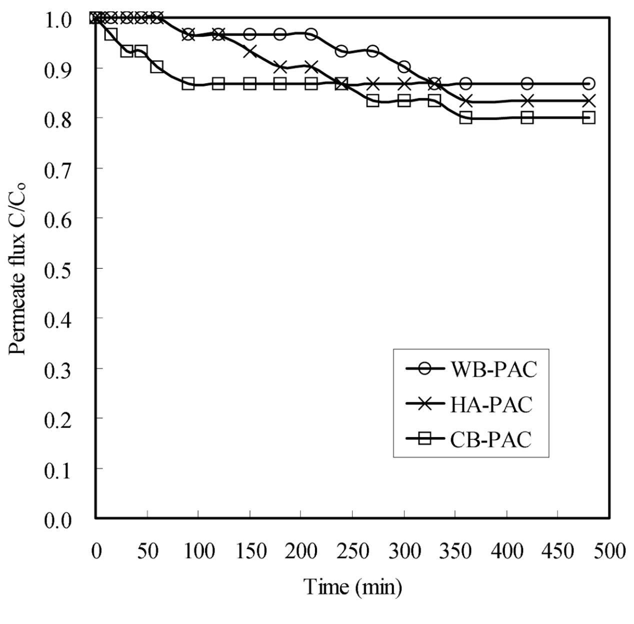

Fig. 3. Performance of the pre-coated membrane for three different PACs in terms of permeate flux (Amounts of PAC pre-coated: HA-458 mg, WB-497 mg and CB-906 mg; Initial flux: 348.8 L/m^{2}h).

Turbidity removal performance of pre-coated membrane is shown in Fig. 4. At higher PAC coatings the membrane was consistently able to remove and maintain the permeate turbidity below 0.2 NTU for all the three activated carbons. The average initial turbidity amount of the wastewater was 1.0 NTU. Here again, WB-coated membrane had the maximum capacity with turbidity removal of up to 89%.

Notably, apart from the ability of PAC pre-coated membrane to effectively reduce membrane fouling and remove turbidity, significant amount of organic removal was also observed. Figs. 5, 6 and 7 show the organic removal performance of WB, CB and HA coated membranes, respectively. The figures give the organic amounts based on UV_{254} absorbance values in the tank as well as in the permeate. At low amount of WB and CB-PAC coatings, the membrane was not able to retain any organic material. However, interestingly, it was observed that low amount of HA-PAC pre-coated membrane was able to remove up to 52% of initial organic material from the wastewater. The UV_{254} value of the original wastewa-

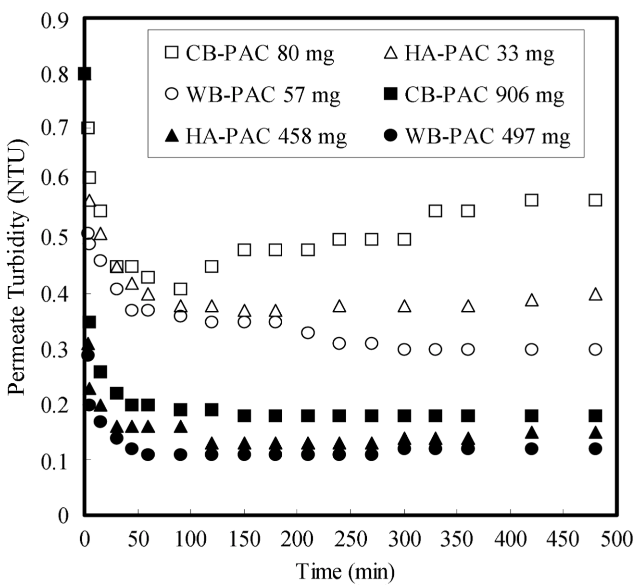

Fig. 4. Turbidity removal performance of the PAC pre-coated membrane (Initial turbidity of wastewater=1 NTU).

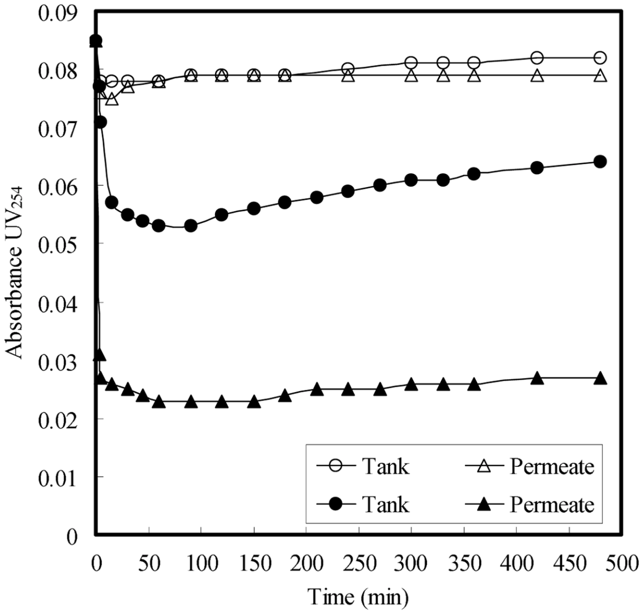

Fig. 5. Organic removal performance of the WB-PAC pre-coated membrane (For non-shaded symbols WB coating amount=57 mg, shaded symbols WB coating amount=497 mg, Initial UV_{254} absorbance=0.085).

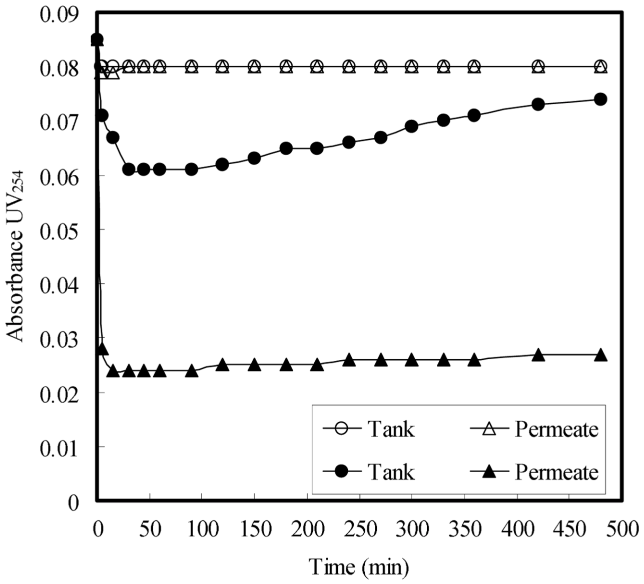

Fig. 6. Organic removal performance of the CB-PAC pre-coated membrane (For non-shaded symbols CB coating amount=80 mg, shaded symbols CB coating amount=906 mg, Initial UV_{254} absorbance=0.085).

ter was found to be 0.085. The difference in organic amounts between the tank and the permeate gives the retention ability of the coated membrane. After 1 hour of operation, about 35% of organic retention ability was observed for low amount (33 mg) of HA-coated membrane. At higher PAC coating, WB, CB and HA coated membrane achieved significant organic removal. The overall maximum organic removal obtained from the higher amount of PAC coated membrane are as follows: WB-PAC (497 mg)=73%, CB-PAC (906

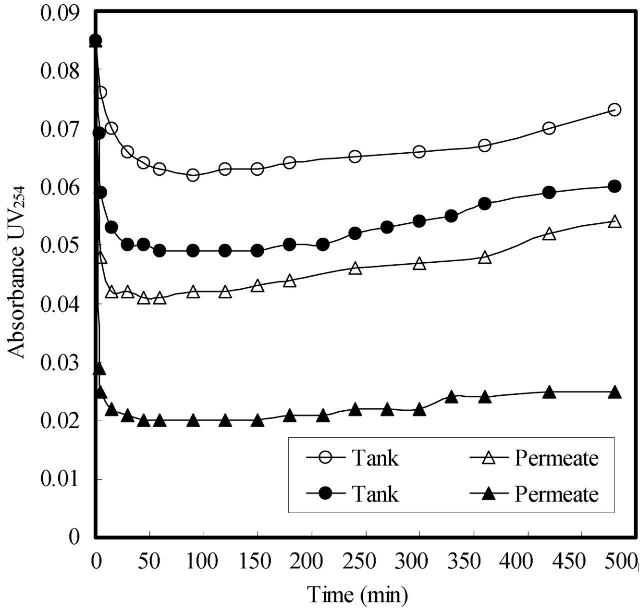

Fig. 7. Organic removal performance of the HA-PAC pre-coated membrane (For non-shaded symbols HA coating amount=33 mg, shaded symbols HA coating amount=458 mg, Initial UV_{254} absorbance=0.085).

mg)=72% and HA-PAC (458 mg)=76%. The organic retention ability of membrane increased with time reaching 58, 59 and 64% for HA, CB and WB PACs, at the end of 8 hours of operation. The organic reduction in the tank might largely be due to the adsorption by some amount of activated carbon detached from the coated membrane because of the agitation in the tank. It is also possible that very small amount of organic material might be adsorbed onto the PAC cake surface in the coated membrane. The PAC that strongly adheres onto the membrane surface does not seem to act as an adsorbent, as it forms a gelatinous micro-porous cake on the membrane. This was evident from the results with low-coated amounts of WB and CB, where there was very little PAC detachment from the pre-coated membrane and hence almost negligible amount of organic reduction.

In membrane processes, formation of the rejected external cake layer on the membrane surface is considered undesirable, as it can alter the performance. However, in some cases, the cake layer serves as a secondary membrane, which can aid in separation [Kuberkar and Davis, 2000]. The size of PAC particles (Table 2) is much greater than the pore size of the membrane (Table 3). So, the coated PAC particles will have a negligible effect on the permeability of the wastewater. However, upon combination with the organic material, an effective PAC-organic/PAC particle multiplayer matrix is formed on the membrane surface, which can alter the rejection of organic materials and thus reduce the amount of fouling material clogging the membrane. Fig. 8 shows the SEM images of clean membrane surface and the cross section of a membrane module with and without PAC coating.

More studies are required to identify the underlying phenomena and understand the exact mechanism behind the capacity of the coated membrane to remove organic material and prevent membrane fouling. A similar phenomenon of increased rejection of polyethyl-

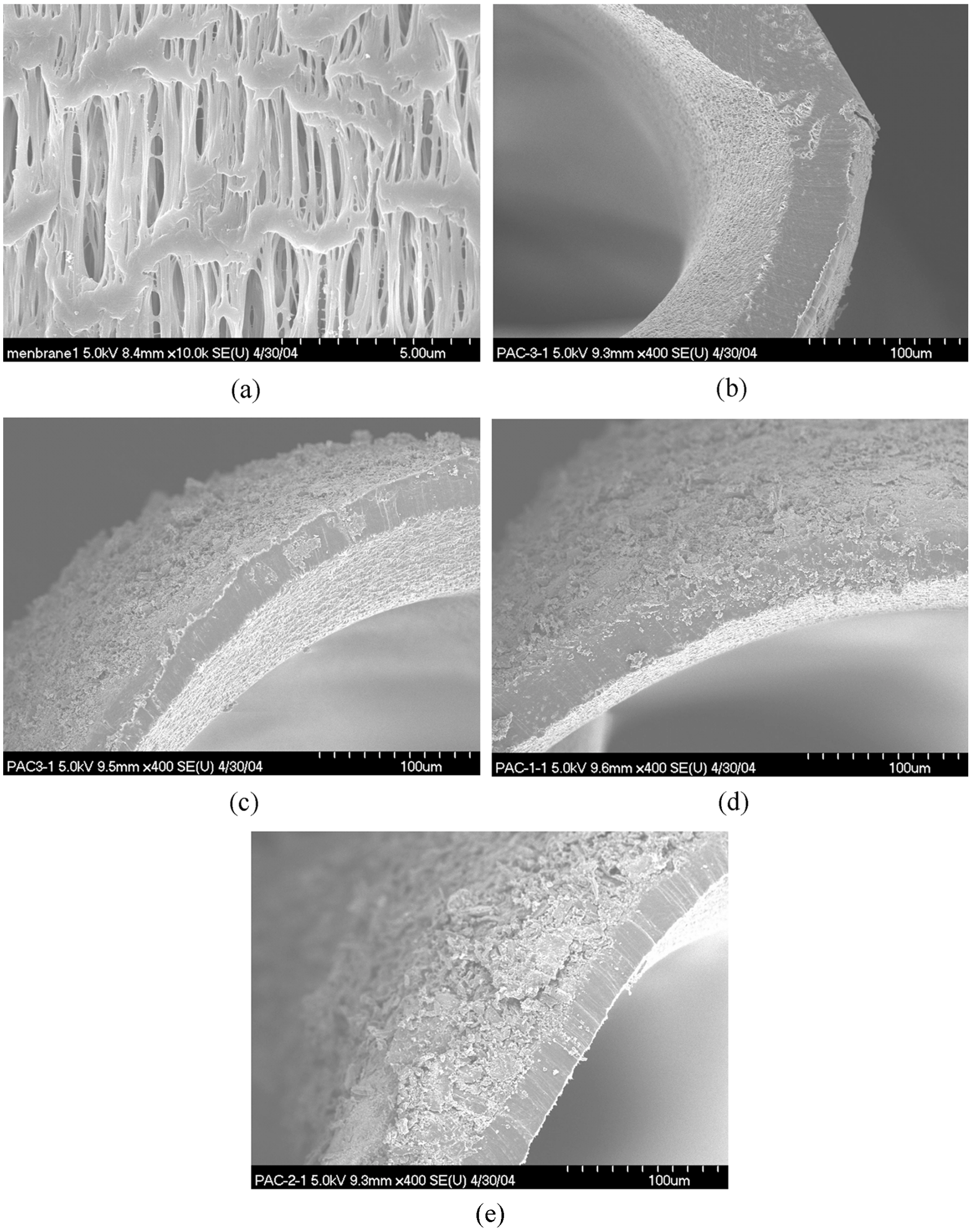

Fig. 8. SEM images showing the surface of clean membrane and the cross section of a membrane module with and without PAC coating ((a) surface of clean membrane (b) cross sectional view of membrane module (c) WB-PAC coated on the membrane (d) CB-PAC coated on the membrane (e) HA-PAC coated on the membrane).

ene glycol (PEG) and dextran due to the deposition of bovine serum albumin (BSA) and silica sol as secondary membrane was observed in earlier studies [Oers et al., 1995].

It was also observed that the pre-coated membrane performed much better than the system where PAC was added into the reaction tank instead of pre-coating [Thiruvenkatachari et al., 2004]. Detailed investigation on the performance evaluation of the three PACs introduced into the tank without pre-coating the membrane was reported earlier [Thiruvenkatachari et al., 2004]. Table 5 gives the overall performance of the hybrid system using uncoated membrane with optimum PAC dose introduced into the influent tank and compares with the performance obtained with pre-coated membrane. During membrane operation, PAC is deposited gradually on the membrane when it is placed in the PAC suspension. It can be seen from Table 5 that the amount of PACs deposited on the membrane after 8 hours of operation is 196 mg, 694 mg and 70 mg for WB, CB and HA-PACs, respectively. However, most of the flux decline happens during the initial phase of the operation, even before the PAC cake is formed on the membrane. This is prevented in the case of pre-coated membrane. Studies are being carried out to identify

Table 5. Performance of the hybrid process with PAC pre-coated membrane and when optimum amounts of PAC introduced in the tank for uncoated membrane

Parameters	PAC pre-coated			Without pre-coating (PAC in tank)		
	HA-PAC	WB-PAC	CB-PAC	HA-PAC	WB-PAC	CB-PAC
PAC amount	458 mg	497 mg	906 mg	125 mg/L	250 mg/L	750 mg/L
Amount of PAC deposited on membrane after 8 hrs expet. run (mg/L)	N/A	N/A	N/A	70	196	694
Maximum overall organic removal in terms of UV_{254} absorbance (%) (Initial 0.085)	76	73	72	70	68	65
Permeate flux decline (%)	17	14	20	33.3	40	50
Maximum turbidity removal (%) (Initial 1 NTU)	85	88	82	87.5	83.7	80

the optimum amount and thickness of PAC to be pre-coated on the membrane that can be effective in limiting membrane fouling and the rate of flux decline and maximize organic removal.

CONCLUSIONS

Preliminary studies on the performance of the PAC pre-coated membrane hybrid system were found to be very promising. Pre-coating the membrane with PAC successfully lowered membrane fouling, especially during the important early stages of membrane operation. With the PAC pre-coating amounts of 458 mg, 497 mg and 906 mg of HA, WB and CB PACs, the reduction in permeate flux was as low as 20% even after 8 hours of operation. Even without pre-treatment or PAC addition in the tank, the pre-coated membrane also had the ability to remove organic materials. The type of PAC coated on the membrane and the amount coated could determine the flux decline and organic removal performance of the system.

Efforts are underway to formulate an effective coating procedure, evaluate the optimum PAC coating amounts/thickness, and identify the exact mechanism involved in the organic removal mechanism and fouling abatement.

Some of the main advantages of the PAC pre-coated membrane operation are (i) simple and single step operation without any pretreatment for secondary and tertiary treatment, (ii) avoids additional PAC addition into influent tank, which reduces the strain on the membrane, (iii) significantly lowers membrane fouling, which could improve membrane life, enhance process performance and reduce membrane cleaning time.

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