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Preparation of Cellulose Acetate Membranes for Ultra- Nano- Filtrations

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ABSTRACT

Cellulose acetate (CA) membranes were prepared from CA powder, formamide and acetone by phase inversion. Production conditions used included evaporation times of 20, 30 and 60 seconds, gelation temperature of 1 – 2 °C and annealing temperature of 70 and 75°C. The product membranes were coded CA620-70, CA630-70 CA660-70, CA620-75, CA630-75 and CA660-75 and were tested to have Molecular weight cutoff (MWCO) between 1500 and 10000 Da. The pure water flux tests classified the membranes CA620-70, CA630-70 CA660-70, CA620-75 as ultra-filtration type and CA630-75 and CA660-75 as nano-filtration membranes. Tannin was easily filtered with the rejection of 78 - 100 % for different membrane types and pressures. Rejection of protein BSA was successful at nearly 100 % rejection for all the product membranes. SEM micrographs showed an average pore longest axis of 0.066 ± 0.029 micron and pore densities of 1.95 – 3.02 pores/micron^2. The membrane strength was tested to have the ultimate tensile strength of 1.64 – 2.82 N, Young's modulus of 54.74 – 175.36 MPa and the percent elongation at failure of 15.57 – 23.00

Key words: CA membrane, cellulose acetate, PEG, BSA protein, tannin

INTRODUCTION

Membrane filtration or separation is the most efficient way in separation and concentration treatments. It can be successfully used in nano-scale filtration of nano particles. The membranes with different pore sizes can be made by varying production conditions which include 2 main parameters, evaporation time and annealing temperature.

Cellulose acetate is an environmental friendly substance for making membranes since it is a non-toxic material and low can be available at cost. Membranes made from cellulose acetate have been used for brackish water or seawater desalination and for filtering methanol, ethanol, and urea in a reverse osmosis process. The process is used to separate substances in fluid mixtures under high pressure between 5.6-10.5 MPa for seawater desalination and between 1.4-4.2 MPa for brackish water desalination. Salt reject and permeate flux characteristics are essential to provide knowledge for the appropriate usage of the membranes.

This work was aimed to develop a wide range of CA membranes for ultra- to nano-filtrations by varying production parameters. Some product membranes was tested to separate tannin from tsunami-induced tannin-contaminated well water collected from Phang Nga province.

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MATERIALS AND METHODS

Preparation of membranes

Membranes were prepared from a mixture of 20 % cellulose acetate (Eastman Chemical, USA), 33 % formamide (AR grade, Ajax, Australia) and 47% acetone (AR grade, Merck, Germany). They were then cast on a glass plate at a 120-140 μm thickness forming a paste, The paste is left to evaporate time for 20, 30 or 60 seconds. The resulting polymer films are directly immersed for 30 minutes in distilled water at 1 - 2 °C. The membranes were then annealed for 3 minutes at 70 or 75 °C. After annealing process, the membranes were ready to use and stored in distilled water, and named according to the membrane production parameters, CA620-70, CA620-75, CA630-70, CA630-75, CA660-70 and CA660-75. For example, The CA620-70 was named by using the evaporation time of 20 second and annealing temperature of 70°C. Permeation tests under pressures were performed using a dead-end stirred cell (Bhongsuwan *et al.,* 2002).

Characterization of membranes

Permeation tests

The permeation tests are carried out at 25°C under an operating pressure of 20 - 80 psi for UF-membrane and 100 - 400 psi for NF membrane using a conventional dead-end stirred cell (Figure 1; Bhongsuwan *et al.,* 2002). The stirred cell is made of stainless steel to resist high pressure (0 - 400 psi). Pressure-controlled N_2 gas feeds water or salt solution in the closed storage into the stainless steel test cell. When salt rejection is studied, a magnetic stirrer in the system is started as soon as the feed is introduced into the cell which holds a circular piece of laboratory-prepared membrane of 2.3×10^{-3} m^2. Permeate is collected continuously and weighed (Satorius electronic balance) at the end of several period of time. Permeate flux is calculated by equation (1). The percentage of rejection (%R) of the contaminant (i.e., the PEG, tannin and BSA protein) in feed water can be determined from equation (2), (Field, 1993).

$$Permeate\ Flux = \frac{Volume\ of\ Permeate}{Time \times Area\ of\ Membrane} \quad (1)$$

$$\%\ R = 1 - \left(\frac{Concentration\ of\ contaminant\ in\ Permeate}{Concentration\ of\ contaminant\ in\ Feed} \right) \times 100 \quad (2)$$

Permeate flux is a plot of pure water flux ($Lm^{-2}hr^{-1}$) versus applied pressure (kPa). When the applied pressure was increased, the flux generally increases (Figure 2). In calculating the expected behavior at the higher pressure, it was assumed that the hydraulic permeability, Lp (flux divided by the effective pressure) remained constant. To change the unit of flux/pressure in $Lm^{-2}hr^{-1}$ kPa^{-1} to the unit of the hydraulic permeability ($ms^{-1}Pa^{-1}$) the value was multiplied by the constant 2.77×10^{-10}. Table 2 shows the slope, the hydraulic permeability and membrane classes of the product membranes. It was showed that membranes CA620-70, CA630-70 CA660-70 and CA620-75 are classified as the UF type while membranes CA630-75 and CA660-75 are of the NF type.

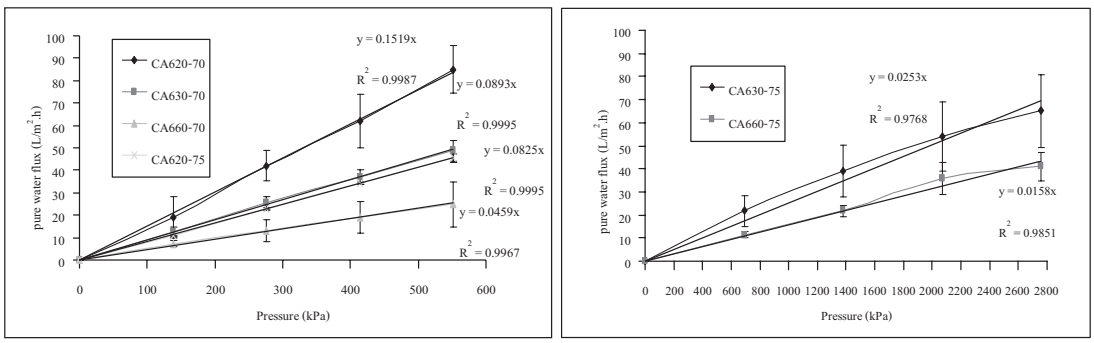
Table 1 Casting solution composition and film casting condition.

Membrane	CA6 (CA : Acetone : Formamide = 20 : 47 : 33)					
	CA620-70	CA620-75	CA630-70	CA630-75	CA660-70	CA660-75
Cast conditions						
- Evaporation time (Sec)	20		30		60	
- Annealing temperature (°C)	70	75	70	75	70	75
- Annealing time (Min)	3		3		3	
- Gelation medium (temp.)	Water (1 – 2 °C)		Water (1 – 2 °C)		Water (1 – 2 °C)	

The membrane molecular weight cut-off (MWCO) from the PEG tests

Molecular weight cut-off of the product pre-classified UF and NF membranes were determined from the PEG filtration tests at different molecular weights of PEG, i.e., PEG1500, 3000, 8000, 10000 and 20000 Da and at PEG concentration of 50 ppm.

Figure 1 A dead-end stirred-cell filtration system used in this study.



(a) (b)

Figure 2 Pure water permeation flux (PWF) measured at trans-membrane pressure (ΔP) of (a) 138 - 552 kPa for the membranes CA620-70, CA630-70 CA660-70 and CA620-75, and (b) 670 - 2758 kPa for membranes CA630-75 and CA660-75.

Table 2 Membrane characterization: L_p ($ms^{-1}Pa^{-1}$) and membrane classes.

Type of Mb	L_p (l/m^2 .h/kPa)	L_p ($ms^{-1}Pa^{-1}$)	Membrane class
CA620-70	0.1519	4.21×10^{-11}	UF
CA630-70	0.0893	2.47×10^{-11}	UF
CA660-70	0.0459	1.27×10^{-11}	UF
CA620-75	0.0825	2.29×10^{-11}	UF
CA630-75	0.0253	7.01×10^{-12}	NF
CA660-75	0.0158	4.38×10^{-12}	NF

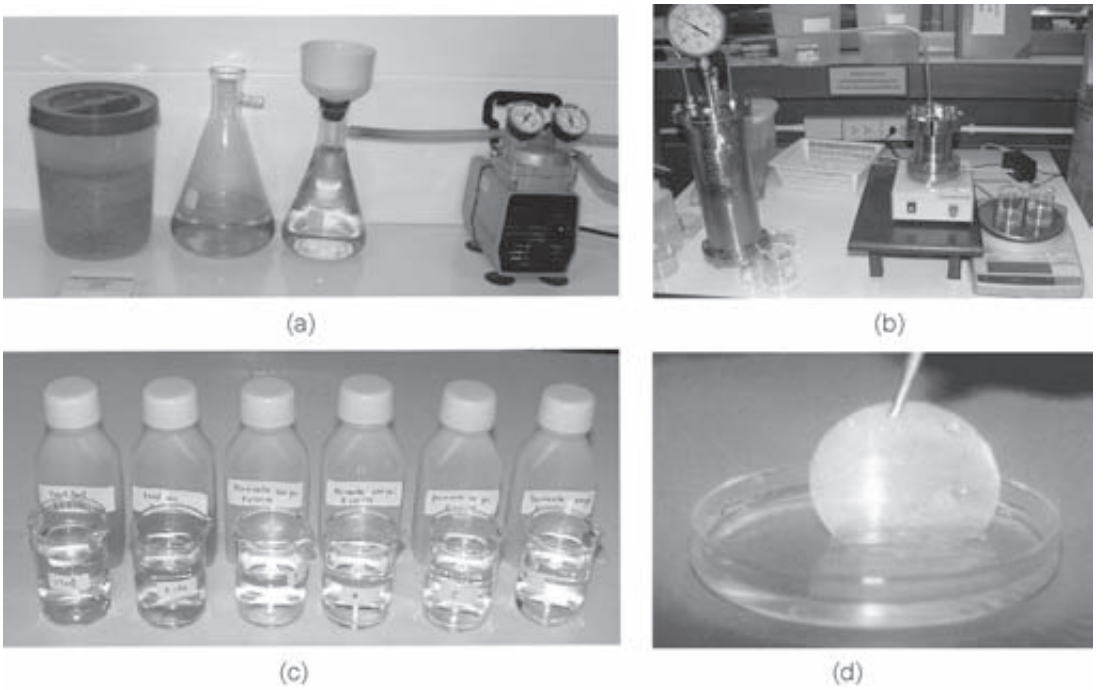


Figure 3 Filtration tests, (a) Sampled tannin contaminated well water from Ban Thung Dab, Mu 1 (after tsunami B.E. 2548), (b) after membrane filtration using membrane CA630-70 with a dead end stirred cell, (c) raw water (brown color, the two from the left) before filtration by membrane CA630-70 and after membrane filtration at pressures 100, 200, 300 and 400 psi, (d) membrane feature after filtration.

Tannin rejection from water

Tannin contaminated well water was sampled from the village's wells in Ban Thung Dab, Mu 1, Thambol Kao Phra Thong, Amphoe Kuraburi, Phang Nga province. The water has been affected by Tsunami event (B.E. 2548). The brown-color tannin water has been filtered using a 4.5 micron fiber glass filter (Figure 3a), which was unsuccessful in indicating a sub-micron range of tannin molecules. In filtration tests using our product membranes, clear permeate water was successfully obtained at pressures as low as 20 psi (Figure 3b, 3c). Table 3 shows the tannin rejection of the product membranes at pressures 60 psi. Membranes CA660 gave the most efficient tannin rejection among the membranes prepared using annealing temperature of 70 °C, while membranes CA630 and CA660 gave the highest rejection among the membranes with annealing temperature of 75 °C. Membrane production parameters, evaporation time and annealing temperature, clearly affected the membrane filtration properties.

Rejection of protein in water

Bovine Serum Albumin (BSA) protein filtration test of the product membranes is performed using BSA solution (Sigma, USA). BSA concentration was analyzed using the method of Lowry *et al.* (1951) by spectrophotometer (Lambda 25, Perkin Elmer, USA). The results show that all product membranes give nearly 100 % rejections at all pressures (Table 3)

Mechanical properties

Table 3 Product membranes properties after conditioning

Properties	Product membranes					
	CA620-70	CA630-70	CA660-70	CA620-75	CA630-75	CA660-75
MWCO (Da)	9000	9000	< 3000	7000	< 1500	< 1500
L_p (l/m^2 .h/kPa)	0.1519	0.0893	0.0459	0.0825	0.0253	0.0158
BSA reject (%) at 60 psi	99.7	100	100	100	100	100
Tannin reject (%) at 60 psi	78.25	79.36	95.22	80.49	97.26	100
Modulus of Elasticity (MPa)	54.74	69.70	84.25	73.93	106.34	175.36
Tensile strength (MPa)	1.93	1.68	2.06	1.64	1.92	2.82

Membrane morphological study using scanning electron microscope

Membrane morphology was examined using a SEM (JSM-5800LV, JEOL, Japan) at a maximum magnification of x10000. Magnification over x10000 was not possible as the sample were burnt by the high intensified electron beams. Analysis of pore sizes and density was performed by using a computer program called Carnoy version 2.0 (Schols and Smets, 2001). Pore sizes of most product membranes were not visible in the SEM micrographs at a magnification of x10000 (Figures 4-7), except for membranes CA620-70 and CA660-70 of which pores could be visible in SEM micrographs (Figures 4b and 6b). They were analyzed and shown in Table 4. Membrane CA620-70 has an average longest pore axis of 0.066 micron (S.D. = 0.029 micron), average pore area of 0.0035 micron^2 (S.D. = 0.0029 micron^2) and pore density of 1.95 pores/micron^2. Membrane CA660-70 has an average longest pore axis of 0.0656 micron (S.D. = 0.0292 micron), average pore area of 0.0034 micron^2 (S.D. = 0.0036 micron^2) and pore density of 3.02 pores/micron^2. Both visible and invisible pores in SEM micrographs at x10000 clearly indicate the sub-micron pore sizes of all product membranes.

Table 4 Product membranes pore sizes and distribution.

Mb Type	Pore area (micron^2)				Longest pore axis (micron)				Ref.
	Min	Mean	Max	Std.dev.	Min	Mean	Max	Std.dev.	
CA620-70	~ 0	0.0035	0.0233	0.0029	0.0211	0.0660	0.2316	0.0293	Figure 4b
CA660-70	~ 0	0.0034	0.0509	0.0036	0.0105	0.0656	0.2316	0.0292	Figure 6b

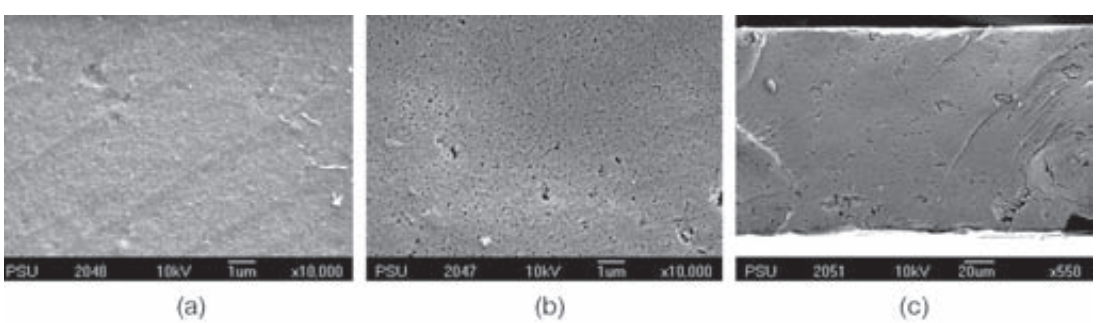


Figure 4 SEM micrographs of membrane CA620-70 at X10000, (a) the top surface, (b) the bottom layer, (c) the cross-section at X550.

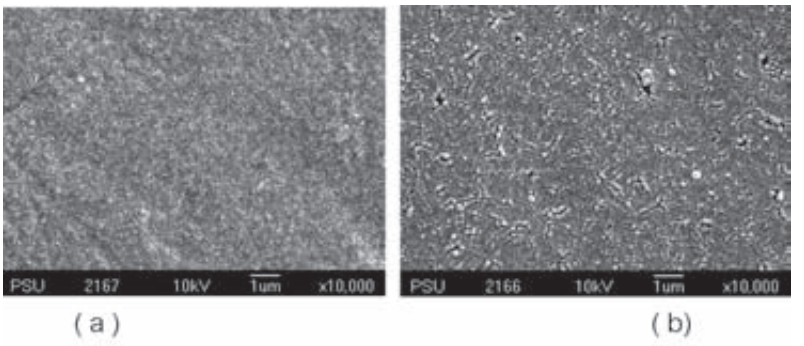


Figure 5 SEM micrographs of membrane CA630-70 at X10000, (a) the top surface, (b) the bottom layer.

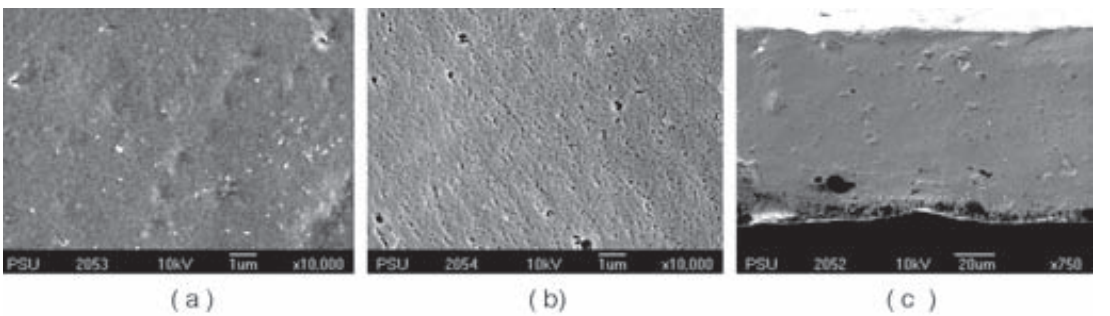


Figure 6 SEM micrographs of membrane CA660-70 at X10000, (a) the top surface, (b) the bottom layer, and (c) the cross-section at X 750.

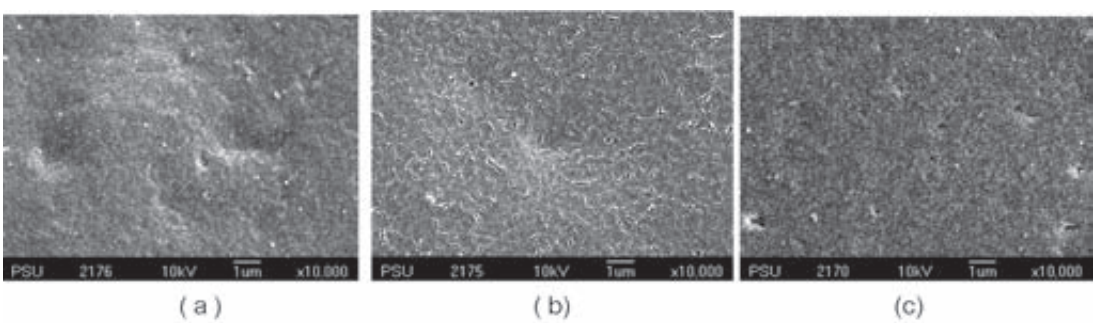


Figure 7 SEM micrographs of membrane CA620-75 at X10000, (a) the top surface, (b) the bottom layer, (c) the top surface of membrane CA630-75 at X10000.

CONCLUSIONS

CA membranes, prepared in the laboratory, were successfully used in experiments for sea food processing wastewater treatment. With regard to the MWCO of the product membranes, two kinds of membranes can be distinguished in relation with the two filtration processes: Ultra-filtration and Nano-filtration. Effect of evaporation time (20, 30 and 60 second) clearly indicated that longer evaporation times resulted in thickening skin layers and lessening the water fluxes, but increasing rejection efficiencies. Effect of annealing temperature (70 and 75 °C) showed that

raising the annealing temperatures reduced the water fluxes but improved the rejection efficiencies.

Morphological studies using a scanning electron microscope indicated a sub-micron range of pore size which could be seen in micrographs with x10000. Some pore sizes could be seen with average pore axis of 0.066 ± 0.029 micron and pore densities of 1.95 – 3.02 pores/micron^2. Tannin was easily filtered by the product membranes with the efficiencies of 78.25% rejection by membrane CA620-70 and 100% rejection by membrane CA660-75. Protein BSA rejection was successfully separated by using all the product membranes at nearly 100 % rejection.

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