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DEVELOPMENT OF CELLULOSE ACETATE MEMBRANES FOR NANO- AND REVERSE OSMOSIS FILTRATION OF CONTAMINANTS IN DRINKING WATER

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Abstract. Cellulose acetate (CA) membrane was produced from CA powder, formamid, and acetone. Annealing temperature of 80°C and evaporation times of 30, 60, and 90 seconds were chosen in preparation of the CA membranes named R530, R560, and R590, respectively. The membranes were tested using a dead-end stirred cell for filtration of NaCl salt, iron, manganese, and arsenic in the laboratory-prepared water and groundwater. Results of the tests using a membrane R530 at 400 psi showed, that the rejection efficiencies for salt, iron, and manganese in laboratory-prepared water with 3000 ppm NaCl , 2.0 ppm Fe, and 2.0 ppm Mn were 87%, 99%, and 92%, respectively, with a permeate flux of 21 Lm⁻²hr⁻¹. Tests for the groundwater containing 4815 ppm NaCl and 5.48 ppm Mn without acid treatment showed that membrane R530 gave the flux and rejection for salt and manganese at 24 Lm⁻²hr⁻¹, 85% and 98%, and for iron and manganese at 21 Lm⁻²hr⁻¹, 93% and 99%, respectively. In the filtration of arsenic, the prepared membrane had a As rejection of 68 – 70% at 300 and 400 psi when the feed was the laboratory prepared 1 ppm As⁺³ contaminated water but it was found to be more than 82 – 96% when the feed was a natural water. This is probably because the prepared membrane had a higher rejection efficiency for As⁺⁵ ions than As⁺³ ions. Ion selective capability of the CA membrane shows the potential to use the membrane in filtration of selective ions.

Keywords: Cellulose acetate membrane, reverse osmosis, nano-filtration, contaminated water, dead-end stirred cell

1.0 INTRODUCTION

Cellulose acetate is an environmental friendly substance for making membranes since it is a non-toxic material and not costly. 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 pressures between 5.6 - 10.5 MPa for seawater desalination and between 1.4 - 4.2 MPa for brackish water desalination [1].

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Charaterisation of salt rejection and permeate flux is essential to provide knowledge for the appropriate usage of the membranes.

Coastal villages in South Thailand are becoming increasingly dependent on brackish bore water for household usage during the extensive dry season, when the salinity was increased up to 3000 ppm. There is, therefore, a need to develop reverse osmosis membranes for these villagers so that cheap and good enough system can be provided in producing drinking water (WHO allowed total dissolved solid in drinking water at 1500 ppm salinity). In previous work, locally made cellulose acetate membranes were studied for salt rejection [2] using a cross-flow test unit, where the retentate was sent back into the system. This limited the possibility for a continuous study on the same membrane since the re-circulation would cause an increase in water temperature, which might affect membrane properties. Membrane characterization in this work was therefore, made using a dead-end stirred cell instead. The advantage is that it utilizes less amount of feed solution, and more information on membrane behavior during a long time filtration can be obtained.

This work describes the result of tests on membranes manufactured in terms of permeate flux, and salt (NaCl) rejection (SR%). As reported by Shah *et al.* [3], salinity limit for human use was between 3100-5000 ppm, the same salinity level as obtained from bore water in Sa-Ting-Pra district, Songkla Province. This study therefore, used NaCl concentration of 5000 ppm for the membrane SR test and the percentage of SR was estimated as solution conductivity. De-ionised water was used as a solvent in all cases, to avoid unexpected fouling during the dead-end testing. The study was made in comparison to a commercial reverse osmosis membrane.

2.0 MATERIALS AND METHOD

2.1 Membrane Ppreparation

The membranes R530, R560, and R590 used in this research were hand-made in the Membrane Science and Technology Research Center, Faculty of Science, Prince of Songkla University. They were made from cellulose acetate (CA, Eastman Chemical, USA) using the phase inversion process, in which CA (23.5%; Eastman Chemical, USA) was dissolved in acetone (46.5%, Merck, Germany), and formamide (30%; Merck, Germany) was used as the additive. After being well mixed, the CA solution was casted on a glass plate to form a thin liquid film of ca. 120 – 150 mm thick. This membrane was evaporated in air under room temperature at 25°C. Evaporation time was varied from 30, 60, and 90 seconds to ensure that the dense layer (or skin layer) of the membrane was formed and salt permeability was minimum [4]. Membrane gelation was made in ice water. During this process, a double-diffusion process occurred. Acetone and formamide (swelling agent) had escaped the membrane while water had diffused into it and porous layer of the membrane was formed. Gelation temperature was controlled $(0 - 3^{\circ}C)$ because higher gelation temperature could

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increase water permeability but decrease the salt permeability. Membrane annealing process was conditioned in water at 3 minutes and the annealing time was varied at 75, 80, and 85°C water temperature. This process was needed to increase the density of skin layer, and modify pore size and porosity of the membrane. After annealing process, the membranes were ready to use and were stored in distilled water. A test for salt permeation under pressures was performed using a dead-end stirred cell. A parallel study was performed on a commercial membrane Nitto Denko LES-90 [5].

2.2 Filtration Procedure

Filtration tests were performed using a dead-end filtration system (Figure 1). The stirred cell is made of stainless steel to resist high pressure (0 – 400 psi). N₂ pressure fed NaCl solution in the closed storage into the stainless steel test cell. When salt rejection was studied, a magnetic stirrer in the system was started as soon as the feed was introduced into the cell. A piece of laboratory-prepared membrane of 2.3×10^{-3} m² was placed into the cell. Permeate was collected continuously and weighed (Satorius eletronic balance) at the end of several period of time. Permeate flux was calculated from equation (1), using the density of water. The percentage of rejection (%R) of the contaminant (NaCl salt, iron, manganese and arsenic) in feed water can be determined from equation (2) [6].

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

$$\% R = \left(1 - \frac{\text{Concentration of contaminant in permeate}}{\text{Concentration of contaminant in feed}}\right) \times 100$$
(2)

The NaCl concentration was estimated through the conductivity value (Activon Model 301). Salt rejection from both sides of the membranes was studied to test for their homogeneity. Arsenic concentration was determined using the silver diethyldithiocarbamate method and the ICP-AES (Perkin Elmer). Iron and manganese were analysed using spectrophotometric method (Spectroquant NOVA 60).

2.3 Sampling and Preparation of Contaminated Feed Water

Feed water used in the filtration experiments comes from 2 main sources, (1) natural contaminated water and (2) laboratory preparation of contaminated water. Natural contaminated water is sampled from the area, where contamination of water causes problems to people living there. The district of Sathing Phra of the Songkhla province is well known to have a problem of high salinity of well water. It is also true for iron and manganese contamination in well water from this area. Another potential pollutant found in well water is arsenic, which causes a serious problem in the district of

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High pressure N₂ gas Feed Feed Stirred cell Porous substrate Permeate Magnetic stirrer Balance

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Figure 1 Flow diagram of the dead-end stirred-cell filtration system

Ronphiboon of the Nakorn Srithammarat province. This area is also well known to have a high number of human skin cancer cases for the villagers, who live in the area of abandoned tin mining zones. It is now known that the skin cancer evidences in this area are caused by arsenic content in well water. This arsenic has been leaching from arsenic sulfide minerals, which are associated in tin mineralization in this land. Standard contaminated water with known concentration of pollutants was prepared in our laboratory. Salt, iron, manganese and arsenic were selected as the contaminants dissolved with distilled water. The contaminants concentration was prepared in comparable with those found in natural water.

3.0 RESULTS AND DISCUSSIONS

3.1 Effect of Evaporation Time and Annealing Temperature During Membrane Preparation

Various membranes were produced using different evaporation time and annealing temperatures, and found that the suitable range of evaporation time and annealing temperature is between 30 - 90 seconds, and $75 - 85^{\circ}$ C, respectively. We had further prepared our membranes by fixing the evaporation time at 60 seconds while the annealing temperature had been varied at 75, 80, and 85°C. The membranes prepared with different annealing temperatures were tested for filtration properties, i.e., pure water flux and salt rejection efficiency using a dead-end stirred cell (Figure 1).

At a fixed evaporation time of 60 seconds, the result showed that membrane produced using an annealing temperature of 75°C had the highest fluxes at 400 psi operating pressure, both for pure water and salt water at 22.6 and 21.1 L hr⁻¹ m⁻², respectively (Figure 2a), but lowest salt rejection at 71.6 %, comparing with %SR of 83.5 and 85.1, when the annealing temperatures of 80 and 85°C were used, respectively (Figure 2b). As higher flux membranes are always obtained with lower salt rejection property, we designed to prepare the membrane by choosing the annealing temperature

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of 80°C, which is the optimum condition in between the highest flux and the highest salt rejection at 75 and 85°C, respectively.

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The new membranes were then prepared using the optimum annealing temperature of 80°C and annealing time of 3 minutes with varying evaporation time of 30, 60, and 90 seconds, and coded R530, R560, and R590, respectively. The filtration tests in terms of flux and salt rejection were then performed using the new membranes R530, R560, and R590.

In this filtration tests, we used a 3000 ppm NaCl solution as the feed water in order to determine both flux and contaminant rejection efficiency of the prepared membranes. Filtration results showed that the permeate fluxes obtained at 0 - 400 psi operating pressure of the membrane R530 (evaporation time = 30 seconds) ranged from 5 to 20 L m⁻² hr⁻¹, which was much higher than those (5 – 10 L m⁻² hr⁻¹) of the membranes R560 and R590 (evaporation time of 60 and 90 seconds, respectively), especially at high pressure (Figure 3a), while the salt rejections were not different for all three membranes (Figure 3b). This is the reason for choosing to prepare and use membrane R530 in further filtration tests.

3.2 Filtration of Salt, Iron and Manganese in Laboratory-Prepared Contaminated Water

Membrane R530 was used in this filtration tests. Feed solution was prepared in the laboratory by dissolving the contaminants, i.e., salt (NaCl), iron, and manganese in distilled water. The concentration of salt, iron, and manganese in the laboratory prepared



Figure 2 Effect of annealing temperature to the produced membrane property (a) Permeate flux and (b) % Salt rejection. The operating pressure is fixed at 400 psi.



Figure 3 (a) The effects of evaporation time in membrane preparation to permeate flux and salt rejection efficiency

Figure 3 (b) The effects of evaporation time in membrane preparation to permeate flux. The feed water is a 3000 ppm NaCl solution.

as contaminated water is 3000, 2.0, and 2.0, ppm, respectively. Filtration result shows that permeate flux varied from $8 - 21 \text{ Lm}^{-2} \text{ hr}^{-1}$ at the operating pressure of 100 - 400 psi (Figure 4a). Salt, iron, and manganese rejections at the same range of operating pressures are 68 - 87 %, 98 - 99 %, and 89 - 92 %, respectively. Result indicates that our membrane R530 was suitable for filtration of iron and manganese in water. However, in natural water which may contain many species of dissolved contaminants, the result may be different.

3.3 Filtration of Salt, Iron and Manganese in Natural Contaminated Water

Natural contaminated water used in this experiment was collected from Sating-Phra district, Songkhla province. This raw groundwater is contaminated with saline (NaCl), iron, and manganese of 4815, 0.06, and 5.48 ppm, respectively. Groundwater was separately sampled into 2 set of 50 litres each. The first part was acidified with HNO₃ to prevent oxidation. The second part was left in its natural condition in which, the precipitation occurred within a few hours. Membrane R530 was used in this filtration tests. Filtration results show that permeate flux (9-24 L m⁻² hr⁻¹,) of non-acidified feed water, as shown in Figure 5a. Salt and manganese rejections in non-acidified feed water were 67 – 85% and ca.98%, respectively while in acidified feed water, the iron and manganese rejections



Figure 4 Filtration results of the membrane R530. Concentrations of NaCl, iron, and manganese in laboratory-prepared feed water were 3000, 2.0, and 2.0 ppm, respectively. Filtration results included (a) permeate flux and (b) salt, iron, and manganese rejection at different operating pressures.

were 77 - 93 % and 97 - 99 %, respectively (Figures 5b and 5c). Manganese rejection using membrane R530 was almost 100 %, both in acidified and non-acidified feed water. Salt rejection in acidified feed water is not shown because the TDS of acidified water was much lower due to the acid content, and cannot be filtered by membrane R530. In non-acidified feed water, the precipitation of iron oxides due to the oxidation, occurred within a few hours. This resulted in a very low concentration of iron in non-acidified feed water and then, iron rejection (is not shown here).

3.4 Filtration of Arsenic in Natural Contaminated Water

Arsenic contaminated feed water used in this filtration tests includes (1) a laboratoryprepared As contaminated water with As concentration of 1.02 ppm (sample 1 in Table 1), (2) As-contaminated groundwater, acidified, and not-acidified with HNO₃ collected from Ronphiboon district (samples 2.1 and 2.2 in Table 1), and (3) As contaminated shallow well water, acidified and not-acidified collected from Ronphiboon district (samples 3.1 and 3.2 in Table 1). Arsenic concentrations in groundwater and shallow well water collected from Ronphiboon district range 1.67 - 2.71 ppm, and 0.38 ppm, respectively (Table 1). The As contaminations in water collected from Ron Phiboon district are higher than the maximum concentration level for safe drinking water standard.



Figure 5 Filtration results of membrane R530. Concentrations of NaCl, iron, and manganese in natural contaminated feed water were 4815, 0.06, and 5.48 ppm, respectively. Results include (a) permeate flux and (b) iron and manganese rejection in acidified feed water, and (c) salt and manganese rejection in non-acidified feed water.

Filtration of arsenic in feed water using our laboratory prepared membrane R530 was performed at the operating pressure of 300 and 400 psi. Filtration result is shown in Table 1. Result shows that the As rejection of 68 - 70 % was obtained for water sample 1, which was the laboratory prepared As contaminated water, while the As rejection was higher than 96 % for groundwater and higher than 82 % for shallow well water. The difference in As rejection in laboratory prepared and natural feed water is

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most probably a result of arsenic ionic species contents in the feed water. The laboratory prepared feed water contains only As^{3^+} ions as we used As_2O_3 dissolved with distilled water. However, except for As^{+3} ions, the As^{+5} ions have been reported to be presented with a large fraction in natural water. Filtration result indicates that our cellulose acetate membrane R530 had a higher efficiency in filtering out As^{+5} ions than As^{+3} in natural water as having been reported by Urase *et al.* [7].

Table 1 Result of arsenic filtration using R530 membrane in laboratory-prepared As-contaminated water and natural As-contaminated water collected from Ron-Phiboon district, Nakorn Sri Thammarat province.

Water sample code	As conc. in feed water (ppm)	Arsenic conc. in permeate (ppm) at operating pressure		% As rejection	
		300 psi	400 psi	300 psi	400 psi
1	1.02	0.33	0.42	67.9	70.2
2.1 (acidified)	1.67	< 0.07	< 0.07	> 95.8	> 95.8
2.2 (not-acidified)	2.71	< 0.07	< 0.07	> 97.4	> 97.4
3.1 (acidified)	0.38	< 0.07	< 0.07	> 81.6	> 81.6
3.2 (not-acidified)	0.38	< 0.07	< 0.07	> 81.6	> 81.6

Note: Sample 1 is the laboratory-prepared contaminated water with As concentration of 1.02 ppm. Samples 2.1 and 2.2 are groundwater collected from Ronphiboon district, and samples 3.1 and 3.2 are shallow well water sampled from Ronphiboon district. As concentration of 0.07 ppm in the table indicates As detection limit of the ICP-OES at the Scientific Instrumentation Unit, the Faculty of Science, Prince of Songkla University.

3.5 Filtration Tests of the Commercial Membrane Nitto Denko LES90

To compare the filtration property of our laboratory prepared membranes (R530) with the commercial ones, we choose the Nitto Denko LES90 membrane, which is of the same type with our membranes. Filtration results show the permeate fluxes ranged between 3 and $14 \text{ Lm}^{-2} \text{ hr}^{-1}$ (Figure 6a), and the salt and manganese rejections were 79 - 94 %, and 92 - 96 %, respectively (Figure 6b). It is obvious that our laboratory prepared membrane R530 has higher flux than that of the LES90 membrane, but comparable in salt and manganese rejection efficiency.

4.0 CONCLUSIONS

The CA membrane is produced from a mixture of cellulose acetate (23.5 %) formamide (30 %) and acetone (46.5 %). The optimum casting condition for the preparation of CA membrane coded R530 includes the evaporation time of 30 seconds, annealing

Figure 6 Result of filtration tests for commercial membrane Nitto Denko LES90, (a) fluxes over the 200 – 400 psi operating pressure and (b) salt and manganese rejection. Feed water is a groundwater from Sathing Phra district.

temperature and time of 80°C and 3 minutes, respectively. Tests of the prepared membrane in filtration of salt (NaCl), iron, and manganese in natural contaminated water showed the permeate fluxes of $8 - 24 \text{ Lm}^{-2} \text{ hr}^{-1}$, salt rejection of 67 - 85 %, iron rejection of 77 - 93 %, and manganese rejection of 97 - 99 % during the operating pressure of 100 - 400 psi. The manganese rejection was almost 100 % at all tested conditions of feed water.

In the filtration of arsenic, the prepared membrane had a As rejection of 68 - 70 % at 300 and 400 psi, when the feed water was the laboratory prepared As⁺³ contaminated water but it was found to be more than 82 - 96 %, when the feed water was a natural As contaminated water. This is probably because the prepared membrane has a higher rejection efficiency for As⁺⁵ ions than As⁺³ ions. Ion selective capability of the CA membrane shows the potential to use the membrane in a filtration of selective ions.

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