

# Fabrication and Application of Removing Microcystin of CTA-based Forward Osmosis Membrane

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**Abstract**—CTA-based membranes for forward osmosis (FO) were prepared by immersion precipitation. Casting composition and coagulation conditions—solvent/acetone ratio, temperature, evaporation time of coagulation bath—were optimized to obtain membranes with best performance. Membranes were characterized by various available methods to testify the performance in forward osmosis system. The CTA membrane showed a water flux higher than 3.8 LMH and a good NaCl rejection of 95% when using 2 M glucose solution as the draw solution and 0.6 M NaCl solution as feed solution. Besides, experiments were attempted to remove microcystin by applying FO technology. More than 80% of the microcystin removal rate was obtained in this experiment.

**Keywords**--CTA-based membrane; Phase inversion; Component solvent; Microcystin

## I. INTRODUCTION

Water shortage, a global issue resulting from the population explosion and water pollution, is facing an unprecedented challenge. To keep up with the supply of fresh water, tremendous efforts were made by seawater desalination<sup>[1]</sup> and water purification by a lot of researchers. In the past decades, scientists were attracted by FO<sup>[2]</sup>, a novel technology with no massive energy input and high water recovery rates. Moreover, FO has gained vast popularity in the areas, such as desalination of seawater and brackish water<sup>[3]</sup>, concentration of dilute solutions<sup>[4-5]</sup>, fuel cell<sup>[6]</sup>, power generation<sup>[7]</sup>, agriculture water<sup>[8]</sup>.

Recently, a newly proposed forward membrane<sup>[9-10]</sup> was prepared comprising a highly porous sublayer sandwiched between two active layers via phase inversion. ICP<sup>[11-13]</sup> was well mitigated by this membrane, while water flux also decreased due to the two layer structure.

In this article, optimized FO membranes were prepared by immersion precipitation to reduce ICP. CTA-based membranes were prepared by using different ratios of NMP and dioxane. And acetone is considered as a volatile constituent in the component solvent. Different additives contents and coagulation conditions were also discussed to obtain the homogeneous casting solution. The objective of this paper is to reveal the effect of volatile solute and additives on the structure of membrane. The novel potential application of FO was successfully to remove the residual microcystin.

## II. EXPERIMENT

In this work, the fabrication of CTA-based membranes was based on the immersion precipitation [14]. After solidification, the membrane was taken away from the glass,

and rinsed with DI water to remove the residual solvent before undergoing heat treatment [15] for performance test.

Compositions of casting dope were optimized to enhance performance by attempting various ratios of acetone/solvent (1:7, 1:5, 1:3 and 1:1). The influence of coagulation conditions—temperature, evaporation time — were investigated with a unchanged casting solution of 14 % CTA, 60 % dioxane, 14% NMP, 8% acetone, 4% TEP.

These membranes prepared by phase inversion were named as M-A, M-B, M-C, M-D, M-E, M-F, M-G, M-H, M-I, M-J, M-K, M-L, M-M, M-N, M-O, M-P in the following paper.

### A. FO Performance Tests

As shown in Fig 1, tests of FO performance were conducted on a lab-scale cross-flow filtration setup. The water flux ( $J_w$ , Lm<sup>2</sup>h<sup>-2</sup>, abbreviated as LMH) was calculated by the volume change of the DS resulting from the permeating water as formula (1):

$$J_w = \frac{\Delta V_w}{A_M \times \Delta t} \quad (1)$$

where  $\Delta V_w$  (L) is the volume of water flowed across the membrane from the feed side to the draw side in certain time interval  $\Delta t$  and  $A_M$  is the area of the effective membrane, which was 0.00385 m<sup>2</sup> used in this FO module.

The salt reverse flux was calculated using the following equation:

$$J_s = \frac{\Delta(C_t \times V_t)}{A_M \times \Delta t} \quad (2)$$

where  $C_t$  and  $V_t$  are the salt concentration and the volume of the feed solution at the end of test, respectively.

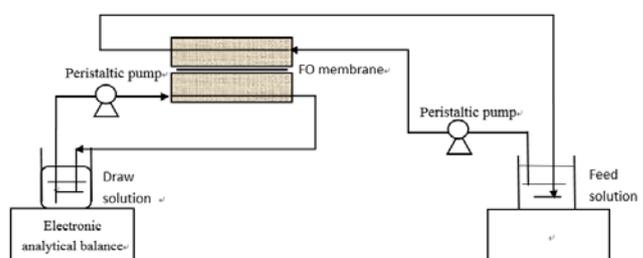


Fig.1: Process of FO

And for rejection test, 2000ppm NaCl solution was used as feed solution and the 2M Glucose as draw solution. The salt rejection  $R$  (%) was calculated as follows:

$$R(\%) = \left(1 - \frac{C_{permeate}}{C_{feed}}\right) \times 100\% \quad (3)$$

where  $C_{permeate}$  and  $C_{feed}$  were NaCl concentration of permeate and feed solution, respectively.

### B. Analytical tools

#### 1) Scanning electron microscopy (SEM)

Surface and cross-sectional of membrane was observed by SEM(S-3400N, Japan).

#### 2) Mean pore size and pore size distribution (PSD) [16]

The pore size and pore size distribution of CTA membranes were determined by modeling the rejection of simple uncharged solutes under hydraulic pressure as described in references [17].

#### 3) Porosity

For the measurement of porosity, weight of membranes was measured for wetted sample ( $m_0$ ) and freeze-dried sample ( $m_p$ ). Since the density of water ( $\rho_w$ , 1.00g/cm<sup>3</sup>) and CTA material( $\rho_p$ , 1.33g/cm<sup>3</sup>) are known, the overall porosity  $P$  (%) is obtained:

$$P(\%) = \frac{V_{water}}{V_{total}} \times 100\% = \frac{(m_0 - m_p) / \rho_w}{(m_0 - m_p) / \rho_w + m_p / \rho_p} \times 100\% \quad (4)$$

#### 4) HPLC of the microcystin residues [18]

The concentration of microcystin was measured by HPLC, and MC-RR was dissolved with 300  $\mu$ L of methanol. Mobile phase was prepared by methanol and phosphoric acid at ratio of 66% and 34% respectively, and pH was set 3.00 $\pm$ 0.01. The injection volume was 30 $\mu$ L and the flow rate was 0.8mL/min at 40  $^{\circ}$ C.

### III. RESULTS AND DISCUSSION

The cross section of the membrane was observed as shown in Fig 2. The dense layer of top surface was formed due to rapid evaporation of acetone when the casting solution quickly immersed in the coagulation bath (usually deionized water). The big open-pore structure was well accorded with Hansen parameter [19]. It was the fact that water diffused to polymer solution more quickly than the diffusion between solvents and water. It is evident that adaptation of membrane morphology adjustment to specific needs of treated solution may be obtained by an appropriate choice of acetone.

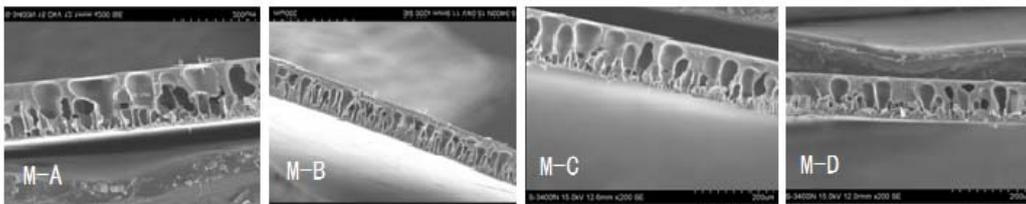


Fig.2: SEM images of cross section in CTA membranes

Concentrations of 12-16% of CTA was studied in this research. As shown in Fig 3, with the increasing concentration of CTA, the porosity decreased. It is well established that the higher is the polymer concentration in

the casting solution, the denser is the active layer and the closer is the pore size distribution. This was mainly attributed that polymer concentration in the interface increased with the initial increased concentration.

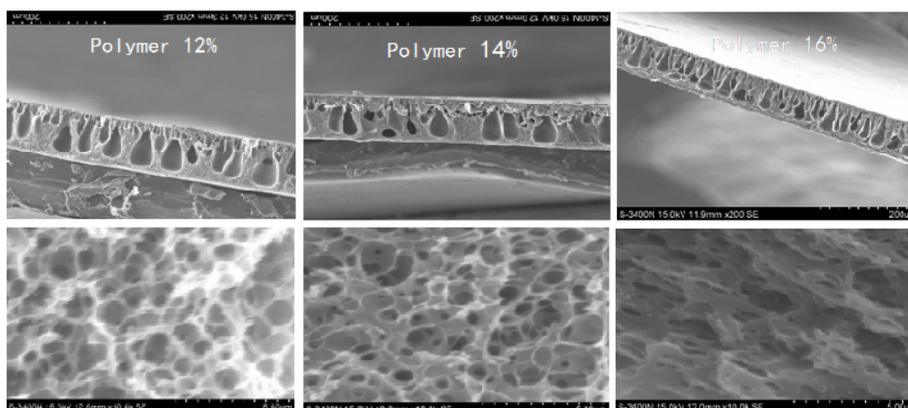
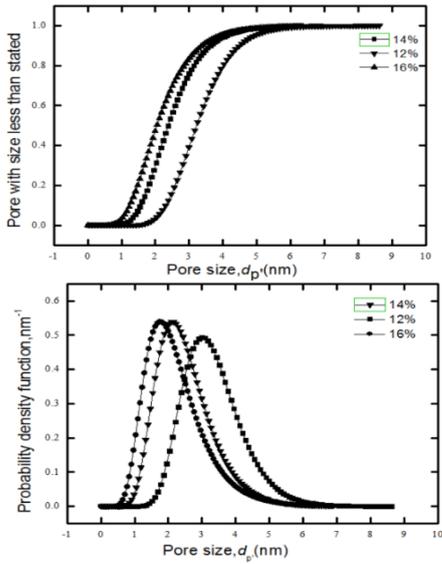


Fig.3: Effect of CTA concentrations on membrane cross structure



List	$\mu$ (nm)	$\sigma$	MWCO(Da)
M- Q ( CTA=14% )	2.37	1.39	4479.67
M- R ( CTA=12% )	3.21	1.30	6591
M- S ( CTA=16% )	2.04	1.47	3952

Fig.4: Cumulative pore size distribution curves and probability density function curves were obtained under different contents of CTA.

Due to low-boiling-point of acetone, NMP and dioxane were brought out from the casting with solution evaporating in the room temperature. Macropore appeared in the surface of membrane and mean pore diameter increased with the increase of evaporation time. Therefore, it can be safely concluded that shortening the evaporation time was in favour of forming membrane with good separation performance. The relationship between evaporation time and performance of membrane was shown in Fig 5.

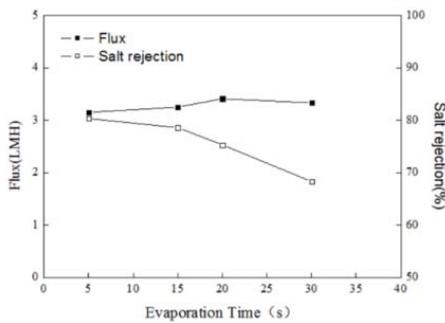


Fig.5: Effects of different evaporation time on water flux and salt rejection

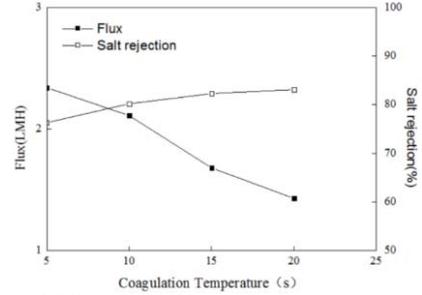


Fig.6: Effects of different coagulation bath temperature on water flux and salt rejection

As shown in Fig6, effect of coagulation temperature on the performance of membrane was observed. From 5 to 20 $^{\circ}$ C in coagulation bath, flux decreased from 1.83 to 1.43 L/m $^2$ h (LMH), while rejection increased from 76.3 to 81.9%. Increasing temperature accelerated the diffuse between solvent and non-solvent and exacerbated the movement of macromolecule chain, and made the membrane structure more thick. To obtain good permeability and selectivity, the coagulation bath temperature was selected 5  $^{\circ}$ C, which can get thin porous support layer.

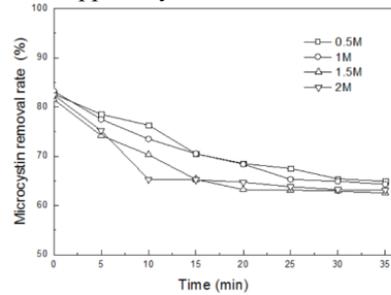


Fig.7: Microcystin removal rate curve at different draw solution concentrations

Since microcystin has been widely studied in environmental fields, while knowledge for dealing it by membrane separation was rare. The obtained results (Fig 7) clearly show a linear variation of removal rate vs. time within 10 min. Besides, microcystin removal rates was depended on concentration of draw solution, the higher concentration, lower the removal rate was. This was attributed to the osmotic pressure of high concentration of draw solution, which made the removal more thoroughly.

#### IV. CONCLUSIONS

CTA-based forward osmosis membranes were prepared by immersion precipitation with different casting compositions and coagulation conditions, and optimized with high water flux and good removal of microcystin. The optimal casting component were 74% solvents, 14% CTA, 8% acetone, 4% TEP with evaporation time of 15 s at room temperature and at the coagulation bath of 5  $^{\circ}$ C.

Further studies will focus on the two scenarios. Draw solution need to be re-cycled. In addition, FO may be integrated with RO to treat seawater and wastewater simultaneously.

## REFERENCES

- [1] Quintanilla, V.Y; Li, Z.Y; Valladares,W; Li, Q.Y; Amy, G. Indirect desalination of Red Sea water with forward osmosis and low pressure. *Desalination* 2011, 280, 160-166.
- [2] Chung, T.S; Zhang, S; Wang, K.Y; Su, J.C; Ling, M.M. Forward osmosis processes: Yesterday, today and tomorrow. *Desalination* 2012, 278, 78-81.
- [3] Wei,J; Tang,C.Y; Qiu,C; Wang,Y; Wang,R. Comparison of NF-like thin film composite forward osmosis membrane in osmotically driven membrane processes. *Procedia Engineering* 2012, 44, 267-268.
- [4] Phuntsho, S; Hong, S; Elimelech, M; Shon, H.K. Forward osmosis desalination of brackish groundwater: Meeting water quality requirements for fertigation by integrating nanofiltration. *Journal of Membrane Science* 2013, 436, 1-15.
- [5] Garcia-Castello, E.M; McCutcheon, J.R. Dewatering press liquor derived from orange production by forward osmosis. *Journal of Membrane Science* 2011, 372, 97-101.
- [6] Sant'Anna, V; Marczak, L.D.F; Tessaro,I.C. Membrane concentration of liquid foods by forward osmosis: Process and quality view. *Journal of Food Engineering* 2012, 11, 483-489.
- [7] Werner, C.M; Logan, B.E; Saikaly, P.E; Amy G.L. Wastewater treatment, energy recovery and desalination using a forward osmosis membrane in an air-cathode microbial osmotic fuel cell. *Journal of Membrane Science* 2013, 428, 116-122.
- [8] Kim, Y.C; Elimelech, M. Potential of osmotic power generation by pressure retarded osmosis using seawater as feed solution: Analysis and experiments. *Journal of Membrane Science* 2013, 429, 330-337.
- [9] Phuntsho, S; Shon, H.K; Hong, S; Lee, S; Vigneswaran, S; Kandasamy, J. Fertiliser drawn forward osmosis desalination: the concept, performance and limitations for fertigation. *Rev Environ Sci Biotechnol* 2012, 11,147-168.
- [10] Gray, G. T.; McCutcheon, J. R.; Elimelech, M., Internal concentration polarization in forward osmosis: role of membrane orientation. *Desalination* 2006, 197, 1-8.
- [11] Yu, S; Liu, M; Liu X.S; Gao, C.J. Performance enhancement in interfacially synthesized thin-film composite polyamide-urethane reverse osmosis membrane for seawater desalination. *Journal of Membrane Science* 2009, 342, 313-320.
- [12] Qiu, C.Q; Qi, S; Tang, C.Y. Synthesis of high flux forward osmosis membranes by chemically crosslinked layer-by-layer polyelectrolytes. *Journal of Membrane Science* 2011, 381, 74-80.
- [13] Herron, J; Corvallis; OR. Asymmetric forward osmosis membranes.US Patent.2008, US007445712B2.
- [14] Sairam, M; Sereewatthanawut, E; Li, K; Bismarck, A; Livingston, A.G. Method for the preparation of cellulose acetate flat sheet composite membranes for forward osmosis— Desalination using MgSO4 draw solution. *Desalination* 2011,273, 299-307.
- [15] Kong, L; Zhang, D.L; Shao, Z.Q; Han, B.X; Lv, Y.X; Gao, K.Z; Peng, X.Q. Superior effect of TEMPO-oxidized cellulose nanofibrils (TOCNs) on the performance of cellulose triacetate (CTA) ultrafiltration membrane. *Desalination* 2014, 332, 117-125.
- [16] Ong, R.C; Chung, T.S. Fabrication and positron annihilation spectroscopy (PAS) characterization of cellulose triacetate membranes for forward osmosis. *Journal of Membrane Science* 2012, 394-395, 230-240.
- [17] Zhao, Y.L; Li, W.Y; Zhang, M; Dong, B.Z. Study on the removal mechanisms and influencing factors of microcystins by ultrafiltration membrane. *Industrial Water Treatment* 2010, 30, 26-29.
- [18] Thi, P.P; Yun, E.T; Kim, I.C; Kwon, Y.N. Preparation of cellulose triacetate/cellulose acetate (CTACA)-based membranes for forward osmosis. *Journal of Membrane Science* 2013, 433, 49-59.
- [19] Swinyard, B.T; Barrie, J.A. Phase separation in non-solvent dimethylformamide polyethersulphone and non-solvent dimethylformamide polysulphone systems. *British Polymer Journal* 1988, 20(4), 317-321.