

Utilization of Ammonium Bicarbonate as Draw Solution in Forward Osmosis Process: A Case Study of Cooling Water Reuse

Mahisorn Maneechan^{1,4}, Patiparn Punyapalaku^{2,4}, and Aunnop Wongrueng^{3,4}

Abstract—In order to maintain the cooling facilities and heat exchanging efficiency of cooling tower unit, many chemicals such as scale and corrosion inhibitors are added into the cooling make up water. However, those chemicals might cause the decreasing of reuse cycle of cooling water due to the limitation of TDS and some specific ion species. This study aimed to evaluate the possibility to treat discharged high TDS cooling water by forward osmosis (FO) process. Semi-permeable membrane, namely, CM-1 membrane was applied. Three draw solutions, i.e. sodium chloride, calcium chloride, and ammonium bicarbonate were examined. Synthesized cooling wastewater was prepared from 1,000 mg/L of NaCl solution. The results showed that ammonium bicarbonate solution had the highest potential to be used as draw solution. Optimal applied pressure was 0.1 MPa. Water flux of CM-1 membrane in FO process using ammonium bicarbonate as draw solution was 8.0 LMH for pure water and 4.0 LMH for synthesized cooling wastewater. In comparison between FO and reverse osmosis (RO) process by using CM-1 membrane, FO process showed higher water flux than RO process. Air blower can be used to separate ammonium bicarbonate from draw solution easily in a recovery step.

Keywords—Cooling water, Forward osmosis, Draw solution, Ammonium bicarbonate

I. INTRODUCTION

WATER cooling system is widely used in industrial plants, hospitals, super stores, office buildings and other facilities. The main objective of cooling water in cooling system is to remove thermal energy (heat) by evaporation of water as the heat-exchange mechanism [1], [2]. In order to maintain the cooling facilities and heat exchanging efficiency of cooling tower unit, many chemicals such as scale inhibitors, corrosion inhibitors and biocides are added into the cooling make up water. However, those chemicals might cause the decreasing of reuse cycle of

cooling water due to the limitation of Total dissolved solid (TDS) and some specific ion species such as chloride ion, calcium ion, etc.[3], [4].

Moreover, chlorine compounds and chlorophenols are the commonly used as the biocide as broad spectrum to kill and control microbial in cooling water system. Chlorine compounds finally can increase the concentration of chloride ions and cause the reduction of concentration cycle of cooling water system. And, chlorophenols can expose to the environment by contamination in discharged cooling water. Chlorophenol can be accumulated and affected to biota in water resources [5].

Forward osmosis (FO) is the term to describe the natural phenomena whereby a side of lower osmotic pressure solvent flows pass through a selective semi-permeable membrane to a side of higher osmotic pressure solvent. The driving force for this phenomena is osmotic pressure gradient. FO can be the candidate method to treat discharge wastewater from water cooling system in order to return low TDS water to the cooling system and reduce the cost to purchase clean water from other water resources [6], [7].

Draw solution is a concentrated solution that has a high osmotic pressure to draw water from feed solution side by pass through semi-permeable membrane [8]. The appropriate draw solution should have high solubility in water, high osmotic pressure and should be easily separable from water in low energy consumption [9]. Other factors which should be considered before select draw solutions are low cost, zero toxicity, no damage to membrane and stability at or near natural pH [10]. Using ammonium bicarbonate (NH_4HCO_3) together with ammonium hydroxide (NH_4OH) as draw solution can get water fluxes depending on the concentrations of draw solution [11].

The thin film composited (TFC) polyamide membrane was investigated to reject various organic compounds and got rejection efficiency ranging from 94-97% [12]. Normally, inorganic compound and organic compounds that used as chemical adding in cooling system have molecular structure size larger than sodium and chloride ions. Hence, the membrane process has the possibility to reject chlorophenol or any organic compounds that dissolved in discharged cooling water.

This study aimed to evaluate the possibility to treat discharged cooling water which high TDS by FO process by

Mahisorn Maneechan¹ International Postgraduate Programs in Environmental Management, Graduate School, Chulalongkorn University, Bangkok 10330, Thailand (corresponding author's phone: +6686 222 0446; e-mail: m.mahisorn@hotmail.com).

Patiparn Punyapalaku², Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand (e-mail: p_patiparn@yahoo.com).

Aunnop Wongrueng³ Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai 50200, Thailand (e-mail: aunnop@eng.cmu.ac.th).

No.4 is the Center of Excellence on Hazardous Substance Management (HSM), Chulalongkorn University, Bangkok 10330, Thailand

using ammonium bicarbonate as draw solution. Semi-permeable membrane, namely, CM-1 membrane was applied in this research.

II. MATERIALS AND METHODS

A. Feed solution (FS)

Solid sodium chloride (NaCl) which molecular weight 58.44 g. was diluted in deionized water to be a solution of sodium chloride 1,000 mg/L. Both sodium chloride solution and deionized water were tested in RO Mode to find the water flux baseline of each solution. Cooling water from one factory in Rayong province, Thailand was used in FO mode. Each solution was measured electrical conductivity value by EC meter before and after the experiment of each batch.

B. Draw solution (DS)

Solid ammonium bicarbonate which molecular weight 79.06 g. was diluted in deionized water and used as DS. Ammonium bicarbonate decomposed in water to be ions of NH_4^+ and CO_3^- and can be removed from water by heating at the temperature 60 °C to get NH_3 and CO_2 in gas form [10]. The differential concentration of DS (0.1, 0.5 and 1.0 M) was tested in FO mode, to compare the potential and water flux gained from each concentration experiments. Electrical conductivity value of DS was measured by EC meter before and after the experiment of each batch.

C. Flat sheet thin film composite (TFC) polyamide membrane

A commercial flat sheet in thin film composite polyamide membrane type namely CM-1 which have 98% salt rejection efficiency was used in each experiment. The filtration area is 60 cm². The membrane has 2 layers which is a thin active layer is aromatic polyamide and a thick supporting layer is polymer fiber. The maximum operating limitations of flat sheet membrane on active layer side are the temperature 45°C, pH range 2-11 and hydraulic pressure 1 MPa. Picture of flat sheet membrane are shown in Fig. 1



Fig.1 Picture of flat sheet TFC polyamide membrane

D. Membrane module

The membrane module was operated by cross-flow membrane condition.

E. Reverse Osmosis (RO) Mode

RO mode was tested to obtain water flux baseline for compare water flux with FO Mode. This experiment was controlled the temperature of feed solution at temperature 25 °C and the magnetic gear pump (MP) is the main force to took water pass through the membrane was fixed the hydraulic pressure at 0.1 MPa. Valve (V1) was used to control the hydraulic pressure of MP and show the value on screen of pressure indicator (PI). FS was contact on the active layer of the membrane along the operation of RO Mode. Permeated water passed through the membrane from FS side to permeate water tank. The number on screen of the digital weight balance is increasing along with the time, because the volume of permeated water was increased. The diagram of RO mode are shown in Fig. 2

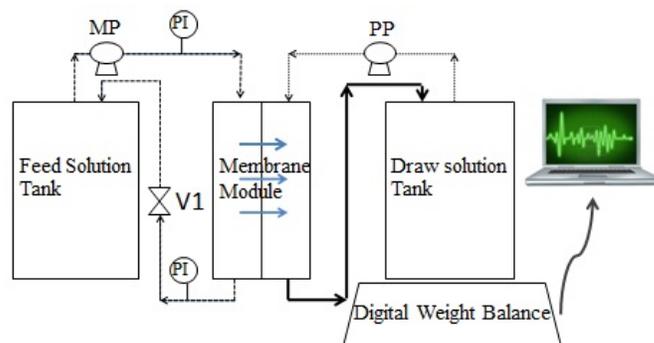


Fig. 2 Experimental diagram of RO Mode

F. Forward Osmosis (FO) Mode

FO mode was tested to compare the osmotic pressure potential of ammonium bicarbonate solution at differential concentration. The temperature of FS was fixed at 25 °C and a MP for operating FS was fixed at 0.1 MPa. The peristaltic pump (PP) was used to circulate draw solution by fixing speed at 20 rpm. Both of the FS and DS were maintained and kept contacting with active layer side and the supporting layer side of a membrane, respectively, along with the operating time. The concentration of DS was diluted by permeated water along the operating time of FO Mode. The digital weight balance is function as same as RO mode. The diagram of FO mode are shown in Fig. 3

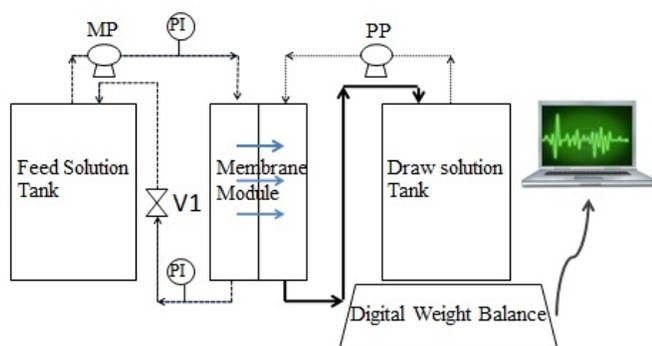


Fig. 3 Experimental diagram of FO Mode

G. Distillation set

Ammonium bicarbonate was removed from draw solution by distillation process at temperature 60 °C up to 6 hrs. The air blower was setting in distillation process to activate the separation process of ammonium bicarbonate.

III. RESULT AND DISCUSSION

A. Results of RO mode

The results of RO mode with different types of feed solution had different water flux, because the total ionic concentration in solution might obstruct the phenomena of water passing through membrane. The absolutely dissolve of compound in solution gave ions from of added compounds or elements.

The concentration of each feed solution after 2 hrs. of RO mode filtration was increased due to the water in the FS tank was separated pass through the membrane pores to permeate tank. The water flux after 1 hour of operation time by RO mode was reduce because membrane layer was compressed by hydraulic pressure from magnetic gear pump. And the compression of membrane layer will reduced the pore size of membrane. Equation (1) illustrates the water flux of permeated water, where J_w is water flux (LMH), ΔV is the change of permeated water volume in each operation time (L), A is the filtration area of membrane (m^2) and T is the duration time in each operation time (hr).

$$J_w = \Delta V / A \cdot T \tag{1}$$

Electrical conductivity of FS and water flux of RO mode are shown in Table.I and Fig.4.

TABLE I
ELECTRICAL CONDUCTIVITY OF FS AND WATER FLUX OF RO MODE

Feed solution types	Initial		Final	
	EC ($\mu S/cm$)	Flux (LMH)	EC ($\mu S/cm$)	Flux (LMH)
DI-water	7.2	4.3	10	4.0
NaCl 1000 mg/L	1416	1.57	2600	1.54

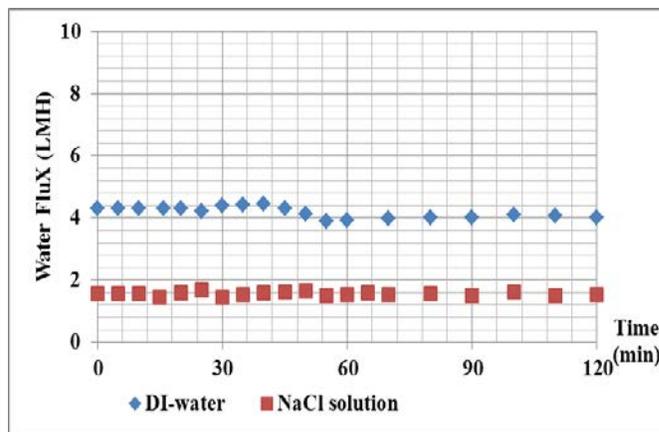


Fig.4 Water flux in RO Mode

B. Results of FO mode

Discharged cooling water was filtrate by FO mode with different concentration of DS. Water from cooling water side was passed through the membrane to DS side by the osmotic pressure of DS and the EC value of discharged cooling water was increasing along the operation time of FO mode. From the obtained EC results, it can be supposed that the organic biocides or other chemical additive compounds that used as in cooling system, can be rejected or removed by filtration process using FO mode.

Equation (2) showed the equation to describe the relationship between electrical conductivity and TDS, where TDS is the concentration of total dissolved solid in solution (mg/L), 0.66 is the relation factor number and EC is the electrical conductivity of solution ($\mu S/cm$) [13]

$$TDS (mg/L) = 0.66 \times EC (\mu S/cm) \tag{2}$$

The different EC results of cooling water in each batch of the FO mode are shown in Table.II

TABLE II
ELECTRICAL CONDUCTIVITY OF DISCHARGED COOLING WATER

Operation batch of DS (M)	Initial		Final	
	EC ($\mu S/cm$)	TDS (mg/L)	EC ($\mu S/cm$)	TDS (mg/L)
0.1	806	531.96	837	552.42
0.5	806	531.96	863	569.58
1.0	806	531.96	891	588.06

The higher concentration of DS had higher water flux than lower concentration of DS. The osmotic force of DS in each concentration was decreased along with the time increase, because concentration of DS was diluted by the water from FS side. And the permeated water flux was increased too.

Equation (3) shows the relationship for calculating the osmotic pressure that was the main driving force in FO mode. Where π is osmotic pressure (MPa); C is concentration of solute (mol/L); R is the gas constant ($R = 8.31451 \text{ Pa}\cdot\text{m}^3/(\text{mol}\cdot\text{K})$) and T is the absolute temperature (K) [14].

$$\pi = CRT \quad (3)$$

The EC value of DS was decreased along with the time increase. The EC value and water flux trend line are shown in Table.III and Fig.5 respectively

TABLE III
ELECTRICAL CONDUCTIVITY OF DRAW SOLUTION

Concentration of DS (M)	Osmotic Pressure of DS (MPa)	Initial EC ($\mu\text{S}/\text{m}$)	Final EC ($\mu\text{S}/\text{m}$)
0.1	0.252	6100	5820
0.5	1.26	22700	20400
1.0	2.52	39300	38300

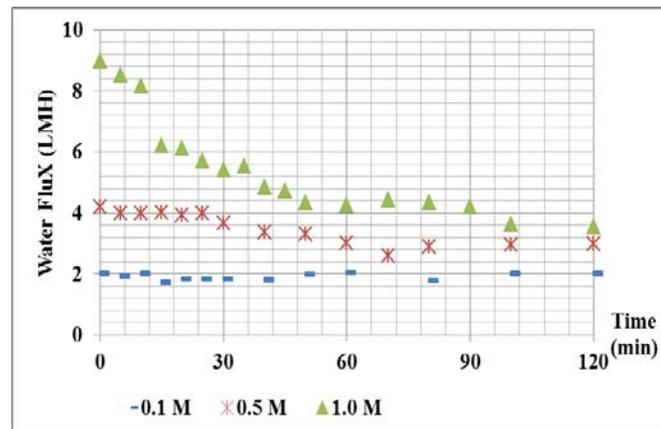
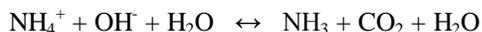


Fig.5 Trend of water flux in FO Mode

C. Results of ammonium bicarbonate removal

Ammonium bicarbonate was removed from DS by distillation process at the temperature 60°C upto 6 hrs. The ionic concentration of ammonium bicarbonate was decreased along with the time increase. The air blower was set to produce the turbulence in bulk of DS and enhanced the separation process of ammonium bicarbonate from permeated water. Ammonia released for distillation process can be trapped and reused as DS. The ammonia production was shown by the below chemical equation



The results of experiment are show in Table.IV and Table.V

TABLE IV
ELECTRICAL CONDUCTIVITY OF AMMONIUM BICARBONATE IN DISTILLATION PROCESS AT 60°C FOR 6 HRS

Conc. of DS	Initial		Final	
	EC ($\mu\text{S}/\text{cm}$)	TDS (mg/L)	EC ($\mu\text{S}/\text{cm}$)	TDS (mg/L)
0.1 M	5820	3841.2	200	132
0.5 M	20400	13464	2600	1716

(The Japan Refrigeration and Air Conditioning Industry Association recommended EC value for makeup water should be $\leq 300 \mu\text{S}/\text{cm}$)

TABLE V
AMMONIA PRODUCTION AFTER 6 HRS. OF DISTILLATION PROCESS

Conc. of DS in each batch of distillation process (M)	Volume (ml.)	EC ($\mu\text{S}/\text{m}$)
0.1	105	4060
0.5	97	17770

IV. CONCLUSION

The different concentration of ammonium bicarbonate can affect to the quantity of permeated water flux solution. Ammonium bicarbonate has the potential to be used as a draw solution in forward osmosis application. The recovery of ammonium bicarbonate can be processed by separation of ammonia from solution in DS by adding air blower to make the turbulence in bulk of DS. From obtained data, it might be concluded that the possibility to apply FO process was quite low. Since the DS concentration at 0.1 M can be removed ammonium ion easier than 0.5 M. The temperature at 60°C was suitable for separation of ammonia ion from water in DS.

REFERENCES

- [1] San Jose/Santa Clara Water Pollution Control Plant and The City of San Jose Environmental Service Department, *Guidelines for Managing Water in Cooling Systems*. SJ : San Jose Environmental Service Department, 2002, ch. 1.
- [2] M. Seneviratne, *A Practical Approach to Water Conservation for Commercial and Industrial Facilities*, Massachusetts: Elsevier, 2007, ch. 5.
- [3] San Diego County Water Authority, *Technical Information for cooling Towers Using Recycled Water*. California, 2009, ch. 2.
- [4] T. Keister, *Cooling Water Management Basic Principles and Technology*, Pennsylvania: Prochemtech International, Inc., 2008
- [5] U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, *TOXICOLOGICAL PROFILE FOR CHLOROPHENOLS*. Georgia, United States, 1999
- [6] T. Y. Cath, A. E. Childress, and M. Elimelech, "Forward osmosis: Principles, applications, and recent developments," *Journal of Membrane Science*, vol. 281, Sep. 2006. pp. 70-87. <http://dx.doi.org/10.1016/j.memsci.2006.05.048>
- [7] P. Nicoll, N. Thompson, V. Gray, "Forward osmosis applied to evaporative cooling make-up water". The 2012 Cooling Technology Institute Annual Conference, Houston, Texas, Feb, 2012. Paper no. TP12-06

- [8] Q. Ge, M. Ling, and T. S. Chung, "Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future," *Journal of Membrane Science*, vol. 442, Sep. 2013. pp. 225-237.
<http://dx.doi.org/10.1016/j.memsci.2013.03.046>
- [9] C. Kim, S. Lee, H. K. Shon, M. Elimelech, and S. Hong, "Boron transport in forward osmosis: Measurements, mechanisms, and comparison with reverse osmosis," *Journal of Membrane Science*, vol. 419-420, Nov. 2012. pp. 42-48.
<http://dx.doi.org/10.1016/j.memsci.2012.06.042>
- [10] S. Zhao, L. Zou, C. Y. Tang, and D. Mulcahy, "Recent developments in forward osmosis: Opportunities and challenges," *Journal of Membrane Science*, vol. 396, April. 2012. pp. 1-21.
<http://dx.doi.org/10.1016/j.memsci.2011.12.023>
- [11] J. R. McCutcheon, R. L. McGinnis, and M. Elimelech, "Desalination by ammonia-carbon dioxide forward osmosis: influence of draw and feed solution concentrations on process performance," *Journal of Membrane Science*, vol. 278, July. 2006. pp. 114-123.
<http://dx.doi.org/10.1016/j.memsci.2005.10.048>
- [12] X. Jin, J. Shan, C. Wang, J. Wei, and C. Y. Tang, "Rejection of pharmaceuticals by forward osmosis membranes," *Journal of Hazardous Materials*, vol. 227-228, August. 2012. pp. 56-61..
- [13] Osmonics Inc, *Pure Water Handbook*. Minnesota : United States, 1997, pp. 18
- [14] C. N. Nguyen, S. S. Chen, H. Y. Yang, N. T. Hau, "Application of forward osmosis on dewatering of high nutrient sludge," *Bioresource Technology*, vol.132, 2013. Pp. 224-229
<http://dx.doi.org/10.1016/j.biortech.2013.01.028>