USING AMMONIUM BICARBONATE AS DRAW SOLUTION IN FORWARD OSMOSIS PROCESS FOR REMOVAL OF p-CHLOROPHENOL IN DISCHARGED WATER FROM COOLING SYSTEM

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2013

การใช้แอมโมเนียมไบคาร์บอเนตเป็นสารดึงในกระบวนการฟอร์เวิร์ดออสโมซิสเพื่อกำจัดสารพาราคลอโรฟีนอลในน้ำทิ้งจากระบบหล่อเย็น

นายมหิศร มณีจันทร์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2556

Thesis Title	USING AMMONIUM BICARBONATE AS DRAW SOLUTION IN FORWARD OSMOSIS PROCESS FOR REMOVAL OF p-CHLOROPHENOL IN DISCHARGED WATER FROM COOLING SYSTEM
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มหิศร มณีจันทร์ : การใช้แอมโมเนียมไบคาร์บอเนตเป็นสารดึงในกระบวนการฟอร์เวิร์ดออสโมซิสเพื่อกำจัดสารพาราคลอโรฟีนอลในน้ำทิ้งจากระบบหล่อเย็น. (USING AMMONIUM BICARBONATE AS DRAW SOLUTION IN FORWARD OSMOSIS PROCESS FOR REMOVAL OF p-CHLOROPHENOL IN DISCHARGED WATER FROM COOLING SYSTEM) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.ปฏิภาณ ปัญญาพลกุล, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: อ. ดร.อรรณพ วงศ์เรือง, 4 หน้า.

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาสภาวะการดำเนินการกรองด้วยกระบวนการฟอร์เวิร์ดออสโมซิส (FO process) ที่เหมาะสม ในการกำจัดสารพาราคลอโรฟีนอล (p-Chlorophenol) ที่ปนเปื้อนในน้ำทิ้งจากระบบหล่อเย็น จากการศึกษาพบว่าค่าแรงดันที่น้อยที่สุดที่ยังสามารถดำเนินการกรองได้คือ 0.1 เมกะปาสคาล (MPa) โดยสารดึงที่นำมาศึกษาได้แก่ โซเดียมคลอไรด์ (NaCl) และ แอมโมเนียมไบคาร์บอเนต (NH4HCO3) ที่ความเข้มข้น 0.5 โมลาร์ (M) ของแต่ละสารดึงจะสามารถให้แรงออสโมติก 2.49 และ 3.735 MPa ตามลำดับ ลำดับประสิทธิภาพในการดึงน้ำของของสารดึงได้แก่ NH4HCO3 และ NaCl ตามลำดับ ดังนั้น สาร NH4HCO3 จึงมีความเหมาะสมที่จะนำมาใช้เป็นสารดึงในการกรองแบบฟอร์เวิร์ดออสโมซิส การปรับเปลี่ยนความเข้มข้นของสารดึง NH4HCO3 ที่ 0.05, 0.1, 0.5 และ 1.0 M เพื่อกำจัดสาร p-chlorophenol ในน้ำทิ้งสังเคราะห์ (NaCl ความเข้มข้น 0.017 M) พบว่า p-chlorophenol มีความเข้มข้นลดลงจากจุดเริ่มต้น 5.14 %, 5.72 %, 10.19 % และ 15.32 % ตามลำดับ นอกจากนี้สาร p-chlorophenol ในน้ำทิ้งจริงจากระบบหล่อเย็นนั้นความเข้มข้นมีค่าลดลงจากจุดเริ่มต้น 4.19 %, 4.39 % , 7.83 % และ 9.72 % ตามลำดับ และตรวจวัดไม่พบปริมาณสาร p-chlorophenol ในฝั่งสารดึง ดังนั้นสาร p-chlorophenol ถูกควบคุมโดยกระบวนการคัดขนาดของกระบวนการฟอร์เวิร์ดออสโมซิส และปริมาณความเข้มข้นที่ลดลงของสาร p-chlorophenol ในน้ำทิ้งจากระบบหล่อเย็นเกิดจากการระเหยตัวตามธรรมชาติ และการย่อยสลายโดยใช้แสง การศึกษาการแยกแอมโมเนีย (NH3) ออกจากสารละลาย NH4HCO3 ที่ใช้เป็นสารดึง พบว่าที่ความเข้มข้นของสารดึงที่ต่ำคือ 0.05 M NH3 จะแยกตัวได้ดี และได้น้ำที่มีคุณภาพเหมาะแก่การนำกลับไปใช้ในระบบหล่อเย็น ส่วนที่ความเข้มข้นของสารดึงที่สูงคือ 0.5 และ 1.0 M NH3 บางส่วนยังคงละลายอยู่ในสารดึง ดังนั้นน้ำที่ได้จึงมีค่าการนำไฟฟ้าที่สูงและไม่เหมาะแก่การนำกลับมาใช้ในระบบหล่อเย็น การเพิ่มอุณหภูมิและเวลาในการกลั่นทำให้ประสิทธิภาพการแยก NH3 ออกจากสารดึงสูงขึ้น

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต ....

ปีการศึกษา 2556 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม ....

5587596020 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS: COOLING WATER / FORWARD OSMOSIS / DRAW SOLUTION / AMMONIUM BICARBONATE / P-CHLOROPHENOL

MAHISORN MANEECHAN: USING AMMONIUM BICARBONATE AS DRAW SOLUTION IN FORWARD OSMOSIS PROCESS FOR REMOVAL OF P-CHLOROPHENOL IN DISCHARGED WATER FROM COOLING SYSTEM. ADVISOR: ASST. PROF. PATIPARN PUNYAPALAKUL, Ph.D., CO-ADVISOR: AUNNOP WONGRUENG, Ph.D., 4 pp.

This study examined the optimal condition of forward osmosis process (FO process) for remove p-chlorophenol in discharged cooling water. The lowest applied pressure for operate the filtration process was 0.1 MPa. Two draw solutions (e.g. sodium chloride (NaCl) and ammonium bicarbonate (NH4HCO3)) were applied in this study. The same concentration of 0.5 M of two draw solutions (NaCl and NH4HCO3) produced osmotic pressure 2.49 and 3.735 MPa, respectively. Hence, the NH4HCO3 was selected to be draw solution in FO process for further study. Concentration of NH4HCO3 solution as draw solution was varied as 0.05, 0.1, 0.5 and 1.0 M for remove p-chlorophenol in synthetic wastewater (NaCl 0.017 M), the concentrations of p-chlorophenol were decreased from the initial state 5.14 %, 5.72 %, 10.19 % and 15.32 %, respectively. In case of real discharged cooling water, the concentrations of p-chlorophenol were decreased from the initial state 4.19 %, 4.39 %, 7.83 % and 9.72 %, respectively. The concentration of p-chlorophenol in draw solution cannot be detected. Hence, p-chlorophenol was rejected by size exclusion mechanism. However, the concentration of p-chlorophenol in feed solution might be reduced due to evaporation and photodegradation. Separation of ammonia (NH3) in NH4HCO3 solution as draw solution was operated by distillation process in order to obtain a good quality of water. At the low concentration of draw solution (e.g., 0.05 M), NH3 can be separated easily and the quality of obtained water was appropriate to return to cooling system. In the contrast, some of NH3 still remained in the draw solution at the high concentration of draw solution e.g., 0.5 and 1.0 M. which caused the high electrical conductivity and was not appropriate to return into cooling system. The increasing of temperature and the distillation time can enhance NH3 separation efficiency.

Field of Study: Environmental Management Student's Signature ....
Academic Year: 2013 Advisor's Signature ....
Co-Advisor's Signature ....

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere gratitude to Asst. Prof. Dr. Patiparn Punyapalakul and Dr. Aunnop Wongrueng, my thesis advisor and co-thesis advisor for their both valuable suggestion, guidance and a great encouragement during the thesis work

I also thankful to Asst. Prof. Dr. Tawan Limpiyakorn, Chairperson of the committee, Assoc.Prof.Dr. Pisut Painmanakul, Asst. Prof. Dr. Monthon Thanuttamavong, committees for their encouragement and useful comments.

I gratefully to Ms.Benja Sookwong and Ms.Katunchalee Phadunghus, both master students in Environmental management, Graduate school, Chulalongkorn Uninversity for their helpful in the experiment of my thesis.

My appreciation also goes to Center of Excellence on Hazardous Substance Management for (HSM), Chulalongkorn University, Thailand for providing scholarship and all equipment to support my thesis work.

Finally, I would like to express my deepest appreciation and gratitude to my family, who provide the strong encouragement, love, financial support and inspiration.

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ABBREVIATIONS AND SYMBOLS

π	Osmotic pressure
%R	Percentage rejection
µg/L	Micro gram per liter
µm	Micro meter
µS/cm	Micro siemens per centimeter
C_{DS}	Concentration of draw solution
C_{FS}	Concentration of feed solution
cm^2	Square centimeter
CTA	Cellulose triacetate
Da	Dalton
DS	Draw solution
EC	Electrical conductivity
FO	Forward osmosis
FS	Feed solution
g/mol	Gram per molar
J_w	Permeate water flux
$L/m^2 \cdot hr$	Liter per square meter hour
M	Molar
MF	Micro filtration
mg/L	Milli gram per liter
Mpa	Mega Pascla
mS/cm	Milli siemens per centimeter

MWCO	Melecular weight cut-off
MΩ	Micromho
NF	Nano filtration
nm	Nano meter
p-CPN	para-Chlorophenol
RO	Reverse osmosis
TFC	Thin film composite
TMP	Transmembrane pressure
UF	Ultra filtration

CHAPTER 1

INTRODUCTION

1.1 Motivation

Water is the essence for life on the earth for drinking, washing, agriculture, industrial, transportation and other activities (Palaniappan et al., 2010). Water shortages and energy crises have threatened many areas. Population in the world is around 7 billion. 1.2 billion is disable to access clean and drinking water and 2.6 billion is lack adequate sanitation (Zhao et al., 2012)

Over last a few decades, the continued growth of population and industrialization have effected to the degradation of numerous ecosystem around human. Human uses water in many activities and discharges wastewater to river and ocean with or without adequate treatment. The wastewater can cause the septic condition in water resources. Moreover, wastewater contains high levels of inorganic compounds (metal, sodium and phosphate etc.) and high loading of organic compounds in forms of Total Suspended Solids (TSS), Biochemical Oxygen Demand (BOD_5), or Chemical Oxygen Demand (COD). These parameters were hardly to be degraded by the process of purification (Chan et al., 2009)

Cooling water is used in industries to control temperature or heat of machines in the production process by reducing the temperature and transfer the heat from machine to water (Heat Exchange) (Seneviratne, 2007). After the heat exchange process, cooling water is contaminated with high total dissolved solid (TDS). High TDS cooling water may cause the scaling which can clog the piping system in cooling unit (San Diego County water Authority, 2009). Hence, TDS in cooling water is the important parameter which is always measured and controlled.

When the TDS is higher than designed concentration, cooling water is discharged as wastewater (NALCO-Corp, 2005). Then, clean water is added into the cooling system to replace the discharged high TDS cooling water. However, clean water is quite costly. Lacking of clean water is the major problem for many regions. (Pattaravichian, 2006).

Microorganisms can grow on the surface of equipment which contact to the cooling water causing the formation of biological fouling layers (biofilm). Biofilm decreases the heat transfer between cooling water and hot objects. Moreover, the thickness of biofilm can retard the movement of cooling water in pipe line and it can reduce the efficiency of cooling system (Keister, 2008).

Biocide such as p-chlorophenol is added into cooling system to control biological growth. p-Chlorophenol can kill many types of microorganisms. Hence, discharged water contains p-chlorophenol can toxic to fish and aquatic invertebrate (U.S.DEPARTMENTOFHEALTHANDHUMANSERVICES, 1999).

Forward osmosis (FO) is a term describing the natural phenomenon whereby a side of lower osmotic pressure solvent passes through a selective semi-permeable membrane to a side of higher osmotic pressure solvent. The main force of the solvent movement in osmotic gradient (Thompson & Nicoll, 2011). FO process is the one of method to treat discharged water from cooling system in order to return clean water to the cooling system and reduce the cost to purchase clean water from other sources (Nicoll et al, 2012).

Therefore, p-chlorophenol in discharged water from cooling system should be concerned and managed properly.

1.2 Objectives

1. To study optimal condition of forward osmosis process to treat discharged cooling water.
2. To evaluate p-chlorophenol removal efficiency of FO process from discharged water from cooling system by forward osmosis system.

1.3 Hypotheses

1. Solution of ammonium bicarbonate could be used as draw solution for forward osmosis process to reject biocide in discharged water from cooling system.
2. Solution of ammonium bicarbonate could be evaporated from draw solution by heating at 60 °C.
3. FO osmosis process could reject p-chlorophenol in discharged cooling water by size exclusion mechanism.

1.4 Scope of the study

1. The study was focused on optimization of operating condition based on water flux and quality of feed and draw solutions after treatment by FO process.
2. FO experiment was operated in a laboratory-scale reactor with both synthesized discharged cooling water and real discharged cooling water.
3. The flat sheet membrane in Reverse osmosis type (RO-1) was used in this study.
4. RO experiment was conducted to compare the permeate water flux with FO process.

5. Solution of ammonium bicarbonate was applied as draw solution at concentration from 0.05 to 1.0 M.
6. p-Chlorophenol was added into feed solution at the concentration of 42.5 mg/L.
7. Ammonium bicarbonate in draw solution was evaporated by heating at 60 °C for 6 hrs.

1.5 Benefit of this study

1. The knowledge of this study can be applied for treatment of discharged water from cooling system.
2. Develop the process to separate draw solution out of water which passed the filtration process by FO process.

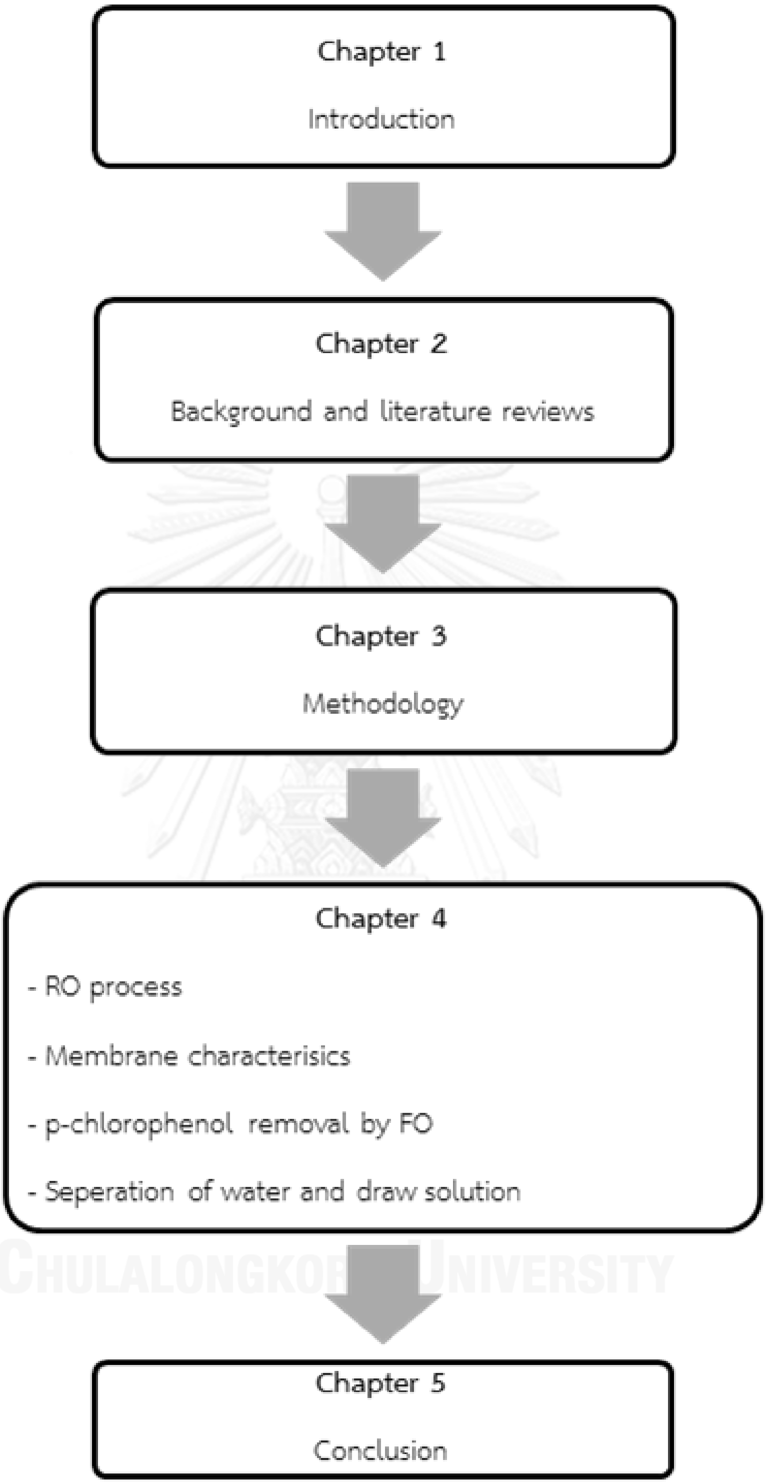


Figure 1 Diagram of thesis in each chapter

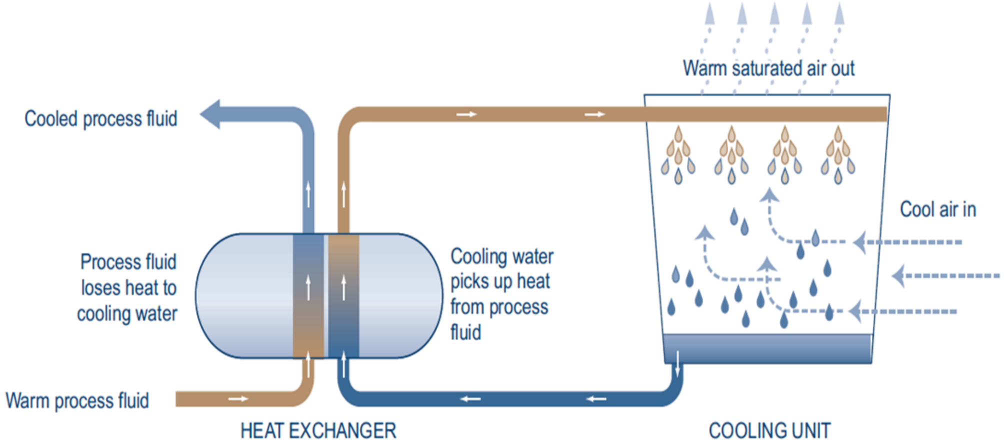
CHAPTER 2

BACKGROUND AND LITERATURE REVIEWS

2.1 Cooling Water

The temperatures and pressures in the process are control by cooling water system by transferring heat from hot fluid into cooling water which takes the heat away (NALCO-Corp, 2005).

Cooling water system were consists of a heat exchanger and a cooling unit. The heat exchanger was accomplice with cooling water to remove heat from hot fluid with direct or indirect contact. The cooling unit removed the heat which carried by the contact cooling water in the heat exchanger, the heat was removed from returning cooling water by exchanging the heat to cool air via evaporation process (San Jose/San Clara Water pollution control plant and the City of San Jose Environmental Service Department, 2002). Common heat exchanging process of cooling systems was summarized in **Figure 2**



(Source: San Jose/San Clara Water pollution control plant, 2002)

Figure 2 Heat exchanging process of cooling system

Loop of cooling water system was cooling water which can transfer the heat from hot fluid in the heat exchanger. After transferring the heat, cooling water has higher temperature, which needs to reduce the temperature by contacting with external air. However, during cool down process, cooling water would be lost by evaporation, drift, blowdown and leakage. Hence, makeup water was needed to be added for recirculation water system and replaces the water lost.

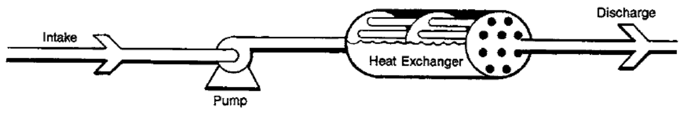
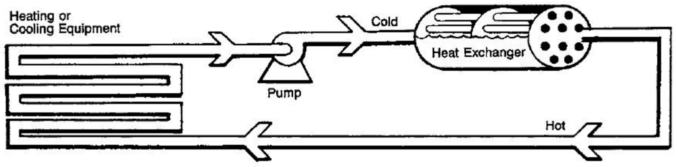
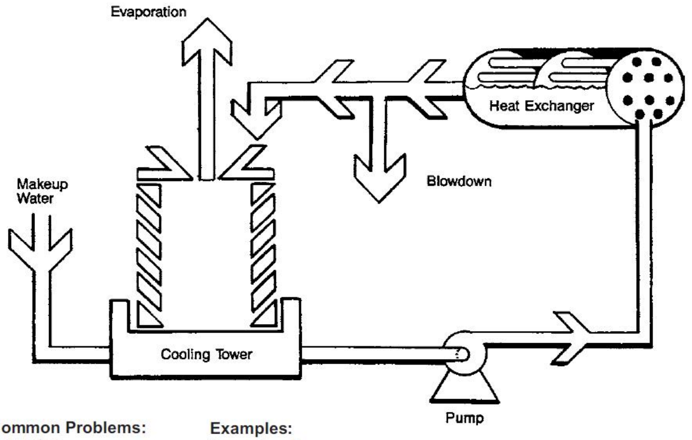
2.1.1 Types of cooling water system

Cooling water system could be categorized to be three types as following (Seneviratne, 2007):

1. Once-through systems – They uses large amounts of water and the water in the system is use only one time. This system was commonly used in thermal power plant and steel mills industries. The Once-through system has high potential to environmental damage from thermal shock of hot water discharges.
2. Closed re-circuit systems – The cooling water of these systems were completely localized in the pipe systems and heat exchangers. These systems were used for control temperature of industrial processes such as cooling gas engines, compressors. The design of this system was not for water leak.
3. Open re-circuit systems – The cooling water was lost by evaporation at cooling unit. These systems were commonly used to control temperature in the huge office buildings. The makeup water was used to replace water

lost in the system. The schematics of cooling water system types are shown in **Table 1**

Table 1 The schematic types of cooling water system

System	Schematic
Once-through systems	 **Common Problems:** Corrosion Fouling Scale Microbiological Contamination **Examples:** Potable Water Systems Process Water General Service Amount of Water Used: Extremely Large
Closed re-circuit systems	 **Common Problems:** Corrosion Fouling Leakage Microbiological Contamination **Examples:** Diesel Engine Jackets Automobile Radiators Chilled Water Systems Amount of Water Used: Negligible
Open re-circuit systems	 **Common Problems:** Corrosion Fouling Scale Wood Decay Microbiological Contamination **Examples:** Spray Ponds Cooling Towers Evaporative Condensers Amount of Water Used: Moderate

(Source: NALCO Company Operation, Cooling water treatment, 2005)

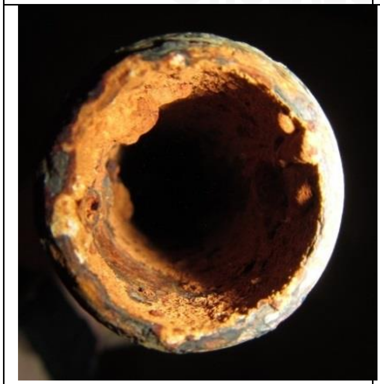
Three main problems in cooling water system that may cause of the failure of the systems can be concluded as following (U.S. Army for Center for Public Works, 1998):

1. Scaling: The causes of scaling in the cooling system was calcium carbonate in the form of calcite including calcium phosphate, calcium sulfate, magnesium silicate and silica. The decrease of increase solubility of calcium carbonate was complex function with temperature, TDS, total alkalinity and pH.

2. Fouling: The causes of fouling on the surface of heat exchanger were silt, dust, suspended solids and microbial.

3. Corrosion: The dilapidation of a metal in cooling system was occurred at the contact area between metal surface and cooling water. At contact area, electron can transfer from metal to cooling water as the electric currents from anode part to cathode part via cooling water. **Table 2** Illustrated the damage in pipelines caused by untreated cooling water.

Table 2 The problem in pipeline of cooling water system

Scaling	Fouling	Corrosion
		

2.1.2 Biocide

Chemical production was used to control the growth of microorganisms such as algae, fungi and bacteria in cooling water system and protect the fouling problem. Biocides were stable in long period, were not lost from systems through evaporation and were not decomposed by high temperatures.

Keister (2008) concluded two major classes of biocide were oxidizing biocides and non-oxidizing biocide. Oxidizing biocides destroys the cellular structure of the organism and kill the organisms by chemical oxidation function. Oxidizing biocides were rapid effect to organisms in low dosage. While non-oxidizing biocides function by interference with the metabolism of the organisms, and most of non-oxidizing biocides function were not effect to corrosion and scaling in the system. Biocides that uses in the present are shown in **Table 3.**

Table 3 Oxidizing biocide and non-oxidizing biocides

Types	Chemicals	Efficiency Concentrations
Oxidizing biocides	Hydantoin	12 – 36 mg/L
	p-Chlorophenol	42.5 mg/L
	Stabilized bromine	5.25 mg/L
Non-oxidizing biocides	Carbamates	40- 60 mg/L
	Isothiazolin	883 ppm
	Sodium hypochlorite	3.75 mg/L

(Source: Keister, 2008)

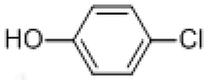
2.1.3 p-Chlorophenol

p-Chlorophenol was a one of chlorophenol compounds and was widely used pesticides, fungicides, preservative agent of wood, industrial leather and antifouling agent (Yin et al., 2014). Chlorophenols exposed to environment by contaminated to discharged wastewater and it was concerned as aquatic biota degradation (Zhou et al., 2013). Moreover, it was a most toxic pollutant and was listed as a pollutant by the US EPA (Duan et al., 2013).

p-Chlorophenols could expose to the environment while they were made or used as biocides and contaminated in discharged cooling water. Most of the chlorophenols released into the environment go into water, with very little entering the air. Normally, the compounds of chlorophenol were going to the water but mono- and di-chlorophenol are likely going to the air because they were the most volatile. Monochlorophenols and dichlorophenol were volatile to atmosphere easier than trichlorophenols and tetrachlorophenols. However, chlorophenols were volatile by a small fraction approximately 5% (Scow et al., 1982).

The main factor affected to the fate and transport of p-chlorophenol was pH. But other factors were considered too, e.g., water solubility, molecular structure, Henry's law constant and volatilization rate. Chlorophenols stick to soil and sediments at the bottom of water resources (U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 1999). The properties of p-chlorophenol was shown in **Table 4.**

Table 4 Physicochemical properties of p-chlorophenol

Formula	C_6H_5ClO
Molecular weight	128.56 g/mol
Molecular structure	
Physical state	Solid
Odor	Medicinal odor
Boling point	220 °C
Melting point	41 - 44 °C
Solubility in water	27 g/L
Density @20 °C	1.31 g/ml
pKa	9.26
Log K_{ow}	2.4
Log K_{oc}	1.2 - 2.7
Henry's law constant @25 °C	9.2×10^{-7} atm-m^3/mol
Average mass	128.556305 Da

(Source : U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 1999) p-Chlorophenol's waste was released into the environment from chlorophenol's production and its use as biocide or pesticide. The partition of p-chlorophenol into different environmental compartments was shown in **Table 5.**

Table 5 Partition of p-chlorophenol in environmental compartments

Compartment	%
Water	89.1
Air	7.6
Soil	1.7
Sediment	1.6

(Source: EuroChlor, 2002)

In the atmosphere, p-chlorophenol go into the atmosphere due to its properties was volatile compounds and was released from the incinerator. p-Chlorophenol in the atmosphere were degraded by photolytic degradation and hydroxyl redical attack and the degradation per hour were 0.022 % and 41 % respectively (Bunce & Nakai, 1989)

In the soil and sediment, p-chlorophenol was released into soil and sediment by the process of leaking from landfill, atmospheric deposition, accidental released and discharged wastewater (U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 1999). p-Chlorophenol was partitioned into soil and sediment due to its log K_{ow} was >1 (Scow et al., 1982). However, the prediction of modeling study of chlorophenols in the river found that 72 % presented in water and 28 % presented in sediment (U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 1999).

In the water, 85 % of chlorophenols that releases into environment were detected at surface water (Scow et al., 1982). p-Chlorophenol was a most frequently found from the discharged source into the water resources and its was detected from the bleaching straw mill process at the concentration of 5.3 μg/L (U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 1999). p-Chlorophenol had the potential to accumulate in aquatic biota and the values of bioconcentration factor was predict by mathematics equation (Veith et al, 1980). The photolysis and reaction of hydroxyl redical might be the main process to degrade p-chlorophenol near water surface but the water conditions and properties should be effected too (U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 1999). The degradation of p-chlorophenol in estuarine and distilled water by photolysis process were similar and the half-life of p-chlorophenol in two types of water were 63 hours (Hwang & Hodson, 1986). p-Chlorophenol in water at the concentration of 0.5 μg/L. was not concerned for bioaccumulation and biodegradation but at the high concentration was affected directly to organisms of aquatic biota (Euro Chlor,2002).

Most of p-Chlorophenol exposed into the environment by contaminated with discharged wastewater. The amount of p-chlorophenol in the environment was concerned to the bioaccumulation and biodegradation (U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 1999).

Yogesh et al, (2008) investigated the separation performances of chlorophenol compound in water by using four types of thin film composite membranes. The mechanisms to reject chlorophenol compounds in water by membrane filtration were size exclusion and polarity of the molecules. The results of experiments were shown in **Table 6.**

Table 6 Performance data of all four membranes

Types	Performance for NaCl 1000 ppm.		Performance for the phenols compounds 50 ppm					
			2,6-Dichorophenol		m-Chlorophenol		p-Chlorophenol	
	Flux ($L/m^2 \cdot hr$)	% R	Flux ($L/m^2 \cdot hr$)	% R	Flux ($L/m^2 \cdot hr$)	% R	Flux ($L/m^2 \cdot hr$)	% R
MB-1	631.7	77.3	868.6	48.88	552.7	33.03	592.2	21.21
MB-2	671.1	56.75	908.0	43.92	651.4	27.62	532.9	19.63
MB-3	437.7	43.24	572.5	38.58	552.7	21.59	513.2	16.95
MB-4	2881.9	5.55	1934.5	13.22	1776.6	8.32	1677.9	2.45

2.1.4 Cooling water characteristics

The Japan Refrigeration and Air Conditioning Industry Association (JRA) suggested the standard of water quality guideline for cooling water to obtain the cooling water system and protect the problem of corrosion and scaling in the cooling water system in **Table 7.**

Table 7 Water quality standards for cooling

Items		Circulating water system		Tendency	
		Circulating water	Makeup water	Corrosion	Scaling
Std. value	pH (25°C)	6.5-8.2	6.0-8.0	O	O
	EC (mS/m)	≤ 80	≤ 30	O	O
	Chloride ion (mg/l)	≤ 200	≤ 50	O	
	sulfate ion (mg/l)	≤ 200	≤ 50	O	
	total hardness (mg/l)	≤ 200	≤ 70		O
	calcium hardness (mg/l)	≤ 150	≤ 50		O
Ref.	ionized silica (mg/l)	≤ 50	≤ 30		O
	iron (mg/l)	≤ 1.0	≤ 0.3	O	O
	sulfide ion(mg/l)	ND	ND	O	
	ammonium ion (mg/l)	≤ 1.0	≤ 0.1	O	
	residual chlorine (mg/l)	≤ 0.3	≤ 0.3	O	
	free carbon dioxide (mg/l)	≤ 4.0	≤ 4.0	O	

(Source: The Japan Refrigeration and Air Conditioning Industry Association. (1994), ND = Not to be detected, O = The factor relevant to corrosion or scaling)

Raw water may contain many types of substances depending on the source and activity of surround water used. Common substances found in natural raw water are inorganic and organic substances. Some types of the contaminants can affect to cooling water system. Types of substances found in raw water are shown in **Table 8.**

Table 8 Types of substances found in cooling water

Types of substances	**Example**
Dissolved	
Positive ions	Calcium, magnesium, sodium, potassium
Negative ions	Carbonate, bicarbonate, phosphate, chloride, cyanide
Disinfectants	Chlorine
Heavy metals	Copper, nickel, chromium, lead, mercury
Gases	Oxygen, carbon dioxide, ammonia, hydrogen sulphide
Physical	
Color	Dissolved organic matter, iron, manganese, dyes, algae
Taste and odor	Geosmin, sulphide, chlorine
Appearance	Silt-suspended solids, plankton, oil fats, petroleum hydrocarbons

(Source: (Seneviratne, 2007)

Evaporation of cooling water at the heat exchanger and cooling unit could cause the water lost in cooling system. The total dissolved solid (TDS) in the cooling water system become higher and could reach the recommended maximum TDS concentration. For preventing the TDS to make damage in the equipment of cooling system, concentrated cooling water was discharged (blowdown process) and new makeup water was added to reduce TDS concentration and replace the water lost (San Diego County Water Authority, 2009)

The TDS was the sum of dissolved minerals including the carbonates, chlorides and sulfates. The TDS can contribute to both scaling and corrosion in heat-transfer equipment. Hence, the concentrated cooling water can cause the corrosion and scaling in pipe lines of cooling water system.

Total solid (TS) was the sum of Total Dissolved Solids (TDS) and Total Suspended Solids (TSS). The dissolved contaminant was measured in the unit of mg/L and µg/L. In the field of water analysis, TDS which relate to specific salt solution could be measured approximately by a conductivity meter. TDS concentration could be roughly calculated by multiple the conductivity with the factor of 0.66 (Osmonics Inc, 1997). Types of solid substance in water were shown in **Table 9**.

Table 9 Types of solid substances found in water

TDS		TSS	
Organic	Inorganic	Organic	Inorganic
Humic acid	Reactive silica (dissolved)	Algae	Silt
Tannin		Fungi	Rust
Pyrogens	Salt ions	Bacteria	Clays

Water’s electrical conductivity was used to evaluate total ionic concentration. The electrical conductivity is easily to measure and it was used in daily quality control. The unit of electrical conductivity was microsiemens/cm (μS/cm). Resistivity was the reverse of conductivity and the unit of resistivity was megaohm-cm (MΩ-cm) (Osmonics Inc, 1997). The relationship of concentration of dissolved minerals versus conductivity and Resistance were shown in **Table 10**.

Table 10 Relationship of concentration of dissolved minerals versus conductivity and resistance at 25 °C

NaCl (mg/L)	TDS (mg/L as $CaCO_3$)	Conductivity (µS/cm)	Resistance (ohms/cm)
0.05	0.043	0.105	9523800
0.1	0.085	0.212	4716980
0.5	0.425	1.06	943396
5.0	4.25	10.6	94339
10.0	8.5	21.2	47169
100.0	85	212	4716

(Source: Osmonics Inc, 1997)

The equation to show the relationship between conductivity and TDS (Seneviratne, 2007). The equation was shown in **Eq. 1.1.**

TDS = 0.55–0.8 × conductivity. The average is 0.64. (1.1)

Table 11 Factors for converting conductivity to TDS

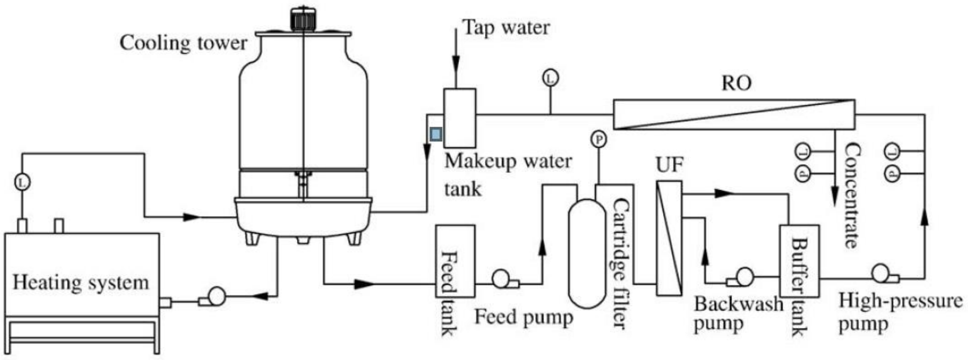
Unit	To convert	Multiply by	To obtain
Conductivity	µS/cm or µmho/cm (when <5000µS/cm) (when >15000µS/cm)	 0.64 0.8	 mg/L mg/L
TDS	mg/L	1.0	ppm
Water salinity	deciSiemens/metre (dS/m) or millimho/cm	1000.0	µS/cm or µmho/cm

2.1.5 Methods to treat cooling water discharged

Concentrated cooling water was discharged to drainage system or natural water resource that may cause the contamination of TDS and turbidity problem in natural water resources. Moreover, residual chemical in discharged cooling water was toxic to biota and that toxicity could be accumulated in the ecosystem.

Water treatment was the process to control corrosion and scaling in cooling water system. Including reduce the problem of deficient water resource and utilized water as high worth (U.S. Army Center for Public Works, 1998).

UF membrane pretreatment and RO membrane were used to treat blow down water from air conditioning cooling water system in the pilot test scale. The UF-RO were optimized the operation of cooling water system and ensure the quality of cooling water within the JRA (The Japan Refrigeration and Air Conditioning Industry Association) water standard (Yan et al., 2010). The schematic and the results of the reported experiments are shown in **Figure 3** and **Table 12**, respectively.



(Source: Yan et al., 2010)

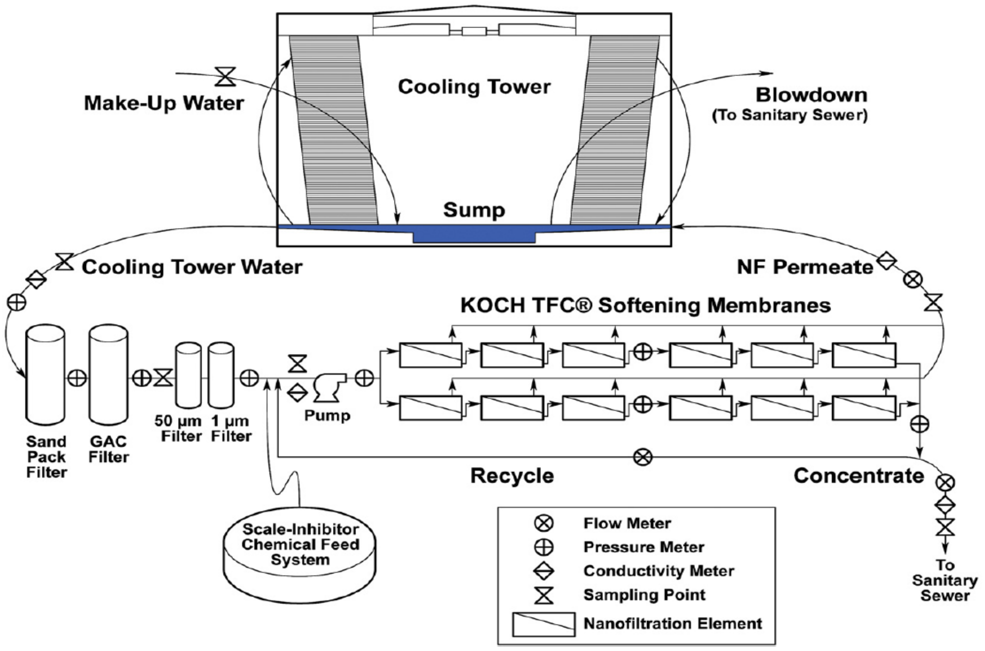
Figure 3 Schematic diagram of the pilot test system

Table 12 Water quality of each sampling point

Items	JRA standard	Tap Water quality	Feed water	UF-RO product
pH	6.5-8.2	7.2-7.6	8.4	7.29
Conductivity, (μS/cm)	≤ 800	230-270	340.0	24.00
Total hardness, (mg $CaCO_3$/L)	≤ 200	92-172	192.0	5.00
Ca^{2+}, (mg $CaCO_3$/L)	≤150	83-120	145.0	4.00
Alkalinity, (mg $CaCO_3$/L)	≤ 100	59-94	104.0	3.75
SiO_2, (mg/L)	≤ 50	< 1	1.3	0.68
Cl^{-}, (mg/L)	≤ 200	30-42	51.0	2.20
SO^{2-}_4, (mg/L)	≤ 200	30.57-40.2	59.0	1.60

(Source: Yan et al., 2010)

The application of NF membrane (KOCH TFC® softening membranes) for reverse osmosis process to treat re-circulated cooling water in order to reduce water usage and discharge. The average applied pressure for nanofiltration process in the experiment is 8.6 psi. The treated permeate water was returned to the cooling water system, the concentrated permeate water was discharged to sanitary sewer (Altman et al., 2012). The schematic and the results of the experiments are shown in **Figure 4** and **Table 13,** respectively.



(Source: Altman et al., 2011)

Figure 4 Schematic of nanofiltration pilot flow diagram

Table 13 Summary of water chemistry data

Constituent	Make up	Cooling tower	Feed	Permeate	concentrate
Ca, (mg/L)	37	115	148	10	172
Mg, (mg/L)	6.6	22	28	2	33
K, (mg/L)	3.6	20	22	5.7	26
Na, (mg/L)	27	103	126	32	139
Cl^-, (mg/L)	22	90	105	30	118
F^-, (mg/L)	0.6	2	2.5	0.5	2.9
SO^{2-}_4, (mg/L)	36	121	157	5.2	179
HCO^-_3,(mg/L)	113	401	506	72	562
SiO_2, (mg/L)	27	116	136	38	151

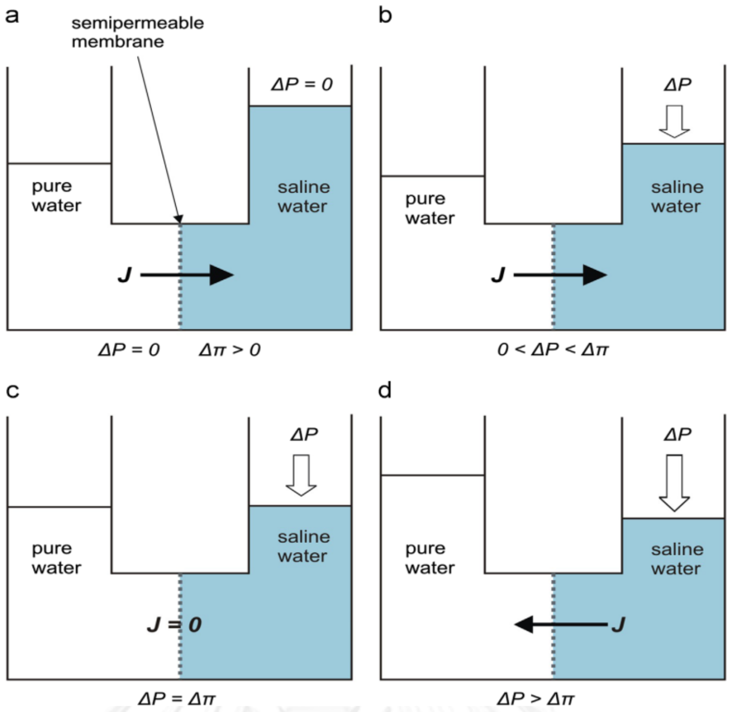
(Source: Altman et al., 2011)

2.2 Forward osmosis

2.2.1 Background

Osmosis was the movement of water selectively passes through semi-permeable membrane from a side of higher water chemical potential to the side of lower water chemical potential, water would across membrane by the differential concentration of water solution. Osmotic pressure (π) has been applied in Forward Osmosis (FO) process by using the differential osmotic pressure ($\Delta\pi$) between feed solution side and draw solution side, draw solution side must has osmotic pressure higher than feed solution side and water would across membrane from feed solution side to draw solution side by osmotic differential force. At the present, the applications of FO were used in many fields such as wastewater treatment, food processing, and seawater/brackish water desalination (Cath et al., 2006).

Helfer et al, (2014) showed four possible osmotic processes via semi-permeable membrane that might be occurred by using pure water as feed solution and saline water as draw solution. The schematics of 4 osmotic phenomena were shown in **Figure 5.**



(Source: Helfer et al., 2013)

Figure 5 Schematic representations of four osmotic phenomena

In **Figure 5**, J = water flux, $\Delta\pi$ = the osmotic pressure differential between the feed and the draw solution and ΔP = hydrostatic pressure differential between the feed and the draw solution

Yangali-Quintanilla et al, (2011 proposed the equation to calculate the osmotic flux for FO membrane as described below:

$$J_w = \frac{\Delta V}{At} \tag{2.1}$$

Where Jw was the water flux (L/m^2·hr); ΔV is the differential volume changed of draw solution (L); *A* was the area of membrane (m^2); and t was the time that used in FO process (hr).

Nguyen et al, (2013) proposed the equation to describe the osmotic pressure (π) driving force and water flux (Jw) across the FO membrane in FO process:

$$\pi = iCRT \qquad (2.2)$$

Where π was the osmotic pressure (Pa); i was a number of ions produced during dissociation of solute, C was the concentration of solute (mol/L); R was the gas constant (R = 0.082 L·atm/(mol·K)) and T was the absolute temperature (K).

$$\text{With } J_w = A_w (\pi_{\text{Draw solution}} - \pi_{\text{Feed solution}}) \qquad (2.3)$$

Where Jw was the water flux; A_w was the permeability coefficient of membrane; $\pi_{\text{Draw solution}}$ was the osmotic pressure of draw solution and $\pi_{\text{Feed solution}}$ was osmotic pressure of feed solution.

2.2.2 Draw solution

Draw solution was the concentrated solution that has a high osmotic pressure to draw water from feed solution side which consists with water and other solutions by pass through semi-permeable membrane. The requirements of an ideal draw solution were following. 1. It could be produced high osmotic pressure and the osmotic pressure difference (osmotic gradient) between draw solution and feed solution which was the main force to driving FO process. 2. The reverse flux of the draw solution might be minimal. Because most of FO membranes were not ideally semi-permeable, the draw solution would diffused to feed solution that affects to reduce the driving force and contaminated to feed solution. 3. Easy to regenerate the diluted draw solution after passed FO process. 4. Draw solution should have a small molecular weight and low viscosity in its liquid solution (Ge et al., 2013).

The appropriate draw solution should have high solubility in water and high osmotic pressure to draw water from feed solution side to get high water flux passed through the semi-permeable membrane, draw solution should be easily separable from water in low energy consumption. And draw solution should be easily separable from water in low energy consumption (Kim et al., 2012). 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 (Zhao et al., 2012).

Jin et al, (2012) investigated the rejection efficiency of pharmaceutical compounds (e.g. carbamazepine, diclofenac, ibuprofen and naproxen) by cellulose triacetate (CTA) membrane and thin film composited (TFC) polyamide membrane by forward osmosis process. The condition was fixed by feeding solution contained 250 μg/L of each pharmaceutical compound and 10 mM NaCl at pH 6. The draw solution contained 2 M NaCl. TFC polyamide membrane exhibited rejection efficiency ranging from 94-97%, and CTA membrane exhibited rejection efficiency ranging from 64-96%.

Kim et al, (2012) used three draw solutions which were NaCl (monovalent), $CaCl_2$ (divalent) and $LaCl_3$ (trivalent) to draw Boron that dissolved in water 02-14.0 mg/L. The highest boron solute flux was obtained from $LaCl_3$ draw solution and the lowest boron solute flux was obtained from NaCl draw solution that follow the basic theory of osmotic pressure that the multivalent solution has more osmotic pressure than monovalent solution.

McCutcheon et al, (2006) proposed mixing of ammonium bicarbonate (NH_4HCO_3) with ammonium hydroxide (NH_4OH) as draw solution in wide range of concentration (1.1 – 6 M) for investigate influence of process performance. Water fluxes ranging from 3.6 – 36.01 L/m^2·hr, depending on the concentration of draw solution. High concentration of draw solution got more water flux than low concentration of draw solution due to the osmotic force of draw solution. Concentration of feed solution is affected water flux in draw side due to the phenomena of concentrative-concentration polarization on active layer surface membrane.

2.2.3 Membrane filtration

Membrane filtration was applied to separate unwanted components from water by semipermeable membrane. Two basic criteria to describe membrane filtration were the process must have pressure to remove particles lager than 1 μm by using barrier via s size exclusion mechanism and the process must have the measurement of target particulate removal efficiency (US EPA, 2005).

The membrane was a specific filter to reject suspended solid or other substances but let water pass through. The category of membranes could be separated by using their ability to remove particles and solute in solution by a mechanism of sieving on the size of membrane pores. Four common types of membrane were MF, UF, NF and RO (Gupta & Ali, 2013). The characteristics of each membrane type are shown in **Table 14.**

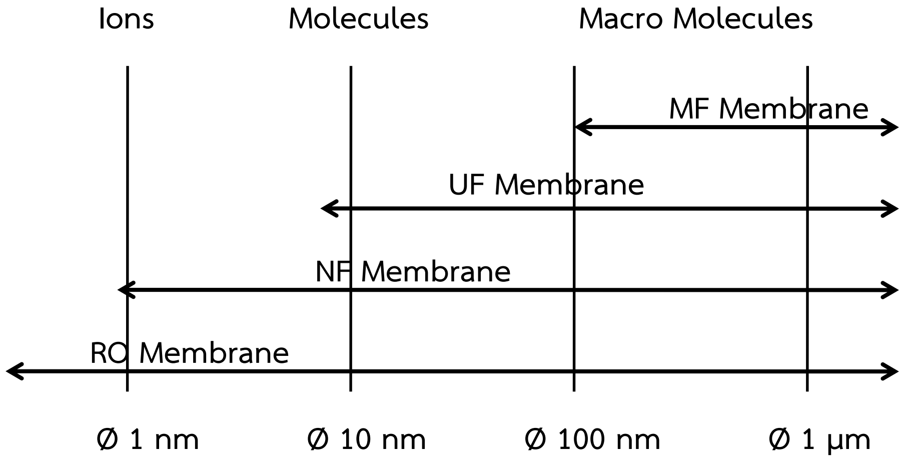
Table 14 The characteristics of membrane in each type

	RO membrane	NF membrane	UF membrane	MF membrane
Structure	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical Symmetrical
Pore size	< 0.002 µm	< 0.002 µm	0.2 - 0.02µm	4 – 0.02 µm
Rejection	HMWC, LMWC glucose, amino acids	HMWC, polyvalent neg. ions	Macro molecules, polysaccharides	Particles, clay
Membrane material	Cellulose acetate, Thin film composite	Cellulose acetate, Thin film composite	Polysulfone, Thin film composite	Ceramic, Polysulfone
Operating pressure	1.5-15 MPa	0.5-3.5 MPa	0.1-1 MPa	< 0.2 MPa
Method	Dead-end filtration Cross-flow filtration	Dead-end filtration Cross-flow filtration	Dead-end filtration Cross-flow filtration	Dead-end filtration Cross-flow filtration

(Source: Wongrueng, 2005)

The MF membrane and the UF membrane were used for eliminating particulate matter which was larger particles, permeate water flux of these two membrane were high while the apply pressure were low. When the water was contaminated with ions or small molecules, NF membrane and RO membrane were used to remove those contaminants. In contrast, permeate water flux of these membranes were low and the applied pressure were high.

Figure 6 illustrates the operating range of each membrane to remove particulate matter that contaminated in water. It can be concluded that the RO membrane has the widest operating range to remove almost all particulate matter in water while the MF membrane has the narrowest operating range to remove particulate matter and the MF membrane should be used as a pretreatment unit.



(Source: Gupta and Ali, 2013)

Figure 6 Operating of membranes on undesirable components

Zhao et al, (2012) were collected data of the membrane types for using in FO process. After the 2000s FO membrane was developed. And the development of FO membranes types and materials were shown in **Table 15.**

Table 15 FO membranes developments

Year	Membranes	Materials
2005	Capsule wall membrane	Cellulose acetate or ethyl cellulose
2007	Hollow fiber NF	Polybenzimidazole (PBI)
2008	Flat sheet cellulose acetate membrane	Cellulose acetate
2009	Dual-layer hollow fiber NF	PBI–PES/PVP
2010	Hollow fiber NF	Cellulose acetate
2010	Flat sheet TFC membrane	Polysulfone (PSf) support, Polyamide active layer
2010	Double dense-layer membrane	Cellulose acetate
2011	Modified RO	PSf support modified by polydopamine
2011	Flat sheet composite	Cellulose acetate cast on a nylon fabric
2011	Flat sheet TFC polyamide	PES/SPSf substrate, Polyamide active layer
2011	Flat sheet TFC	PSF support, polyamide active layer
2011	Flat sheet TFC polyamide	PES nanofiber support, polyamide active layer

(Source: Shuaifei Zhao, 2012)

2.2.4 RO membrane

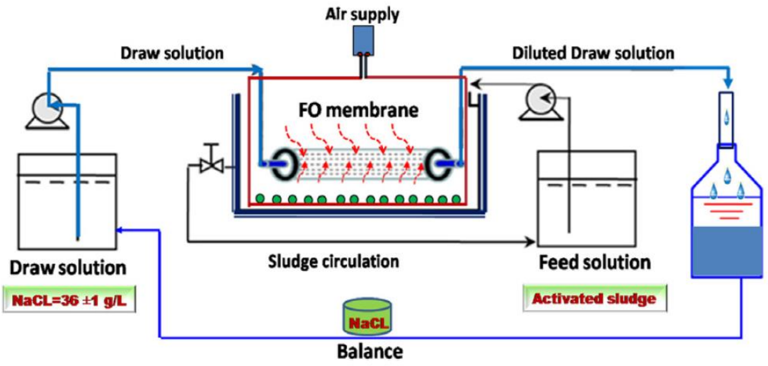
The RO Membranes were widely used in wastewater treatment and especially in sea water desalination. Because the pore size of RO Membrane is very small (< 0.1 nm), it could be rejected the contaminants which have the size larger than 0.1 nm. The ability of RO membrane could be treat wastewater or sea water which contained bacteria, viruses, colloids particles or organic/inorganic ions.

The RO membranes types were commonly used in form of thin film composite polyamide membrane (TFC polyamide). The active layer of membrane were consists of polyamide (Amine functional group and Carboxyl functional group) and the approximately dense of active layer was 0.1 nm. The supporting layer of membrane were consists of polysulfone and the approximately dense was 100 nm. The RO membranes could be categorized to be many types depending on the operating condition.

2.2.5 Applications of forward osmosis

2.2.5.1 Sludge Dewatering

Application of FO was used to dewatering high nutrient sludge from Taipei wastewater treatment plant. Mixed Liquor Suspended Solids (MLSS) concentration of sludge was 3000-8000 mg/L and used as feed solution (FS) in the FO process. 36 mg/L NaCl solution was used as DS. After 28 hours of sludge dewatering, the in concentration of sludge 3000 mg/L and 8000 mg/l were changed to be 21511 mg/L and 28500 mg/L respectively. The schematic of the FO application was shown in **Figure 7.**



(Source: Nguyen et al., 2013)

Figure 7 Schematic of the high nutrient sludge dewatering FO system

Hau et al, (2014) used EDTA sodium salt as DS in FO process to dewatering sludge. The concentration 0.3 M of DS was fixed at pH 8.0. The NF membrane is the barrier in the FO process. Initial MLSS concentration of sludge was 8000 mg/L and was used as FS. After operation the process 18 hours concentration of FS was changed to be 32000 mg/L.

Zhu et al, (2012) investigated the possibility of forward osmosis process to dewatering the waste activated sludge. After 19 days operation, The MLSS concentration was changed from 7 g/L to 39 g/L. The activated sludge was obtained from WTTP located in the northern part of Beijing and used as DS.

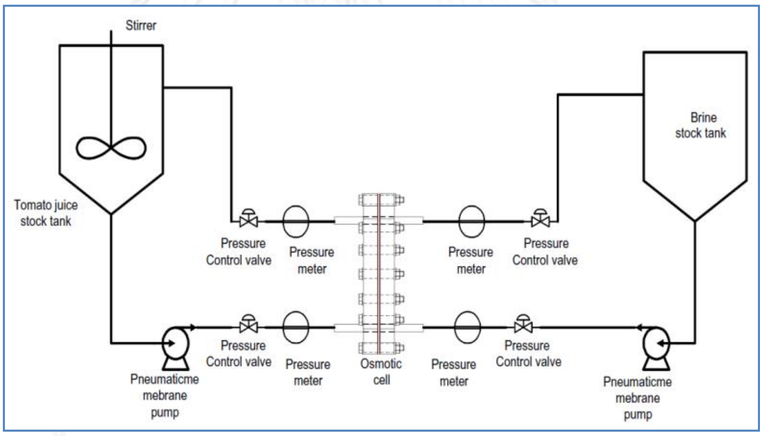
2.2.5.2 Pharmaceutical treatment

Jin et al, (2012) investigated the efficiency of CTA membrane and TFC membrane to reject pharmaceuticals by FO process. carbamazepine, diclofenac, ibuprofen and naproxen dissolved in FS. The feed solution contained 250 μg/L of each pharmaceutical and 10 mM NaCl. Draw solution was solution of NaCl 2 M. TFC membrane exhibited high water flux and high of all pharmaceuticals rejection

(> 94%). The pharmaceuticals rejection by CTA membrane at pH 8.0 were diclofenac (99%) > carbamazepine (95%) > ibuprofen (93%) ≈ naproxen (93%).

2.2.5.3 Food concentration

Petrotos et al, (2010) used forward osmosis application to increase concentration of tomato juice. The hydraulic pressure of pump was fixed at 0.4 MPa for feed side and 0.15 MPa for draw side. The TFC-RO was used as barrier. Fresh tomato juice was used as feed solution and solution of NaCl as draw solution. After 11 hours operation concentration of tomato juice is changed from 5.5 to 16.0 °Brix. The schematic of forward osmosis application to concentrated tomato juice is shown in **Figure 8.**



(Source: Petrotos et al., 2009)

Figure 8 Schematic of forward osmosis application to concentrate tomato juice

Garcia-Castello et al, (2009) investigated performance evaluation of sucrose concentration by using forward osmosis process. Flat sheet of cellulosic membrane (CA) and AG reverse osmosis were used process. Draw solution was NaCl solution and sucrose was feed solution. The result of the experiment is shown in **Table 16.**

Table 16 Results of each experimental condition in FO process

Membrane	Concentration of sucrose as FS (M)	Concentration of NaCl solution as DS (M)	Flux @ differential Temp. (L/m^2·hr)	
			20 °C	30 °C
CA	0 – 1.65	2	17 – 4	26 - 5
CA	0 – 1.65	4	24 – 7.5	34 - 10
AG	0 – 0.7	4	1.5 – 1	2.5- 2

(Source: Garcia et al., 2009)

2.2.5.4 Sea water desalination

Zhao et al, (2012) investigated brackish water desalination by a forward osmosis-nanofiltration system. Real brackish water from Mawson Lakes, South Australia which total dissolved solids of 3970 mg/L was used as feed solution. The concentration 0.06 M of Na_2SO_4 was used to be the draw solution and obtained permeate water flux 8.5 L/m^2·hr pass through the NF 270 membrane.

Bamaga et al, (2011) investigated the osmotic potential of NaCl solution as draw solution. Draw solution was prepared by dissolved 99.9% NaCl in tap water. Tap water was used as feed solution. Four concentration of draw solution were 35, 50, 75 and 100 g/L were tested. The approximately permeate water flux from draw solution were 7.5, 9.5, 11 and 13.5 L/m^2·hr, respectively.

CHAPTER 3
METHODOLOGY

3.1 Source of cooling water

The discharged cooling water was collected from one cooling tower in Chulalongkorn University. It was collected in March, 2014. Characteristics of discharged cooling water are shown in **Table 26.**

3.2 Materials

3.2.1 DI-water

Deionized water (DI-water) with resistivity of 18.2 M$\Omega\cdot$cm at 25 °C was used for preparing all solution in this study.

Figure 9 Deionized water (DI-water)

3.2.2 Membrane module

Nitto Denko C-10T was used as test cell to filtrate discharged cooling water by cross-flow operation. The filtration area of test cell is 60 cm^2.

Figure 10 Membrane module

3.2.3 Flat sheet membrane

The thin film composite (TFC) polyamide membrane in reverse osmosis type (RO-1) was purchased from FilmTec corp, Dow chemical company. The membrane was kept in DI-water at the temperature 4 °C. The characteristics of RO-1 membrane were provided in **Table 17.**

Table 17 Characteristics and operating limits of RO-1 membrane

Membrane type	Polyamide thin film composite (flat sheet)
Maximum operating temperature	45 °C
Maximum operating Pressure	2.1 MPa
pH Range, Continuous operation	2 - 11

Figure 11 Flat sheet membrane (RO-1)

3.2.4 Magnetic gear pump

The magnetic gear pump (Iwaki, Japan) was used to pressurized water. The maximum velocity and the maximum pressure of the pump are 2.4 L/min and 0.55 MPa respectively.

Figure 12 Magnetic gear pump

3.2.5 Peristaltic pump

The peristaltic pump (Watson-Marlow Bredel, England) was used for recirculation of draw solution. The range of speed is 0-250 rpm.

Figure 13 Peristaltic pump

3.2.6 Needle valve

The needle valve was used to adjust the hydraulic pressure of feed solution in a recirculation line.

Figure 14 Needle valve

3.2.7 Pressure indicator

Two pressure indicators were used to measure the hydraulic pressure of feed solution in the feed-in line and feed-out line. The capacity of pressure indicator is 0 - 0.5 MPa.

Figure 15 Pressure indicator

3.2.8 Electrical conductivity meter

Electrical conductivity values of feed solution and draw solution were measured by an electrical conductivity meter (CON900, Cond, AMTAST).

Figure 16 Electrical conductivity meter

3.3 Chemical reagents

3.3.1 Sodium chloride Laboratory grade Carlo Erba Company Ltd.

Solid sodium chloride was diluted in DI-water to be sodium chloride solution. Sodium chloride solutions were used as feed solution and draw solution in RO mode and FO mode.

3.3.2 Ammonium bicarbonate Laboratory grade Ajax Finechem Pty Ltd.

Ammonium bicarbonate solution was used as draw solution in FO mode.

3.3.3 p-Chlorophenol Laboratory grade Fluka Company Ltd.

p-Chlorophenol was used as biocide in cooling system. The effective concentration of p-chlorophenol in cooling system was 42.5 mg/L (Keister, 2008)

3.4 Membrane filtration experiments

3.4.1 Preparation of the membrane experiment

RO-1 membrane was cut in the oval shape providing 60 cm^2 filtration area and stored in DI-water at 4 °C. Before using the membrane in each experiment, the membrane was immersed in DI-water at the room temperature for 24 hours. Then, put the membrane in test cell.

3.4.2 Membrane experiment of RO mode

The experiment was setup as a cross-flow operation. The equipment consisted of two tanks of feed solution and permeate water. A magnetic gear pump (MP) was used to recirculate feed solution in RO process. Two pressure indicators were set for measuring the hydraulic pressure. A needle valve was used to control hydraulic pressure of feed side. A digital weight balance and a computer record system were applied to weight the permeate water. After that, the weight of permeate water was converse to volume. The schematic of RO mode is shown in **Figure 17.**

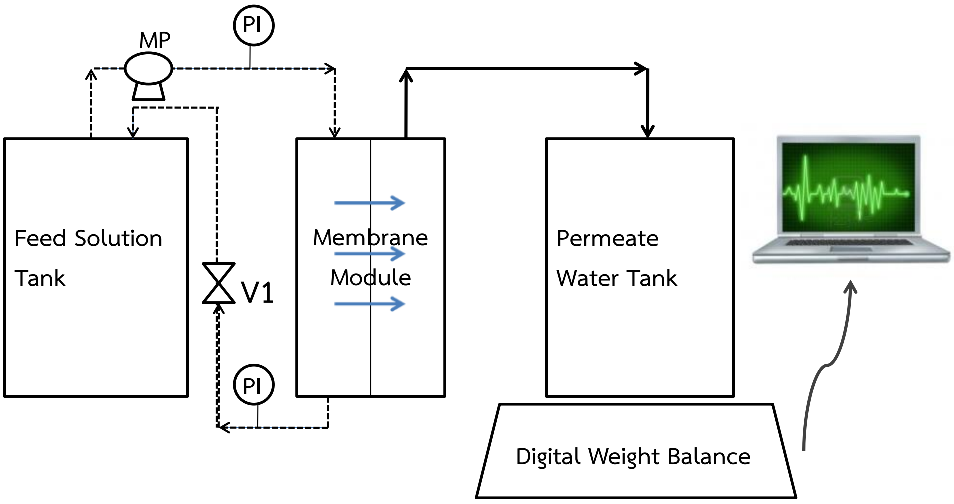


Figure 17 Schematic of reverse osmosis (RO) mode

3.4.3 Characterization of membrane properties

3.4.3.1 Salt rejection

The RO-1 membrane was taken out from the stored place and put in DI-water for 24 hours before use. Sodium chloride solutions were prepared at the concentration of 0.01, 0.05 and 0.1 mol/L, respectively. The sodium chloride solutions were pressurized and flown through the test cell under the pressure of 0.4 MPa.

Then, the samples were collected from the feed line, concentrated line and permeate line for measuring the electrical conductivity and permeate water flux. The electrical conductivity of the samples were further converted to the concentration. Finally, salt rejection was calculated.

3.4.3.2 Isoelectric point

The isoelectric point value was used to describe the pH of solution that can neutralize the membrane surface charge.

RO-1 membrane was brought out from storing place and cut in the small size (4x3 cm) and immersed in DI-water for 24 hours. Solution of sodium chloride (NaCl) was prepared at the concentration of 0.01 mol/L. The pH of sodium chloride solutions were adjusted by 0.01 mol/L hydrochloric acid (HCl) and 0.01 mol/L sodium hydroxide (NaOH). The solution pH was adjusted in a range of 2-10.

Pieces of RO-1 membrane were immersed in each bottle that contained 20 mL of solution at the different pH. Then, pH meter was used to measure the pH of solution in each bottle. All of bottles were shaken by shaker at 200 rpm for 24 hours at the room temperature. Afterward, the pH value of each bottle was measured again. The pH values from before and after the experiment were taken to plot the graph for evaluating the isoelectric point.

3.4.3.3 Water flux measurement

Diagram of the experiment in RO mode is shown in **Figure 3.10**

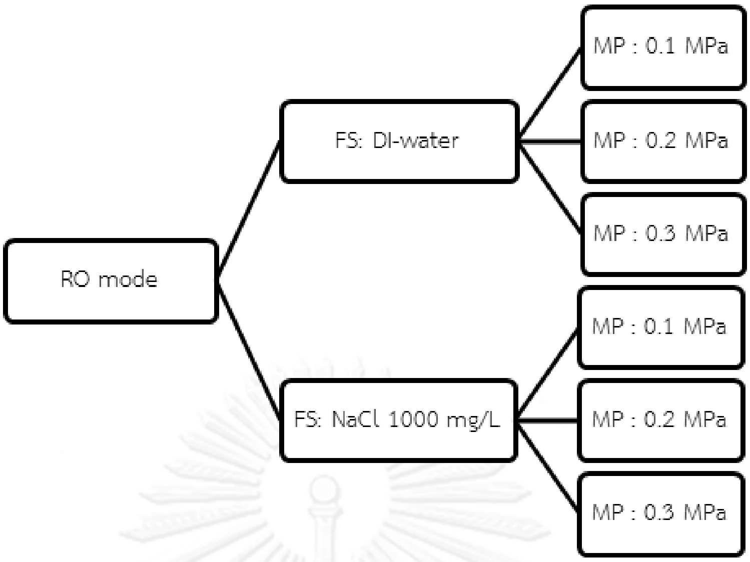


Figure 18 Diagram of the experiment in RO mode

a) Water flux of DI-water as feed solution in RO mode with a variety of applied pressure.

1) DI-water was used as feed solution.

2) The MP sent feed solution to a test cell at the pressure of 0.1 MPa. Permeate water passed through the membrane to a permeate tank.

3) The number on screen of the digital scale is increasing along with the time. The number was recorded by a camera every 5 minutes to calculate the permeate water flux. The operating times of experiment were 2 hours.

4) The pressure of MP were changed to 0.2 MPa and 0.3 MPa respectively. All of the processes after changed the pressure were followed 2) and 3) respectively.

b) Water flux of sodium chloride solution 1000 mg/L as feed solution in RO process with a variety of applied pressure.

1) Sodium chloride solution was prepared at the concentration of 1000 mg/L and used as feed solution.

2) The MP sent feed solution to a test cell at the pressure of 0.1 MPa. Permeate water passed through the membrane to a permeate tank.

3) The number on screen of the digital scale is increasing along with the time. The number was recorded by a camera every 5 minutes to calculate the permeate water flux. The operating times of experiment were 2 hours.

4) The pressure of MP were changed to 0.2 MPa and 0.3 MPa respectively. All of the processes after changed the pressure were followed 2) and 3) respectively.

5) The appropriate pressure of MP was chosen for recirculating the feed solution in the FO mode.

3.4.4 Membrane experiment of FO mode

3.4.4.1 Experiment set up of FO mode

The experiment was setup as a cross-flow operation. The schematic of FO mode and the experimental diagram of FO mode are shown in **Figure 19 and Figure 20.**

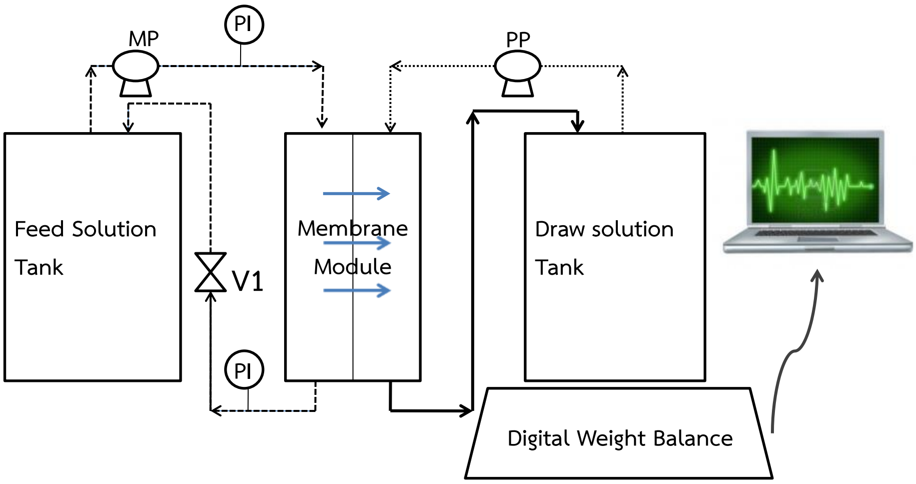


Figure 19 Schematic of forward osmosis (FO) mode

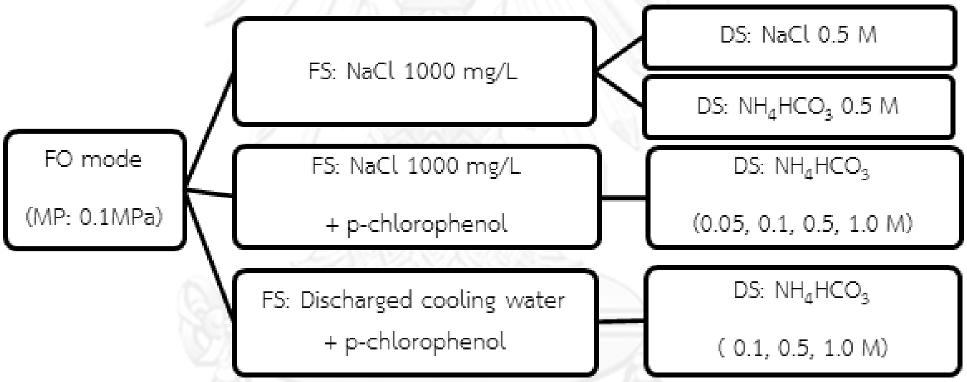


Figure 20 Diagram of the experiment in FO mode

The equipment consisted of two tanks of feed solution and permeate water. A magnetic gear pump (MP) was used to re-circulate feed solution in FO mode. A peristaltic pump (PP) was applied to recirculate draw solution. Two pressure indicators were set for measuring the hydraulic pressure. A needle valve was used to control the pressure of feed side. A digital scale and computer record system were applied to weight the permeate water. After that, the weight of permeate water was converse to volume.

3.4.4.2 Appropriation of draw solution

Appropriation of draw solutions at the concentration of 0.5 M to draw NaCl solution 1000 mg/L. were followed below.

1) Sodium chloride solution was prepared at the concentration of 1000 mg/L and used as feed solution.

2) Sodium chloride solution and ammonium bicarbonate solution were prepared at the concentration of 0.5 M. to use as draw solution.

3) The MP sent feed solution to a test cell at the pressure of 0.1 MPa. The PP sent draw solution (NaCl 0.5M) to a test cell with the speed 20 rpm. The osmosis phenomenon occurred inside the membrane layer. Some of water from feed tank passed through the membrane to the draw tank.

4) The number on screen of the digital scale is increasing along with the time. The number were recorded by a camera every 5 minutes to calculate the permeate water flux. The operating times of experiment were 2 hours.

5) Draw solution was changed from sodium chloride solution to ammonium bicarbonate solution, respectively. All of the processes after changed the draw solution were followed 3) and 4) respectively.

6) Ammonium bicarbonate solution was chosen as the appropriate draw solution.

3.4.4.3 Influence of ammonium bicarbonate concentration on water flux

All of processes were followed ***3.5.4.2.*** Ammonium bicarbonate solutions were prepared at the concentration of 0.05, 0.1, 0.5 and 1.0 M respectively. Feed solutions were changed to sodium chloride solution at the concentration 1000 mg/L mixed with p-chlorophenol at the concentration of 42.5 mg/L and discharged cooling water mixed with p-chlorophenol at the concentration of 42.5 mg/L, respectively.

3.4.4.4 Rejection of p-chlorophenol

p-chlorophenol was measured by UV-vis analyzer at the wavelength 280 nm (U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 1994). The removal of p-chlorophenol by FO mode was calculated from the initial concentration of p-chlorophenol in sodium chloride solution at the concentration 1000 mg/L and p-chlorophenol in draw solution after 5 hours of operation. Measurement of p-chlorophenol in FO mode were followed the steps below.

1) Sodium chloride solution at the concentration 1000 mg/L was used as a blank.

2) p-Chlorophenol were mixed into sodium chloride solution at the concentration 1000 mg/L at the concentrations of 0.5, 5.0, 10, 25, 50 and 70 mg/L respectively. Then, measure the concentration of p-chlorophenol and plot the graph.

3) Sodium chloride solution 1 L. at the concentration 1000 mg/L was mixed with p-chlorophenol 42.5 mg. and used as feed solution in FO mode. Separated that feed solution 20 mL to measure the initial concentration of p-chlorophenol. Then, the residual feed solution was filtrated by mode process. After 5 hours of operating time, feed solution and diluted draw solution were collected to measure the concentration of p-chlorophenol.

4) Discharged cooling water was used as a blank.

5) p-Chlorophenol were mixed into discharged cooling water at the concentrations of 0.5, 5.0, 10, 25, 50 and 70 mg/L respectively. Then, measure the concentration of p-chlorophenol and plot the graph.

6) Discharged cooling water 1 L. was mixed with p-chlorophenol 42.5 mg. and used as feed solution in FO mode. Separated that feed solution 20 mL to measure the initial concentration of p-chlorophenol. Then, the residual feed solution was filtrated by mode process. After 5 hours of operating time, feed solution and diluted draw solution were collected to measure the concentration of p-chlorophenol.

3.4.5 Separation of the product water

NH_4HCO_3 was removed from diluted draw solution by heating or distillation at 60 °C (McCutcheon, McGinnis, & Elimelech, 2005). The distillation process in shown in **Figure 21.**

Figure 21 Experiment setup for NH_4HCO_3 removal

3.4.5.1 Experimental set up of distillation at 60 °C

1) Ammonium bicarbonate solution was prepared at the concentration of 0.05, 0.1, 0.5 and 0.5 M, respectively. 1 L of each draw solution concentration was distilled to separate water and ammonia.

2) The temperature was fixed at 60 °C along the operating time 6 hours. The air blower was set up in the process to made turbulence in bulk concentration of diluted draw solution.

3) The electrical conductivity value and pH of draw solution were measured before and after 6 hours of the operating time.

4) Ammonia product in a flask were measured the quantity of volume, pH and electrical conductivity.

3.4.5.2 Qualities of FS and DS

Qualities of FS and DS were determined by electrical conductivity value. Electrical conductivity values of FS and DS were measured before and after the distillation process. The percentage of ammonia removal was calculated by using electrical conductivity value. Quality of water after separated out of DS by distillation process was compared to cooling water standard.

3.4.5.3 Ammonia production

Ammonia in collecting flask after distillation for 6 hours was measured the quantity of volume. Other qualities of ammonia were measured by pH meter and electrical conductivity meter.

3.5 Analytical instruments

3.5.1 UV-vis analyzer

Concentration of p-chlorophenol in discharged cooling water and draw solution were measured by UV-vis analyzer at wavelength 280 nm.

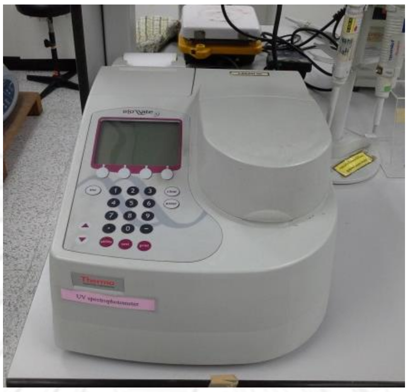


Figure 22 UV-vis analyzer

3.5.2 pH meter

The pH of each solution was measured by a pH/mV meter (pH 3210 SET 2, Germany) which an accuracy of ± 0.01 pH unit. The pH was calibrated before using by buffer solution at the pH levels of 4, 7 and 10 respectively.

Figure 23 pH meter

3.5.3 Thermometer

The temperature of feed solution in feed tank was measured by thermometer. The temperature of feed solution was controlled at 27 °C.

CHAPTER 4

RESULTS AND DISCUSSIONS

The results of experiments and their analyses were shown in the following pages.

4.1 Membrane properties

4.1.1 Permeate water flux

RO-1 membrane was used in this study under crossflow operation and reverse osmosis mode. Permeate water flux of RO-1 was evaluated. DI-water was used as feed solution. The operating pressure ranges were 0.1 – 0.3 MPa, respectively. The permeate water flux was measured along the operating times and were shown in **Appendix A**. The permeate water flux was calculated by using **Eq. 4.1**

$$J_w = \frac{\Delta V}{A \times T} \tag{4.1}$$

Where J_w = Permeate water flux ($L/m^2 \cdot hr$)

ΔV = The differential volume change of permeate water (L)

A = Surface area of RO-1 membrane (60×10^{-4} m^2)

T = Sampling time (hr)

Transmembrane pressure (TMP) is the pressure gradient between feed and concentrate pressure and permeate pressure (Water Environmental Federation, 2006). TMP for crossflow operation of RO mode was calculated as follows **Eq. 4.2**.

$$\text{TMP} = \frac{(P_f + P_c)}{2} - P_p \qquad (4.2)$$

Where TMP = Transmembrane pressure (MPa)

P_f = Feed pressure (MPa)

P_c = Concentrate pressure (MPa)

P_p = Permeate pressure (MPa)

The results of TMP and permeate water flux in the experiments were reported in **Table 18** and **Figure 24,** respectively.

Table 18 Operating transmembrane pressure and permeate water flux of RO-1 membrane

Feed pressure (MPa)	Concentrate Pressure (MPa)	Permeate pressure (MPa)	TMP (MPa)	Average permeate water flux (L/m^2·hr)
0.1	0.07	0	0.085	4.3
0.2	0.17	0	0.185	8.8
0.3	0.28	0	0.290	14.6

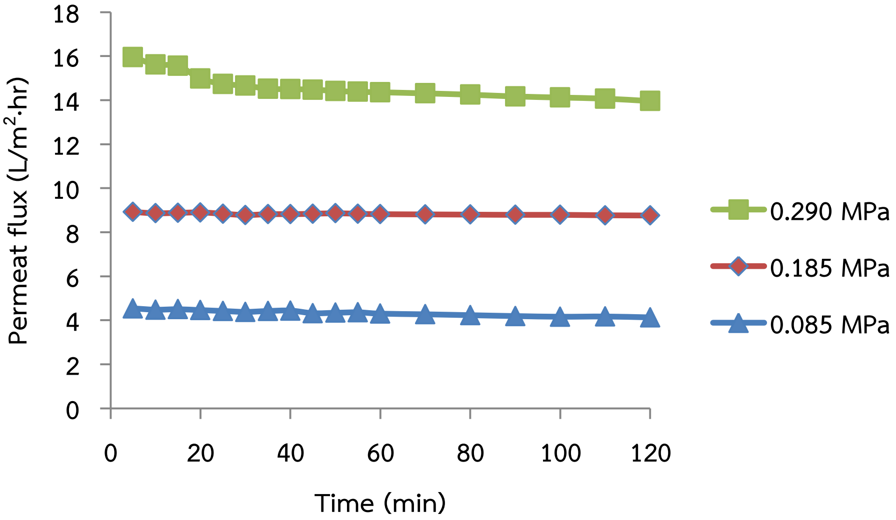


Figure 24 Permeate water flux at various apply pressure

Reverse osmosis is the process to separate liquid solution by using membranes (He et al., 2009). Quantity of permeate water is depending on the applied pressure. Permeate water flux increased with increasing applied pressure (Koyuncu & Topacik, 2003). Permeate water flux at the TMP of 0.085, 0.185 and 0.290 MPa were 4.3, 8.8 and 14.6 L/m^2·hr, respectively.

The volume of water that passed through the area of membrane was defined by the pure water permeability (K_w). The relation between permeate water flux and TMP were used to evaluate K_w by using **Eq. 4.3**. The slope of the graph was presented to K_w. The pure water permeability of RO-1 membrane is shown **Figure 25**.

$$J_w = K_w \times (TMP - \pi) \qquad (4.3)$$

Where K_w = Pure water permeability (L/m^2·hr·MPa)

J_w = Permeate water flux (L/m^2·hr)

TMP = Transmembrane pressure (MPa)

π = Osmotic pressure of DI-water (MPa)

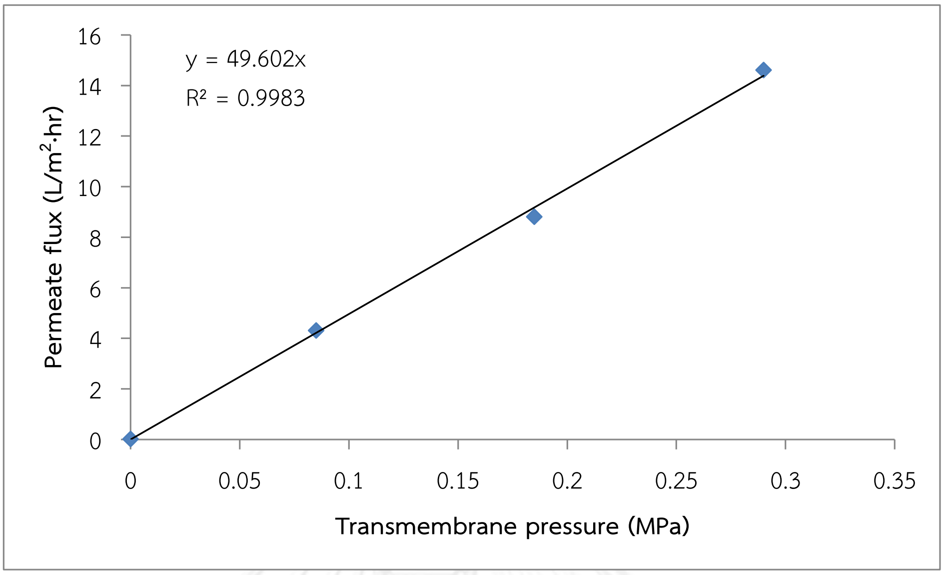


Figure 25 The permeate water fluxes at the steady state of RO-1 membrane

Figure 25 Illustrated the permeate water flux at the steady state of RO-1 membrane as a function of TMP. The linear correlation shown high coefficient (R^2 = 0.998) of RO-1 membrane.

4.1.2 Water flux of NaCl solution

Permeate water flux of DI-water passed through the membrane easily and obtained high permeate water flux because DI-water was the high quality water and pass through the membrane by applied pressured directly.

Water flux of NaCl solution was investigated to study the quality of water that effect to permeated water flux. NaCl solution was used as discharged cooling water in section **4.1.2**. Permeate water fluxes of DI-water and NaCl solution were compared. The lowest applied pressure which the capacity to produce permeate water was chosen to operate feed solution in FO process.

Permeate water flux was obtained by pressurized NaCl solution against RO-1 membrane. Permeate water flux was different in each experiment because the applied pressure was effect directly to permeate water. Permeate water fluxes of NaCl solution were shown in **Table 19** and **Figure 26.**

Table 19 Operating transmembrane pressure and permeate water flux of RO-1 membrane

Feed pressure (MPa)	Concentrate Pressure (MPa)	Permeate pressure (MPa)	TMP (MPa)	Average permeate water flux (L/m^2·hr)
0.1	0.07	0	0.085	1.6
0.2	0.17	0	0.185	5.5
0.3	0.28	0	0.29	10.4

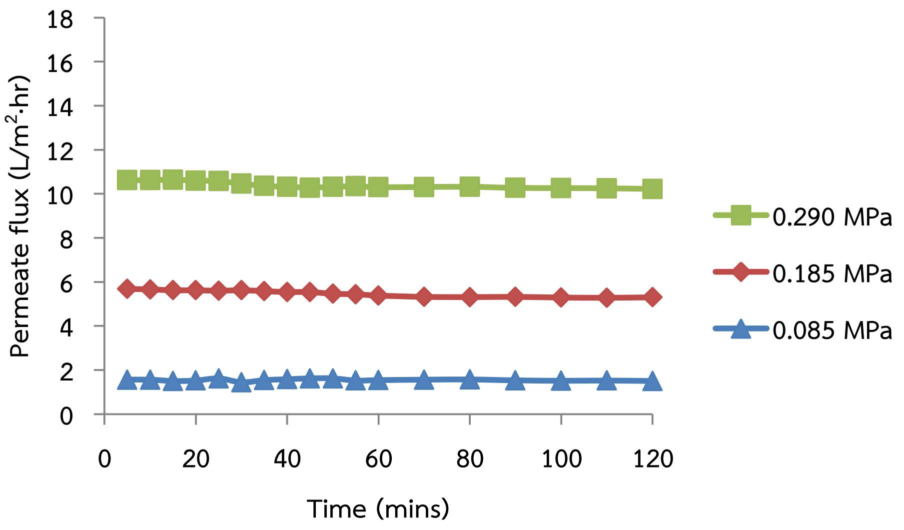


Figure 26 Permeate water flux of NaCl solution at various apply pressure

Permeate water flux of NaCl solution passed through the membrane by applied pressure that was the same reason as **section 4.1.1**. Permeate water flux of NaCl solution at the TMP of 0.085, 0.185 and 0.290 MPa were 1.6, 5.5 and 10.4 L/m^2·hr, respectively. The comparison of permeate water of DI-water and NaCl solution were shown in **Figure 27.**

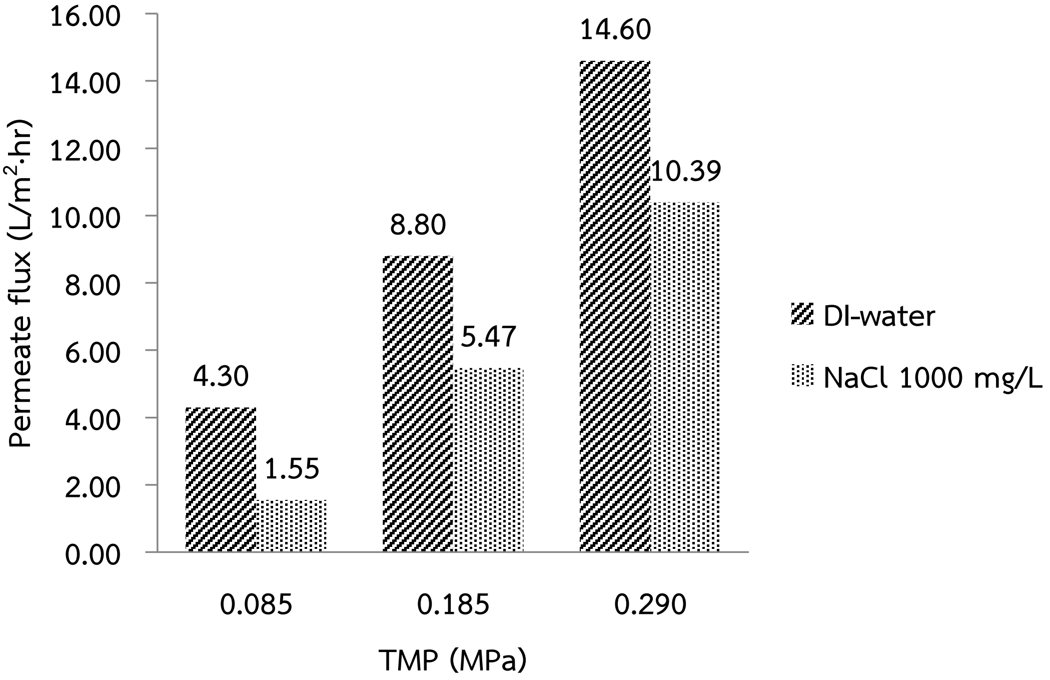


Figure 27 Permeate water flux of DI-water and NaCl solution

Figure 27 was shown permeate water flux of NaCl solution is lower than permeate water flux of DI-water due to osmotic pressure of NaCl solution. The high concentration of feed solution in RO mode produced osmotic pressure higher than the low concentration of feed solution, which reduced effective TMP (Lee & Lueptow, 2001). Therefore, permeate water flux in RO mode depends on TMP and osmotic pressure of feed solution. Osmotic pressure for strong electrolyte solution was calculated by **Eq. 4.4**

$$\pi = iCRT \tag{4.4}$$

Where π = Osmotic pressure (MPa)

i = Number of ions produced during dissociation of solute

C = Concentration of feed solution (mol/L)

R = Universal gas constant (8.31451 $Pa{\cdot}m^3/(mol{\cdot}K)$)

T = The absolute temperature (K)

The osmotic pressure of NaCl solution as feed solution in RO mode was calculated and shown in **Table 20.**

Table 20 Osmotic pressure of NaCl solution

MW (g/mol)	Conc. (mg/L)	Conc. (mol/L)	Number of ions	Universal gas constant ($Pa{\cdot}m^3/mol{\cdot}K$)	Absolute temperature (K)	Osmotic pressure (MPa)
58.44	1000	0.017	2.0	(8.31451)	300	0.0854

4.1.3 Salt rejection

Membrane technology is widely use in conventional desalination to reject salt in sea water (Padaki et al., 2011). Salt rejection is the most important value to show the performance of membrane (Dolar et al., 2011). High salt rejection value show the high performance of membrane to reject salt in feed solution and allow the high quality of water pass through membrane to permeate side. The salt rejection values of RO-1 membrane under various concentration of feed solution were shown in **Appendix B**. and **Table 21.** The percent salt rejection of RO-1 membrane was calculated by using **Eq. 4.5**

$$\% R = \left(1 - \frac{C_p}{C_c}\right) x\ 100 \qquad (4.5)$$

Where R = Rejection of salt (%)

C_p = Concentration of permeate solution (M)

C_c = Concentration of concentrate solution (M)

Phadunghus, (2014) showed the percent salt rejection of RO-1 membrane by varying the concentration of NaCl solution and pressurized the solution at TMP of 0.375 MPa. The percent salt rejection of NaCl solution at the concentration of 0.010, 0.048 and 0.094 M were 90.91, 84.91 and 72.50 %, respectively. The data of salt rejection experiment were shown in **Table 21**.

Table 21 Percent rejection of salt under various concentration of NaCl solution at TMP 0.375 MPa

Conc. of NaCl in feed solution (M)	Conc. of NaCl in concentrate solution (M)	Conc. of NaCl in permeate solution (M)	% Salt rejection	Permeate flux (L/m^2·hr)
0.010	0.011	0.001	90.91	15
0.048	0.053	0.008	84.91	9.17
0.094	0.102	0.028	72.50	5

(Source: Phadunghus et al., 2014)

Table 21 shows the decreasing of salt concentration increases percent salt rejection (Hagmeyer & Gimbel, 1998). The salt rejection decreased as the feed concentration increased due to the electrostatic interaction between charges of membrane and ions in feed solution (He et al., 2009). The increasing of NaCl solution concentration is related to the weakened donnan potential that present in the strong negative charged of membrane. The weakening donnan potential allowed negative charge passed through the membrane easier than the low concentration of NaCl solution (Higa et al., 1998).

4.1.4 Isoelectric point of RO-1 membrane

In the process of membrane filtration, sub-micron particles in fluids were filtrated by sieving mechanism. Only sieving was not appropriate for the particles that smaller than the membrane pores size. Consequently, the interaction of particles and membrane near the isoelectric point was investigated (Duclos-Orsello et al., 2004).

Electrical charges in solution interact with surface functional groups on the membrane surface (Lanteri et al., 2009). Isoelectric point is the net charge of solution and membrane surface become zero. The isoelectric point of membrane was defined as the pH value (Shinagawa et al., 1992).

The relationship of pH value before and after immersing RO-1 membrane into sodium chloride solution for 24 hours at various pH conditions is shown in **Figure 28.** The isoelectric point of RO-1 membrane from the experiment was nearby at pH of 6.

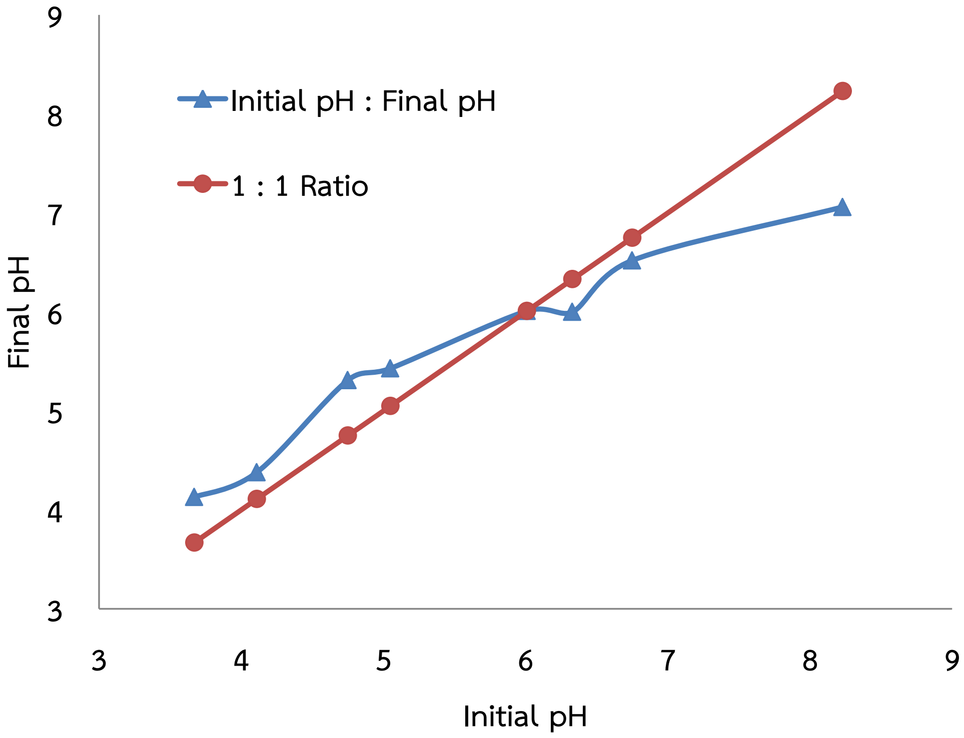


Figure 28 The isoelectric point of RO-1 membrane

A thin polyamide skin layer or active layer of RO membrane consist of two functional groups, carboxyl group (-COOH) and amine group (-NH_2) (Mouhounmed et al., 2014). The functional groups on active layer of membrane can interact with feed solution by exchange the ions. Therefore, pH value of feed solution effected to membrane surface.

At the isoelectric point, net charges of solution and membrane surface were a neutral or nearly zero. Therefore, it can be concluded that the pH value of feed solution was higher than the isoelectric point and the charge on membrane surface became negative due to carboxyl functional group on active layer released proton (de-protonation). Whereas, the pH value of feed solution was lower than the isoelectric point, the charge on the membrane surface became positive because amine functional group on active layer received proton (protonation).

4.2 Membrane filtration of FO mode

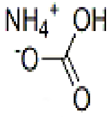
4.2.1 Appropriation of draw solution

In **section 4.1.2** single NaCl solution was the representative of discharged cooling water which reducing effective TMP. Osmotic pressure was the main driving force in FO process, which generated by high concentrated draw solution (Mi & Elimelech, 2008). FO process relied on the low energy consumption by operate the process at low TMP (Lee et al., 2010). Hence, the TMP of 0.085 MPa was produced by applied pressure 0.1 MPa and was chosen to operate feed solution in FO process.

FO mode was set to investigate the performance of three draw solutions e.g. NaCl and NH_4HCO_3 by using NaCl solution at the concentration of 1000 mg/L as same as **section 4.1.2**. A draw solution which highest performance of permeate water flux was chosen to study in the next step.

Osmotic pressure of draw solution is the main force to drive water from feed solution across membrane to draw solution side in FO mode (Kim et al., 2012) . The characteristics of draw solution should have high solubility, high recovery, nontoxic, nonreactive with membrane and easily separable from water (Chanukya et al., 2013). Characteristics of each draw solution are provided in **Table 22.**

Table 22 Physicochemical properties of draw solution

Properties of draw solution	Sodium chloride (NaCl)	Ammonium bicarbonate (NH_4HCO_3)
Molecular Weight (g/mol)	58.44	79.06
Molecular structure	Na^+ --- Cl^-	
Boling point (°C)	695 - 1413	386.5
Solubility in water at 25 °C (g/L)	315	232
Amount (mol) of ions in solution (i)	2	3
Osmotic pressure at concentration of 0.5 M. (MPa)	2.49	3.735
Method of recovery	Desalination	Heating/Distillation

NaCl solution at the concentration of 1000 mg/L was used to represent the cooling water because NaCl was strong electrolyte that dissociate to sodium ion (Na^+) and Chloride ion (Cl^-). NaCl solution was used as feed solution and was run across the membrane at the operating pressure of 0.1 MPa. Then, draw solution at the concentration of 0.5 M was run against supporting layer membrane to draw water from feed solution. Weighting of permeate water that solute in draw solution was measured by digital scale. The results from a digital scale were converted to volume and permeate water flux. The data was provided **in Appendix C, Table C.1-C.2**

Osmotic pressure of each draw solution was calculated from **Eq. 4.4.** Performances of draw solution in FO mode were shown in **Table 23 and Figure 29.**

Table 23 The performance of each draw solution that used in FO mode

Concentration of DS (0.5 M)	π_{DS} (MPa)	Initial EC (mS/cm)	Initial permeate water flux (L/m^2·hr)	Final EC (mS/cm)	Final permeate water flux (L/m^2·hr)
NaCl	2.49	29.70	1.90	29.00	1.68
NH_4HCO_3	3.735	23.80	4.42	23.70	2.54

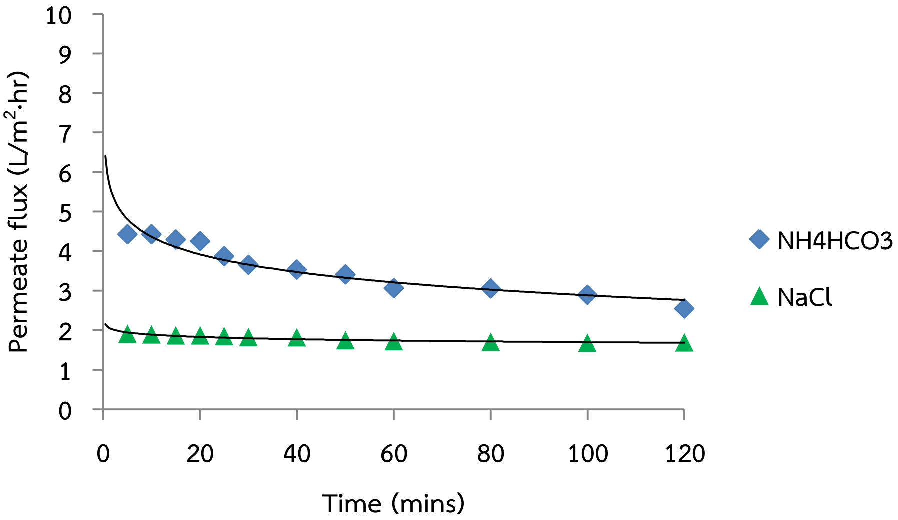


Figure 29 Permeate water flux of each draw solution as function of operating times of 2 hours

The EC value and permeated water flux of each draw solution in **Table 23** were decreased along the operating time because draw solution was diluted by permeate water. The EC value of draw solution can be evaluated the osmotic pressure of draw solution directly (Yangali-Quintanilla et al., 2011).

At the same concentration of two draw solutions produced different osmotic pressure. NH_4HCO_3 solution is produced osmotic pressure more than NaCl solution. The draw solution which high ionic solutes were the most favorable in FO process (Ge et al., 2013). NH_4HCO_3 solution obtained permeate water flux higher than NaCl solution because NH_4HCO_3 generated high osmotic pressure. NH_4HCO_3 solution gained high water flux and could be easily separated out of water (McCutcheon et al., 2005). Hence, it was chosen to be a best appropriate draw solution.

The concentrative external concentration polarization and dilutive internal concentration polarization are common phenomena which cause the reduction of effective osmotic pressure gradient in FO mode (Zhao et al., 2012). Both concentration polarizations are shown in **Figure 30.**

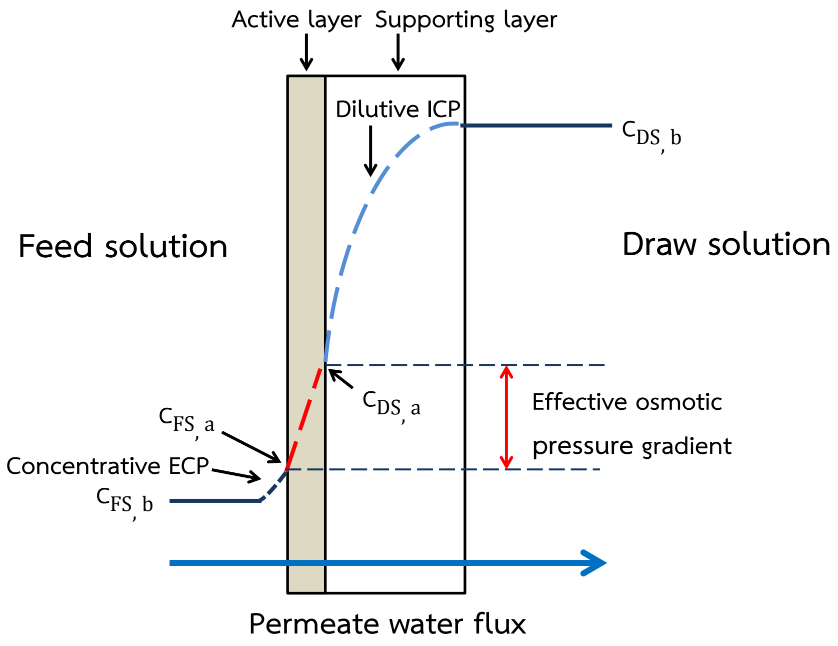


Figure 30 Illustration of concentrative external concentration polarization and dilutive internal concentration polarization across the membrane

The concentrative external concentration polarization occurs on the surface of active layer and can be minimized by increasing turbulence at the membrane surface (Cath et al., 2006). The FO mode experiment with metal mesh obtained water flux higher than the FO mode experiment without metal mesh spacer because the metal mesh spacer increase the turbulence and reduce the concentrative external concentration polarization on the surface membrane (Zhang et al., 2014). In this study operated feed solution with low applied pressure 0.1 MPa and used a plastic mesh as a feed spacer. Hence, the concentrative external concentration polarization was not play a dominant role.

Moreover, The dilutive internal concentration polarization phenomenon that occurs inside porous supporting layer of the membrane was the main problem to concern in FO mode because it can reduce the osmotic pressure of draw solution (Chanukya et al., 2013).

In this study solution of NaCl at the concentration of 1000 mg/L was used as feed solution in RO mode and FO mode. In RO mode NaCl solution was pressurized at 0.1 MPa and obtained permeate water flux 1.6 $L/m^2 \cdot hr$. In FO mode, NaCl solution at the concentration of 0.5 M produced osmotic pressure 2.49 MPa and obtained permeate water flux 1.9 $L/m^2 \cdot hr$. The driven pressure of FO mode is greater than RO mode about 25 times, but obtained permeate water more than a little due to the dilutive internal concentration polarization phenomenon.

Likewise, the result of Emadzadeh et al.,(2014) that investigated the dilutive internal concentration polarization by using TFC membrane and DI-water as feed solution. In RO mode at the applied pressure 0.1 MPa obtained permeate water flux

1.31 L/m^2·hr. In FO mode, NaCl solution at the concentration of 0.5 M produced osmotic pressure 2.49 MPa and obtained permeate water flux 3.0 L/m^2·hr.

The severity of internal concentration polarization in FO mode is depending on the type of membrane and it can be controlled by reduce the thickness and increase the porous of supporting layer (Zhou et al., 2014).

4.2.2 Influence of ammonium bicarbonate concentration on permeate water flux and rejection of p-chlorophenol in NaCl solution

NH_4HCO_3 was chosen from FO mode **section 4.2.1** as the appropriate draw solution. FO mode **section 4.2.2** was set to investigate the influence of NH_4HCO_3 solution concentration on permeate water flux and the rejection of p-chlorophenol in NaCl solution. NaCl solution at the concentration of 1000 mg/L was used to represent the cooling water as same as **section 4.2.1**.

p-Chlorophenol was used to be a biocide in cooling water (Keister, 2008). It was added into NaCl solution at the concentration of 42.5 mg/L and used as feed solution.

The solution of NH_4HCO_3 was used to draw water by varying the concentration of NH_4HCO_3 solution. Permeate water flux and other data of these experiments was provided in **Appendix C, Table C.3-C.6.**

The performance of NH_4HCO_3 solution with the difference of four concentrations were shown in **Table 24.**

Table 24 The performance of each concentration of draw solution that used in FO mode

Concentration of NH_4HCO_3 (M)	π_{DS} (MPa)	Initial EC (mS/cm)	Initial permeate water flux ($L/m^2 \cdot hr$)	Final EC (mS/cm)	Final permeate water flux ($L/m^2 \cdot hr$)
0.05	0.249	3.13	0.88	3.03	0.72
0.1	0.499	5.68	0.94	4.98	0.77
0.5	2.494	23.1	4.46	21.00	1.81
1.0	4.988	38.2	9.46	37.10	2.36

The higher concentration of NH_4HCO_3 solution had higher osmotic pressure than lower concentration of NH_4HCO_3. Hence, concentration of draw solution was function to permeate water flux directly (Yong et al., 2012).

The permeate water flux of draw solution in each concentration was decreased along with the time increase, because concentration of draw solution was diluted by the water from feed solution side. Therefore, the osmotic pressure in each draw solution was decreased by permeate water flux. The performance of various concentration of draw solution is shown in **Figure 31.**

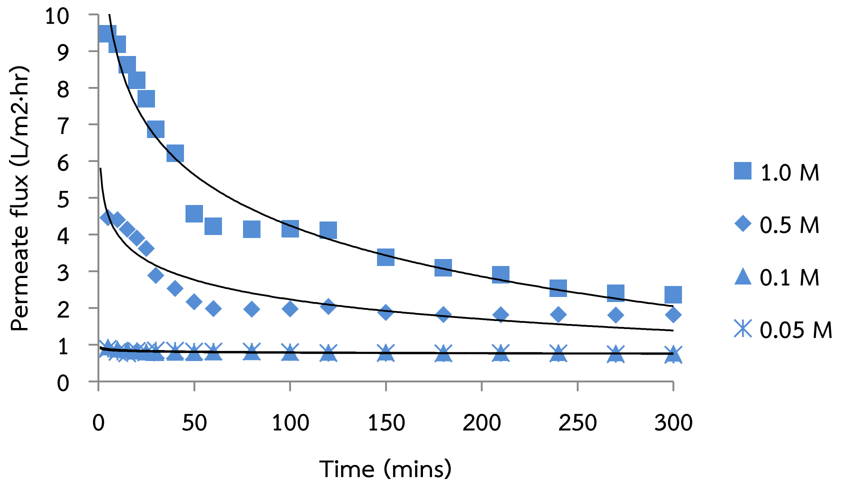


Figure 31 Permeate water flux of each concentration of draw solution as function of operating time 5 hours

p-Chlorophenol added was not changed the form because pKa of p-chlorophenol was 9.26 and pH of NaCl solution was 6.0. Hence, p-Chlorophenol did not released their ions into NaCl solution. The small amount of p-chlorophenol have a little affect to permeate water flux due to the size of p-chlorophenol might obstruct the pore size of membrane because the size of p-chlorophenol is larger than the pore size of RO-1 membrane. Because of, molecular weight cut-off of RO membrane was 100 Da (Dolar et al., 2011) but diameter size of p-chlorophenol was 128.56 Da.

In each experiment batch of FO mode in **section 4.2.2**, The concentrations of p-chlorophenol in NaCl solution and draw solution were measured before and after run through the test cell. The wave length of UV-vis analyser to detect p-chlorophenol was 280 nm and provided the absorbance unit (AU), the absorbance value was converted to concentration (mg/L) by using calibration curve. The concentration of p-chlorophenol in each experiment and the calibration curve were provided in **Appendix D.** Concentration and percent rejection of p-chlorophenol in NaCl solution and draw solution were reported in **Table 25.**

Table 25 Percent rejection of p-chlorophenol by RO-1 membrane under FO mode in section 4.2.2

Conc. of DS in each batch (M)	Mass of p-CPN in NaCl solution (mg)		% loss of p-CPN	Mass of p-CPN in draw solution (mg)		% rejection of p-CPN
	Initial	Final		Initial	Final	
0.05	42.03	39.87	5.14	0.00	0.00	100
0.10	42.34	39.92	5.72	0.00	0.00	100
0.50	42.58	38.24	10.19	0.00	0.00	100
1.00	42.48	35.97	15.32	0.00	0.00	100

Concentrations of p-chlorophenol in NaCl solution under the different concentration of draw solution were shown in **Figure 32.**

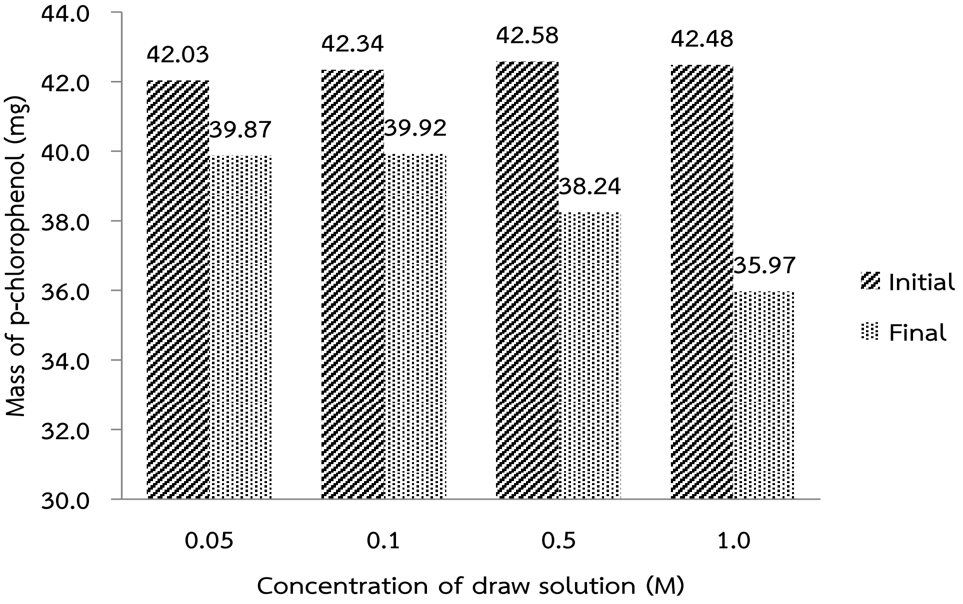


Figure 32 Concentration of p-chlorophenol in NaCl solution before and after FO mode

Monochlorophenols volatile to atmosphere easier than dichlorophenols, trichlorophenols and tetrachlorophenols but monochlorophenols volatile by a small fraction approximately 5% (Scow et al., 1982). The half-life of p-chlorophenol by photodegradation is 63 hours (Euro Chlor, 2002). Hence, p-chlorophenol is loss from the system by photodegradation and its volatile property. The percent loss of p-chlorophenol in draw solution at the concentration of 0.05, 0.1, 0.5 and 1.0 M were 5.14 %, 5.72 %, 10.19 % and 15.32 %, respectively. The evaporation rate of p-chlorophenol is directly related to the depth of water (U.S. Department of health and human services, 1999).

The decreasing of feed solution volume is high at the high concentration of draw solution due to the osmotic force of draw solution. Therefore, the percent loss of p-chlorophenol in feed solution depends on the concentration of draw solution.

Percent rejections of p-chlorophenol in each concentration of draw solution were shown in **Figure 33.**

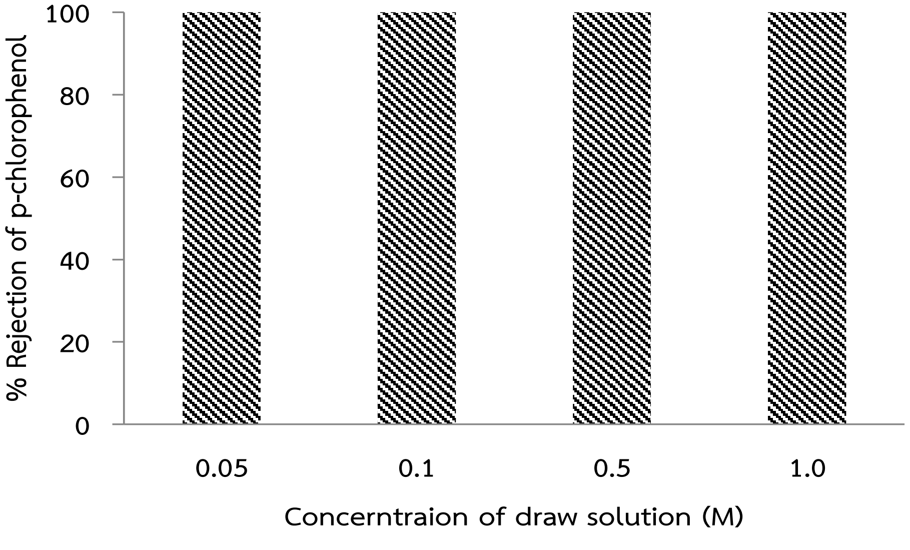


Figure 33 Percent rejection of p-chlorophenol in draw solution

All of **experiments** in **Figure 33** were shown the rejection of p-chlorophenol by RO-1 membrane in FO mode was 100%. p-Chlorophenol could not pass through the membrane from NaCl solution to draw solution because the size of p-chlorophenol is larger than the pore size of RO-1 membrane.

4.2.3 Influence of Ammonium bicarbonate concentration to draw water from discharged cooling water and rejection of p-chlorophenol in discharged cooling water

FO mode **section 4.2.3** was set to investigate the influent of NH_4HCO_3 concentration on the permeate water flux under the condition as same as **section 4.2.2** and the rejection of p-chlorophenol in discharged cooling water.

Discharged cooling water was used as feed solution in this experiment. The discharged cooling water was filtrated by filter paper (Whatman filter papers No.42) which pore size 2.5 μm. for reducing the fouling on the membrane surface. The characteristics of discharged cooling water were shown in **Table 26.**

Table 26 Characteristics of discharged cooling water

Parameters	Amount
pH	8.91
EC	3280.00 μS/cm
TDS	2164.80 mg/L

p-Chlorophenol was added into discharged cooling water at the concentration of 42.5 mg/L and used as feed solution. The feed solution was run through the test cell by varying the concentration of draw solution. Permeate water flux and other data of these experiments were provided in **Appendix C, Table C.7-**

C.10. The performance of various concentration of draw solution is shown in **Figure 34.**

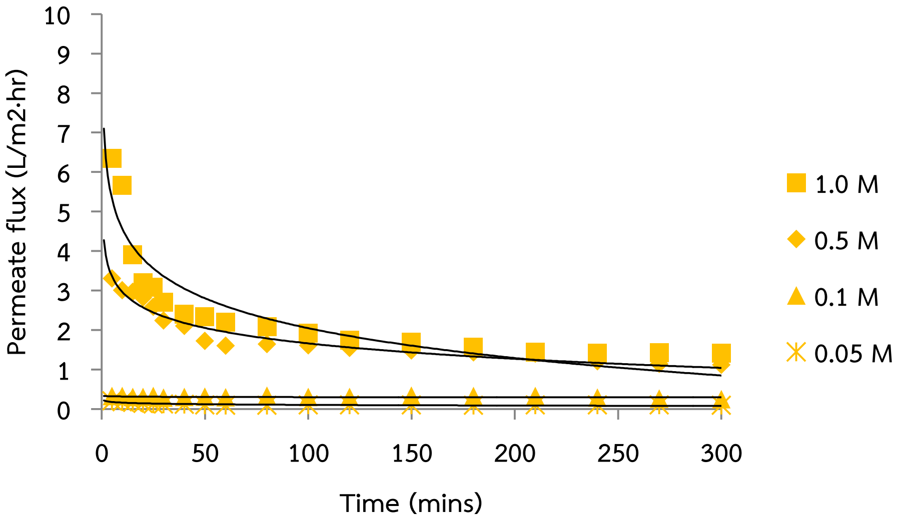
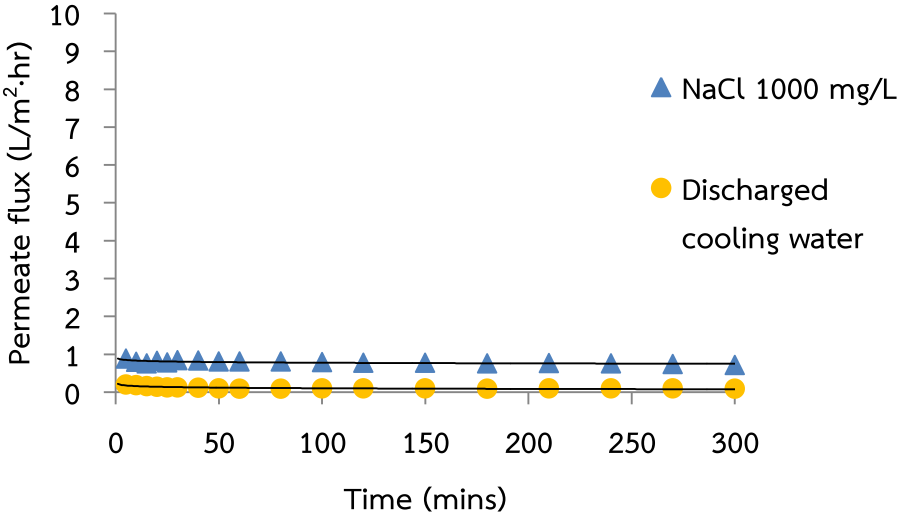


Figure 34 Permeate water flux of each concentration as function of operating time 5 hours

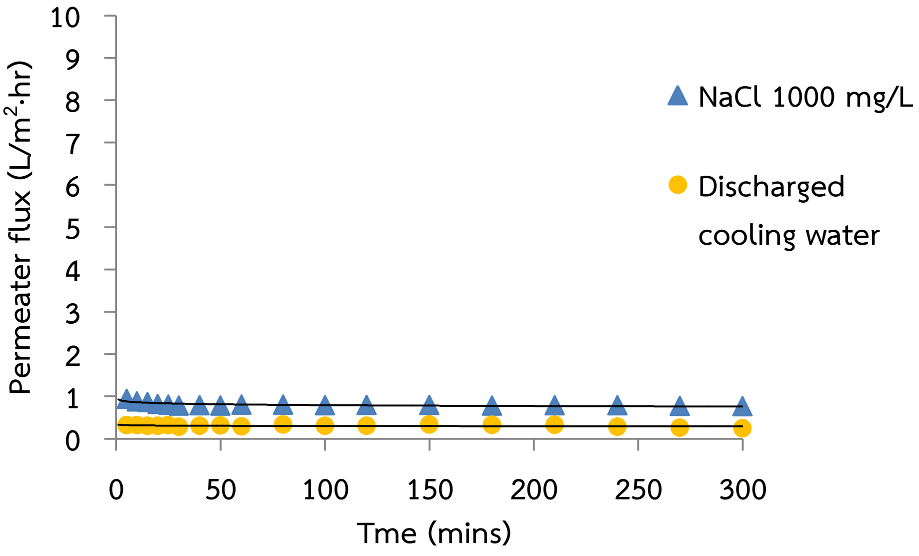
Figure 34 described permeate water flux of draw solution in each concentration decreased along with the time increase as same as **section 4.2.2**.

Figure 35 described the permeate water flux of NaCl solution higher than discharged cooling water. Discharged cooling water was concentrated than NaCl solution and the EC values were 3280 μs/cm and 1345 μs/cm, respectively. The high concentration of discharged cooling water might contained many types of ions that react with the charge of membrane and obstruct the pore size of membrane. Therefore, permeate water flux of discharged cooling water was less than NaCl solution.

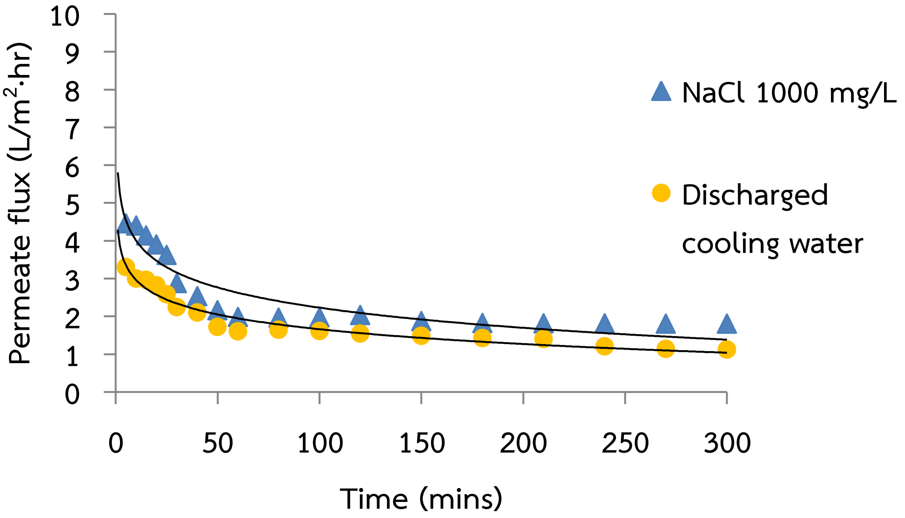
(a) Draw solution at the concentration of 0.05 M



(b) Draw solution at the concentration of 0.1 M



(c) Draw solution at concentration of 0.5 M



(d) Draw solution at the concentration of 0.1M

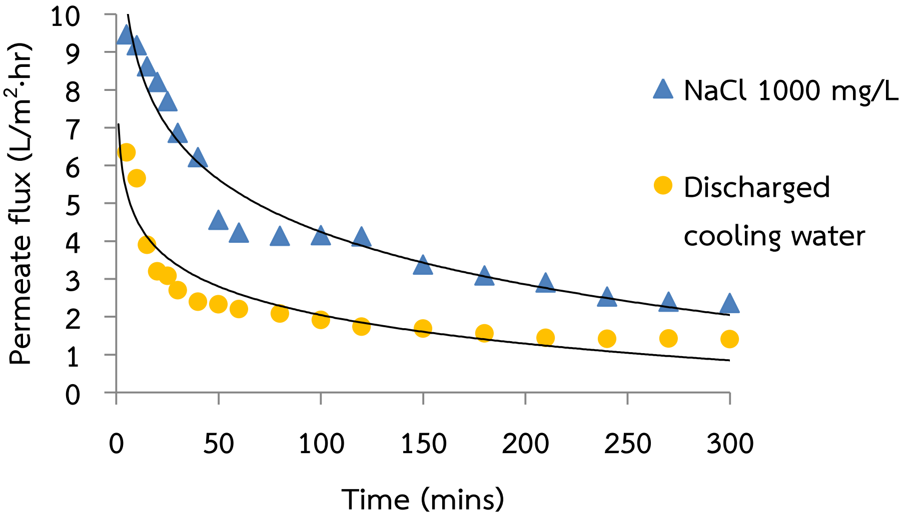


Figure 35 Permeate water flux of NaCl solution and discharged cooling water at the different concentration of draw solution

pH of discharged cooling water in **Table 4.9** was 8.91 but pKa of p-chlorophenol was 9.26. Hence, p-Chlorophenol did not released their ions into discharged cooling water as same as **section 4.2.2**. The concentration of p-chlorophenol in each experiment and the calibration curve were provided in **Appendix D.** Concentration and percent rejection of p-chlorophenol in discharged cooling water and draw solution were reported in **Table 27**.

Table 27 Permeate rejection of p-chlorophenol by RO-1 membrane under FO mode in section 4.2.3

Concentration of DS in each batch (M)	Mass of p-CPN in discharged cooling water (mg)		% loss of p-CPN	Mass of p-CPN in draw solution (mg)		% rejection of p-CPN
	Initial	Final		Initial	Final	
0.05	42.23	40.46	4.19	0.00	0.00	100
0.1	41.94	40.10	4.39	0.00	0.00	100
0.5	41.49	38.24	7.83	0.00	0.00	100
1.0	42.38	38.26	9.72	0.00	0.00	100

Concentrations of p-chlorophenol in discharged cooling water under the different concentration of draw solution were shown in **Figure 36.**

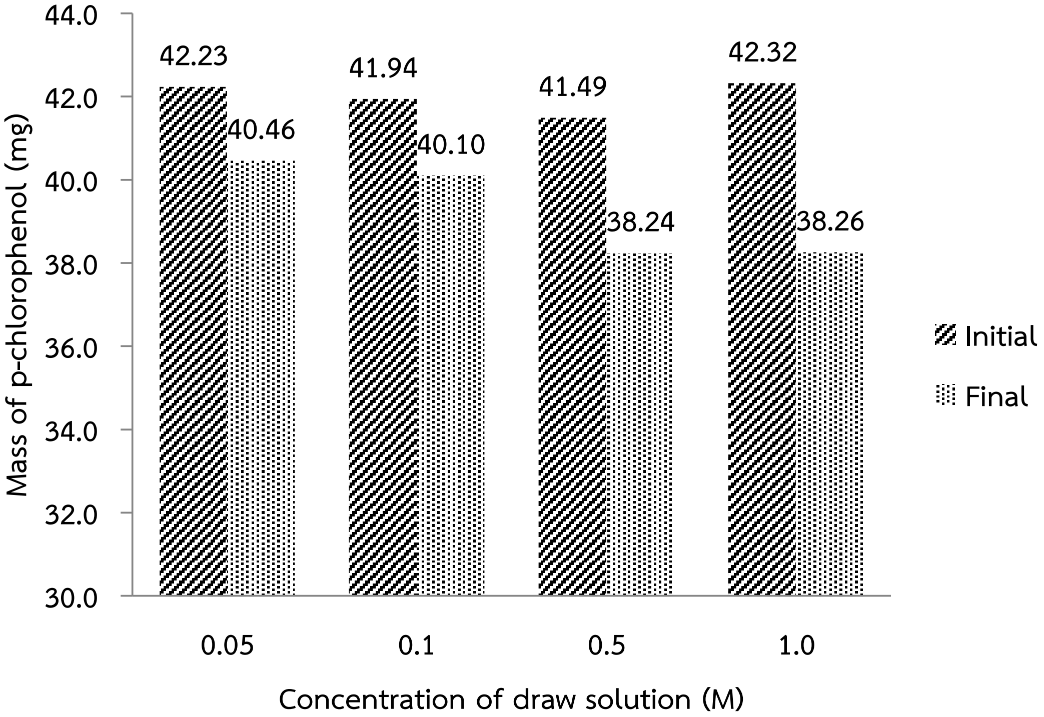


Figure 36 Concentration of p-chlorophenol in discharged cooling water before and after FO mode

The percent loss of p-chlorophenol in feed solution at the draw solution concentration of 0.05, 0.1, 0.5 and 1.0 M were 4.19 %, 4.39 %, 7.83 % and 9.72 %, respectively.

Percent rejections of p-chlorophenol in each concentration of draw solution were shown in **Figure 37.**

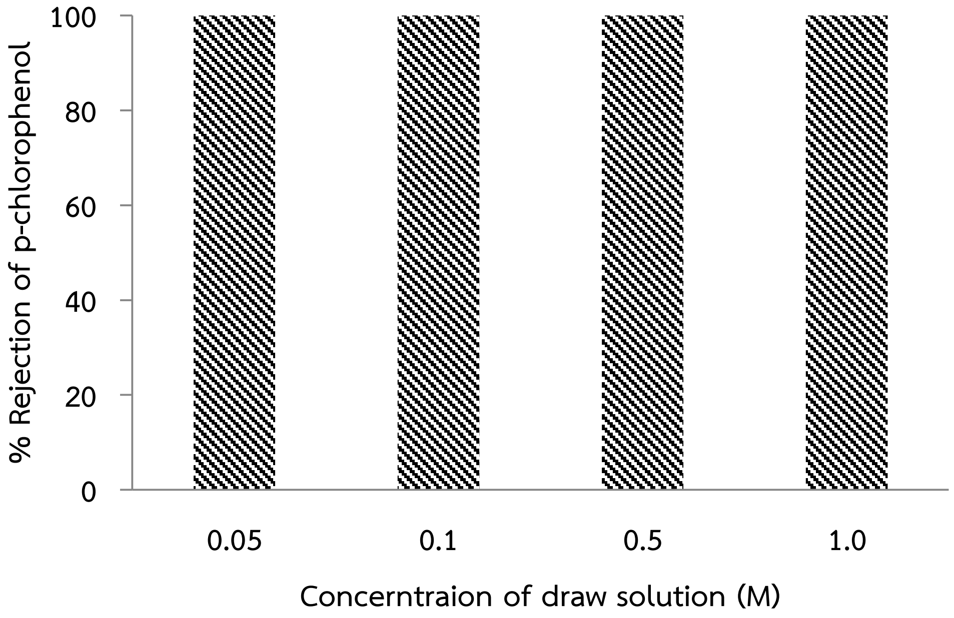


Figure 37 Percent rejection of p-chlorophenol in draw solution

All of **experiments** in **Figure 37** were shown the rejection of p-chlorophenol by RO-1 membrane in FO mode was 100%. p-Chlorophenol could not pass through the membrane from discharged cooling water to draw solution because the size of p-chlorophenol is larger than the pore size of RO-1 membrane and p-chlorophenol was not changed the form as same as **section 4.2.2**. Hence, the main mechanism to reject p-chlorophenol in discharged cooling water was size exclusion.

4.3.5 Separation of water in draw solution

Permeate water that solute in draw solution could be separated out by moderate heating around 60 °C (McCutcheon et al., 2005). At the temperature 60 °C NH_4HCO_3 solution decomposed to ammonia (NH_3) and carbon dioxide gases (CO_2) and were separated out of permeate water (Ge et al., 2013). The distillation process of NH_4HCO_3 solution obtained the NH_3 and could be mixed with CO_2 to use as new draw solution and the quality of water after distillation at temperature 60 °C might be contained ammonia and carbon dioxide gases less than 1 ppm. that appropriate to use again (McGinnis & Elimelech, 2007).

All of researchers proposed the method to permeate water and draw solution by heating at 60°C but qualities and quantities of water and draw solution in the experiment were not presented.

In this experiment NH_4HCO_3 were prepared at the concentration of 0.05, 0.1, 0.5 and 1.0 M, respectively. Zhaung et al, (2012) proposed the chemical equation of NH_4HCO_3 in DI-water was shown below.

$$NH_4HCO_3 + H_2O \longrightarrow NH_4^+ + H^+ + CO_3^{2-} + H_2O$$

The solution was distilled at the temperature 60°C and an air blower was set to make turbulence in bulk solution. The qualities of draw solution were measured before distillation process. After 6 hours of distillation process, draw solution was determined as water due to ammonia was separated out and collected in other flask. The qualities of water and ammonia were measured after distillation process. The separation of water in draw solution was shown by below equation

$$NH_4^+ + H^+ + CO_3^{2-} + H_2O \longrightarrow NH_3 + CO_2 + 2H_2O$$

The properties of NH_4HCO_3, water and ammonia in separation process by distillation were shown in **Table 28.**

Table 28 Properties of water and ammonia after distillation at the temperature 60 °C

Conc. of DS (M)	Parameters before recovery process			Parameters after recovery process					
	DS (NH_4HCO_3)			Water (H_2O)			Ammonia (NH_3)		
	Vol. (ml)	EC (µS/cm)	pH	Vol. (ml)	EC (µS/cm)	pH	Vol. (ml)	EC (µS/cm)	pH
0.05	1000	3310	7.80	930	285	8.74	68	2020	9.29
0.1	1000	6410	7.91	916	350	9.08	85	4280	9.51
0.5	1000	22900	7.86	914	1415	9.39	86	26200	9.50
1.0	1000	37700	7.86	910	4360	9.77	92	618000	9.58

The results in **Table 28** described the EC values of ammonium bicarbonate decreased due to ammonia and carbon dioxide gases were vaporized out along the distillation time. EC values of water in distillation batch at the concentration of 0.05 M was 285 µS/cm, that appropriate to use as new make-up water in cooling system (The Japan Refrigeration and Air Conditioning Industry Association, 1994).

EC values of water in distillation batch at the concentration of 0.1, 0.5 and 1.0 M were 350, 1415 and 4360 µS/cm, respectively. There were not appropriate to use in cooling system due to the high EC value.

pH of water in every experiment batches were higher than pH of ammonium bicarbonate solution in that batch because carbon dioxide gases separated out the ammonium bicarbonate better than ammonia. pKa of HCO_3^- was 6.37 and pKa of NH_3

was 9.3. Thus, pH value of water after distillation process was higher than pH value of ammonium bicarbonate solution before distillation process.

NH_3 was separated out the ammonium bicarbonate solution harder at the high concentration. The operating time 6 hours of distillation process was not appropriate for high concentration of ammonium bicarbonate and the qualities of water after distillation was not reach the quality of make-up water.

In this study, the ammonium bicarbonate solution at concentration of 0.05 M was the best appropriate draw solution because NH_3 was separated out easily in distillation process. If consider to volume of permeate water, ammonium bicarbonate solution at the concentration of 0.5 and 1.0 M should be chosen. Therefore, the extension of operating time and the increasing of temperatures should be applied in distillation process.

CHAPTER 5
CONCLUSIONS

In RO mode, permeate water flux of DI-water at the TMP 0.085, 0.185 and 0.290 MPa were 4.34, 8.83 and 14.61 L/m^2·hr, respectively. Permeate water flux of NaCl solution at the concentration of 1000 mg/L at the TMP 0.085, 0.185 and 0.290 MPa were 1.55, 5.48 and 10.94 L/m^2·hr, respectively. As a result, permeate water of both solutions increased along the operating TMP increased. But the permeate water flux of NaCl solution was less than DI-water due to osmotic pressure from NaCl solution can reduce the effective TMP. At the TMP 0.085 MPa (obtained from applied pressure of 0.1 MPa) permeate water flux still can be detected. Hence, the applied pressure of 0.1 MPa was used to operate feed solution in FO mode. Moreover, the iso-electric point of RO-1 membrane was detected at the pH of 6.

The solution of NaCl and NH_4HCO_3 at the concentration of 0.5 M were used as draw solution in FO mode. The osmotic pressure of NaCl and NH_4HCO_3 solution were calculated as 2.48 and 3.735 MPa, respectively. The performance of draw solution e.g. NaCl and NH_4HCO_3 to draw water from synthetic feed solution (by NaCl) that shown in the term of initial permeate water flux were 1.9 and 4.42 L/m^2·hr, respectively. Hence, NH_4HCO_3 was selected to be used as the draw solution in FO mode for further study.

In FO mode by using synthetic feed solution (NaCl solution) with p-chlorophenol, the higher concentration of NH_4HCO_3 solution had higher osmotic pressure and obtained higher permeate water than lower concentration of NH_4HCO_3 solution. p-Chlorophenol was added into NaCl solution and run through the test cell by using the draw solution at the concentration of 0.05, 0.1, 0.5 and 1.0 M. The percent loss of p-chlorophenol in feed solution depends on the concentration of draw solution. Rejection percentage of p-chlorophenol in all experiments were 100%. The retention of p-chlorophenol in NaCl solution by FO mode was controlled by size exclusion mechanism. The size of p-chlorophenol was larger than pore size of the membrane. Thus, p-chlorophenol could not pass through the pore size of RO-1 membrane.

The permeate water flux of discharged cooling water is less than NaCl solution because discharged cooling water was concentrated and might contained many types of ions that could obstruct the pore size of membrane. The percent loss of p-chlorophenol was very similar in all of draw solution concentration.

NH_3 was separated out from NH_4HCO_3 solution by distillation process. The quality of water was determined by EC value. NH_4HCO_3 solution at the concentration of 0.05, 0.1, 0.5 and 1.0 M were distilled at 60 °C upto 6 hours, respectively. The EC value of water after distillation process in each experiment were 285, 350, 1415 and 4360 μS/cm, respectively. Thus, obtained water from the distillation process of draw solution at the concentration of 0.05 M. could be returned to cooling system.

According to the volume of permeate water fluxes in FO mode and qualities of water after distillation process, the low concentration of draw solution was not appropriate to be applied in FO process because it obtained very low volume of permeate water. The high concentration of draw solution obtained high permeate water but the quality of water after distillation process was not reach the standard of new make-up water. The increasing of temperature and the distillation time can enhance NH_3 separation efficiency.

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APPENDIX

APPENDIX A

Table A.1 Permeate water flux of RO-1 membrane at TMP 0.085 MPa under RO mode by using DI-water as feed solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	2.27	2.27	0.006	4.54
10	5	4.51	2.24	0.006	4.48
15	5	6.76	2.25	0.006	4.5
20	5	8.99	2.23	0.006	4.46
25	5	11.2	2.21	0.006	4.42
30	5	13.39	2.19	0.006	4.38
35	5	15.6	2.21	0.006	4.42
40	5	17.82	2.22	0.006	4.44
45	5	19.98	2.16	0.006	4.32
50	5	22.15	2.17	0.006	4.34
55	5	24.33	2.18	0.006	4.36
60	5	26.48	2.15	0.006	4.3
70	10	30.75	4.27	0.006	4.27
80	10	34.98	4.23	0.006	4.23
90	10	39.17	4.19	0.006	4.19
100	10	43.33	4.16	0.006	4.16
120	10	51.63	4.13	0.006	4.13
Average permeate water flux					4.34

Table A.2 Permeate water flux of RO-1 membrane at TMP 0.185 MPa under RO mode by using DI-water as feed solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	
5	5	4.46	4.46	0.006	8.92
10	5	8.89	4.43	0.006	8.86
15	5	13.33	4.44	0.006	8.88
20	5	17.78	4.45	0.006	8.90
25	5	22.2	4.42	0.006	8.84
30	5	26.59	4.39	0.006	8.78
35	5	31	4.41	0.006	8.82
40	5	35.41	4.41	0.006	8.82
45	5	39.83	4.42	0.006	8.84
50	5	44.26	4.43	0.006	8.86
55	5	48.68	4.42	0.006	8.84
60	5	53.09	4.41	0.006	8.82
70	10	61.9	8.81	0.006	8.81
80	10	70.7	8.8	0.006	8.8
90	10	79.49	8.79	0.006	8.79
100	10	88.28	8.79	0.006	8.79
110	10	97.05	8.77	0.006	8.77
120	10	105.81	8.76	0.006	8.76
Average permeate water flux					8.83

Table A.3 Permeate water flux of RO-1 membrane at TMP 0.29 MPa under RO mode by using DI-water as feed solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	7.98	7.98	0.006	15.96
10	5	15.79	7.81	0.006	15.62
15	5	23.57	7.78	0.006	15.56
20	5	31.06	7.49	0.006	14.98
25	5	38.43	7.37	0.006	14.74
30	5	45.76	7.33	0.006	14.66
35	5	53.02	7.26	0.006	14.52
40	5	60.27	7.25	0.006	14.50
45	5	67.51	7.24	0.006	14.48
50	5	74.72	7.21	0.006	14.42
55	5	81.91	7.19	0.006	14.38
60	5	89.09	7.18	0.006	14.36
70	10	103.4	14.31	0.006	14.31
80	10	117.65	14.25	0.006	14.25
90	10	131.82	14.17	0.006	14.17
100	10	145.94	14.12	0.006	14.12
110	10	160.01	14.07	0.006	14.07
120	10	173.97	13.96	0.006	13.96
Average permeate water flux					14.61

Table A.4 Permeate water flux of RO-1 membrane at TMP 0.085 MPa under RO mode by using sodium chloride solution 1000 mg/L as feed solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	0.78	0.78	0.006	1.56
10	5	1.56	0.78	0.006	1.56
15	5	2.31	0.75	0.006	1.5
20	5	3.07	0.76	0.006	1.52
25	5	3.88	0.81	0.006	1.62
30	5	4.6	0.72	0.006	1.44
35	5	5.37	0.77	0.006	1.54
40	5	6.16	0.79	0.006	1.58
45	5	6.97	0.81	0.006	1.62
50	5	7.78	0.81	0.006	1.62
55	5	8.54	0.76	0.006	1.52
60	5	9.31	0.77	0.006	1.54
70	10	10.87	1.56	0.006	1.56
80	10	12.44	1.57	0.006	1.57
90	10	13.97	1.53	0.006	1.53
100	10	15.48	1.51	0.006	1.51
120	10	18.5	1.5	0.006	1.50
Average permeate water flux					1.55

Table A.5 Permeate water flux of RO-1 membrane at TMP 0.185 MPa under RO mode by using sodium chloride solution 1000 mg/L as feed solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	2.84	2.84	0.006	5.68
10	5	5.67	2.83	0.006	5.66
16	5	8.48	2.81	0.006	5.62
20	5	11.29	2.81	0.006	5.62
25	5	14.09	2.8	0.006	5.6
30	5	16.9	2.81	0.006	5.62
35	5	19.69	2.79	0.006	5.58
40	5	22.46	2.77	0.006	5.54
45	5	25.23	2.77	0.006	5.54
50	5	27.96	2.73	0.006	5.46
55	5	30.68	2.72	0.006	5.44
60	5	33.37	2.69	0.006	5.38
70	10	38.69	5.32	0.006	5.32
80	10	44	5.31	0.006	5.31
90	10	49.32	5.32	0.006	5.32
100	10	54.61	5.29	0.006	5.29
110	10	59.89	5.28	0.006	5.28
120	10	65.19	5.3	0.006	5.30
Average permeate water flux					5.48

Table A.6 Permeate water flux of RO-1 membrane at TMP 0.29 MPa under RO mode by using sodium chloride solution 1000 mg/L as feed solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	5.31	5.31	0.006	10.62
10	5	10.62	5.31	0.006	10.62
15	5	15.94	5.32	0.006	10.64
20	5	21.24	5.3	0.006	10.60
25	5	26.53	5.29	0.006	10.58
30	5	31.76	5.23	0.006	10.46
35	5	36.94	5.18	0.006	10.36
40	5	42.1	5.16	0.006	10.32
45	5	47.24	5.14	0.006	10.28
50	5	52.4	5.16	0.006	10.32
55	5	57.57	5.17	0.006	10.34
60	5	62.72	5.15	0.006	10.30
70	10	73.03	10.31	0.006	10.31
80	10	83.35	10.32	0.006	10.32
90	10	93.62	10.27	0.006	10.27
100	10	103.88	10.26	0.006	10.26
120	10	124.35	10.22	0.006	10.22
Average permeate water flux					10.39

APPENDIX B

Table B.1Calibration curve to convert the electrical conductivity unit (µS/cm) of sodium chloride solution to the concentration unit (Molar, M)

Concentration of sodium chloride solution (M)	Electrical conductivity (µS/cm)
0.002	171.3
0.004	341
0.006	499
0.008	666
0.01	838
0.02	1593
0.04	3160
0.06	4380
0.08	6030
0.1	7330

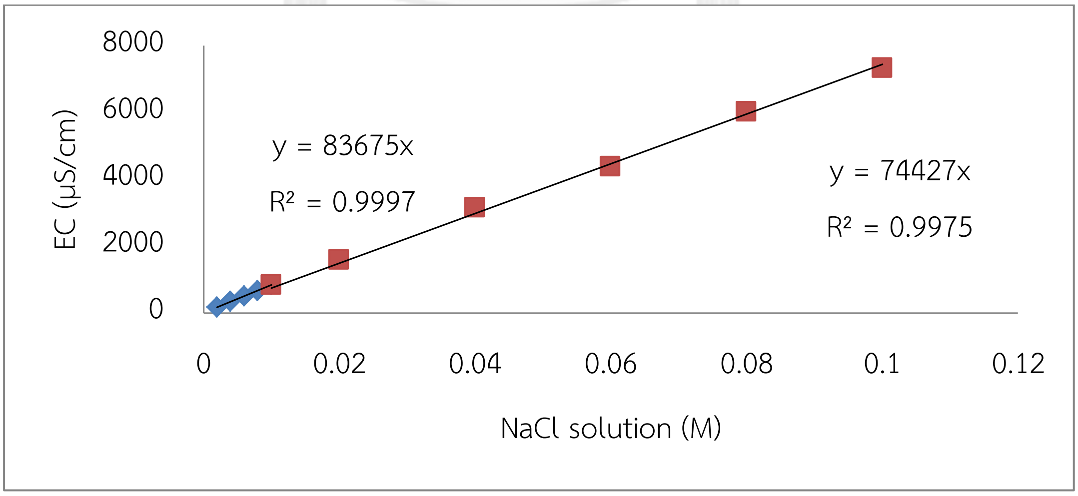


Figure B.1 Calibration curve to convert the electrical conductivity unit (µS/cm) of sodium chloride solution to the concentration unit (Molar, M)

Table B.2 The calculating data for salt rejection of RO-1 membrane at TMP 0.375 MPa

Feed solution		Concentrate solution		Permeate solution		% Salt rejection	Flux ($L/m^2 \cdot hr$)
Conc. of NaCl (M)	EC (μS/cm)	EC (μS/cm)	Conc. of NaCl (M)	EC (μS/cm)	Conc. of NaCl (M)		
0.01	779	848	0.011	85.6	0.001	90.91	15.00
0.048	3600	3970	0.053	642.0	0.008	84.91	9.17
0.094	7020	7590	0.102	2360.0	0.028	72.50	5.00

APPENDIX C

Table C.1 Permeate water flux of RO-1 membrane under FO Mode by using sodium chloride solution 1000 mg/L as feed solution and sodium chloride solution at the concentration of 0.5 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	0.95	0.95	0.006	1.90
10	5	1.89	0.94	0.006	1.88
15	5	2.82	0.93	0.006	1.86
20	5	3.75	0.93	0.006	1.86
25	5	4.67	0.92	0.006	1.84
30	5	5.58	0.91	0.006	1.82
40	10	7.39	1.81	0.006	1.81
50	10	9.13	1.74	0.006	1.74
60	10	10.84	1.71	0.006	1.71
80	20	14.23	3.39	0.006	1.70
100	20	17.58	3.35	0.006	1.68
120	20	20.94	3.36	0.006	1.68

Table C.2 Permeate water flux of RO-1 membrane under FO mode by using sodium chloride solution 1000 mg/L as feed solution and ammonium bicarbonate solution at the concentration of 0.5 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	2.21	2.21	0.006	4.42
10	5	4.42	2.21	0.006	4.42
15	5	6.56	2.14	0.006	4.28
20	5	8.68	2.12	0.006	4.24
25	5	10.61	1.93	0.006	3.86
30	5	12.43	1.82	0.006	3.64
40	10	15.95	3.52	0.006	3.52
50	10	19.35	3.4	0.006	3.40
60	10	22.4	3.05	0.006	3.05
80	20	28.49	6.09	0.006	3.05
100	20	34.25	5.76	0.006	2.88
120	20	39.32	5.07	0.006	2.54

Table C.3 Permeate water flux of RO-1 membrane under FO mode by using sodium chloride solution 1000 mg/L mixed with p-chlorophenol at the concentration of 42.5 mg/L as feed and ammonium bicarbonate solution at the concentration of 0.05 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	0.44	0.44	0.006	0.88
10	5	0.84	0.4	0.006	0.80
15	5	1.22	0.38	0.006	0.76
20	5	1.63	0.41	0.006	0.82
25	5	2.02	0.39	0.006	0.78
30	5	2.44	0.42	0.006	0.84
40	10	3.27	0.83	0.006	0.83
50	10	4.08	0.81	0.006	0.81
60	10	4.89	0.81	0.006	0.81
80	20	6.5	1.61	0.006	0.81
100	20	8.08	1.58	0.006	0.79
120	20	9.62	1.54	0.006	0.77
150	30	11.93	2.31	0.006	0.77
180	30	14.2	2.27	0.006	0.76
210	30	16.5	2.3	0.006	0.77
240	30	18.77	2.27	0.006	0.76
300	60	23.13	2.15	0.006	0.72

Table C.4 Permeate water flux of RO-1 membrane under FO mode by using sodium chloride solution 1000 mg/L mixed with p-chlorophenol at the concentration of 42.5 mg/L as feed and ammonium bicarbonate solution at the concentration of 0.1 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	0.47	0.47	0.006	0.94
10	5	0.91	0.44	0.006	0.88
15	5	1.34	0.43	0.006	0.86
20	5	1.75	0.41	0.006	0.82
30	5	2.54	0.39	0.006	0.78
40	10	3.33	0.79	0.006	0.79
50	10	4.11	0.78	0.006	0.78
60	10	4.91	0.8	0.006	0.80
80	20	6.52	1.61	0.006	0.81
100	20	8.1	1.58	0.006	0.79
120	20	9.69	1.59	0.006	0.80
150	30	12.08	2.39	0.006	0.80
180	30	14.41	2.33	0.006	0.78
210	30	16.76	2.35	0.006	0.78
240	30	19.12	2.36	0.006	0.79
300	60	23.74	2.3	0.006	0.77

Table C.5 Permeate water flux of RO-1 membrane under FO mode by using sodium chloride solution 1000 mg/L mixed with p-chlorophenol at the concentration of 42.5 mg/L as feed and ammonium bicarbonate solution at the concentration of 0.5 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	2.23	2.23	0.006	4.46
10	5	4.43	2.2	0.006	4.40
15	5	6.5	2.07	0.006	4.14
20	5	8.45	1.95	0.006	3.90
25	5	10.26	1.81	0.006	3.62
30	5	11.7	1.44	0.006	2.88
40	10	14.23	2.53	0.006	2.53
50	10	16.39	2.16	0.006	2.16
60	10	18.37	1.98	0.006	1.98
80	20	22.3	3.93	0.006	1.97
100	20	26.24	3.94	0.006	1.97
120	20	30.31	4.07	0.006	2.04
150	30	35.92	5.61	0.006	1.87
180	30	41.38	5.46	0.006	1.82
210	30	46.81	5.43	0.006	1.81
240	30	52.25	5.44	0.006	1.81
300	60	63.08	5.42	0.006	1.81

Table C.6 Permeate water flux of RO-1 membrane under FO mode by using sodium chloride solution 1000 mg/L mixed with p-chlorophenol at the concentration of 42.5 mg/L as feed and ammonium bicarbonate solution at the concentration of 1.0 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	4.73	4.73	0.006	9.46
10	5	9.32	4.59	0.006	9.18
15	5	13.63	4.31	0.006	8.62
20	5	17.73	4.1	0.006	8.20
30	5	25.01	3.43	0.006	6.86
40	10	31.23	6.22	0.006	6.22
50	10	35.79	4.56	0.006	4.56
60	10	40.01	4.22	0.006	4.22
80	20	48.28	8.27	0.006	4.14
100	20	56.59	8.31	0.006	4.16
120	20	64.83	8.24	0.006	4.12
150	30	74.95	10.12	0.006	3.37
180	30	84.22	9.27	0.006	3.09
210	30	92.93	8.71	0.006	2.90
240	30	100.52	7.59	0.006	2.53
300	60	114.79	7.08	0.006	2.36

Table C.7 Permeate water flux of RO-1 membrane under FO process by using discharged cooling water mixed with p-chlorophenol at the concentration of 42.5 mg/L as feed and ammonium bicarbonate solution at the concentration of 0.05 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux (L/m^2•hr)
0	0	0	0	0.006	0.00
5	5	0.1	0.00033	0.006	0.20
10	5	0.09	0.00030	0.006	0.18
15	5	0.08	0.00027	0.006	0.16
20	5	0.07	0.00023	0.006	0.14
30	5	0.06	0.00020	0.006	0.12
40	10	0.11	0.00018	0.006	0.11
50	10	0.1	0.00017	0.006	0.10
60	10	0.09	0.00015	0.006	0.09
80	20	0.18	0.00015	0.006	0.09
100	20	0.2	0.00016	0.006	0.10
120	20	0.19	0.00016	0.006	0.10
150	30	0.29	0.00016	0.006	0.09
180	30	0.27	0.00015	0.006	0.09
240	30	0.28	0.00015	0.006	0.09
270	30	0.28	0.00015	0.006	0.09
300	60	0.27	0.00015	0.006	0.09

Table C.8 Permeate water flux of RO-1 membrane under FO mode by using discharged cooling water mixed with p-chlorophenol at the concentration of 42.5 mg/L as feed and ammonium bicarbonate solution at the concentration of 0.1 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	0.16	0.16	0.006	0.32
10	5	0.32	0.16	0.006	0.32
15	5	0.47	0.15	0.006	0.30
20	5	0.62	0.15	0.006	0.30
25	5	0.78	0.16	0.006	0.32
30	5	0.92	0.14	0.006	0.28
40	10	1.22	0.30	0.006	0.30
50	10	1.53	0.31	0.006	0.31
60	10	1.82	0.29	0.006	0.29
80	20	2.48	0.66	0.006	0.33
100	20	3.08	0.60	0.006	0.30
120	20	3.68	0.60	0.006	0.30
150	30	4.68	1.00	0.006	0.33
180	30	5.65	0.97	0.006	0.32
240	30	7.48	0.85	0.006	0.28
270	30	8.26	0.78	0.006	0.26
300	60	8.98	0.72	0.006	0.24

Table C.9 Permeate water flux of RO-1 membrane under FO mode by using discharged cooling water mixed with p-chlorophenol at the concentration of 42.5 mg/L as feed and ammonium bicarbonate solution at the concentration of 0.5 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2\cdot hr$)
0	0	0	0	0.006	0.00
5	5	1.65	1.65	0.006	3.30
10	5	3.15	1.5	0.006	3.00
15	5	4.63	1.48	0.006	2.96
20	5	6.04	1.41	0.006	2.82
25	5	7.33	1.29	0.006	2.58
30	5	8.45	1.12	0.006	2.24
40	10	10.55	2.1	0.006	2.10
50	10	12.27	1.72	0.006	1.72
60	10	13.87	1.6	0.006	1.60
80	20	17.15	3.28	0.006	1.64
100	20	20.37	3.22	0.006	1.61
120	20	23.46	3.09	0.006	1.55
150	30	27.9	4.44	0.006	1.48
180	30	32.18	4.28	0.006	1.43
210	30	36.37	4.19	0.006	1.40
240	30	39.97	3.6	0.006	1.20
270	30	43.38	3.41	0.006	1.14
300	60	46.73	3.35	0.006	1.12

Table C.10 Permeate water flux of CM-1 membrane under FO mode by using discharged cooling water mixed with p-chlorophenol at the concentration of 42.5 mg/L as feed and ammonium bicarbonate solution at the concentration of 1.0 M as draw solution

Time (min)	Sampling time (min)	Weighting (g)	Gradient volume (mL)	Area (m^2)	Flux ($L/m^2 \cdot hr$)
0	0	0	0	0.006	0.00
5	5	3.17	3.17	0.006	6.34
10	5	6	2.83	0.006	5.66
15	5	7.95	1.95	0.006	3.90
20	5	9.55	1.6	0.006	3.20
25	5	11.09	1.54	0.006	3.08
30	5	12.44	1.35	0.006	2.70
40	10	14.84	2.4	0.006	2.40
50	10	17.17	2.33	0.006	2.33
60	10	19.37	2.2	0.006	2.20
80	20	23.53	4.16	0.006	2.08
100	20	27.36	3.83	0.006	1.92
120	20	30.83	3.47	0.006	1.74
150	30	35.89	5.06	0.006	1.69
180	30	40.56	4.67	0.006	1.56
210	30	44.88	4.32	0.006	1.44
240	30	49.13	4.25	0.006	1.42
270	30	53.4	4.27	0.006	1.42
300	60	57.63	4.23	0.006	1.41

APPENDIX D

Table D.1 Concentration of p-chlorophenol in NaCl solution under operating time 5 hours of FO mode by using ammonium bicarbonate solution at the concentration of 0.05 M as draw solution

Sample	Concentration of p-CPN by preparation (mg/L)	Absorbance (AU)	Concentration of p-CPN by calculation (mg/L)
Std.1	0.5	0.023	1.87
Std.2	5.0	0.061	4.96
Std.3	10.0	0.128	10.41
Std.4	25.0	0.307	24.96
Std.5	50.0	0.619	50.32
Std.6	70.0	0.862	70.08
Blank	0.0	0.000	0.00
Initial FS	42.5	0.517	42.03
Final FS	-	0.497	40.81
DS after 5 hrs of FO mode	-	-0.001	0.00

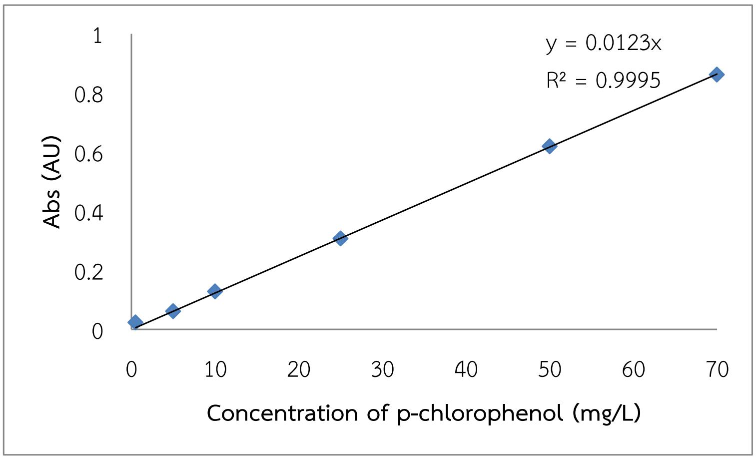


Table D.2 Concentration of p-chlorophenol in NaCl solution under operating time 5 hours of FO mode by using ammonium bicarbonate solution at the concentration of 0.1 M as draw solution

Sample.	Concentration of p-CPN by preparation (mg/L)	Absorbance (AU)	Concentration of p-CPN by calculation (mg/L)
Std.1	0.5	0.009	0.73
Std.2	5.0	0.066	5.32
Std.3	10.0	0.12	9.68
Std.4	25.0	0.317	25.56
Std.5	50.0	0.612	49.35
Std.6	70.0	0.876	70.64
Blank	0.0	0.00	0.00
Initial FS	42.5	0.525	42.34
Final FS	-	0.507	40.89
DS after 5 hrs of FO mode	-	-0.001	0.00

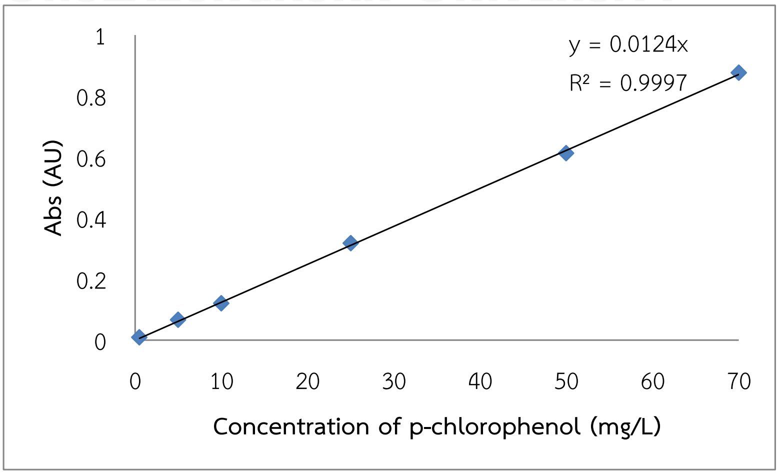


Table D.3 Concentration of p-chlorophenol in NaCl solution under operating time 5 hours of FO mode by using ammonium bicarbonate solution at the concentration of 0.5 M as draw solution

Sample.	Concentration of p-CPN by preparation (mg/L)	Absorbance (AU)	Concentration of p-CPN by calculation (mg/L)
Std.1	0.5	0.004	0.32
Std.2	5.0	0.064	5.16
Std.3	10.0	0.117	9.43
Std.4	25.0	0.316	25.48
Std.5	50.0	0.628	50.64
Std.6	70.0	0.866	69.84
Blank	0.0	0.000	0.00
Initial FS	42.5	0.528	42.58
Final FS	-	0.506	40.81
DS after 5 hrs of FO mode	-	0.000	0.00

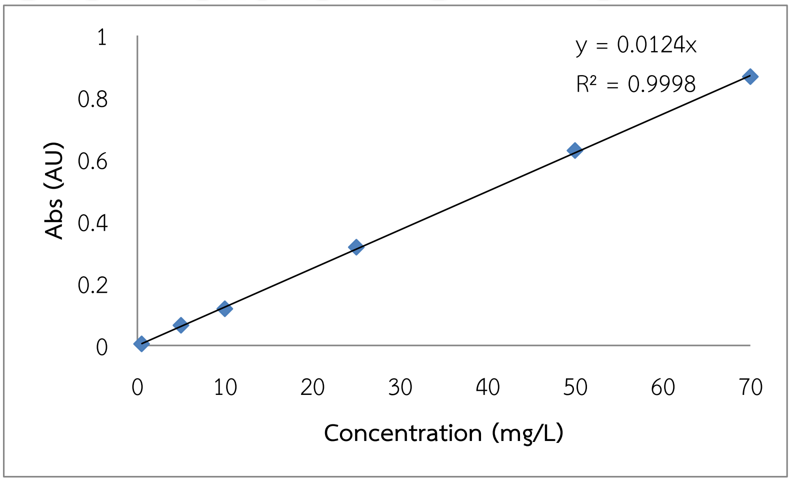


Table D.4 Concentration of p-chlorophenol in NaCl solution under operating time 5 hours of FO mode by using ammonium bicarbonate solution at the concentration of 1.0 M as draw solution

Sample	Concentration of p-CPN by preparation (mg/L)	Absorbance (AU)	Concentration of p-CPN by calculation (mg/L)
Std.1	0.5	0.008	0.64
Std.2	5.0	0.065	5.20
Std.3	10.0	0.122	9.76
Std.4	25.0	0.319	25.52
Std.5	50.0	0.615	49.20
Std.6	70.0	0.877	70.16
Blank	0.0	0.000	0.00
Initial FS	42.5	0.531	42.48
Final FS	-	0.508	40.64
DS after 5 hrs of FO mode	-	0.000	0.00

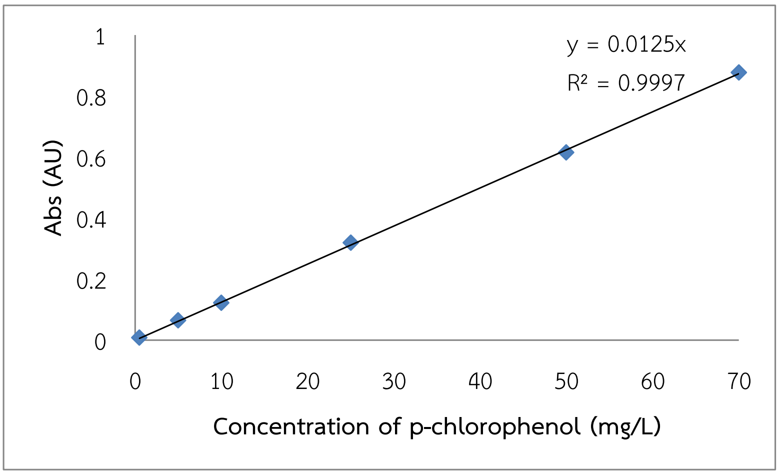


Table D.5 Concentration of p-chlorophenol in draw solution by using ammonium bicarbonate solution at the concentration of 0.1 M as background solution.

Sample	Concentration of p-CPN by preparation	Absorbance (AU)	Concentration of p-CPN by calculation
Std.1	0.5	0.01	1.00
Std.2	5.0	0.049	4.90
Std.3	10.0	0.098	9.80
Std.4	25.0	0.251	25.10
Std.5	50.0	0.496	49.60
Std.6	70.0	0.698	69.80
Blank	0.0	0.002	0.20
DI water	0.0	0.002	0.20

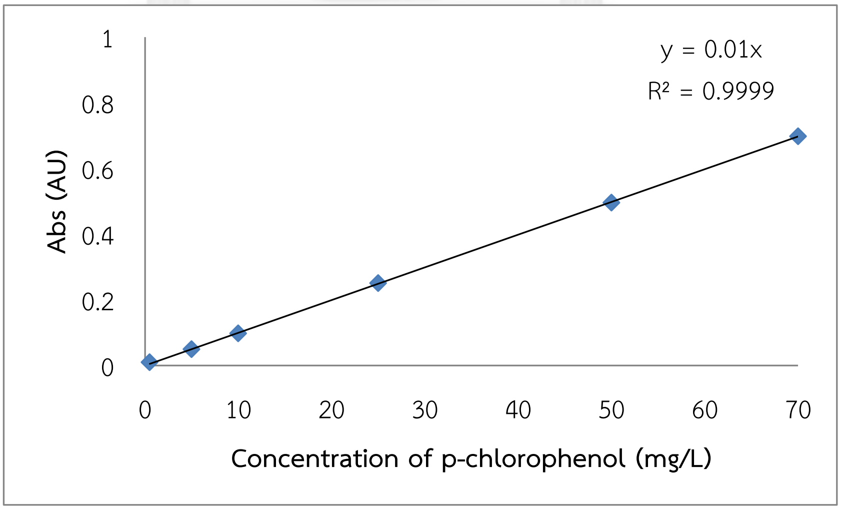


Table D.6 Concentration of p-chlorophenol in draw solution by using ammonium bicarbonate solution at the concentration of 0.5 M as background solution.

Sample.	Concentration of p-CPN by preparation	Absorbance (AU)	Concentration of p-CPN by calculation
Std.1	0.5	0.008	0.89
Std.2	5.0	0.046	5.12
Std.3	10.0	0.091	10.12
Std.4	25.0	0.225	25.00
Std.5	50.0	0.425	47.22
Std.6	70.0	0.649	72.11
Blank	0.0	0.002	0.22
DI water	0.0	0.000	0.00

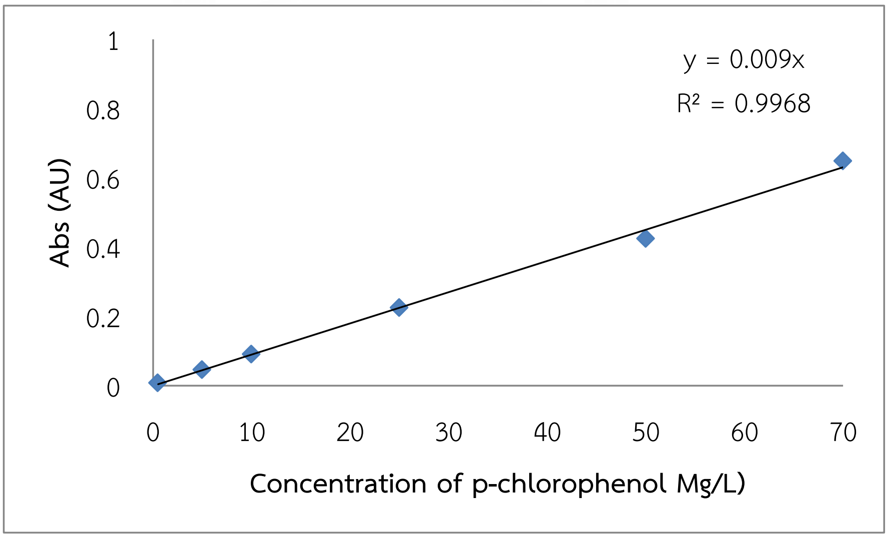


Table D.7 Concentration of p-chlorophenol in discharged cooling water under operating time 5 hours of FO mode by using ammonium bicarbonate solution at the concentration of 0.05 M as draw solution

Sample.	Concentration of p-CPN by preparation (mg/L)	Absorbance (AU)	Concentration of p-CPN by calculation (mg/L)
Std.1	0.5	0.005	0.49
Std.2	5.0	0.048	4.66
Std.3	10.0	0.098	9.51
Std.4	25.0	0.247	23.98
Std.5	50.0	0.514	49.90
Std.6	70.0	0.723	70.19
Blank	0.0	-0.002	0.00
Initial FS	42.5	0.435	42.23
Final FS	-	0.418	40.58
DS after 5 hrs of FO mode	-	-0.001	0.00

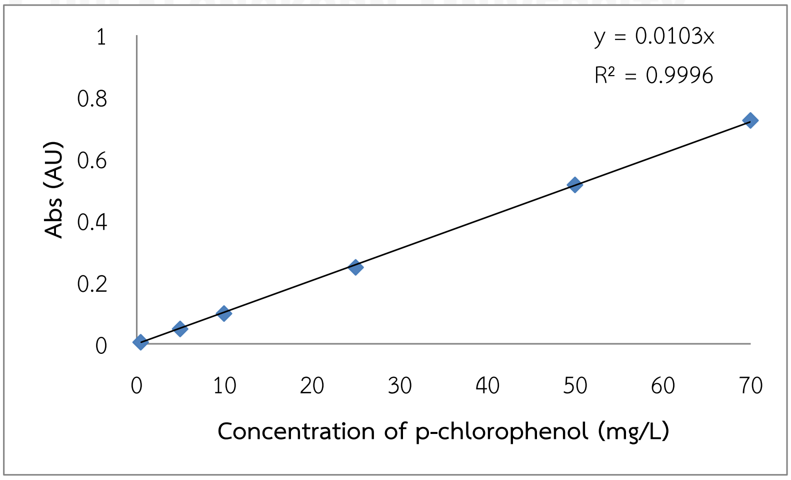


Table D.8 Concentration of p-chlorophenol in discharged cooling water under operating time 5 hours of FO process by using ammonium bicarbonate solution at the concentration of 0.1 M as draw solution

Sample.	Concentration of p-CPN by preparation (mg/L)	Absorbance (AU)	Concentration of p-CPN by calculation (mg/L)
Std.1	0.5	0.005	0.46
Std.2	5.0	0.052	4.81
Std.3	10.0	0.107	9.91
Std.4	25.0	0.256	23.70
Std.5	50.0	0.543	50.28
Std.6	70.0	0.755	69.91
Blank	0.0	-0.002	0.00
Initial FS	42.5	0.453	41.94
Final FS	-	0.437	40.46
DS after 5 hours of FO mode	-	-0.001	0.00

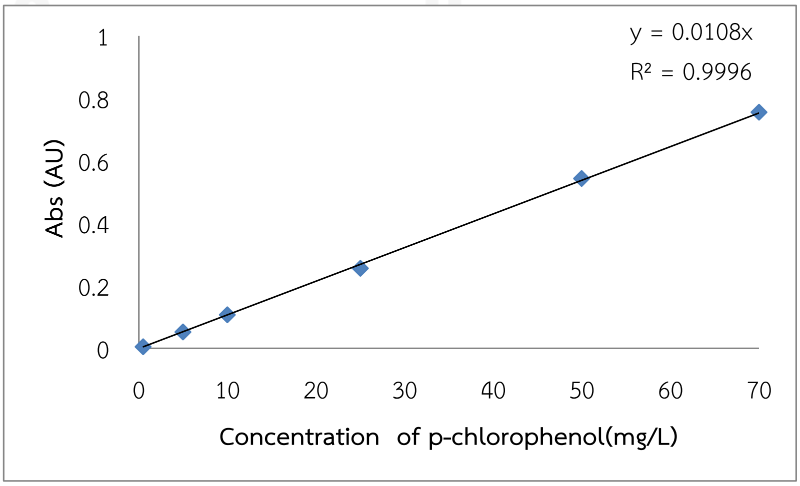


Table D.9 Concentration of p-chlorophenol in discharged cooling water under operating time 5 hours of FO mode by using ammonium bicarbonate solution at the concentration of 0.5 M as draw solution

Sample.	Concentration of p-CPN by preparation (mg/L)	Absorbance (AU)	Concentration of p-CPN by calculation (mg/L)
Std.1	0.5	0.003	0.35
Std.2	5.0	0.043	4.94
Std.3	10.0	0.087	10.00
Std.4	25.0	0.22	25.29
Std.5	50.0	0.435	50.00
Std.6	70.0	0.613	70.46
Blank	0.0	-0.002	0.00
Initial FS	42.5	0.361	41.49
Final FS	-	0.349	40.11
DS after 5 hrs of FO mode	-	-0.001	0.00

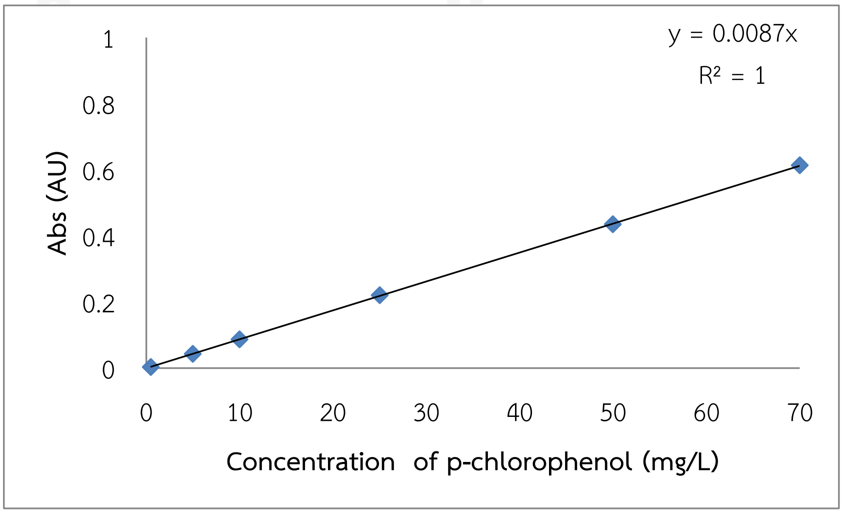
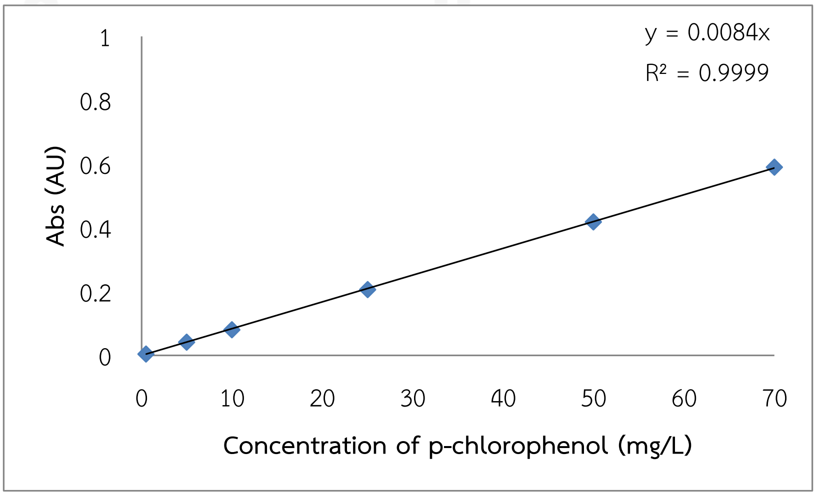


Table D.10 Concentration of p-chlorophenol in discharged cooling water under operating time 5 hours of FO mode by using ammonium bicarbonate solution at the concentration of 1.0 M as draw solution

Sample.	Concentration of p-CPN by preparation	Absorbance (AU)	Concentration of p-CPN by calculation
Std.1	0.5	0.004	0.48
Std.2	5.0	0.041	4.88
Std.3	10.0	0.08	9.52
Std.4	25.0	0.206	24.52
Std.5	50.0	0.418	49.76
Std.6	70.0	0.59	70.24
Blank	0.0	-0.001	0.00
Initial FS	42.5	0.356	42.38
Final FS	-	0.341	40.60
DS after 5 hrs of FO mode	-	-0.002	0.00



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Presentation

Mahisorn Maneechan, Patiparn Punyapalakul and Aunnop Wongrueng, Utilization of ammonium bicarbonate as draw solution in forward osmosis process: A case study of cooling water reuse, International Conference on Agricultural, Environmental and Biological Sciences (AEBS-2014), April 24-25, 2014 Phuket(Thailand).