TREATMENT OF N-NITROSODIMETHYLAMINE PRECURSORS IN COAGULATED WATER
BY NANOFILTRATION AND REVERSE OSMOSIS MEMBRANES

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การบำบัดสารตั้งต้นของสารเอ็น-ไนโตรโซไดเมทิลเอมีนในน้ำที่ผ่านการโคแอกกูเลชันด้วยเยื่อ
กรองนาโนและรีเวิร์สออสโมซิส

นางสาวสกาวรัตน์ สัมพัฒนวรชัย

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สกาวรัตน์ สัมพัฒนวรชัย : การบำบัดสารตั้งต้นของสารเอ็น-ไนโตรโซไดเมทิลเอมีนใน
น้ำที่ผ่านการโคแอกกูเลชันด้วยเยื่อกรองนาโนและรีเวิร์สออสโมซิส. (TREATMENT OF
N-NITROSODIMETHYLAMINE PRECURSORS IN COAGULATED WATER BY
NANOFILTRATION AND REVERSE OSMOSIS MEMBRANES) อ.ที่ปรึกษา
วิทยานิพนธ์หลัก: ผศ. ดร. จรงค์พันธ์ มุสิกะวงศ์ , 57 หน้า.

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการกำจัดสารตั้งต้นของสาร   N-
Nitrosodimethylamine (NDMA) ในน้ำดิบประปาจากโรงผลิตน้ำประปาบางเขนและโรงผลิต
น้ำประปาบางเลน ด้วยการโคแอกกูเลชันด้วย polyaluminium chloride (PACl) ร่วมกับการ
กรองด้วยเยื่อกรองชนิด nanofiltration (NF) และ reverse osmosis (RO) น้ำดิบประปาถูกเก็บ
มาจากโรงงานผลิตน้ำประปาทั้ง 2 โรงหนึ่งครั้ง การโคแอกกูเลชันด้วย PACl 80 มก./ลิตร ที่พีเอช
7 และ PACl 150 มก./ลิตร ที่พีเอช 7 ใช้เป็นการบำบัดเบื้องต้นของน้ำดิบประปาบางเขนและบาง
เลนตามลำดับ   กระบวนการกรองดำเนินการโดยใช้แรงดัน 4 บาร์ น้ำดิบประปาบางเขนมีค่า
dissolved organic carbon (DOC) เท่ากับ 4.2 มก./ลิตร และมีค่า dissolved organic
nitrogen (DON) เท่ากับ 0.24 มก./ลิตร น้ำดิบประปาบางเลนมีค่า DOC เป็น 7.9 มก./ลิตร และ
มีค่า DON เป็น 0.28 มก./ลิตร สำหรับน้ำดิบประปาบางเขนการโคแอกกูเลชันลดค่า DOC ได้ร้อย
ละ 32 และค่า DON ได้ร้อยละ 34 สำหรับน้ำดิบประปาบางเลน การโคแอกกูเลชันลดค่า DOC
ได้ร้อยละ 41 และค่า DON ได้ร้อยละ 37 การทดลองโคแอกกูเลชันร่วมกับการกรองด้วยเยื่อ
กรองชนิด NF ลดค่า DOC ได้ร้อยละ 92 และค่า DON ได้ร้อยละ 69 จากน้ำดิบประปาบางเขน
ขณะที่การทดลองโคแอกกูเลชัน ร่วมกับการกรองด้วยเยื่อกรองชนิด RO ลดค่า DOC ได้ร้อยละ
95 และค่า DON ได้ร้อยละ 85 ส่วนน้ำดิบประปาบางเลน การทดลองโคแอกกูเลชันร่วมกับการ
กรองด้วยเยื่อกรองชนิด NF ลดค่า DOC ได้ร้อยละ 97 และค่า DON ได้ร้อยละ 70 ขณะที่การ
ทดลองโคแอกกูเลชันร่วมกับการกรองด้วยเยื่อกรองชนิด RO ลดค่า DOC ได้ร้อยละ 97 และค่า
DON ได้ร้อยละ 79 การโคแอกกูเลชันร่วมกับการกรองด้วยเยื่อกรองชนิด RO กำจัด DON ได้
ดีกว่าเมื่อเทียบกับการโคแอกกูเลชันร่วมกับการกรองด้วยเยื่อกรองชนิด NF น้ำดิบประปาบางเขน
มีค่า DOC ของ HPO เป็น 2.0 มก./ลิตร และมีค่า DOC ของ HPI เท่ากับ 2.2 มก./ลิตร ส่วนน้ำ
ดิบประปาบางเลน มีค่า DOC ของ HPO เท่ากับ 3.7 มก./ลิตร และมีค่า DOC ของ HPI เท่ากับ
3.9 มก./ลิตร การโคแอกกูเลชันเพียงอย่างเดียวมีประสิทธิภาพในการลดค่า DOC ของ HPO ได้
ดีกว่าการค่า DOC ของ HPI การโคแอกกูเลชันร่วมกับการกรองด้วยเยื่อกรองชนิด RO กำจัดค่า
DOC ของ HPO และค่า DOC ของ HPI ได้เกือบจะทั้งหมดสำหรับค่าโอกาสในการก่อตัวของสาร
NDMA ในตัวอย่างน้ำดิบประปา น้ำที่ผ่านการโอแอกกูเลชัน และน้ำที่ผ่านกรองกรองด้วยเยื่อ
กรองชนิด RO นั้นตรวจไม่พบสารดังกล่าว เมื่อทำการตรวจวัดด้วยวิธีการที่มีค่าความเข้มข้นต่ำสุด
ที่ตรวจวัดได้เป็น 542 นาโนกรัม/ลิตร

สาขาวิชา	การจัดการสิ่งแวดล้อม	ลายมือชื่อนิสิต	....
ปีการศึกษา	2556	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก	....

5587628420 : MAJOR ENVIRONMENTAL MANAGEMENT

SAGAORAT SUMPATTANAVORACHAI: TREATMENT OF N-NITROSODIMETHYLAMINE PRECURSORS IN COAGULATED WATER BY NANOFILTRATION AND REVERSE OSMOSIS MEMBRANES. ADVISOR: ASST. PROF. CHARONGPUN MUSIKAVONG, Ph.D., 57 pp.

This research is aimed at investigating the removal of N-Nitrosodimethylamine (NDMA) precursors in raw water supplies from the Bangkhen water treatment plant (WTP) and the Banglen WTP by polyaluminum chloride (PACl) coagulation combined with nanofiltration (NF) and reverse osmosis (RO) membrane. Raw water supplies were collected once time. The PACl of 80 mg/L at pH 7 and PACl of 150 mg/L at pH 7 were conducted as pre-treatment for raw water of the Bangkhen WTP and the Banglen WTP, respectively. NF270 and TW30 membranes were used in NF and RO experiments, respectively. The operating pressure of 4 bars was used. Dissolved organic carbon (DOC) of 4.2 mg/L and dissolved organic nitrogen (DON) of 0.24 mg/L were found in raw water of the Bangkhen WTP. DOC and DON of raw water of the Banglen WTP were 7.9 and 0.28 mg/L, respectively. The coagulation reduced DOC and DON from raw water of the Bangkhen WTP and the Banglen WTP by 32 and 34% and 41 and 37%, respectively. In the case of the Bangkhen WTP, the coagulation combined with NF reduced DOC and DON by 92 and 69%, respectively. DOC of 95% and DON of 85% could be reduced by coagulation combined with RO filtration. For the Banglen WTP, coagulation combined with NF reduced DOC and DON by 97 and 70%, respectively. DOC of 97% and DON of 79% could be reduced by coagulation combined with RO filtration. The PACl coagulation combined with RO filtration showed better results on DON removal when compared with coagulation combined with NF filtration. DOC of hydrophobic organic fraction (HPO) of 2.0 mg/L and DOC of hydrophilic organic fraction (HPI) of 2.2 mg/L were detected in raw water of the Bangkhen WTP. DOCHPO and DOCHPI of raw water of the Bangkhen WTP were 3.7 and 3.9 mg/L, respectively. The PACl coagulation, alone, showed better result on reduction of HPO than that of HPI. The PACl coagulation combined with RO filtration could reduce nearly 100% of both HPO and HPI. NDMA formation potential of raw water supplies, coagulated waters, and permeate waters could not be detected under the detection limit of the method at 542 ng/L.

Field of Study: Environmental Management   Student's Signature ....

Academic Year: 2013   Advisor's Signature ....

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CHAPTER 1

INTRODUCTION

1.1   Motivation

Natural waters contain not only significant levels of dissolved organic carbon (DOC), but also dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN), which includes ammonium, nitrite and nitrate. In surface water, DON concentrations can vary from less than 0.1 mg N/L to more than 10 mg N/L with an approximate median DON concentration of 0.3 mg N/L (Westerhoff & Mash, 2002)

Nitrogenous disinfection by-products (N-DBPs) can be formed during a water treatment process from the reaction of DON with the chlorine (Cl2) used for disinfection. DON and N-nitrodimethylamine formation potential (NDMA-FP) serve as the primary N-nitrodimethylamine (NDMA) precursors. Ultraviolet adsorption at wavelength 254 nm (UV-254), DOC, and SUVA were classified the secondary precursors of NDMA (Roux, Gallard, & Croué, 2011; S. Yoon, Nakada, & Tanaka, 2011). NDMA is one of N-DBPs in the group of N-Nitrosamines compounds. The United State Environmental Protection Agency (US.EPA.) classifies a NDMA as a probable human carcinogen; a NDMA concentration of 0.7 ng/L in drinking water has a 10-6 risk level of cancer (USEPA., 1987). World Health Organization (WHO) also set the guideline value of NDMA concentration in drinking water of 100 ng/L.

Nowadays, raw water supplies from reservoirs and rivers are facing more serious problems due to contamination by DOC and DON. This can be attributed to the expansion of residential, industrial, and agricultural areas. High levels of DOC and DON in water increases the potential for high levels of carbonaceous-DBPs (C-DBPs) and N-DBPs in the water supply. A fractionation technique using this resin could be utilized to separate dissolved organic matter (DOM) in raw water supply into hydrophobic organic fraction (HPO) and hydrophilic organic fraction (HPI) (Leenheer, Noyes, & Steer, 1982). It was used by researchers to characterize the nature of organic matter in raw water and water supply (Kanokkantapong, Marhaba, Wattanachira, Panyapinyopol, & Pavasant, 2006; Panyapinyopol, Marhaba, Kanokkantapong, & Pavasant, 2005).

The Bangkhen Water Treatment Plant (WTP), the largest water treatment plant in Bangkok, Thailand, utilizes raw water from the Chao Phraya River. Approximately 3.7 million cubic meters of water supply is produced daily and distributed to around 6 million people in Bangkok and nearby provinces. The Banglen Water Treatment Plant (WTP) is operated by the Provincial Waterworks Authority (PWA). The Banglen WTP utilizes raw water from the Tha-Jeen River for producing an approximate 440,000 m^3 per day. The Banglen WTP distributed water supply to serve water consumers in Nakorn Pathom and Samut Sakorn provinces.

The treatment process of the Bangkhen and Banglen WTPs mainly consisted of alum and polyaluminium chloride (PACl) coagulation, sedimentation, filtration, and chlorine disinfection. The coagulation has been proven to remove efficiency organic matter. Due to the simplicity and effectiveness of the coagulation process, the coagulation is commonly used for removing contaminants from raw water supplies (Lee & Westerhoff, 2006).

The increasing levels of DOC and DON being found in raw water could affect a water treatment plant's capability to produce safe water supply. Alternative water treatment processes, therefore, have been developed to mitigate this situation. Nanofiltration (NF) and reverse osmosis (RO) membrane filtration have been developed to remove micropollutants from raw water supplies. These treatment processes could be used after the coagulation to remove the remaining micropollutants from the coagulated water (Kimura, Toshima, Amy, & Watanabe, 2004). NF can filter DON by approximately 80% (Xu et al., 2010), and could remove more than 90% of DOC in water (Hongthong, Mattaraj, & Jiraratananon, 2009). The rejection of organic substances by RO filtration and NF depended on the size of the organic substances. The molecular weight, charge and polarity of organic substances could be used as indicators in this case. Organic matter that was relatively small in size tended to have lower rejection rate (Ozaki & Li, 2002; Van der Bruggen, Schaep, Maes, Wilms, & Vandecasteele, 1998; Van der Bruggen, Schaep, Wilms, & Vandecasteele, 1999).

Previous studies have characterized DOM and its potential to form C-DBPs in the source water of Bangkok (Kanokkantapong et al., 2006; Panyapinyopol et al., 2005). However, the study on level of NDMA precursors and their reductions by the PACl coagulation, PACl coagulation followed by the NF filtration, and PACl coagulation followed by the RO filtration are limited. Therefore, in this study we choose to investigate the reduction of NDMA precursors and their HPO and HPI in raw water supplies of the Bangkhen WTP and the Banglen WTP, Thailand. The PACl coagulation was employed as the pre-treatment. The NF and RO filtration were utilized for removing NDMA precursors in this work. The water treatment that facing the problem of DOM and DON contamination can be applied results obtained from this work to develop the additional treatment units for mitigating their problem.

1.2   Objective

To determine the reduction of NDMA precursors in raw water supplies and their HPO and HPI by using PACl coagulation as the pre-treatment of nanofiltration and reverse osmosis processes.

1.3   Hypothesis

NDMA precursors and their HPO and HPI in raw water supplies from different sources can be removed variously when using PACl as pre-treatment and followed by NF and RO filtration.

1.4   Scope of Study

- Raw water supplies were collected once from the Bangkhen WTP and the Banglen WTP.

- The PACl was used as coagulant in coagulation experiments with dosage of 80mg/L for the water sample from the Bangkhen WTP, and with dosage of 150mg/L for the water sample from the Banglen WTP.

- A jar test apparatus were used for performing coagulation experiments.

- NF membrane (NF270) and RO membrane (TW30) were used in this study. The membrane filtration was conducted with a C-10T membrane unit, under the cross-flow operation.

- The effect of pressure on DON rejection was studied under 3 pressures.

- The DAX-8 resin was used in the fractionation experiment to separate HPO and HPI. The resin fractionation was performed in accordance with the method developed by Thurman and Malcolm (1981).

- Water samples for DON analysis was prepared in accordance with the method developed by Xu *et al*., (2010).

- Samples for analysis of NDMA were extracted in accordance with Standard Method 521 (APHA, AWWA, and WPCF, 1995).

- NDMA was analyzed by using Gas Chromatography/with Nitrogen Phosphorus Detector. Limit of detection (LOD) of NDMA is 300 µg/L.

1.5   Benefit of this work

- The process could be applied into the water treatment operation of the water treatment plant.

CHAPTER 2

THEORETICAL BACKGROUNDS AND LITERATURE REVIEWS

2.1   Dissolved organic matter (DOM)

Natural waters consist of many kinds of organic matter. Dissolved organic matter (DOM) is produced naturally when organisms die. Depending on its source and extent of degradation, DOM can be greatly variable. These include temperature, humidity, light, microbial populations and geography. DOM consists of hydrocarbon structures, which are aromatic and aliphatic, that have contained ketone, carboxyl, amide, and other functional groups. An aggregation of heterogeneous molecules in natural water increases DOM complexity (Leenheer et al., 1982). DOM can be divided into 2 groups which are humic and non-humic substances (Thurman, 1985). The DOM fraction and chemical groups are shown in Table 1.

Table 1 Dissolved organic matter fractions and chemical groups

Fraction	Chemical groups
Hydrophobic	
Acid	
Strong	Humic and fuvic acid, high MW alkyl monocarboxylic and dicarboxylic acids, aromatic acids.
Weak	Phenols, tannins, intermediate MW alkyl monocarboxylic and dicarboxylic acids, aromatic acids.
Base	Proteins, aromatic amines, high MW alkyl amines
Neutrals	Hydrocarbon, aldehydes, high MW methyl ketones and alkyl alcohols, ethers, furan, pyrrole.
Hydrophilic	
Acid	Hydroxyl acids, sugars, sulfonics, low MW alkyl monocarboxylic and dicarboxylic acids
Base	Amino acids, purines, pyrimidines, low MW alkyl amines
Neutrals	Polysaccharides; low MW alkyl alcohols, aldehydes

Sources: (Leenheer & Noyes, 1984; Leenheer et al., 1982; Reckhow, Bose, Bexbarua, Hesse, & McKnight, 1992)

2.2 Surrogate parameters for DOM

2.2.1 Total organic carbon (TOC) and dissolved organic carbon (DOC)

To measure the content of organic carbon in water directly is to measure its total organic carbon (TOC), however an implication of the aromaticity, aliphatic nature, functional groups, or chemical bonding associated with natural organic molecules does not included. An important factor in explaining why differ sources of water which contain similar concentration of TOC will form various concentrations of DBPs under the same disinfection conditions and halogenated levels is the reactivity between the chemical bonds and the functional groups (USEPA., 1999).

Dissolved organic carbon (DOC) is commonly used as a measurement of surrogate DBP precursors. DOC is identified as a part of TOC. Dissolves organics can be more reactive than particulate organics. A relatively high ratio of DOC/TOC could be used to indicate that much of the organic matter is in form of soluble. The ratio of DOC/TOC might also be taken into account as a significant factor in explaining why differ sources of water which have the similar concentration of TOC will form various concentrations of DBP under the same disinfection condition.

Physical treatments, for example flocculation and filtration, are expected to be used to take away a great amount of the organic matter in water. Therefore, other treatments, for instance coagulation, adsorption using granular activated charcoal, and media filtration are necessary in achievement of significant removal.

2.2.2 Ultraviolet Light Absorbance at 254 nm

One of the most widely used surrogates in drinking water research is to measure the ultraviolet light absorption ability of water at a specific wavelength, a wavelength of 254 nm (UV-254). The absorbance of UV-254 can be used to imply the concentration of organic molecules with extended conjugation (USEPA., 1999).

Some inorganic species, which also absorb UV light at wavelength of 254 nm, can interfere in the use of UV-254 as an indicator of unit process for DBPs precursor removal. For example, monochloramine absorb ultraviolet light at wavelength of 243 nm. This potential intervention should be taken into account as an evaluation of unit process performance for the removal of UV-254 (USEPA., 1999).

2.2.3 Specific Ultraviolet Absorption

There is evidence showed that SUVA can be used as a reliable indicator of the humic content in water. SUVA is defined as UV-254 (measured in m^{-1}) divided by DOC concentration (in mg/L), resulting in SUVA unit of L/mg-m. Equation 1 shows the calculation of SUVA.

$$SUVA = UV_{254} / DOC \qquad \text{(Equation 1)}$$

By using the SUVA results, the capability in removal of water treatment processes is predictable. Enhanced coagulation could reduce large SUVA and TOC. High SUVA containing water limited large reductions in SUVA and TOC as a result of enhanced coagulation. While low SUVA containing water, however, limited pretty low in SUVA and TOC reductions.

2.2.4   Dissolved organic nitrogen (DON)

Organic nitrogen, ammonium ion (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-) are species of nitrogen found in secondary and tertiary treated wastewater effluents. Organic nitrogen consists of DON and particulate organic nitrogen (PON). DON plays an important role as precursor of many N-DBPs during water treatment process. A study found that N-DBPs have higher teratogenic, mutagenic, and carcinogenic capability than carbon-containing disinfection byproducts (C-DBPs), such as trihalomethanes (THMs) (Plewa *et al.*, 2008). DON cannot be measured directly, but can be calculated by the following equation (Equation 2).

$$DON = TN - NO_3^- - NO_2^- - NH_4^+ \qquad \text{(Equation 2)}$$

Where DON is concentration of DON, TN is concentration of total nitrogen, NO_3^- is concentration of nitrate, NO_2^- is concentration of nitrite, and NH_4^+ is concentration of ammonium ion.

2.3   Nitrosamine

Nitrosamines are probable human carcinogens which are classified by united state environmental protection agency (USEPA., 1987). Nitrosamines are polar compounds and usually soluble in water. The properties of the nitrosamines are listed in Table 2.

Table 2 the properties of the nitrosamines

Nitrosamine (Abbreviation)	Formula	Molecular weight (g/mol)	Standard US EPA cancer classification group	MCL for $R=10^{-6}$ (ng/L)
N-nitrosodimethylamine (NDMA)	$C_2H_6N_2O$	74,082	B2	0.7
N-nitrosomethylethylamine (NMEA)	$C_3H_8N_2O$	88,108	B2	2
N-nitrosodiethylamine (NDEA)	$C_4H_{10}N_2O$	102,135	B2	0.2
N-nitroso-di-n-propylamine (NDPA)	$C_6H_{14}N_2O$	130,188	B2	5
N-nitroso-di-n-butylamine (NDBA)	$C_8H_{18}N_2O$	158,241	B2	6
N-nitroso-di-phenylamine (NDPhA)	$C_{12}H_{10}N_2O$	198,221	B2	7,000
N-nitrosopyrrolidine (NPYR)	$C_4H_8N_2O$	100.1	B2	20
N-nitrosopiperidine (NPIP)	$C_5H_{10}N_2O$	114.15	B2	
N-nitrosomorpholine (NMOR)	$C_4H_8N_2O_2$	116.12	2B (IARC)	

Remark; MCL: maximum contaminant level for risk 10^{-6}, (The abbreviations are used throughout the text) Source: (Nawrocki & Andrzejewski, 2011).

2.4 N-Nitrosodimethylamine (NDMA)

The formula of NDMA is $C_2H_6N_2O$. Nitrosamines are classified as carcinogenic, mutagenic and teratogenic substances. NDMA is an organic compound and a member of nitrosamines. Their cancer potencies are much higher than those of the THMs (Richardson, Plewa, Wagner, Schoeny, & DeMarini, 2007). The USEPA evaluates a 10^{-6} risk level of cancer from NDMA concentration of 0.7ng/L in drinking water (USEPA., 1987).

NDMA is a yellow liquid which has no typical odor. Once NDMA was loose into air, sunlight can destroy it. Sunlight and/or biological processes can also decompose NDMA when it was in water. During water chlorination and chloramination, formation of NDMA as DBPs could take place.

NDMA shows a strong tendency to harm the liver of humans and animals. Animals which are exposed to environments with high concentration of NDMA for a short periods of time (hours until few days) get liver diseases but not cancer. Animals exposed to a low NDMA concentration for long time, might have liver and lung cancer. A secondary amine compound, dimethylamine (DMA), is classified as a precursor of NDMA formation during chlorination and chloramination (Choi and Valentine, 2002; Mitch and Sedlak, 2002). Many researchers have been studied on the Mechanisms of NDMA formation (Chen & Young, 2008; Oya, Kosaka, Asami, & Kunikane, 2008).

2.5 Coagulation

The coagulation is to add aluminium or iron salts, for example aluminium sulphate, polyaluminium chloride, ferric chloride, ferric sulphate or polymers, into the water. These salts added in the water are known as coagulants. These coagulants have a positive charge. The negative charge of particles suspended and dissolved in the water will be neutralize by the coagulant's positive charge. During the coagulation, the particles in the water bind together, or coagulate. When the particles get larger, they rapidly settle to the bottom of the water (Droste, 1997).

In a water treatment line, a rapid mixing will be started after the coagulant was added to the water. The coagulated water can either be filtered directly through a media filter (for example sand and gravel), a microfiltration or ultrafiltration membrane, or it can be moved to a settling tank. In a settling tank, the heavy particles settle to the bottom and are removed, and the water moves on to the filtration step of the treatment process.

Significant amount of organic compounds, which included DOM or DOC, can be efficiency removed during the coagulation. Suspended particles, which include inorganic particles, for instance iron, can also be removed during coagulation. An undesirable taste and odor of water are come from a significant amount of DOC containing in the water. Pathogens may be found in the water, even though large amount of particles and DOM could be removed during the coagulation. These pathogens can normally be removed from the water by attaching to the dissolved substances that are removed by coagulation.

2.6   Polyaluminium chloride (PACl)

Since 1980s, polyaluminum chloride (PACl) coagulant has been developed. Since then, it has been widely used in many water and wastewater treatment processes around the world (Jiang, 2001). When compared to aluminium sultphate, PACl hydrolyses with greater ease and releases an emission of longer chains and greater electrical polyhydroxides in the water, thus contributing to maximize the physical action of the flocculation. Coagulation using PACl as coagulants is obtained better performance when compared to using aluminium sulphate as coagulant at medium and high turbidity waters. The formation of floc using PACl is pretty rapid. The sludge produced by PACl is more compact than that produced by alum (Jiang, 2001).

2.7   Jar-test

The jar test is normally performed to determine for the proper coagulant and the chemical dosage required for the coagulation of water. In this test, various dosages of coagulant are added to a series of beaker, which water is poured into, and then tested under identical conditions. Flocculation is stimulated during the rapid mixing step and the slow mixing step after adding the coagulant. After a given time, the stirring ceased and the floc formed is allowed to settle. The most important aspects to note are the time for floc formation, the percent turbidity, color removal, and the final pH of the coagulated water. The dosage for coagulant

required for the coagulation can be estimated from the dosage of coagulant determined from the jar-test experiment.

2.8   Membrane filtration

A membrane filtration is technology which is applied for water purification. The membrane can be classified, by considering its pore size and the differential pressure on both sides of the membrane, into four categories. There are microfiltration membrane (MF), ultrafiltration membrane (UF), nanofiltration membrane (NF), and reverse osmosis membrane (RO). A comparison of MF, UF, NF, and RO is shown in Table 3.

From Figure 1, membrane with the widest operating ranges for almost all undesirable components in water removal goes to RO membrane, whereas, the narrowest operating range for almost all undesirable components removal membrane is MF membrane.

Table 3 Comparison of MF, UF, NF, and RO

	RO	NF	UF	MF
Structure	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical Symmetrical
Pore size	< 0.001 µm	< 0.002 µm	0.2 - 0.02 µm	4 - 0.02 µm
Rejection	HMWC, LMWC glucose, amino acid	HMWC, polyvalent negatively ions	Macro molecules, polysaccharides	Particles, clay
Membrane material	Cellulose acetate, Thin film composite	Cellulose acetate, Thin film composite	Polysulfone, Thin film composite	Ceramic, Polusulfone
Operating pressure	1.5 - 2.5 MPa	0.5 a 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

Remarks; HMWC: High Molecular Weight Component, LMWC: Low Molecular Weight Component, Source: (Wagner, 2001)
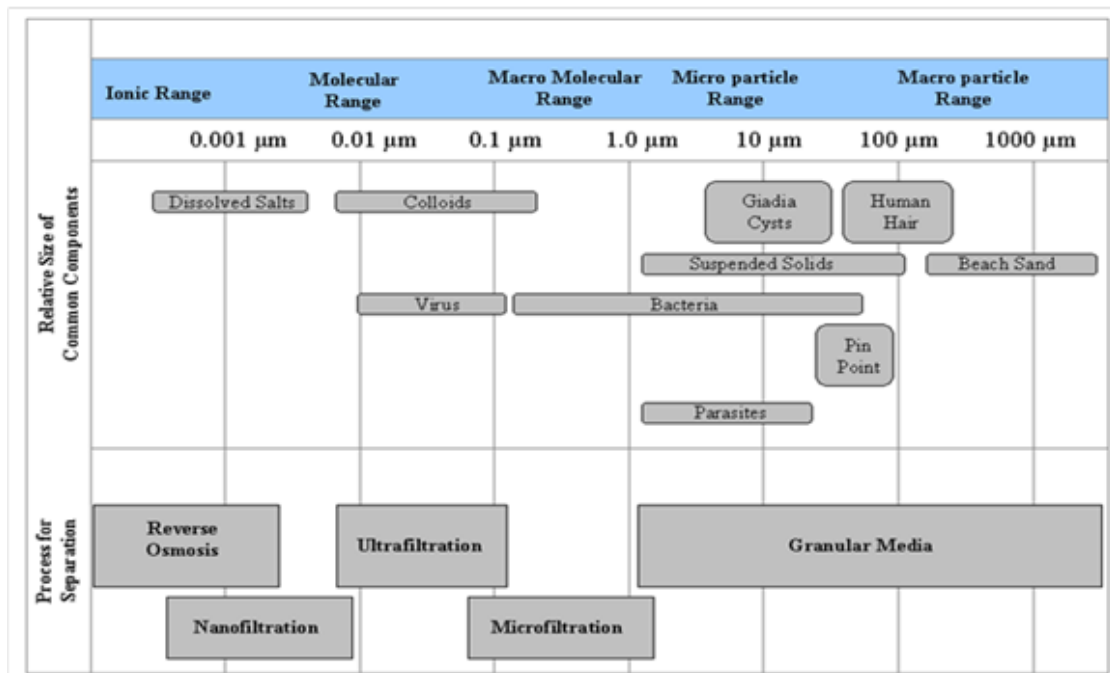
Figure 1 **Operating ranges of membranes for undesirable components removal**

(Wang, Chen, Hung, & Shammas, 2011)

2.9   Cross-flow filtration

For cross-flow filtration, the feed will flow parallel to the membrane surface. Only small part of the feed can pass through the membrane. The cross-flow membrane is preferred in many cases because the rate of fouling in cross-flow operation is lower than that in dead-end operation.
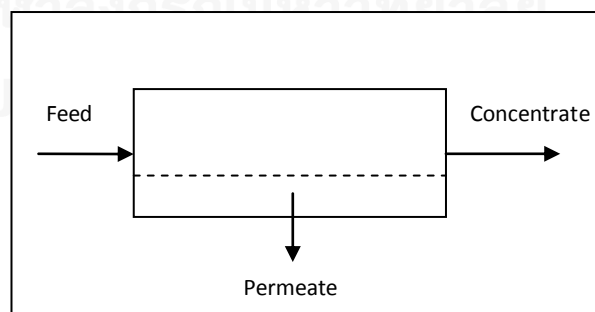
Figure 2 Cross-flow filtration (Cheryan, 1998)

The cross-flow filtration can be categorized into two types which are the single-pass method and the circulation method. Figure 3 shows the schematic diagram of both methods. For the single-pass method, the feed will pass through the module only once, and then the feed volume will decrease with time of operation, whereas the feed in circulation method will be circulated to pass the module for several times. For circulation method, flow velocity and pressure can be adjusted to reduce the pressure drop and also minimize the rate of fouling.
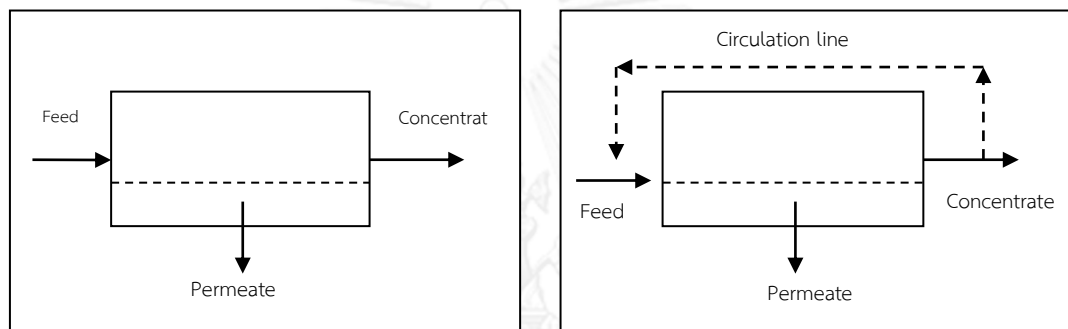
Figure 3 Two types of cross-flow filtration (Cheryan, 1998)

The major separation mechanism of membrane filtration is size exclusion and electrostatic exclusion (Crittenden *et al.*, 2005). In general, the size exclusion is the predominant removal mechanism for separation of uncharged. For separation of ionic compounds, both size exclusion and electrostatic exclusion are responsible (CHILDRESS & ELIMELECH, 2000).

The size exclusion is a porous barrier which can be used to separate the dissolved compounds based on their size or molecular weight. The separation in a sieve-like style is driven by an application of a pressure differential across the size exclusion membrane. In this "pressure-driven" filtration process, smaller particles or molecules pass through the barrier with the solvent (small molecules) as filtrate, whereas, the retentate is a retained larger particles or molecules. The pore size and retentate dimension of the membrane are used to classify the types of filtration membranes. (Kunst & Kosutic, 2008).

The present of charge exclusion of ionic species happens because of electrical charges carried by a membrane. The sulfonic, carboxylic or ammonium groups layer of a membrane have been formed and bonded covalently to a membrane matrix. The dissociation of these functional groups occurs in aqueous solution (pH depending), leaving a membrane negatively or positively charged and repelling ions from the membrane. The pH of the feed water has significant effect on the charge of the membrane surface. For the most thin film composite membranes, the dissociation of the functional groups of the surface of the membrane leads to the negative charge in neutral aqueous solution (Kunst & Kosutic, 2008).

2.10   DOM removal by coagulation

Raw water from two reservoirs and the U-Tapao canal, Songkha, Thailand were collected for study the reduction of trihalomethane formation potential (THMFP) and organic matter by coagulation process. A coagulant used in this study was PACl. The dosage of PACl was selected at 40 mg/L as optimal dosage of coagulant under controlled pH 7. The study showed that major chemical classes in water samples were aliphatic hydrocarbon and organic nitrogen. Under this optimal condition, it could reduce average UV-254 to 57%, DOC to 64%, and THMFP to 42%. The major chemical classed found in coagulated water go to aliphatic hydrocarbon, organic nitrogen and aldehydes and ketones (Musikavong & Wattanachira, 2013).

The raw water supply in Sri-Trang Reservoir, Thailand was taken for investigating the removal of dissolved organic matter and trihalomethane formation potential (THMFP). The coagulation was conducted using polyaluminium chloride (PACl) as coagulant. The DOC and UV-254 were reduced by 52 and 65%, respectively. The DOC of HPI and DOC of HPO were found to be reduced by 46 and 56%, respectively. PACl coagulation showed higher efficiency on reduction of DOC of HPO than that of DOC of HPI. (Kueseng, Suksaroj, Musikavong, & Suksaroj, 2011).

In 2005, the alum and ferric chloride coagulation were used as coagulants for reducing the organic matter and THMFP of treated industrial estate wastewater in the northern Thailand. A coagulants dosage was varied from 10 to 80 mg/L at pH conditions varying from 5 to 6.5. DOC was reduced from an average value of 5.1 mg/L to a level of about 4.0 mg/L by alum and ferric chloride dosages of approximately 40 mg/L. Total THMFP reduction efficiency were comparable at 25 and 28% by alum and ferric chloride coagulation, respectively (Musikavong, Wattanachira, Marhaba, & Pavasant, 2005).

2.11   Resin fractionation

The Bangkok source water was characterized for THMFP precursors. DAX-8, AG-MP-50, and WA-10 were utilized to fractionate DOM. The distribution of DOC in six organic fractions from high to low were hydrophilic neutral fraction (HPIN), hydrophobic acid fraction (HPOA), hydrophilic acid fraction (HPIA), hydrophobic neutral fraction (HPON), hydrophilic base fraction (HPIB), and hydrophobic base fraction (HPOB), respectively. Two main precursors of THMFP in the source water with chlorination were HPIN and HPOA. The chlorination of HPON and HPIN fractions only formed chloroform, while other organic fractions led to the formation of both chloroform and bromodichloromethane (Panyapinyopol et al., 2005).

The raw water from U-tapao Canal, Songkla, Thailand was collected to investigate the reduction of fractionated dissolved organic matter and their trihalomethane formation potential (THMFP) with enhance coagulation. The optimal condition for coagulation process was found at PACl dosage of 40 mg/L at controlled pH 7. Under such a condition, DOC and THMFP were reduced by 55 and 48%, respectively. The coagulated water was fractionated using DAX-8 resin into 2 parts which are hydrophilic organic fraction (HPI) and hydrophobic organic fraction (HPO). The results showed that by using PACl at 40 mg/L could reduce DOC of HPI and DOC of HPO by 48 and 60%, respectively. The THMFP of HPI and THMFP of HPO were reduced by 39 and 57%, respectively (Musikavong, Inthanuchit, Srimuang, Suksaroj, & Suksaroj, 2013).

2.12   NDMA precursors removal by membrane filtration

In 2010, a measurement of DON in water samples with nanofiltration (NF) treatment was developed. The study presented a NF method for increasing accuracy and precision of DON measurements by selectively concentrating DON while passing through dissolved inorganic nitrogen species (DIN). This method could reduce the DIN/total nitrogen (TN) ratio and decrease the effect of DIN for DON measurement. They tested three commercial NF membranes (NF90, NF270, and HL). The rejection efficiency of filtered water from the Yangshupu drinking water treatment plant is 12%, 31%, 8% of nitrate, 26%, 28%, 23% of ammonia, 77%, 78%, 82% of DOC, and 83%, 87%, 88% of UV-254 for HL, NF90, and NF270, respectively. Due to its high DIN permeability and DON retention (~80%), the best performance came from NF270. The DIN/TN ratio was lowered from around 1 to less than 0.6 mg N/mg N by using NF270 (Xu et al., 2010).

Xu et al. studied the characteristics of DON in raw water from the Huangpu River and in water undergoing treatment in the full-scale of the Yangshupu Drink Water Treatment Plant in Shanghai, China. The concentration of DON in raw water was found at 0.34 mg/L. By using a series of ultrafiltration (UF) membranes, the molecular weight (MW) distribution of dissolved organic matter (DOM) was divided into five groups: 30, 10-30, 3-10, 1-3 and less than 1 kDa. The less than 1 kDa fraction dominated the composition of DON as the major N-nitrosodimethylamine formation potential (NDMA-FP) in the raw water. DON fractions cannot be effectively removed in the treatment process, which included pre-ozonation, clarification and sand filtration processes. The results from linear regression analysis showed that DON was strongly correlated to HAAFP and NDMA-FP. (Xu et al., 2011)

A study by Yu *et al* (2009) stated that NDMA precursors, which are dimethylamine (DMA), methylethylamine (MEA), diethylamine (DEA), and dipropylamine (DPA), have high pKa (more than 10.7) and they are positively charged. These positively charged can be well co-rejected by negatively charged membranes. The filtration using a NF membrane (NE90) and brackish water RO (BWRO) membrane showed that the steady-state rejection of all NDMA precursors was almost 98% (Yu, Park, Hyung, Huang, & Kim, 2009).

CHAPTER 3

METHODOLOGY

3.1 Source of the raw water supplies

The Bangkhen water treatment plant (WTP), located in Bangkok, Thailand and the Banglen WTP, located in Nakorn Pathom, Thailand, was selected as the study site in this research. Samples of the plant's raw water supply were collected once. The samples for the analysis of the basic water quality and for the polyaluminium chloride (PACl) coagulation experiments were stored in a cold room under a controlled temperature of 4 °C until analysis.

The Whatman GF/F (0.7 μm nominal pore size) filter paper was pre-combusted at 550 °C for 2 hours and then used to filtrate the raw water prior to the water being analyzed for the following parameters: ultraviolet adsorption at wavelength 254-nm (UV-254), dissolved organic carbon (DOC), dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), NH_4^+, NO_3^-, and NO_2^- values. The samples for the nanofiltration (NF) and reverse osmosis (RO) filtration experiments were filtered through pre-combusted (at 550 °C for 2 hours) Whatman GF/F 0.7 μm nominal pore size filter paper.

3.2 Experimental procedure

The raw water supplies were collected once from the Bangkhen WTP (30th September, 2013) and the Banglen WTP (1st November, 2013). The raw waters, then, were separated into 2 portions. The first portion was used for conducting the PACl coagulation, NF and RO filtrations. The PACl coagulation was employed as the pre-treatment of NF and RO filtrations in this work. The GF/F filter paper was used as microfiltration for NF and RO experiments. The second portion was utilized to determine the distribution of hydrophobic organic fraction (HPO) and hydrophilic organic fraction (HPI) and *N*-nitrosodimethylamine formation potential (NDMA-FP) in raw water supplies.

The pH, turbidity, alkalinity, UV-254, DOC, DON, TDN, NH_4^+, NO_3^-, and NO_2^- values of the raw waters, coagulated waters, and permeate waters from NF and RO processes were measured. After that, one optimal condition for filtration process was selected (NF or RO process) using the DOC and DON results. The HPO, HPI, and NDMA-FP of raw waters, coagulated waters, and permeate waters at optimal condition of filtration process were analyzed. The HPO and HPI of raw waters, coagulated waters, and permeate waters at optimal condition of filtration process was analyzed for theirs UV-254, DOC, DON, TN, NH_4^+, NO_3^-, and NO_2^- values. The experimental framework of this research is presented in Figure 4. The detail of experiment is shown in the following sections.

```
                    ┌─────────────────┐              ┌──────────────────┐
                    │   Raw water     │              │  -  pH           │
                    └────────┬────────┘              │  -  Turbidity    │
                             │                       │  -  Alkalinity   │
                             │                       └──────────────────┘
```

Raw water

- pH
- Turbidity
- Alkalinity

PACl Coagulation

Filtration using GF/F paper

Supernatant

pH
Turbidity
Alkalinity

Filtration using GF/F paper

- DOC
- UV-254
- SUVA
- NH$_3$
- NO$_2^-$
- NO$_3^-$
- TN
- DON
- NDMA-FP

- DOC
- UV-254
- SUVA
- NH$_3$
- NO$_2^-$
- NO$_3^-$
- TN
- DON
- NDMA-FP

NF filtration   RO filtration

Resin fractionation

HPO   HPI

Selection of one optimal condition

- NDMA-FP
- Variation of pressure

- DOC   - NH$_4^+$
- DON   - NO$_3^-$
- TN   - NO$_2^-$

Resin fractionation

Experiment

HPO   HPI

Sample

- DOC
- UV-254
- SUVA
- NH$_3$
- NO$_2^-$
- NO$_3^-$
- TN
- DON

Analysis

Figure 4 **Experimental framework of this research**

3.3   Material

3.3.1   PACl Coagulant

PACl was used as the chemical coagulant in this study. The stock solution of PACl was prepared at a dosage of 80 g/L and 150 g/L. The dosing solution of PACl was then diluted to 80 mg/L and 150 mg/L for the raw water from the Bangkhen WTP and the Banglen WTP, respectively.

3.3.2   Membrane

The NF membrane (NF270) and RO membrane (TW30) was used in this study. They are classified as thin-film composite polyamide membranes. Table 4 summarizes the properties of these two membranes.

Table 4 Properties of membranes used in this study

Membrane type	NF270	TW30
Manufacturer	DOW/Filmtec	DOW/Filmtec
Water permeability (L m^{-2} h^{-1} bar^{-1})	13.5[a]	2[d]
Molecular weight cutoff (Daltons)	170-300[b,c]	100
Contact angle (°)	55.0[a]	N.A.*
Zeta potential (mV)	-19[b,c]	-20.6[e]
NaCl rejection (%)	70%	92%

a (Nghiem, Schafer, & Elimelech, 2005), b (Boussu, 2007), c (Lin, Chiang, & Chang, 2007), d (Yang, Liu, & Li, 2010), e (Qin et al., 2003) *Not available

3.4 Coagulation experiment

A jar test apparatus was used to perform the coagulation experiment. A PACl dosage of 80 mg/L was used under a controlled pH of 7 for the water sample from the Bangkhen WTP. For the water sample from the Banglen WTP, a PACl dosage of 150 mg/L was used under a controlled pH of 7. PACl was added into the raw water supply under a controlled pH of 7 and then the coagulation experiment was started with rapid mixing at 100 rpm for 1 minute, followed by slow mixing at 30 rpm for 30 minutes. After that, each sample was left to settle down for 1 hour. The supernatant was collected and filtrated through a 0.7 μm GF/F filter. The coagulated water, then, was analyzed for its UV-254, DOC, DON, TN, NH_4^+, NO_3^-, and NO_2^- values. The overall procedure of coagulation process is shown in Figure 5.
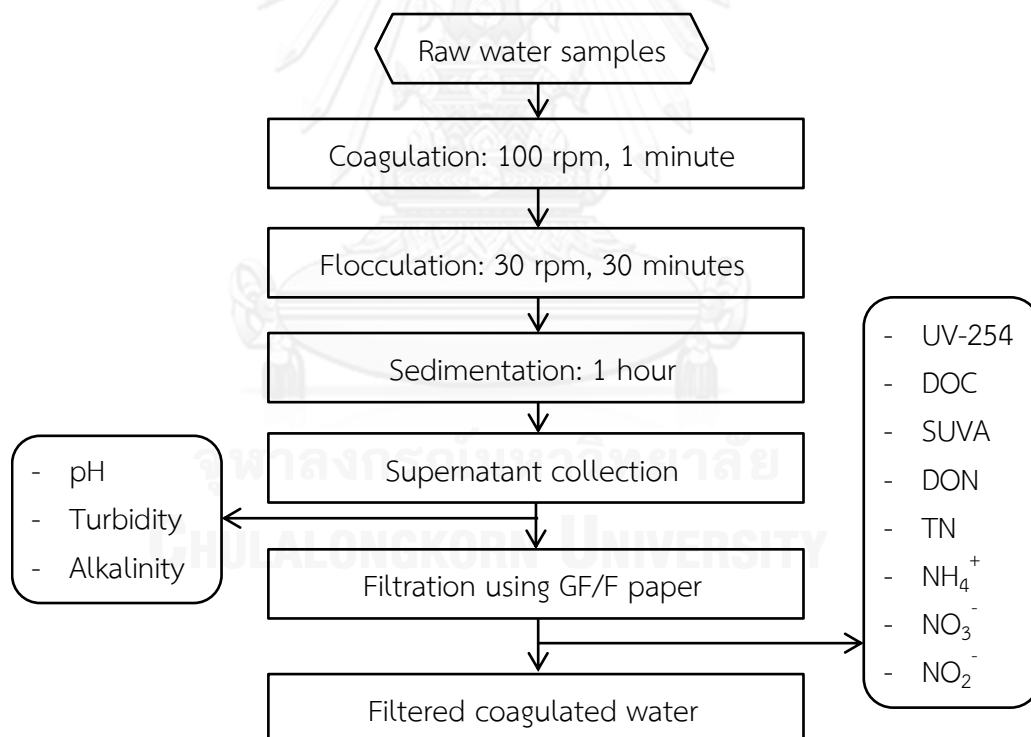
Figure 5 Overall procedure of coagulation process

3.5   Membrane filtration

A cross-flow membrane test unit (C-10T Module, Nitto Denko Corp., Japan) with a membrane area of 60 cm^2 was used for conducting the NF and RO filtration experiments. The system was operated under a feed pressure of 4 bars. The temperature was controlled throughout the experiment at 30 ± 2 ℃. Coagulated water was used as the feed water in the NF and RO filtration experiments. Figure 6 shows a schematic diagram of the cross-flow filtration process that was used. The overall procedure of filtration process is shown in Figure 7.
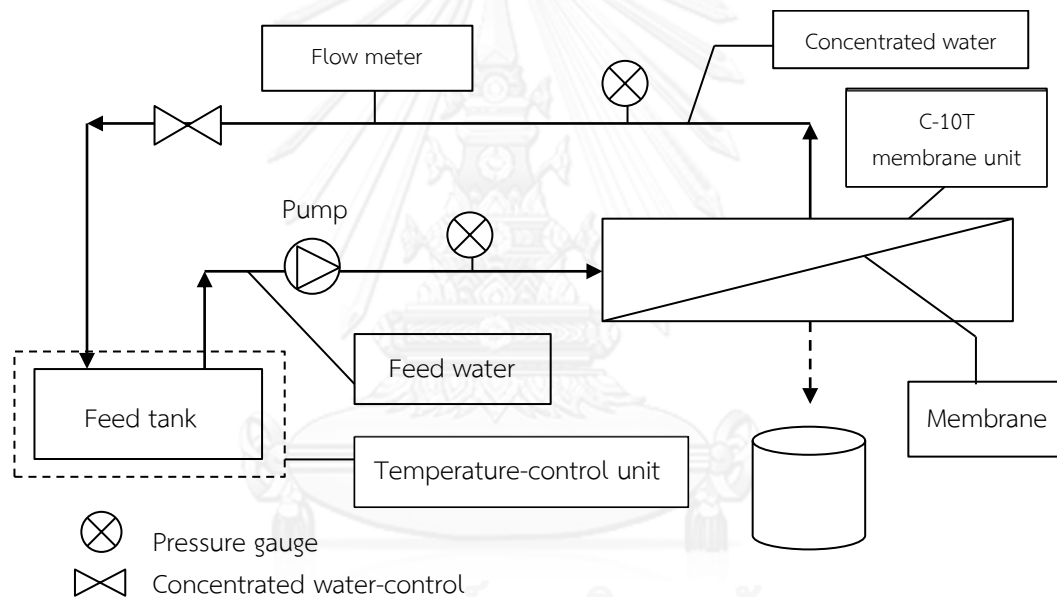
Figure 6 Schematic diagram of cross-flow filtration process (Hong, Faibish, & Menachem, 1997)
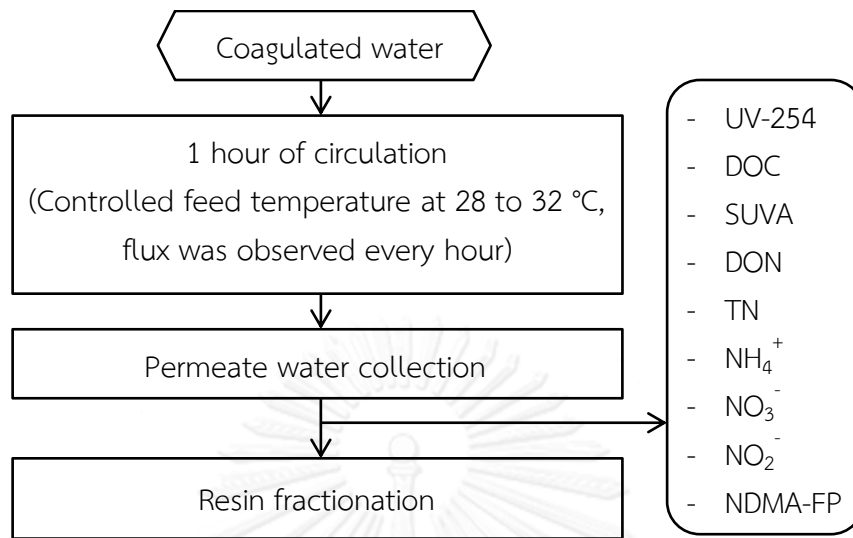
Figure 7 Overall procedure of filtration process

3.5.1 Variation of pressure

The feed pressure was varied (at 2, 3, and 4 bars) to studied the effect of DON rejection on pressure. The system was operated as explained above. The feed water was circulated thought out the experiment. The permeate water was collected after one hour of circulation. The feed temperature was controlled at between 28 to 32 °C. The permeate water then was measured for DOC, DON, TN, NH_4^+, NO_2^-, and NO_3^-.

3.5.2 Flux

Membrane flux was observed every hour during the filtration process. Membrane flux can be calculated using the following equation (Equation 3):

$$\text{Membrane flux} = V \ (cm^3) \ / \ \{A \ (cm^2) * T \ (sec.)\} \qquad \text{(Equation 3)}$$

Where V is volume of permeate, A is Area of membrane (60 cm^2), and T is time.

3.6   Resin fractionation

3.6.1   Preparation of DAX-8

- The DAX-8 was purified with 0.1 N NaOH for 24 hours.

- The DAX-8 was extracted with acetone and hexane for 24 hours in a set of soxhlet extraction apparatus, respectively.

- The extracted DAX-8 resin was kept in methanol.

- The DAX-8 was taken into a column in slurry of methanol.

- The DAX-8, then, was washed with 0.1 N NaOH and 0.1 N HCl, respectively. After that, it was rinsed with milli-Q water until the conductivity and DOC of the effluent water is less than 10 μS/cm and 0.2 mg/L, respectively.

3.6.2   Fractionation procedure

- The water sample was filtered through filter paper with pore size of 0.7 μm GF/F and will have pH adjusted to 2 by 1N H_2SO_4.

- The water sample wais taken into column.

- The effluent from the DAX-8 column was called HPI, whereas HPO was adsorbed on the DAX-8.

- HPO was eluted with 0.1 N NaOH and followed by 0.01 N NaOH.

- The pH of the HPI and HPO was adjusted to neutral prior to analysis for UV-254, DOC, DON, TN, NH_4^+, NO_3^-, and NO_2^- values.

3.7   *N*-nitrosodimethylamine Formation Potential (NDMA-FP) Test

3.7.1   Definition of terms

- N-nitrosodimethylamine ($NDMA_T$) is the total concentration of NDMA at any time T.

- $NDMA_0$ is the total concentration of NDMA at the time of sampling.

- NDMA$_7$ is the total concentration of NDMA during reaction of sample precursors with excess free chlorine over 7-day reaction time at standard reaction conditions which are as follows: free chlorine residual at least 3 mg/L and not more than 5 mg/L at the end of the 7-day reaction (incubation) period with sample incubation temperature of 25±2 °C, and pH controlled at 7±0.2 °C with phosphate buffer.

- NDMAFP is the difference between the NDMA$_7$ and the NDMA$_0$. Figure 8 shows the formation potential test of a sample without free chlorine at the time of sampling. Figure 9 presents the formation potential test of a sample with free chlorine at the time of sampling.

NDMA Concentration

NDMA$_T$
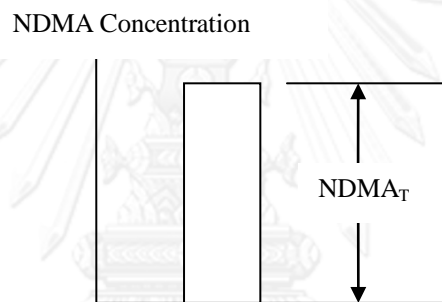
Figure 8 The formation potential test of a sample without free chlorine at the time of sampling (adapted from APHA, AWWA, and WPCF, 1995)

NDMA Concentration

NDMAFP

NDMA$_T$

NDMA$_0$
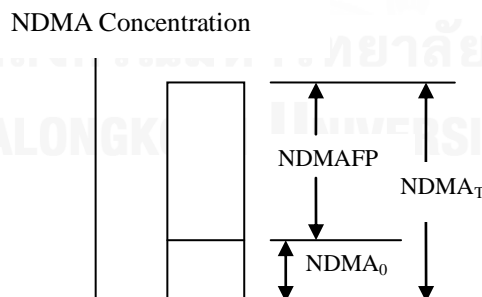
Figure 9 The formation potential test of a sample with free chlorine at the time of sampling; adapted from (APHA, AWWA, & WPCF, 1995)

3.7.2   Analysis of NDMA-FP

Sample collection and preservation

Sodium thiosulfate of 80-100 mg was used to dechlorinate of water samples in accordance with United State Environmental Protection Agency (US.EPA.) method EPA 521 solid phase extraction (US.EPA., 2004). Samples were stored in the lab must be held at 4°C and analyzed with 14 days after collection

To analyze NDMA the US.EPA. method 521, the basic of trihalomethanes formation potential (THMFP) analysis were applied to measure NDMA-FP. This application was done according to studies of Mitch *et al.*, (2003) and Lee *et al.*, (2006) (Lee & Westerhoff, 2006; Mitch, Gerecke, & Sedlak, 2003). The procedures for analysis of NDMA-FP consisted of four major sections including the preparation of calibration curve, the experiment of NDMA-FP, the extraction of NDMA-FP, and the analysis by using gas chromatography.

For the calibration curve preparation, it was modified according to the US.EPA. Method 521 (US.EPA., 2004). In this work, the external standard method was used for preparing the calibration curve. Standard solutions of each concentration for making the calibration curve were prepared in methylene chloride from the primary dilution standard solution (200 mg/L stock standard solutions). The capillary column, Stabilwax (Carbowax polyethylene glycol), with thickness of 0.25 µm, diameter of 25 mm, and length of 30 m with gas chromatography with nitrogen phosphorus detector (GC-NPD) was used in the analysis. The detection limited of GC/NPD was equal to 300 µg/L. 400, 600, 800, and 1000 µg/L of NDMA were prepared and injected to GC/NPD. The calibration curve was presented in Appendix.

By considering the GC/NPD condition, the splitless injection of 1 µL, temperature of injection port of 220 $^{\circ}$C, initial temperature of 40°C, pressure of 19.33 psi, split flow of 60 mL/min, and the helium as carrier gas was used. For the oven condition, the GC was programmed to hold initially at 40°C, heated at 40-110°C at a rate of 7°C/min, heated at 140–240°C at a rate of 15°C/min. Finally, it

was programmed to hold at 240°C for 5 minutes. The NPD detector was set at 250 °C with nitrogen gas as make up at flow rate of 30 mL/min.

For the NDMA-FP experiment, the water sample was analyzed for $NDMA_0$. Then a water sample was incubated with excess chlorine with temperature of 25±2 °C, and pH controlled at 7±0.2 °C with phosphate buffer. After 7-day reaction time the free chlorine residual of water sample must be at least 3 mg/L and not more than 5 mg/L. The NDMA-FP is the difference between the $NDMA_7$ and the $NDMA_0$. The free chlorine residual was analyzed according to Standard method 4500-CI (APHA et al., 1995).

For the extraction, the NDMA extraction was conducted by using Resprep US.EPA. 521 solid-phase extraction cartridges containing 2 grams of coconut activated carbon. Water sample of 1,000 mL was passed through a SPE cartridge. The methylene chloride of 3 mL, methanol of 3 mL and another methanol of 3 mL was used to pre-condition the cartridge, respectively. 3 mL of reagent water was rinsed down the cartridges for 5 times. Water samples were passed through the cartridges at a flow rate of 10 mL/min under a vacuum condition. Air was drawn through the cartridge for 10 minutes after the extraction was completed. Methylene chloride was used eluted NDMA from the cartridge. 1 mL of the extracted sample was collected and preserved at -20 °C prior to injection into the gas chromatograph. All step of extraction process was conducted in the dark room so as to prevent the reaction between NDMA and the ultraviolet light.

The percent recovery must be investigated when the SPE cartridge was used. DI water and raw water supplies from a surface water source were in the experiment for investigating the percent recovery of the extraction method in accordance with US.EPA. 521. 600, and 1000 µg/L of NDMA were added into DI water and raw water supplies samples. Water sample were performed the SPE. The experiment was done in triplicates for each water sample. After SPE, NDMA in DI and raw water supply were analyzed. The accuracy (percent recovery) and precision (RSD) of DI water were 54.4 percent and 7.4, respectively whereas that of raw water supplies were 55.4

percent and 11.9, respectively. By using the percent recovery of 55.4 percent and 1,000 times for the concentrated of the sample and the detection limited of GC/NPD of 300 µg/L. the detection limited of the methods in this work therefore was 542 ng/L or 7.3 nM

3.8   Analytical method and instrument

Table 5 demonstrates all analytical methods and instruments used in this works. At least duplicates of each measurement was conducted.

pH

The pH of water samples was directly measured by a pH meter.

Turbidity

Turbidity meter was used to directly measure for the turbidity of water samples.

Alkalinity

The alkalinity of water samples was analyzed by Titration method, in accordance with Standard method 2320B (APHA, AWWA, and WPCF, 1995).

UV-254

UV-254 of water samples was measured by UV-Vis Spectrophotometer, in accordance with Standard method 5910B (APHA, AWWA, and WPCF, 1995) using a Genesys 10 UV-Vis spectrophotometer (Thermoelectron Corp., USA), with matched quartz cells, which provide a path length of 10 mm.

DOC

The DOC was analyzed in accordance with Standard Method 5310D (APHA, AWWA, and WPCF, 1995), using Shimadzu TOC-V CSN/TOC analyzer.

DON

DON was calculated using Equation 1. To avoid negative DON concentrations, the method developed by Xu *et al.*, (2010) was employed. The water samples was filtered through a dead-end filtration unit with a NF270 membrane, before being measured for NH_4^+, NO_3^-, NO_2^-, and TN. The DON concentrations will be calculated using the following equation (Equation 4):

$$C_F = (C_R (V_F - V_P)) / V_F \qquad \text{(Equation 4)}$$

Where C_F is the DON concentration in the feed water; C_R is the DON concentration in the retentate water; V_F is the volume of the feed water; and V_P is the volume of collected permeate water.

TDN

TDN was measured using a TOC/TN analyzer.

NH_4^+

NH_4^+ was measured in accordance with Standard Method 8038 (APHA, AWWA, and WPCF, 1995), using the DR 2700 Spectrophotometer (Hach Company, Germany).

NO_3^-

NO_3^- was measured in accordance with Standard Method 8192 (APHA, AWWA, and WPCF, 1995), using the DR 2700 Spectrophotometer (Hach Company, Germany).

NO_2^-

NO_2^- was measured in accordance with Standard Method 8507 (APHA, AWWA, and WPCF, 1995), using the DR 2700 Spectrophotometer (Hach Company, Germany).

Table 5 Analytical methods and instruments

Parameter	Analytical method	Standard	Analytical Instrument
pH	Direct measurement	-	pH meter
Turbidity	Direct measurement	-	Hach, 2100 turbidity meter
Alkalinity	Titration method	Standard method 2320B	-
UV-254	Ultraviolet Absorption method	Standard method 5910B	Genesys 10 UV-Vis spectrophotometer
DOC	The wet-oxidation method	Standard method 5310D	
NH_3/NH_4^+	The colorimetric method with a Nessler reagent	Standard method 8038	DR 2700 Portable Spectrophotometer
NO_2^-	The diazotization method	Standard method 8507	DR 2700 Portable Spectrophotometer
NO_3^-	The cadmium reduction method using powder pillows	Standard method 8192	DR 2700 Portable Spectrophotometer
TN	Total bound nitrogen (TNb) method		Multi N/C 3100, TOC Analyzer
Free chlorine residual	Colorimetric method	Standard method 4500-Cl G	DR 2700 Portable Spectrophotometer

Parameter	Analytical method	Standard	Analytical Instrument
$NDMA_0$	Adapted from "Formation of Trihalomethane and Other Disinfection By-Products and Liquid-Liquid Extraction Gas Chromatography Method"	Standard method 5710 and 6232B US.EPA. method 521	GC/NPD
$NDMA_7$	Adapted from "Formation of Trihalomethane and Other Disinfection By-Products and Liquid-Liquid Extraction Gas Chromatography Method"	Standard method 5710 and 6232B US.EPA. method 521	GC/NPD

CHAPTER 4

RESULTS AND DISCUSSION

4.1   Characteristics of the raw water supplies

The characteristics of the raw water supply from the Bangkhen Water Treatment Plant (WTP) are summarized in Table 6. The pH of the raw water supply from the Bangkhen WTP was close to neutral with an alkalinity of 61 mg/L as $CaCO_3$. The ultraviolet adsorption at wavelength 254 nm (UV-254), dissolved organic carbon (DOC), and specific ultraviolet adsorption (SUVA) values were found to be 0.135 cm^{-1}, 4.2 mg/L, and 3.2 L/mg-m, respectively. The concentrations of NH_4^+, NO_2^-, NO_3^-, and dissolved organic nitrogen (DON) were 0.11, 0.005, 0.03, and 0.24 mg/L, respectively.

As can be seen from Table 6, pH of the raw water supply from the Banglen WTP was 7.4, which was close to neutral. The alkalinity of raw water from Banglen WTP was 91 mg/L as $CaCO_3$. The UV-254, DOC, and SUVA values were found to be 0.231 cm^{-1}, 7.9 mg/L, and 2.9 L/mg-m, respectively. The concentrations of NH_3/NH_4^+ of 0.25 mg/L, NO_2^- of 0.012 mg/L, NO_3^- of 0.02 mg/L and DON of 0.28 mg/L were detected.

DOC/DON values of raw water from the Bangkhen WTP and the Banglen WTP were 17 and 28, respectively. These values can be used to estimate the *N*-nitrosodimethylamine formation potential (NDMA-FP) during the disinfection process. A low DOC/DON value indicates a much higher potential for forming N-DBPs than a high DOC/DON value (Dotson, Westerhoff, & Krasner, 2009). A range of DOC/DON values of 10 to 30 was found in drinking water by Lee and Westerhoff (2006). Westerhoff and Mash (2002) found DOC/DON values of 18 for 28 raw waters in the United State of America; a range of DOC/DON value was found from 5 to 100 (Lee & Westerhoff, 2006).

A high SUVA (SUVA > 3 L/mg m) was found in both of the raw water supplies. The high SUVA contained natural organic matter (NOM), which was more humic-like, had a higher apparent molecular weight and was easily removed by coagulation (Musikavong & Wattanachira, 2013; Qin et al., 2003). The DOM in the raw water supply of the Bangkhen WTP could be easily removed by PACl coagulation when compared to that of the Banglen WTP.

The DOC of the raw water of the Bangkhen WTP found in this work was similar to those found in the study by Kanokkantapong *et al.* (2006) (Kanokkantapong et al., 2006). It was reported that DOC of the raw water from the Bangkhen WTP was approximately 4.7 mg/L. DON values from both water sources (0.24 and 0.28 mg/L) were similar to those observed in rivers and lakes (0.04 – 2.5 mg/L) (Westerhoff & Mash, 2002). DOC/DON in range of 10 - 20 of raw water of Kinmen Tai Lake WTP was reported (Chang, Chen, & Wang, 2013).

Table 6 Characteristics of the raw waters of the Bangkhen WTP and Banglen WTP

Parameter	Source of raw waters	
	Bangkhen WTP	Banglen WTP
pH	7.3	7.4
Turbidity (NTU)	50	17
Alkalinity (mg/L as CaCO$_3$)	61	91
UV-254 nm (cm^{-1})	0.135	0.231
DOC (mg/L)	4.2	7.9
SUVA (L/mg m)	3.2	2.9
NH$_3$/NH$_4^+$ (mg/l)	0.11	0.25
NO$_2^-$ (mg/L)	0.005	0.012
NO$_3^-$ (mg/L)	0.03	0.02
DON (mg/L)	0.24	0.28
DOC/DON	17	28
NDMA-FP (ng/L)	ND.*	ND.*

* ND. = not detectable at the detection limit of < 542 ng/L or 7.2 nM

4.2 Removal of precursors of NDMA by PACl coagulation as pre-treatment of membrane filtration

The PACl of 40 mg/L at control pH of 7 was used as the pre-treatment of membrane filtration. Under such conditions, turbidity of raw water from the Bangkhen WTP and the Banglen WTP were dramatically reduced from 50 to 0.90 NTU and from 17 NTU to 0.34 NTU, respectively. A reduction of turbidity of raw water from the Bangkhen WTP and the Banglen WTP were obtained at 98% for both of raw water sources.

UV-254 of raw water from Bangkhen and Banglen WTPs were dramatically reduced from 0.135 to 0.049 cm^{-1} and from 0.231 cm^{-1} to 0.085 cm^{-1}, a reduction of 64 and 63%, respectively. The DOC of raw water from the Bangkhen WTP was reduced by approximately 32%, from 4.2 to 2.9 mg/L. DOC of raw water from the Banglen WTP was reduced by approximately 48%, from 7.9 to 4.1 mg/L. The SUVA values in the coagulated waters from the Bangkhen WTP and the Banglen WTP were declined from 3.2 to 1.7 L/mg-m and from 2.9 to 2.1 L/mg-m, a reduction of about 47 and 29%, respectively. This is because the percentages of the UV-254 reduction were higher than that of DOC. On this basis, it can be stated that aromatic molecules were easily removed by PACl coagulation (Musikavong & Wattanachira, 2013).

The results studied by Musikavong *et al*. (2013) found that the coagulation process, alone, with 40 mg/L of PACl could reduce UV-254 and DOC by approximately 52 and 55%, respectively (Musikavong et al., 2013). PACl coagulation with PACl dosage of 60 mg/L could reduce DOC by 61%, and PACl dosage of 100 mg/L gave 71% of UV-254 reduction (Ciner & Ozer, 2013). Kueseng *et al*. (2011) reported that the coagulation condition with 20 mg/L of PACl at pH 7 could reduce UV-254 and DOC by 65 and 52%, respectively (Kueseng et al., 2011).

The DON in coagulated waters from the Bangkhen WTP and the Banglen WTP were reduced from 0.24 to 0.16 mg/L and from 0.28 mg/L to 0.18 mg/L, respectively. After the PACl coagulation, the DOC/DON of the coagulated water of the Bangkhen WTP slightly rose from 17 to 18. This is because the percentages of the DOC and DON reductions of the coagulated water from Bangkhen WTP by PACl coagulation were similar. While, the DOC/DON of the coagulated water from the Banglen WTP slightly declined from 28 to 24. This is because the percentage of DON reduction was slightly higher than that of DOC. When the DOC/DON value was increased, it could be indicated that the formation of NDMA probably decreased. Characteristics of coagulated water by PACl coagulation of the Bangkhen WTP and the Banglen WTP and theirs percent reduction were summarized in Table 7.

Dwyer *et al*. (2009) noted that using aluminium sulfate (alum) dose of 30 mg/L as aluminum could reduce DON by 42% from a sewage treatment plant effluent. Knight *et al*. (2012) reported that the coagulation using alum as coagulant could remove a mean of DOC and DON by 55 and 80%, respectively. While, that the coagulation using ferric chloride as coagulant could remove a mean of DOC and DON by 60 and 82%, respectively.

Table 7 Characteristics of coagulated water by PACl coagulation of the Bangkhen WTP and the Banglen WTP and theirs percent reduction

Parameter	Source of waters	
	Bangkhen WTP	Banglen WTP
pH	7.0	7.1
Turbidity (NTU)	0.90 (98)	0.34(98)
UV-254 (cm^{-1})	0.049 (64)	0.085 (63)
DOC (mg/L)	2.9 (32)	4.1 (41)
SUVA (L/mg-m)	1.7 (47)	2.1 (29)
DON (mg/L)	0.16 (34)	0.18 (37)
DOC/DON	18	24
NDMA-FP (ng/L)	ND.*	ND.*

* ND. = not detectable at the detection limit of < 542 ng/L or 7.2 nM , ( ) = percent reduction

4.3 Optimal condition for UV-254, DOC, SUVA, and DON removal by membrane filtration

4.3.1 Optimal condition for UV-254, DOC, SUVA, and DON removal from raw water of the Bangkhen WTP by membrane filtration

As shown in Figure 10, it can be seen that the nanofiltration (NF) membrane with PACl coagulation at 80 mg/L as pre-treatment and reverse osmosis (RO)

membrane with PACl coagulation at 80 mg/L as pre-treatment could reduce UV-254 by 94 and 95%, respectively. UV-254 values of 0.008 and 0.006 cm^{-1} were detected in the permeate waters from NF and RO, respectively.

The NF and RO were able to obtain DOC removal of 92 and 95%, respectively, and the DOC in the permeate water from NF and RO were 0.36 and 0.23 mg/L, respectively. NF could reduce DON by 69%, while RO could reduce DON by 85%. DON values of 0.075 and 0.037 mg/L were detected in the permeate waters from NF and RO, respectively.

Figure 10 UV-254, DOC and DON of raw water, coagulated, and permeate waters of water sample from Bangkhen WTP

From Figure 11, it can be obtained that NF and RO could reduce the SUVA by 29 and 19%, respectively, when compare with SUVA of raw water. The percentage reduction of UV-254, SUVA, DOC, and DON by using PACl of 80 mg/L under controlled pH of 7 was used as the baseline. The NF increased the reduction of UV-254, DOC, and DON by 30, 60, and 35%, respectively. The increased in the reduction

of UV-254 of 31%, DOC of 63%, and DON of 51% were obtained by using the RO membrane (Table 8). NF and RO did not increase the percent reduction of SUVA.

Figure 11 SUVA of raw water, coagulated, and permeate waters of water sample from Bangkhen WTP and percentage of SUVA removal

Table 8 Increased reduction of UV-254, DOC, SUVA, and DON of water sample of the Bangkhen WTP by NF and RO

Condition	Increasing reduction (%)			
	UV-254	DOC	SUVA	DON
PACl 80 mg/L, NF	30	60	N.A	35
PACl 80 mg/L RO	31	63	N.A	51

DOC/DON values of water samples after treatment by NF and RO were 4.8 and 6.2. It indicated that the nature of selected NF and RO membrane had better capability in removal of DOC than that of DON. In addition, DOC/DON values of treated water were lower than that of raw water. According to the obtained result in this work, the reactivity of DON in treated water from NF and RO membranes in the formation of NDMA was probably higher than that of raw water.

4.3.2 Optimal condition for UV-254, DOC, SUVA, and DON removal from raw water of the Banglen WTP by membrane filtration

As shown in Figure 12, it can be seen that NF membrane with the PACl coagulation at 150 mg/L as pre-treatment and RO membrane with the PACl coagulation at 150 mg/L as pre-treatment could reduce UV-254 by 97 and 98%, respectively. UV-254 values of 0.006 and 0.005 cm^{-1} were detected in the permeate waters from the NF and RO, respectively.

The NF and RO were able to obtain DOC removal of 97 and 97%, respectively, and the DOC concentrations in the permeate water from NF and RO were 0.27 and 0.25 mg/L, respectively. It can be stated that the NF and RO could reduce the SUVA by 24 and 32%, respectively, when compare with SUVA of raw water (Figure 13). NF could reduce DON by 70%, while RO could reduce DON by 79%. DON values of 0.083 and 0.058 mg/L were detected in the permeate waters from NF and RO, respectively.
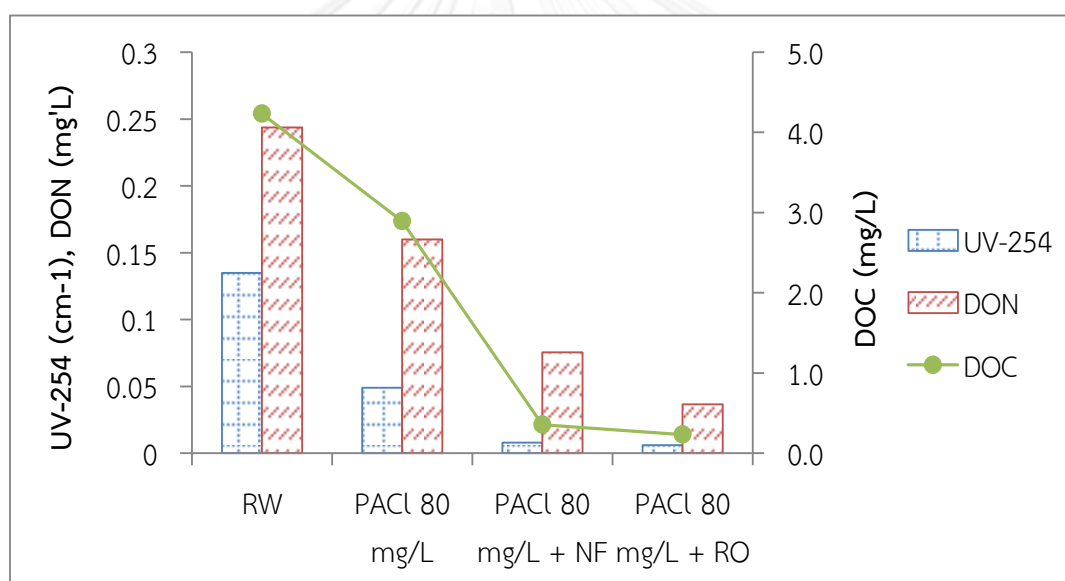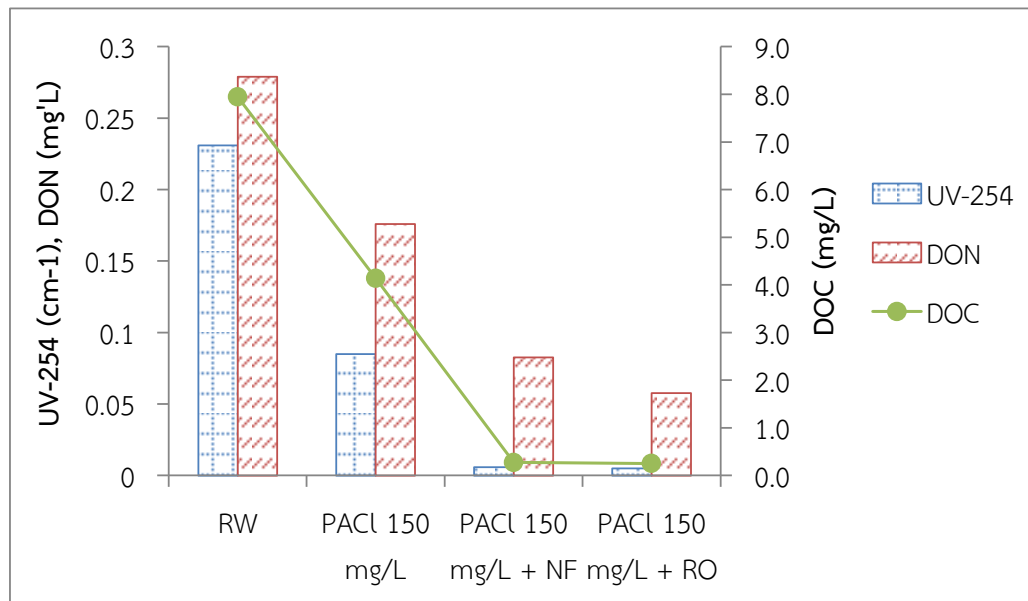
Figure 12 UV-254, DOC and DON of raw water, coagulated, and permeate waters of water sample from Banglen WTP
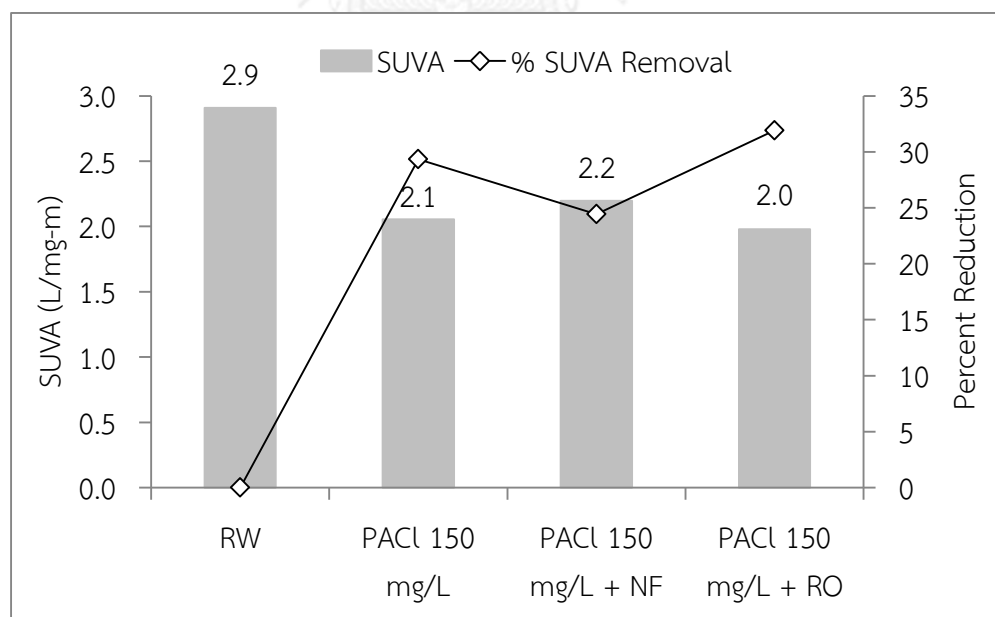
Figure 13 SUVA removals of raw water, coagulated, and permeate waters of water sample from the Banglen WTP and percentage of SUVA

The percent reduction of UV-254, SUVA, DOC, and DON by using PACl of 150 mg/L under controlled pH of 7 was used as the baseline. The NF increased the reduction of UV-254, DOC, and DON by 34, 56, and 33%, respectively (Table 9). The increased in the reduction of UV-254 of 35%, DOC of 56%, and DON of 42% were found by using RO membrane. NF and RO did not increase the percent reduction of SUVA.

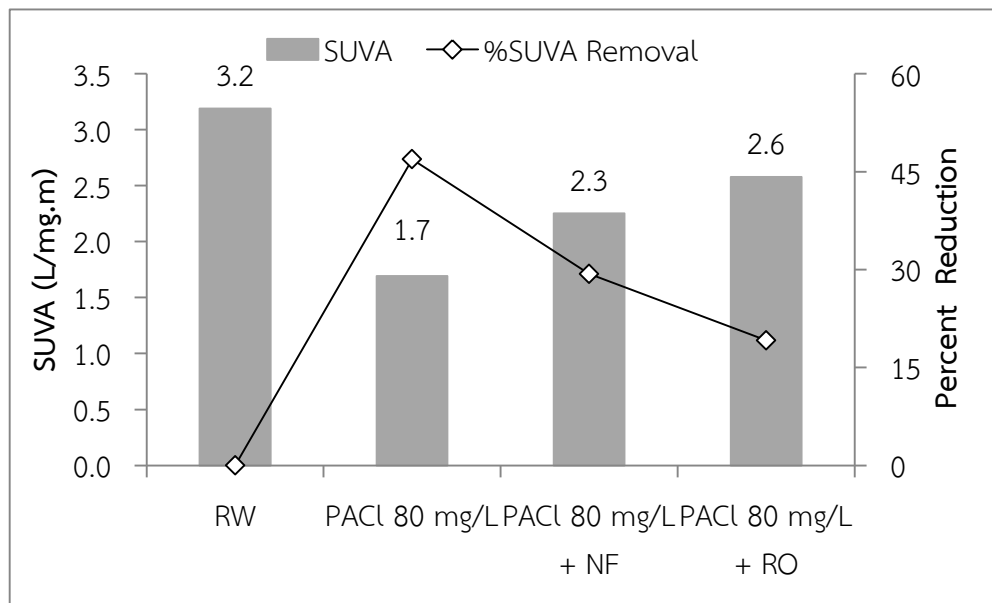**Table 9 Increased reduction of UV-254, DOC, SUVA, and DON of water sample of the Banglen WTP by NF and RO**

Condition	Increasing reduction (%)			
	UV-254	DOC	SUVA	DON
PACl 80 mg/L, NF	30	60	N.A	35
PACl 80 mg/L RO	31	63	N.A	51

DOC/DON values of water samples after treatment by NF and RO were 3.3 and 4.3. It indicated that the nature of selected NF and RO membrane had better capability in removal of DOC than that of DON. In addition, DOC/DON values of treated water were lower than that of raw water. On this basis, the reactivity of DON in treated water from NF and RO membranes in the formation of NDMA was probably higher than that of raw water.

It can be seen that the tendency of SUVA reduction from the Bangkhen WTP and the Banglen WTP was contrasted. This phenomenon could be because of the different in nature of DOM in water. In addition, the higher percentage of HPO could be resulted in higher SUVA value (Hu, Ong, Shan, Kang, & Ng, 2003).

For NF experiments, Song *et al*. (2004) investigated the NOM rejection by nanofiltration. The average rejection of TOC and UV-254 were found to be 93 and 98%, respectively. Xu *et al*. (2010) studied on the measurement of DON and found that the NF-270 membrane could retain DON by approximately 80% (Xu et al., 2010).

For RO experiment, Clair *et al*. (1991) studied the DOC removal by using the RO membrane of 5 raw water samples having DOC within the range of 8.1 - 22.3 mg/L. The percent DOC removal was found between 95.6 and 98.5% (Clair, Kramer, Sydor, & Eaton, 1991). Meylan et al. (2007) reported the percent DOC reduction between 98 and 99% by using the RO membrane. Yoon and Lueptow (2005) used six RO membranes to deal with DON in raw water. The result showed that using RO membranes could remove DON by 65% (Y. Yoon & Lueptow, 2005). Serkiz and Perdue (1990) used a RO membrane to separate natural organic matter (NOM) from river water. The result of the study found that by using RO membrane, DOM rejection was obtained (Serkiz & Perdue, 1990).

Yu *et al*. (2009) reported that NDMA precursors, the secondary amine, are high pKa compounds (pKa > 10.7). These compounds are positively charged at pH of 7. Therefore, they could be efficiently removed by the co-rejection effect with chloride ions. The rejection of NDMA precursors found in the study using NE90 membrane (NF membrane) and BWRO membrane was achieved 98% and 99%, respectively (Yu et al., 2009).

4.4 DOC and DON removal by reverse osmosis membrane (TW30) at various pressures.

RO provided the best results on DOC and DON removals from the raw water of the Bangkhen WTP and the Banglen WTP. RO, therefore, was selected as the optimal membrane used in this study.

By operating the cross-flow membrane unit with (RO) membrane (TW30) (RO), the variation on pressures were conducted to determine the effectiveness of each pressure on DOC and DON removal. Pressures of 2, 3, and 4 bars were applied to each batch experiment in which other conditions were similar. The results showed that these pressures gave mostly similar results on both DOC and DON removals.

For the permeate water of the Bangkhen WTP, DOC was reduced by 94, 94, and 95% when pressures of at 2, 3, and 4 bars were applied, respectively (Figure 14). DOC values of permeate water with applied pressures at 2, 3, and 4 bars were obtained at 0.25, 0.25, and 0.23 mg/L, respectively. DON was decreased by 86, 84, and 85% on the permeate waters which were operated under applied pressures at 2, 3, and 4 bars, respectively. Applied pressures at 2, 3, and 4 bars could reduce DON from 0.24 mg/L (DON value in raw water of the Bangkhen WTP) to 0.035, 0.039, and 0.037 mg/L, respectively. This result could be used to confirm that the selected RO membrane had a performance capability for removal of DOC better than DON.
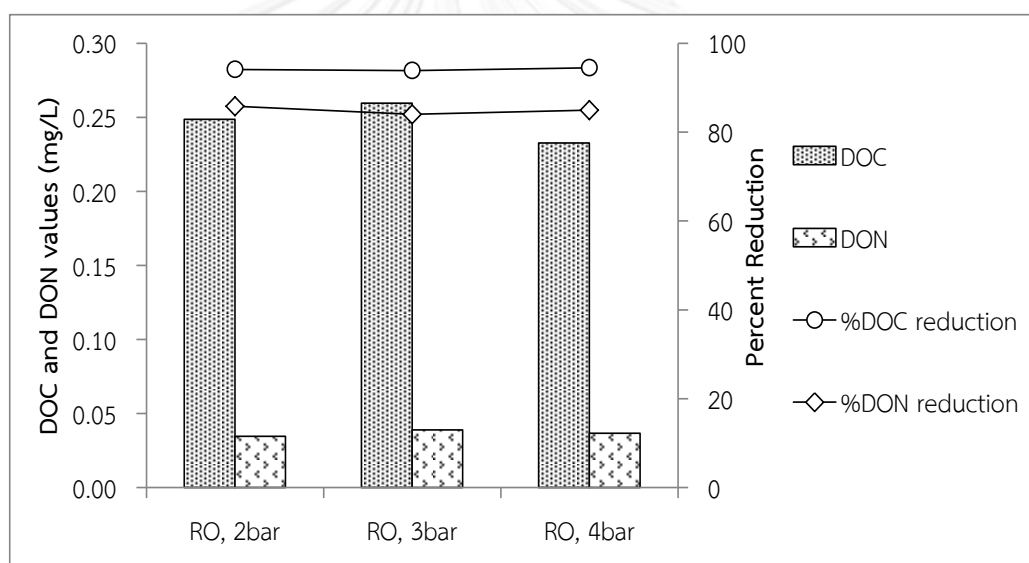
Figure 14 DOC and DON removals from raw water of the Bangkhen WTP by the PACl coagulation with RO (TW30) on various applied pressures

For the permeate water from the Banglen WTP, DOC reductions of 96, 96, and 97% were obtained when pressures of 2, 3, and 4 bars were applied, respectively (Figure 15). DOC values of permeate water with applied pressures at 2, 3, and 4 bars were found at 0.32, 0.33, and 0.25 mg/L, respectively. DON was decreased by 73, 71, and 79% on the permeate waters which were operated under applied pressures at 2, 3, and 4 bars, respectively. Applied pressure at 2, 3, and 4 bars could reduce DON from 0.28 mg/L (DON value in raw water of the Bangkhen WTP) to 0.076, 0.081, and 0.058 mg/L, respectively. This obtained result was corresponded well with

the RO experiment in the previous section. The selected RO membrane had a better efficiency in removal of DOC than DON.
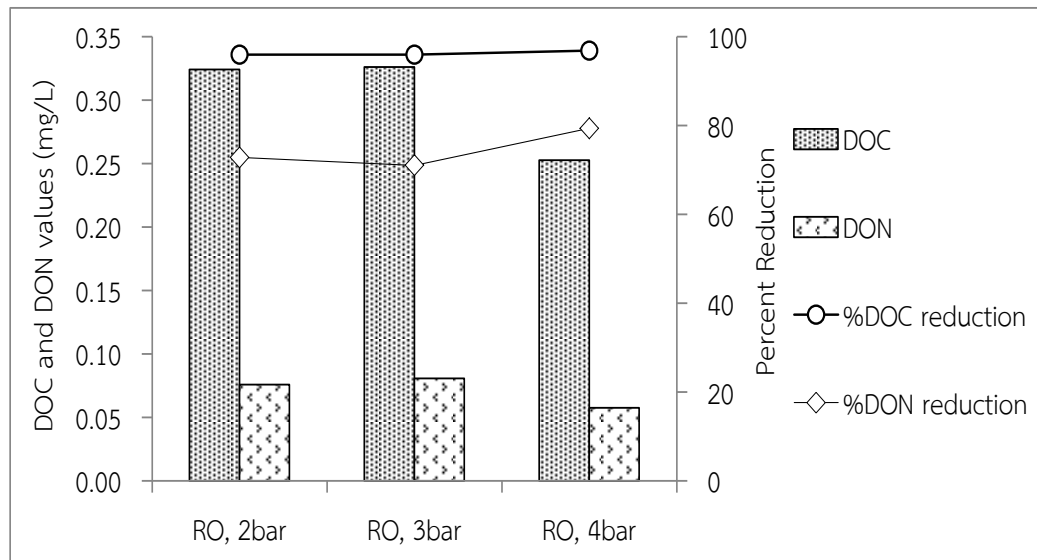
Figure 15 DOC and DON removals from raw water of the Banglen WTP by PACl coagulation with RO (TW-30) on various applied pressures

The DON reduction efficiencies of NF and RO filtration obtained in this work are comparable to those of previous studies. At the Stickney Water Reclamation Plant (Cicero, IL, USA), DON in the water was decreased by 69% using enhanced coagulation and microfiltration (Arnaldos & Pagilla, 2010). In another study, a NF270 membrane removed 80% of the DON when the experiment was conducted with synthetic water (Xu *et al.*, 2010). Size exclusion and electrostatic exclusion are the well-known mechanisms for NOM rejection on RO membrane (Hu et al., 2003). For this study, the pressure had shown no significant on DON removal for both of raw waters. Therefore, it can be stated that the main separated mechanism occurred during filtration experiment was size exclusion. Ates *et al.* (2008) reported that by using NF membrane, TMP showed no significant effect on UV-254 and DOC reductionn(Ates, Kitis, & Yetis, 2008).

4.5   Observation on permeate flux

During each batch experiment, flow was observed in every 1 hour for both source of waters (The Bangkhen and the Banglen WTPs) on both membranes (NF and RO)

4.5.1   Permeate flux on NF experiment

For the NF experiment, only one pressure was applied (pressure of 4 bars). Three batch experiments for each water source were observed for the flow value (mL/min). For the Bangkhen WTP source water, the permeate flow was obtained between 5.0 to 5.3 mL/min. The permeate fluxes were calculated by using these flow values. The permeate fluxes were found between 50 to 53 L/m^2-hr (Figure 16). The variety of flux depends on the feed temperatures at each hour. The higher feed temperature leads to the higher permeate flux. For the Banglen WTP source water, the permeate flow was obtained between 4.9 to 5.5 mL/min. The permeate fluxes were found between 50 to 55 L/m^2-hr (Figure 17).The permeate flux of filtered water from NF of water of the Bangkhen and the Banglen WTP are nearly similar.
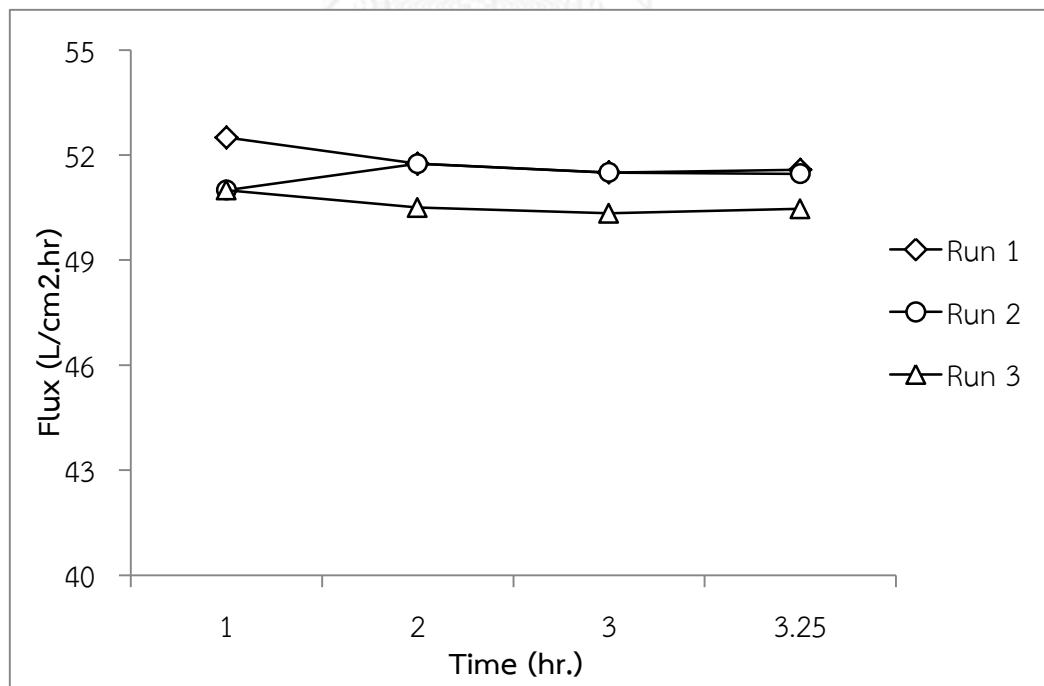
Figure 16 The permeate flux of NF experiment of the Bangkhen WTP source water
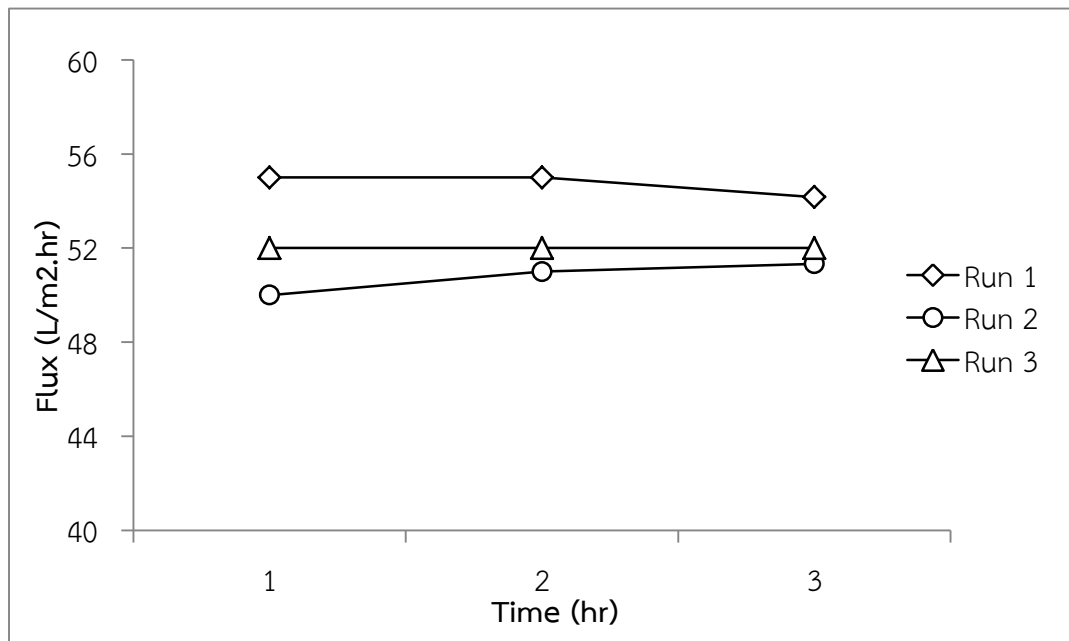
Figure 17 The permeate flux of NF experiment of the Banglen WTP source water

4.5.2 Permeate flux on RO experiment

For the RO experiment, the permeate flow was observed on 3 applied pressures (pressure of 2, 3, and 4 bars) for each batch experiment.

For the Bangkhen WTP source water, the permeate flows were obtained from 1.5 to 1.7, 2.6 to 2.8, and 3.6 to 4.2 mL/min for applied pressure of 2, 3, and 4 bars, respectively. Permeate fluxes were calculated and found between 8 and 9, 14, and 18 and 21 L/m^2-hr for applied pressure of 2, 3, and 4 bars, respectively (Figure 18).

For the Banglen WTP source water, permeate flows of between 2.0 and 2.2 mL/min at 2 bar, between 3.2 and 3.4 mL/min at 3 bar, and between 4.5 and 4.9 mL/min were obtained. Permeate fluxes were found between 10 to 11, 17, and 23 to 24 L/m^2-hr for applied pressure of 2, 3, and 4 bars, respectively (Figure 19).
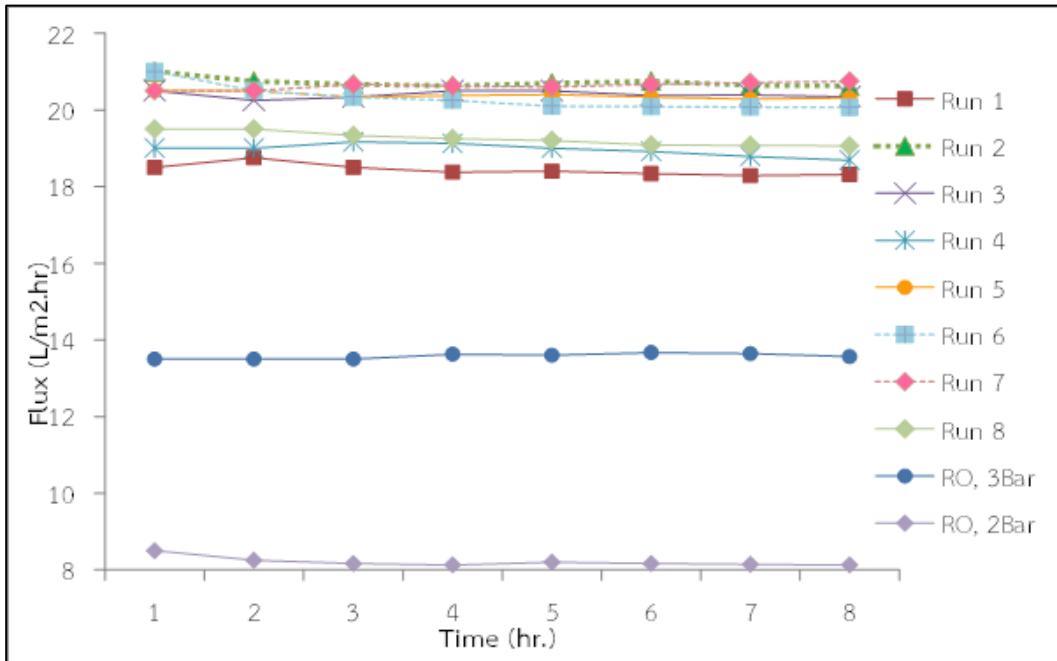
Figure 18 The permeate flux of RO experiment on three various pressures for
the Bangkhen WTP source water
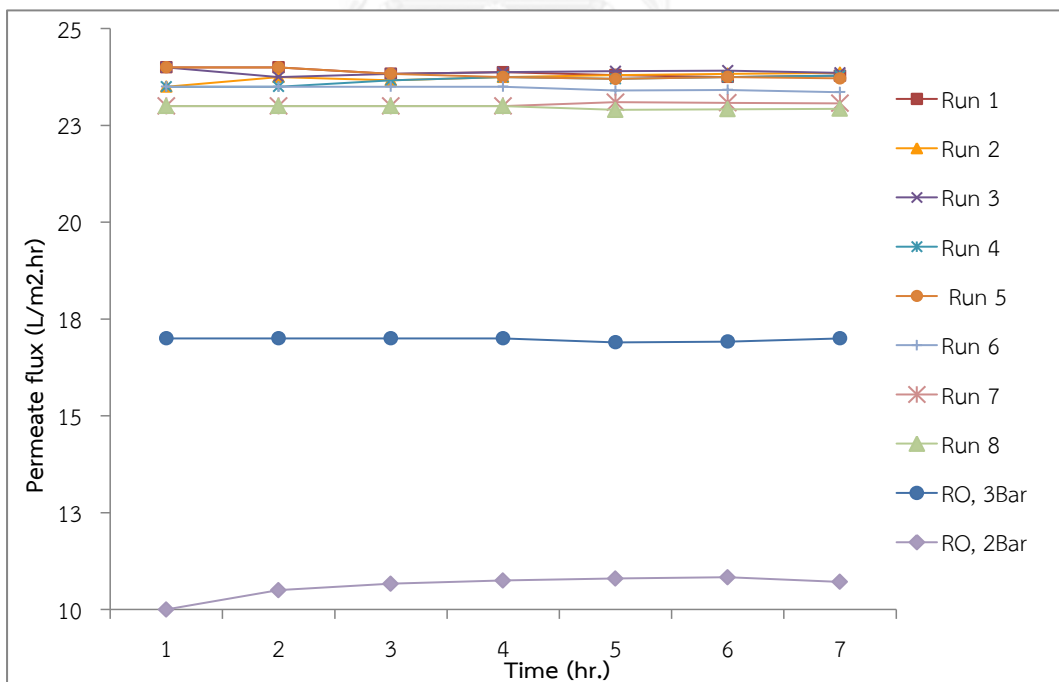
Figure 19 The permeate flux of RO experiment on three various pressures of
the Banglen WTP source water

From these results, it could be concluded that NF experiment showed approximate 2.3 to 5 times higher permeate flux than that of RO experiment. This is because RO membrane have smaller membrane pore than that of NF membrane. The smaller pore allows lower amount of water to get through compare with the higher pore membrane. Mattheus et al. (2002) reported that when the feed temperature decreased, the permeate flux tended to decreased. Moreover, the permeate flux rose when the feed pressure was increased. The studied by Khalaf (2008) also stated that increasing in feed temperature and/or applied pressure could result in an increasing of permeate flux.

4.6   HPO and HPI

4.6.1   DOC of HPI and HPO in raw waters, coagulated waters, and permeate waters

For the Bangkhen WTP source water, as shown in Figure 20, raw water, coagulated water, and permeate water were consisted of DOC of HPO fraction by 48, 42, and 53%, respectively. For HPI fraction, 52, 58, and 47% of DOC were found in raw water, coagulated water, and permeate water of the Bangkhen WTP source water, respectively. The DOCs of HPI found in raw water and coagulated water was a little higher than that of the DOCs of HPO. The higher DOC of HPI can be implied that water the samples contained higher non-humic substances than humic substances. For the permeate water, the result showed that the values of DOC of both HPI and HPO were quite similar (0.14 mg/L for DOC of HPI and 0.15 mg/L for DOC of HPO).
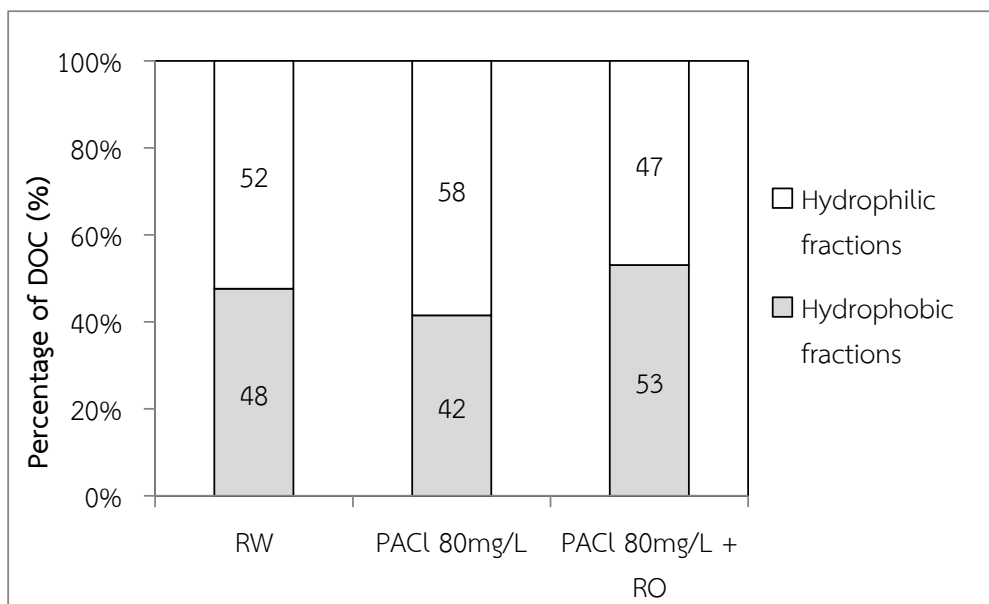
Figure 20 The percentage of DOC of HPI and HPO of the Bangkhen WTP source water

As shown in Figure 21, the PACl coagulation could reduce DOC of HPI and DOC of HPO by 26 and 42%, respectively. The PACl coagulation had better capability on HPO reduction than that of HPI. Using PACl as coagulant alone, the reduction of DOC of HPI and DOC of HPO was found at approximately 46 and 56%, respectively. The DOC of HPI and DOC of HPO were reduced by 60 and 48%, respectively, using PACl dosage of 80mg/L. The RO membrane with PACl coagulation as pre-treatment could reduce DOC of HPI and DOC of HPO by 94 and 92%, respectively. The increasing in HPI and HPO reduction by RO were 68 and 50%, respectively.
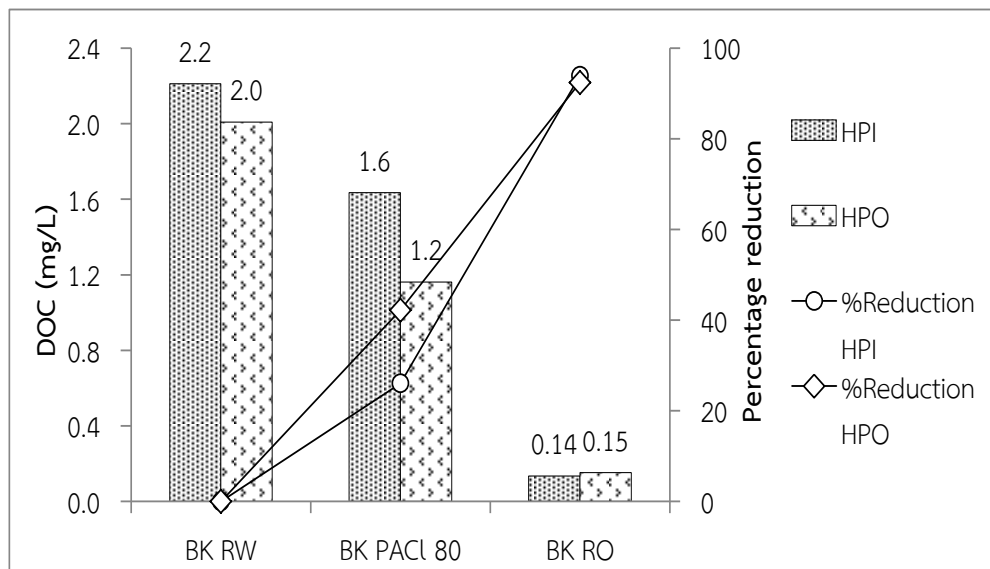
Figure 21 Reduction of DOC of HPI and HPO of the Bangkhen WTP source water by PACl coagulation and PACl coagulation with RO

For the Banglen WTP source water, as shown in Figure 22, raw water, coagulated water, and permeate water were consisted of DOC of HPI fraction by 52, 55, and 48%, respectively. For HPO fraction, 48, 45, and 52% of DOC were found in raw water, coagulated water, and permeate water of the Banglen WTP source water, respectively. The DOCs of HPI found in raw water and coagulated water was a little higher than that of the DOCs of HPO. For permeate water, HPO was slightly higher than HPI. The obtained result in was corresponded well the HPO and HPI in the Bangkhen water source by PACl coagulation and PACl coagulation with RO.

As shown in Figure 23, the PACl coagulation could reduce DOC of HPI and DOC of HPO by 43 and 50%, respectively. The PACl coagulation had better ability on HPO reduction than that of HPI. The PACl coagulation as pre-treatment with RO membrane could reduce DOC of HPI and DOC of HPO by 96 and 96%, respectively. The increasing in HPI and HPO reduction by RO were 53 and 46%, respectively.
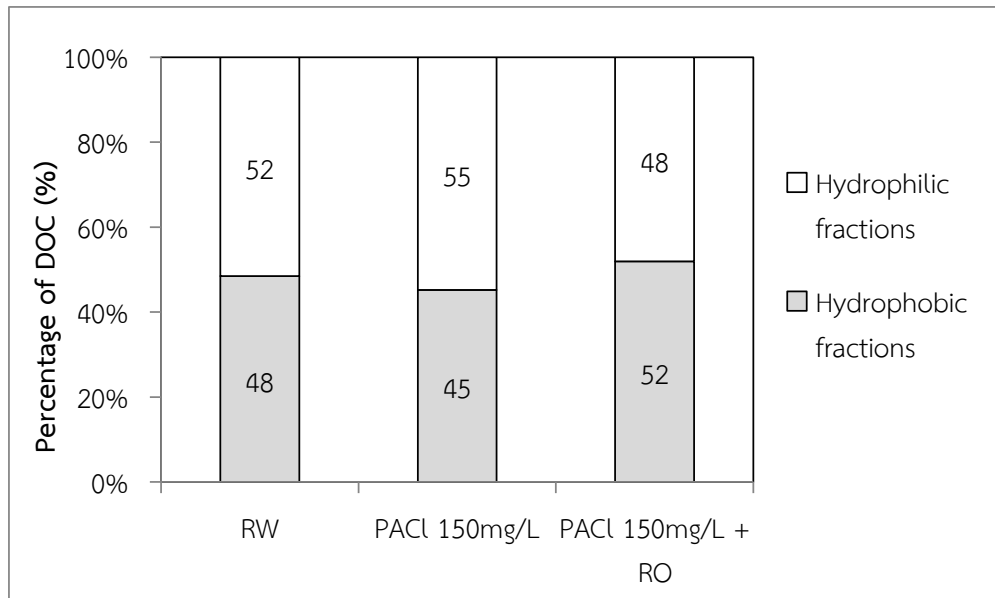
Figure 22 The percentage of DOC of HPI and HPO of the Banglen WTP source
water
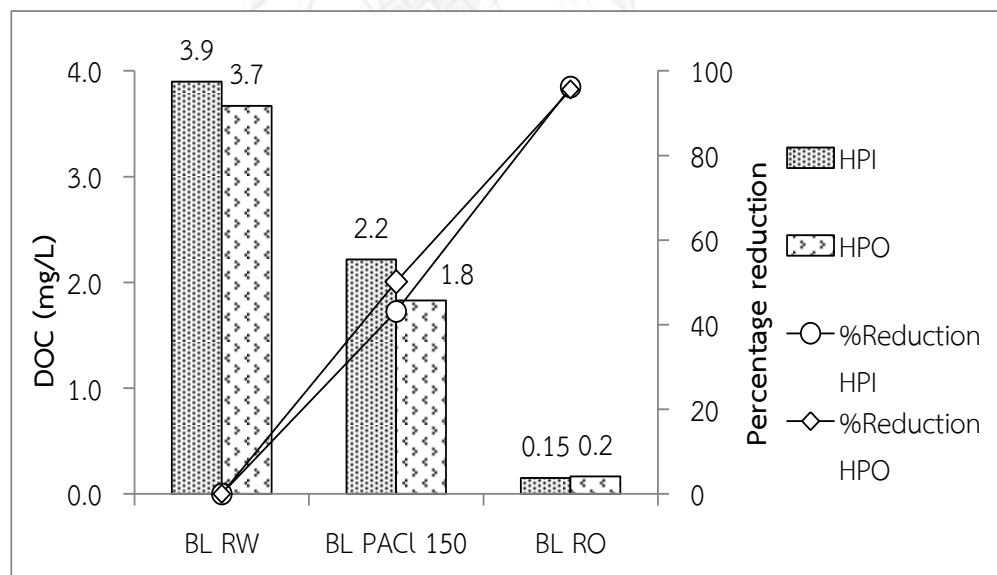
Figure 23 Reduction of DOC of HPI and HPO of the Banglen WTP source water
by PACl coagulation and PACl coagulation with RO

4.6.2 DON of HPO and HPI in raw waters, coagulated waters, and permeate water

Results of DON of HPO and HPI in raw water, coagulated water, and permeate water of the Bangkhen WTP and the Banglen WTP is shown in Appendix. It was found that the summation of DON values of all samples after resin fractionation was higher or lower than 15% of DON values of water before fractionation. This observation could come from the interference of chemical added during the fractionation process on the DON measurement. This is because the membrane technique was used as the pre-treatment of DON measurement. The additional of acid and base during the resin fractionation procedure created the high concentration of inorganic in the water samples. The organic may cause foul on the membrane in pre-treatment process. Therefore, it could lead to the error in DON analysis.

Westerhoff and Mash (2002) reported that DON of HPI were contained more DON contents than that of DON of HPO. However, it could not be concluded that which fraction of DON are more capable of NDMA formation (Westerhoff & Mash, 2002). Shen and Andrews (2013) stated that the maximum formation of NDMA takes place at the pH range of 7 to 8. At pH lower than 7-8, the insufficient of non-protonated amines restrict the reaction. At the higher pH, even though the increasing in non-protonated amine improve the reaction of NDMA formation, the NDMA formation is restricted due to the short of dichloramine. Chang *et al*. (2013) found that very small amounts of nitrosamines were formed in all DON fractions when treated with chlorine (mostly less than 4.3 ng/mg-C). The hydrophilic base fraction was found contained a slightly higher amount of NDMA-FP (6.6 ng/mg-C) (Chang et al., 2013).

4.7   NDMA-FP results

Six water samples, raw water supplies (two samples), coagulated waters (two samples), and permeate waters (two samples) for both sources waters, were extracted in accordance with US.EPA Method 521 (US.EPA., 2004). The extracted water samples were approximately concentrated about 1000 times. The results for NDMA-FP are showed in Table 10, for both sources water samples. The NDMA-FP results were negative, or could not be detected by using Gas Chromatography with

Nitrogen Phosphorus Detector (NPD) with the limit of detection (LOD) of the method for NDMA of 542 ng/L or 7.3 nM. Therefore, it cannot be concluded that PACl coagulation as pre-treatment with RO can remove NDMA-FP or not.

Table 10 NDMA-FP results

sample	Source of raw waters	
	Bangkhen WTP	Banglen WTP
Raw water	ND.*	ND.*
Coagulated water	ND.*	ND.*
Permeate water	ND.*	ND.*

* ND. = not detectable/less than LOD of 542 ng/L or 7.3 nM.

CHAPTER 5

CONCLUSION

1. This research was aimed at investigating the removal *N*-Nitrosodimethylamine (NDMA) precursors and their hydrophobic organic fraction (HPO) and hydrophilic organic fraction (HPI) in raw water supplies of the Bangkhen water treatment plant (WTP) and the Banglen WTP. The PACl coagulation combined with nanofiltration (NF) and reverse osmosis (RO) membrane filtration was employed. The experiment results can be concluded as below:

2. Dissolved organic carbon (DOC) of 4.2 mg/L, ultraviolet adsorption at wavelength 254 nm (UV-254) of 0.135 cm^{-1}, specific ultraviolet adsorption (SUVA) of 3.2 L/mg-m and DON of 0.24 mg/L were found in raw water supply of the Bangkhen WTP. DOC, UV-254, SUVA, and DON of raw water supply of Banglen WTP were 7.9 mg/L, 0.231 mg/L, 2.9 L/mg-m, and 0.28 mg/L, respectively.

3. The PACl coagulation at 80 mg/L and pH of 7 could reduce DOC, UV-254, SUVA, and DON from raw water supply of the Bangkhen WTP by 32, 64, 47, and 34%, respectively. In the case of the Banglen water, DOC of 41%, UV-254 of 63%, SUVA of 29%, and DON of 37% could be reduced by PACl coagulation at 150 mg/L and pH of 7.

4. In the case of the Bangkhen WTP, the PACl coagulation combined with NF could reduce DOC, UV-254, SUVA, DOC and DON by 92, 94, 24, and 86%, respectively. DOC of 95%, UV-254 of 95%, SUVA of 19%, and DON of 85% could be reduced by the PACl coagulation combined with RO filtration. In the case of the Banglen WTP, the PACl coagulation combined with NF could reduce DOC, UV-254, SUVA, DOC and DON by 97, 97, 24, and 70%, respectively. DOC of 97%, UV-254 of 98%, SUVA of 32%, and DON of 79% could be reduced by PACl coagulation combined with RO filtration.

5. The PACl coagulation combined with RO membrane filtration showed better results on DON removal when compared to the PACl coagulation combined with NF membrane filtration.

6. The mechanism of membrane separation took place in this research was size exclusion.

7. Applied pressures on RO membrane filtration had only small effect on DON removal.

8. DOC could be fractionated by using DAX-8 resin, whereas DON which was found very low amount in samples could not be fractionated in this work.

9. DOC of HPO of 2.2 mg/L and DOC of HPI of 2.2 mg/L were detected in the raw water supply of the Bangkhen WTP. DOC of HPO and HPI of the raw water supply of the Bangkhen WTP were 3.7 and 3.9 mg/L, respectively.

10. The PACl coagulation, alone, showed better result on reduction of HPO (42% reduction) than that of HPI (26% reduction). The PACl coagulation combined with RO membrane filtration could reduce nearly 100% of both HPO and HPI.

11. The NDMA-FP in raw water supplies, coagulated waters, and permeate waters could not be detected with limit of detection of the method at 542 ng/L or 7.3 nM.

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APPENDIX

Table 1 Turbidity, UV-254, DOC, DON, SUVA, and their percentage reduction including DOC/DON ratio of raw water, coagulated, and permeate water of water sample from Bangkhen Water Treatment Plant (Bangkhen WTP)

Sample	Turbidity	%turbid Red	UV-254	%UV-254 Red	DOC	%DOC Red	DON	%DON Red	DOC/DON	SUVA	%SUVA Red
RW	50.3	0	0.135	0	4.2	0	0.24	0	17	3.2	0
PACl 80 mg/L	0.90	98	0.049	64	2.9	32	0.16	34	18	1.7	47
PACl 80 mg/L + NF 4bar	0.17	100	0.008	94	0.36	92	0.075	69	4.7	2.3	29
PACl 80 mg/L + RO 4bar	0.17	100	0.006	96	0.23	95	0.037	85	6.3	2.6	19
PACl 80 mg/L + RO 2bar	N/A	N/A	0.007	95	0.25	94	0.035	86	7.2	2.8	12
PACl 80 mg/L + RO 3bar	N/A	N/A	0.007	95	0.26	94	0.039	84	6.7	2.7	15

Table 2 Turbidity, UV-254, DOC, DON, SUVA, and their percentage reduction including DOC/DON ratio of raw water, coagulated, and permeate water of water sample from Banglen Water Treatment Plant (Banglen WTP)

Sample	Turbidity	%Turbid Red	UV-254	%UV-254 Red	DOC	%DOC Red	DON	%DON Red	DOC/DON	SUVA	%SUVA Red
RW	17.4	0	0.231	0	7.9	0	0.28	0	28	2.9	0
PACl 150 mg/L	0.34	98	0.085	63	4.1	48	0.18	37	24	2.1	29
PACl 150 mg/L + NF 4bar	0.23	99	0.006	97	0.27	97	0.08	70	3.3	2.2	24
PACl 150 mg/L + RO 4bar	0.22	99	0.005	98	0.25	97	0.06	79	4.4	2.0	32
PACl 150 mg/L + RO 2bar	N/A	N/A	0.005	98	0.32	96	0.08	73	4.3	1.5	47
PACl 150 mg/L + RO 3bar	N/A	N/A	0.005	98	0.33	96	0.08	71	4.0	1.5	47

Table 3 NO_2^-, NO_3^-, and NH_4^+ values of raw water, coagulated, and permeate water of water sample from Bangkhen WTP

Sample	NO_2^-	NO_3^-	NH_4^+
RW	0.005	0.03	0.11
PACl 80 mg/L	0.007	0.05	0.05
PACl 80 mg/L + NF	0.004	0.13	0.02
PACl 80 mg/L + RO 4bar	0.004	0.01	0.01
PACl 80 mg/L + RO 2bar	0.003	0.02	0.01
PACl 80 mg/L + RO 3bar	0.003	0.02	0.02

Table 4 NO_2^-, NO_3^-, and NH_4^+ values of raw water, coagulated, and permeate water of water sample from Banglen WTP

Sample	NO_2^-	NO_3^-	NH_4^+
RW	0.012	0.02	0.25
PACl 150 mg/L	0.010	0.02	0.18
PACl 150 mg/L+ NF	0.009	0.07	0.08
PACl 150 mg/L + RO 4bar	0.005	0.02	0.05
PACl 150 mg/L + RO 2bar	0.003	0.02	0.01
PACl 150 mg/L + RO 3bar	0.002	0.01	0.03

Table 3 NO_2^-, NO_3^-, and NH_4^+ values of raw water, coagulated, and permeate water of water sample from Bangkhen WTP

Sample	NO_2^-	NO_3^-	NH_4^+
RW	0.005	0.03	0.11
PACl 80 mg/L	0.007	0.05	0.05
PACl 80 mg/L + NF	0.004	0.13	0.02
PACl 80 mg/L + RO 4bar	0.004	0.01	0.01
PACl 80 mg/L + RO 2bar	0.003	0.02	0.01
PACl 80 mg/L + RO 3bar	0.003	0.02	0.02

Table 4 NO_2^-, NO_3^-, and NH_4^+ values of raw water, coagulated, and permeate water of water sample from Banglen WTP

Sample	NO_2^-	NO_3^-	NH_4^+
RW	0.012	0.02	0.25
PACl 150 mg/L	0.010	0.02	0.18
PACl 150 mg/L+ NF	0.009	0.07	0.08
PACl 150 mg/L + RO 4bar	0.005	0.02	0.05
PACl 150 mg/L + RO 2bar	0.003	0.02	0.01
PACl 150 mg/L + RO 3bar	0.002	0.01	0.03

Table 5 DOC of HPI and DOC of HPO of raw water, coagulated, and permeate water of water sample from Bangkhen WTP

Sample	DOC of load sample (mg/L)	DOC mass of load sample (mg)	DOC of HPI (mg/L)	DOC mass of HPI (mg)	DOC of HPO (mg/L)	DOC of HPO (mg)	DOC mass HPI + HPO	%loss	%HPI	%HPO
RW	4.2	8.5	2.21	4.4	2.01	4.0	8.4	0.3	52	48
PACl 80 mg/L	2.9	5.8	1.64	3.3	1.16	2.3	5.6	3.4	58	42
PACl 80 mg/L + RO	0.23	0.5	0.14	0.3	0.15	0.3	0.6	-23.7	47	53

Table 6 The reduction of DOC of HPI and DOC of HPO of raw water, coagulated, and permeate water of water sample from Bangkhen WTP

Sample	% DOC Reduction	
	%DOC HPI	%DOC HPO
RW	0	0
PACl 80mg/L	26	42
PACl 80mg/L + RO	94	92

Table 7 DOC of HPI and DOC of HPO of raw water, coagulated, and permeate water of water sample from Banglen WTP

Sample	DOC of load sample (mg/L)	DOC mass of load sample (mg)	DOC of HPI (mg/L)	DOC mass of HPI (mg)	DOC of HPO (mg/L)	DOC of HPO (mg)	DOC mass HPI + HPO	%loss	%HPI	%HPO
RW	7.9	15.9	3.90	7.8	3.67	7.3	15.1	4.8	52	48
PACl 150 mg/L	4.1	8.3	2.22	4.4	1.83	3.7	8.1	2.3	55	45
PACl 150 mg/L + RO	0.25	0.5	0.15	0.3	0.16	0.3	0.6	-24.1	48	52

Table 8 The reduction of DOC of HPI and DOC of HPO of raw water, coagulated, and permeate water of water sample from Bangkhen WTP

Sample	%DOC Reduction	
	%DOC HPI	%DOC HPO
RW	0	0
PACl 150mg/L	43	50
PACl 150mg/L + RO	96	96

Table 9 DON of HPI and HPO of raw water, coagulated, and permeate water of water sample from Bangkhen WTP

Sample	DON of load sample (mg/L)	DON mass of load sample (mg)	DON of HPI (mg/L)	DON mass of HPI (mg)	DON of HPO (mg/L)	DON of HPO (mg)	DON mass HPI + HPO (mg)	% HPI	% HPO
RW	0.24	0.49	0.32	0.64	0.18	0.36	1.01	64	36
PACl 80 mg/L	0.16	0.32	0.37	0.75	0.16	0.32	1.07	70	30
RO	0.04	0.07	0.13	0.25	0.06	0.11	0.37	69	31

Table 10 DON of HPI and HPO of raw water, coagulated, and permeate water of water sample from Banglen WTP

Sample	DON of load sample (mg/L)	DON mass of load sample (mg)	DON of HPI (mg/L)	DON mass of HPI (mg)	DON of HPO (mg/L)	DON of HPO (mg)	DON mass HPI + HPO (mg)	% HPI	% HPO
RW	0.28	0.56	0.40	0.80	0.22	0.44	1.23	65	35
PACl 150 mg/L	0.18	0.35	0.31	0.62	0.18	0.35	0.97	63	37
PACl 150 mg/L + RO	0.06	0.12	0.19	0.37	0.09	0.17	0.54	69	31

Table 11 Permeate flux of NF experiment of the Bangkhen WTP source water

Flux (L/m2.hr)			
Time (hr.)	Batch 1	Batch 2	Batch 3
0	0	0	0
1	53	51	51
2	52	52	51
3	52	52	50
3.25	52	51	50

Table 12 Permeate flux of NF experiment of the Banglen WTP source water

Flux (L/m2.hr)			
Time (hr.)	Batch 1	Batch 2	Batch 3
0	0	0	0
1	55	50	52
2	55	51	52
3	54	51	52

Table 13 Permeate flux of RO experiment of the Bangkhen WTP source water

Flux (L/m2.hr)										
Time (hr.)	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	RO, 3Bar	RO, 2Bar
0	0	0	0	0	0	0	0	0	0	0
1	19	21	21	19	21	21	21	20	14	9
2	19	21	20	19	21	21	21	20	14	8
3	19	21	20	19	20	20	21	19	14	8
4	18	21	21	19	20	20	21	19	14	8
5	18	21	21	19	20	20	21	19	14	8
6	18	21	20	19	20	20	21	19	14	8
7	18	21	20	19	20	20	21	19	14	8
8	18	21	20	19	20	20	21	19	14	8

Table 14 Permeate flux of RO experiment of the Banglen WTP source water

Time (hr.)	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	RO, 3Bar	RO, 2Bar
Flux (L/m2.hr)										
0	0	0	0	0	0	0	0	0	0	0
1	24	24	24	24	24	24	23	23	17	10
2	24	24	24	24	24	24	23	23	17	11
3	24	24	24	24	24	24	23	23	17	11
4	24	24	24	24	24	24	23	23	17	11
5	24	24	24	24	24	23	23	23	17	11
6	24	24	24	24	24	23	23	23	17	11
7	24	24	24	24	24	23	23	23	17	11

Figure 1 NDMA calibration curves

```
-----------------------------------------------------------------
                       Calibration Table
-----------------------------------------------------------------

Calibration curve of NDMA

Calib. Data Modified  :      7/18/2014 10:58:15 PM

Calculate             :      Area Percent

Rel. Reference Window :      5.000 %
Abs. Reference Window :      0.000 min
Rel. Non-ref. Window  :      5.000 %
Abs. Non-ref. Window  :      0.000 min
Uncalibrated Peaks    :      not reported
Partial Calibration   :      Yes, identified peaks are recalibrated
Correct All Ret. Times:      No, only for identified peaks

Curve Type            :      Linear
Origin                :      Forced
Weight                :      Equal

Recalibration Settings:
Average Response      :      Average all calibrations
Average Retention Time:      Floating Average New 75%

Calibration Report Options :
     Printout of recalibrations within a sequence:
         Calibration Table after Recalibration
         Normal Report after Recalibration
     If the sequence is done with bracketing:
         Results of first cycle (ending previous bracket)

Signal 1: NPD1 A,

RetTime  Lvl   Amount      Area      Amt/Area  Ref Grp Name
 [min] Sig       [uM]
-------|--|--|-----------|-----------|-----------|---|--|----------------
 8.798  1  1    5.36000    1.50000    3.57333 +     NDMA
           2    6.70000    2.10000    3.19048
           3    8.04000    2.30000    3.49565
           4   10.72000    2.80000    3.82857
           5   13.40000    4.30000    3.11628
-----------------------------------------------------------------
                        Calibration Curves
-----------------------------------------------------------------
```

NDMA at exp. RT: 8.798
NPD1 A,
Correlation: 0.99636
Residual Std. Dev.:   0.26361
Formula: y = mx
          m: 2.96340e-1
          x: Amount[uM]
          y: Area

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