REDUCTION OF N-NITROSODIMETHYLAMINE PRECURSORS IN RAW WATER SUPPLY BY ENHANCED COAGULATION WITH POWDER ACTIVATED CARBON

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การลดสารตั้งต้นของสารเอ็น-ไนโตรโซไดเมทิลเอมีนในน้ำดิบประปาด้วยการเพิ่มประสิทธิภาพการโคแอกกูเลชันด้วยถ่านกัมมันต์แบบผง

นางสาวจินดาลักขณ์ คุ้มสุวรรณ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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จินดาลักขณ์ คุ้มสุวรรณ : การลดสารตั้งต้นของสารเอ็น-ไนโตรโซไดเมทิลเอมีนในน้ำดิบประปาด้วยการเพิ่มประสิทธิภาพการโคแอกกูเลชันด้วยถ่านกัมมันต์แบบผง. (REDUCTION OF N-NITROSODIMETHYLAMINE PRECURSORS IN RAW WATER SUPPLY BY ENHANCED COAGULATION WITH POWDER ACTIVATED CARBON) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. จรงค์พันธ์ มุสิกะวงศ์ , 98 หน้า.

การศึกษามีวัตถุประสงค์เพื่อลดสารตั้งต้นของสารเอ็น-ไนโตรโซไดเมทิลเอมีนในน้ำดิบประปาโรงผลิตน้ำประปาบางเขนและบางเลนด้วยการเพิ่มประสิทธิภาพการโคแอกกูเลชันด้วยการดูดติดด้วยถ่านกัมมันต์แบบผง ตลอดจนการเพิ่มประสิทธิภาพการโคแอกกูเลชันและการดูดติดด้วยถ่านกัมมันต์ สารส้มและโพลีอลูมิเนียมคลอไรด์ (polyaluminium chloride, PACl) เป็นสารสร้างตะกอน น้ำดิบประปาถูกเก็บหนึ่งครั้งจากทั้งสองแหล่ง ค่าคาร์บอนอินทรีย์ละลายน้ำในน้ำดิบประปาบางเขน (dissolved organic carbon, DOC) มีค่าเป็น 4.2 มก./ลิตร ส่วนค่าไนโตรเจนอินทรีย์ละลายน้ำ (dissolved organic nitrogen, DON) มีค่าเป็น 0.24 มก./ลิตร น้ำดิบประปาบางเลนมีค่า DOC เท่ากับ 7.3 มก./ลิตร และ DON เท่ากับ 0.34 มก./ลิตร PACl 80 มก./ลิตร ควบคมค่า pH ที่ 7 กำจัด DOC และ DON จากน้ำดิบประปาบางเขนได้ร้อยละ 42 และ 41 ตามลำดับ ส่วนน้ำดิบประปาบางเลน PACl 150 มก./ลิตร ควบคุมค่า pH ที่ 7 ลดค่า DOC และ DON ได้ร้อยละ 38 และ 52 ตามลำดับ สภาวะที่เหมาะสมสำหรับน้ำประปาดิบบางเขนในการลดสารตั้งต้นของสารเอ็น-ไนโตรโซไดเมทิลเอมีน คือ การโคแอกกูเลชันที่ PACl 80 มก./ลิตร ร่วมกับ PAC ที่ 20 มก./ลิตร โดยที่สภาวะดังกล่าวลด DOC และ DON ได้ร้อยละ 77 และ 68 ตามลำดับ ส่วนน้ำประปาดิบบางเลนสภาวะที่เหมาะสมคือ การโคแอกกูเลชันด้วย PACl 150 มก./ลิตร ร่วมกับ PAC ที่ 20 มก./ลิตร โดยที่สภาวะดังกล่าวลดค่า DOC และ DON ได้ร้อยละ 85 และ 70 ตามลำดับ การลดของค่า DOC และ DON โดยการโคแอกกูเลชันร่วมกับ PAC และการโคแอกกูเลชันแล้วตามด้วยการใช้การดูดติดด้วย PAC มีค่าใกล้เคียงกัน ค่า DOC ของ HPO และ HPI ในน้ำดิบประปาบางเขนมีค่าเป็น 2.0 และ 2.2 มก./ลิตร ตามลำดับ การโคแอกกูเลชันด้วย PACl เพียงอย่างเดียวลด HPO และ HPI ได้ร้อยละ 47 และ31 ตามลำดับ การโคแอกกูเลชันด้วย PACl ร่วมกับ PAC ลด HPI และ HPO ได้ร้อยละ 75 และ 80 ตามลำดับ ส่วนน้ำประปาบางเลนนั้นมีค่า DOC ของ HPO และ HPI เป็น 3.7 และ 3.9 มก./ลิตร ตามลำดับ การโคแอกกูเลชันด้วย PACl เพียงอย่างเดียวลด HPO และ HPI ได้ร้อยละ 45 และ42 ตามลำดับ การโคแอกกูเลชันด้วย PACl ร่วมกับ PAC ลด HPO และ HPI ได้ร้อยละ 89 และ 83 ตามลำดับ ค่าโอกาสการก่อตัวของสารเอ็น-ไนโตรโซไดเมทิลเอมีนของน้ำดิบประปา น้ำที่ผ่านโคแอกกูเลชัน น้ำที่ผ่านการเพิ่มประสิทธิภาพการโคแอกกูเลชันด้วยถ่านกัมมันต์แบบผงของทั้งสองแหล่งน้ำนั้นตรวจไม่พบที่ค่าความเข้มข้นต่ำสุดของวิธีการตรวจวัดที่มีค่าเป็น 542 นาโนกรัมต่อลิตร

สาขาวิชา การจัดการสิ่งแวดล้อม	ลายมือชื่อนิสิต ....
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KEYWORDS: NDMA PRECURSORS NDMA FORMATION POTENTIAL (NDMA-FP) PACL ALUM COAGULATION ENHANCED COAGULATION POWDER ACTIVATED CARBON DISSOLVED ORGANIC NITROGEN (DON)

JINDALAK KUMSUVAN: REDUCTION OF N-NITROSODIMETHYLAMINE PRECURSORS IN RAW WATER SUPPLY BY ENHANCED COAGULATION WITH POWDER ACTIVATED CARBON. ADVISOR: ASST. PROF. CHARONGPUN MUSIKAVONG, Ph.D., 98 pp.

This research is aimed at determining the removal of *N*-nitrosodimethylamine (NDMA) precursors in raw water of the Bangkhen water treatment plant (WTP) and the Banglen WTP by enhanced coagulation with powder activated carbon (PAC) and coagulation followed by PAC adsorption. Alum and polyaluminium chloride (PACl) were used as coagulants. Raw water supplies were collected one time. Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) of raw water of the Bangkhen WTP were 4.2 and 0.24 mg/L, respectively. DOC of 7.3 mg/L and DON of 0.34 mg/L were found in raw water of the Banglen WTP. The PACl of 80 mg/L at pH 7 could reduce DOC and DON from raw water of the Bangkhen WTP by 42 and 41%, respectively. The PACl of 150 mg/L at pH of 7 reduced DOC and DON in raw water of the Banglen WTP by 38, and 52%, respectively. The optimal condition at PACl of 80 mg/L combined with PAC of 20 mg/L at pH 7 could reduce DOC and DON in raw water of the Bangkhen WTP by 77 and 68%, respectively. For raw water of the Banglen WTP, the PACl of 150 mg/L combined with PAC 20 mg/L at pH 7 reduce DOC and DON by 85 and 70%, respectively. Percent reductions of DOC and DON by PACl coagulation followed by PAC adsorption were comparable to using PACl coagulation combined with PAC. DOCs of hydrophobic organic fraction (HPO) of 2.0 mg/L and hydrophilic organic fraction (HPI) of 2.2 mg/L were determined in raw water of the Bangkhen WTP. DOC_{HPI} and DOC_{HPO} in raw water of the Banglen WTP were 3.9 and 3.7 mg/L, respectively. For raw water of the Bangkhen WTP, the PACl coagulation reduced HPO and HPI by 47 and 31%, respectively. The PACl coagulation with PAC reduced HPO by 80% and HPI by 75%. For the Banglen WTP, the PACl coagulation reduced HPO by 45% and HPI by 42%. PACl coagulation with PAC reduced HPO and HPI by 89 and 83%, respectively. NDMA formation potentials in raw water, coagulated water, coagulated water at enhanced coagulation of Bangkhen and Banglen source waters were not detectable under detection limit of the methods of 542 ng/L.

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

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

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CHAPTER 1

INTRODUCTION

1.1 Motivation

The Bangkhen Water Treatment Plant (WTP) supplies tap water to approximately 6 million people in Bangkok, Thailand. The major source of raw water supply of the Bangkhen WTP is the Chao Phraya River. The Banglen WTP is located in Nakhonpathom province. It produces water supply to serve an approximate population of 7 hundred thousand people. The main source of raw water supply of the Banglen WTP is the Tahjeen River. The Bangkhen WTP and the Banglen WTP utilize alum and polyaluminuim chloride (PACl) coagulations followed by sedimentation, filtration, and chlorination processes for producing water supply. The expansion of residential, industrial, and agricultural areas are causing more contaminants to be released into the river, deteriorating the quality of the raw water supply. Water suppliers, therefore, must prepare ways of dealing with this situation.

The International Humic Substances Society (IHSS) detected natural organic matter (NOM) in water that contains roughly 40–60% carbon by weight and 1–5% nitrogen by weight. Dissolved organic carbon (DOC) comes from decomposition processes of plants and animals. DOC compounds are the precursors of mutagenic halogenated compounds in water formed after chlorination (Rook, 1974) . DOC is a type of dissolved organic matter (DOM). To characterize the nature of DOM in raw water supply and tap water, the resin fractionation technique was utilized by several researchers to separate DOM into hydrophobic organic fraction (HPO) and hydrophilic organic fraction (HPI). In the water supply process, disinfectants such as chlorine, chlorine dioxide, and chloramines can react with aquatic DOM and form carbonaceous disinfection by-products (C-DBPs), which are toxic and have significant adverse effects on humans (Lee, Westerhoff, Esparza, & Soto, 2006).

Dissolved organic nitrogen (DON) is primarily composed of degraded amino sugars, peptides and poryphyrins (Leenheer, 2004). DON, a large class of NOM, can react with disinfectants such as chlorine and chloramines to produce nitrogenous disinfection by-products (N-DBPs). N-DBPs are more genotoxic, mutagenic, and/or carcinogenic than traditional C-DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Plewa et al., 2008).

DON is the first primary precursor of *N*-nitrosodimethylamine (NDMA) (Aydin et al., 2012). DOC, ultraviolet adsorption at wavelength 254 nm (UV-254), and specific ultraviolet adsorption (SUVA) are the secondary precursor of NDMA (Roux, Gallard, & Croué, 2011; Yoon, Nakada, & Tanaka, 2011). NDMA is produced during chorine disinfection when chloramines react with dimethylamine (Choi & Valentile, 2002) and other nitrogen-containing compounds (Mitch & Sedlak, 2004). NDMA can potentially cause cancer as it has been shown to cause cancers of the liver, lung and kidneys in adult mice, and cancers of the liver and lung in young specimens fed with milk from mothers exposed to NDMA. Experiments on rats, hamsters, guinea pigs, rabbits, ducks, different types of fish, frogs and newts have demonstrated the carcinogenic character of NDMA (Clark & Boutin, 2001). The United State Environmental Protection Agency (US.EPA.) has regulated NDMA in drinking water. The maximum acceptable concentration is 0.7 ng/L with a risk estimate of 10^{-6} (US.EPA., 1999).

When DOC and DON are discharged to sources of water supply of the Bangkhen WTP and the Banglen WTP and chlorine is utilized in the disinfection process. The C-DBPs and N-DBPs can be formed in water supply. The suitable way to reduce the formation of C-DBPs and N-DBPs is the removal of both C-DBPs and N-DBPs precursors prior to the chlorination. A Coagulation process commonly utilized aluminum or irons based salt such as alum, polyaluminium chloride (PACl), ferric sulphate and ferrous sulphate for reducing suspended solids and turbidity in water supplies. Increasing the coagulant dosage can improve DOC removal from water (C. Musikavong & Wattanachira, 2012). In addition, the enhanced coagulation by powder activated carbon (PAC) has been proved to be effectively removed DOM in water (Uyak, Yavuz, Toroz, Din, & Gencili, 2006).

A previous study focused on the characterization and reduction of DOC and C-DBPs in Bangkok source water (Kanokkantapong, Marhaba, Wattanachira, Panyapinyophol, & Pavasant, 2006). However, there has been no report on the level of DON as a primary NDMA precursor and its reduction by alum and PACl coagulations. This work is aimed at determining the levels of primary and secondary NDMA precursors, HPO, and HPI in the raw water supply of the Bangkhen WTP and the Banglen WTP. In addition, we choose PAC for enhancing alum and PACl coagulations for the reduction of NDMA precursors, HPO, and HPI in raw water supply of the Bangkhen WTP and Banglen WTP.

1.2 Objectives

1. To determine the level of primary and secondary NDMA precursors in raw water supplies and their HPO and HPI.

2. To investigate the reduction of primary and secondary NDMA precursors from raw water supplies and their HPO and HPI by alum and PACl coagulations.

3. To determine the reduction of primary and secondary NDMA precursors and their HPO and HPI by the enhanced coagulation with PAC and the coagulation and PAC adsorption.

1.3 Hypothesis

Alum and PACl coagulations and the enhanced coagulation with PAC can remove primary and secondary NDMA precursors from raw water supplies.

1.4 Scope of the study

1. Raw water supplies from the Bangkhen WTP, located in Bangkok, Thailand and the Banglen WTP, located in Nakhonpathom, Thailand were collected once.

2. Coagulation experiments with alum and PACl by using the jar-test apparatus were conducted.

3. Six dosages of alum and PACl from 10 to 100 mg/L were used in the coagulation experiment of raw water from the Bangkhen WTP.

4. Nine dosages of alum and PACl from 10 to 250 mg/L were used in the coagulation experiment of raw water from the Banglen WTP.

5.Coagulation processes were separated to two experiments (I) the coagulation combined with PAC and (II) coagulation and PAC adsorption.

6. In case study II, the amount of PAC was selected from the optimal condition of the coagulation by PACl or alum combined with PAC from the first coagulation experiment.

7. The DON measurement was conducted according to the method developed by Xu et al. (2010).

8. The resin fractionation was performed in accordance with methods developed by E. M. Thurman and Malcolm (1981).

9. The NDMA-FP analysis was conducted based on the trihalomethanes formation potential analysis that was applied with the method developed by Mitch and Sedlak (2004) and Lee *et al*., (2007).

10. The detection limit of a gas chromatography with nitrogen phosphorus detector (GC/NPD) was 300 μg/L.

1.5 Benefit of this study:

1. The characteristic of raw water from the Bangkhen WTP and the Banglen WTP was surveyed.

2. The optimal condition for the reduction of NDMA precursors, HPO, and HPI was obtained and could be applied to be used in the plant operation.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEWS

2.1 **Natural organic matter (NOM)**

NOM is complex compounds of organic substance in natural water. When NOM reacts with chlorine it can create disinfection by-products (DBPs) such as thrihalomethanes (THMs) and haloacetic acids (HAAs). In general, the type of NOM can be divided according to the state of dissolution into 2 parts including dissolved organic matter (DOM) and particulate organic matter (POM)

$$NOM = DOM + POM$$

DOM is the dissolved fraction of organic substance in water. On the contrary POM is non dissolved fraction of organic substance in water that does not dissolve in water. The type of NOM is divided by using different porosity of filter paper (<0.1 μm, <0.45 μm, <1.0 μm) it can be divided to increase in the part of colloidal organic matter (COM) that is the part between DOM and POM

$$NOM = DOM + COM + POM$$

2.2 Dissolved organic matter

DOM can be divided to 2 parts including humic and non-humic substances. The character of 50-65% of a humic substance is polar and it is organic that comes from the decomposition of soil and aquatic plant. A humic substance is commonly classified as hydrophobic organic substance. It consists of humic and fulvic acids. Non-humic substance is organic substance that has hydrophilic character and consists of hydrophilic acids, proteins, amino acids, carbohydrate and carboxylic acids (E.M. Thurman, 1985).

2.3 Surrogate parameters of NOM

In general, the only one surrogate parameters of NOM cannot explain to NOM characteristic. Therefore, total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV-254) and specific ultraviolet absorbance (SUVA) are the surrogate parameters used to present the level of NOM.

2.3.1 Total organic carbon (TOC)

Total organic carbon (TOC) is amount of TOC in water sample. The analytic principle of TOC is oxidation of carbon in organic compound to become carbon dioxide. Then the amount of carbon can be measured. United State Environmental Protection Agency (US.EPA.) purposed the percentage of removal TOC by coagulation. The performance of coagulation for removing TOC depended on the concentration of TOC and alkalinity in raw water as shown in Table 1.

Table 1 Percentage of TOC removal by coagulation process (US.EPA. 1999).

Source water TOC (mg/l)	Source Water Alkalinity (mg/L as CaCO3)		
	0-60	>60-120	>120
2.0 - 4.0	35%	25%	15%
4.0 - 8.0	45%	35%	25%
>8.0	50%	40%	30%

US.EPA. specified the maximum TOC levels of 2 mg/L in treated water and 4 mg/L in source water that is acceptable level in disinfection by-products.

2.3.2 Dissolved organic carbon (DOC)

The sources of DOC come from decomposition processes from dead organic matter such as plant. When water contact organic matter, it can drain to in the rivers and lake as DOC. Organic carbon in natural water consist of particulate organic carbon (POC) and DOC. In a water supply plants, chlorine is used as disinfectant. The reaction of DOC with chlorine can cause DBPs which are all classified as carcinogenic substances. DOC is the fraction of TOC that passes through a 0.45 μm filter paper (Callahhan et al., 2004) that is pre-combusted at 550 ^{o}C

2.3.3 Dissolved organic nitrogen (DON as NDMA precursors)

DON is the first primary of NDMA precursors (Aydin et al., 2012). Monocholramine and organic compounds containing nitrogen such as dimethyl groups are the compounds that take part in the formation of NDMA. Other compounds containing nitrogen such as amino acids and proteins do not form significant concentration of NDMA (Mitch & Sedlak, 2004). DON, a large class of NOM, is an emerging issue in drinking water treatment because of its role as precursor of N-DBPs. N-DBPs have more genotoxic, mutagenic, and/or carcinogenic activity than traditional carbon- C-DBPs like THMs and HAAs (Plewa et al., 2008).

The concentration of DON is determined by subtracting the summation of dissolved inorganic nitrogen (DIN) species from the total dissolved nitrogen (TDN) as shown in equation 1 (Xu *et al*., 2010).

$$\text{DON} = \text{TDN}- \text{DIN} =\text{TDN}- (\text{NO}_3^- + \text{NO}_2+\text{NH}_3/\text{NH}_4) \qquad (1)$$

High DIN/TDN ratio effects to negative DON concentration (Vandenbruwane *et al*., 2007; Soilinger *et al*., 2001; Lee and Westerhoff, 2005). A NF pre-treatment can retain most of the DON in concentrate and DIN species (nitrate, nitrite and ammonia) to pass through into the permeate (Xu e*t al*., 2010). NF membrane was selected for DON experiment. DON concentration from NF pre-treatment can be calculated from mass balance of DON equation 2.

$$C_F=(C_RV_R+C_RV_R)/V_F=C_R(V_F=V_P)/V_F \qquad (2)$$

The DON concentration in the feed water is C_F, the volume of feed water is V_F, the DON concentration in the retentate is C_R, the volume of retentate is V_R ($V_R = V_F – V_P$, around 50 ml).The concentration in the permeate is C_P, and the exact volume of collected permeate is V_P (Xu *et al*., 2010).

2.3.4 UV-254

Ultraviolet (UV) absorption is used as surrogate parameters of measurement of organic substance in water. Moreover it is used to estimate the capability of amount of organic substance that can be removed. Organic substance in water sample will adsorb ultraviolet that relate with the concentration of organic substance in water sample. When the values of it increase the amount of ultraviolet will be increased. Water sample that is measured for it UV-254 must be passed through a 0.7 or 1.1 -μm-pore-diam filter that was pre-combusted at 550 ^{o}C (GF/F,Whatman, Madstone, UK).

2.3.5 Specific Ultraviolet Absorption (SUVA)

SUVA is surrogate parameters of humic in water. SUVA can calculate from UV-254 (cm^{-1}) divide by DOC (mg/L). A water sample that has low SUVA value contain non-humic organic matter and do not proper to use coagulation process to reduce organic substance. However, a water sample that has high SUVA is suitable for employing the coagulation process to remove DOM (Table 2). High SUVA indicates the organic matter that is largely composed of HPO, high MW organic material. Low SUVA indicated the water that contains mainly HPI, low MW and low charge (Matilainen, Vepsalainen, & Sillanpaa., 2010).

Table 2 The relationship between level of SUVA and DOC removal (Edzwald and Tobiason, 1999.)

SUVA (L/mg-m)	Composition	Coagulation	DOC Removals
< 2	Mostly non-Humics low hydrophobicity low molecular weight	NOM has little influence poor DOC removals	< 25% for alum Slightly greater for ferric
2-4	Mixture of aquatic humic and other NOM mixture of hydrophobic and hydrophilic NOM Mixture of molecular weights	NOM influences DOC removal should be fair to good	25-50% for alum Slightly greater for feric
>4	Mostly aquatic humics high hydrophobicity High molecular weight	NOM control Good DOC removals	50% for Alum Slightly greater for ferric

2.3.6 *N*-nitrosodimethylamine (NDMA)

Nitrosamines, mainly NDMA and *N*-nitrosodiethylamine (NDEA), are highly mutagenic compounds that are suspected of carcinogenic activity in the human body (Andrzejewski, Kasprzyk-Hordern, & Nawrocki., 2005). USEPA set that the maximum admissible concentration of these compounds in drinking water is 7 ng/L (NDMA) and 2 ng/L (NDEA) with the risk estimation of 10^{-5} (Choi & Valentile, 2002; Mitch & Sedlak, 2004). NDMA has a carcinogenic effect on rats (Barnes *et al*., 1956). It was found that 90% of 300 compounds have shown to be carcinogenic. The chemical formula of the *N*-nitrosoamines of interest to the US.EPA. due to their probable carcinogenicity are given in Figure 1. A noticeable feature of this group of nitrosoamines is the fact that their carcinogenic properties decrease with an increase of the length of the aliphatic chain. *N*-nitrosodiethylamine, which is characterized by a higher carcinogenicity than NDMA, is the single exception.

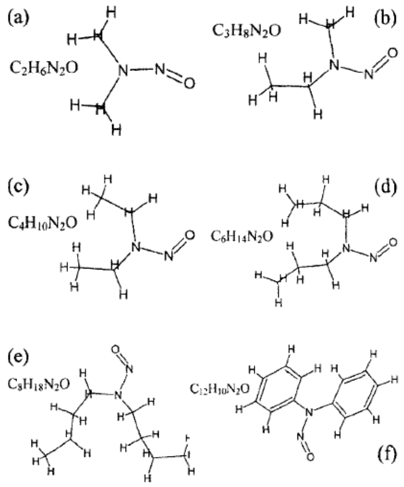

Figure 1 Chemical formular of *N*-nitrosoamines of interest to the US EPA

(a) *N*-nitrosodimethylamine (NDMA); (b) *N*-nitrosomethylethylamine (NDMEA);

(c) *N*-nitrosodiethylamine (NDEA); (d) *N*-nitrosodi-n-propylamine (NDnPA);

(e) *N*-nitrosodibuthylamine (NDBA); (f) *N*-nitrosodiphenylamine (NDPhA).

2.4 Resin Fractionation

NOM fractions and chemical group are shown in Table 3. (Leenheer, Noyes, and Steer, 1982; Leenheer and Noyes, 1984; and Reckhow, Bose, Bexbarua *et al*., 1992). DAX-8 resin was used to fractionate DOM into hydrophobic organic fraction (HPO) and hydrophilic organic fraction (HPI) (Thurman *et al*., 1981). DOMs could be separated into six organic fraction, i.e. hydrophobic acid fraction (HPOA), hydrophobic base fraction (HPOB), hydrophobic neutral fraction (HPON) and hydrophilic acid fraction (HPIA), hydrophilic base fraction (HPIB) and hydrophilic neutral fraction (HPIN) (Leenheer *et al*., 1981).

2.5 Coagulation Process

2.5.1 Alum coagulant

Alumina sulfate or alum is the most popular for coagulation process in Thailand because of it is suitable for water treatment. Moreover it can easy to buy and is not expensive. Molecule formula of Alum is $Al_2(SO_4)_3*H_2O$ and normally * equal 14.3 or 18 when alum is added to water by decomposition to become positive charge and negative charge. Reaction shows in equation 3.

$$Al_2(SO_4)_3 \longrightarrow 2Al^{+3} + 3SO_4^{-2} \quad (3)$$

When alum is added to water, aluminium ion from $Al_2(SO_4)_3$ will be surrounded by molecule of water. Suddenly, it can happen $Al(H_2O)_6^{+3}$ or Al^{3+} or Hydrolysis of Al^{3+} by differ ligands in the water. Especially, OH^- instead of molecule of water and became complex substance between aluminium and hydroxide ion (Hannah *et al.*, 1967)

$$Al^{+3} + H_2O \longrightarrow Al(OH)^{+2} + H^+ \quad (4)$$

$$Al^{+3} + 2H_2O \longrightarrow Al(OH)_2^{+} + 2H^+ \quad (5)$$

$$7Al^{+3} + 17H_2O \longrightarrow Al_7(OH)_{17}^{+4} + 17H^+ \quad (6)$$

If the concentration of alum is higher than the concentration at saturation point, hydrolysis will be continued until the final reaction become $Al(OH)_3$

$$Al^{+3} + 3H_2O \longrightarrow Al(OH)_3(s) + 3H^+ \quad (7)$$

Table 3 Natural organic matter fractions and chemical groups

Fraction	Chemical group
Hydrophobic	
Acids	
Strong	Humic and fulvic acid, high MW alkyl monocarboxylic and dicarboxylic acid, aromatic acids.
Weak	Phenols, tannins, intermediate MW alkyl monocarboxylic and dicarboxylic acid, aromatic acids.
Bases	Proteins, aromatic amines, high MW alkyl Amines.
Neutrals	Hydrocarbon, aldehydes, high MW methyl ketones and alkyl alcohol, ethers, furan, pyrrole.
Hydrophilic	
Acids	Hydroxy acids, sugars, sulforics, low MW alkyl monocarboxylic and dicarboxylic acid.
Bases	Amino acids, purines, pyrimidines, low MW alkyl amines.
Neutrals	Polysaccharides; low Mw alkyl alcohol, aldehydes and ketones

(Leenheer, Noyes, and Steer, 1982; Leenheer and Noyes, 1984; and Reckhow, Bose, Bexbarua *et al*., 1992)

The result of reaction wills adsorption of colloid that is complex substance. It can happen during hydrolysis from Al^{3+} to $Al(OH)_3$. Complex substances may have positive charge or negative charge. It depends on pH of water. If pH of water is higher than zero point of charge of $Al(OH)_{3(s)}$,the complex substance will be negative charge such as $Al(OH)_4^-$, $Al(OH)_5^{-2}$. If pH of water is lower zero point of charge of $Al(OH)_{3(s)}$

that is the normal characteristic in coagulation process. Complex substance will be positive charge such as $Al(OH)^{2+}$, $Al(OH)^{+}_{2}$, $Al(OH)_{17}^{+4}$, $Al_{13}(OH)_{34}^{+5}$ (Figure2).

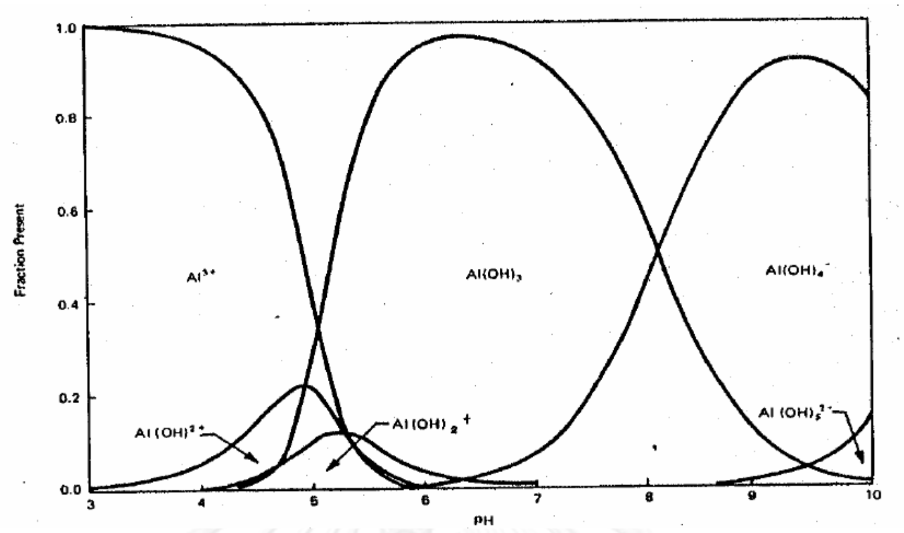

Figure 2 The relationship between complex substance and pH

(Committee Report, 1917)

<u>I.Adsorption and charge neutralization</u>

It happens from complex substance of alum that has positive charge. It breaks down stability of colloid that always has negative charge become neutralization. Small particles include together until become large particles. In addition, it can precipitate by weight of particles. This process is hard to control because the amount of complex substance should be suitable. If it is low amount, the coagulation process will not happen. In opposite if the complex substance is high, it will absorb more particles and make the particles change to be positive charge. Moreover, dregs that happen from this process can separate from water easily.

<u>II. Sweep coagulation</u>

The concentration of alum more over until the reaction can continue to be $Al(OH)_3$ (Equation 4.). Breaking down stability of colloid particles by this process can happen when much alum is added until the concentration is over saturation point. $Al(OH)_3$ will happen that be sticky crystal and it can envelop the particle. Furthermore it is not indicate the influence of electric charge.

III. Combination coagulation

It is breaking down stability of particles of colloid with adsorption and sweep coagulation (Breaking down electric charge). It happens when amount of alum increase more than adsorption process and breaking down electric charge. Figure 3 shows the suitability of pH of sweep coagulation is 6.8 to 8.2

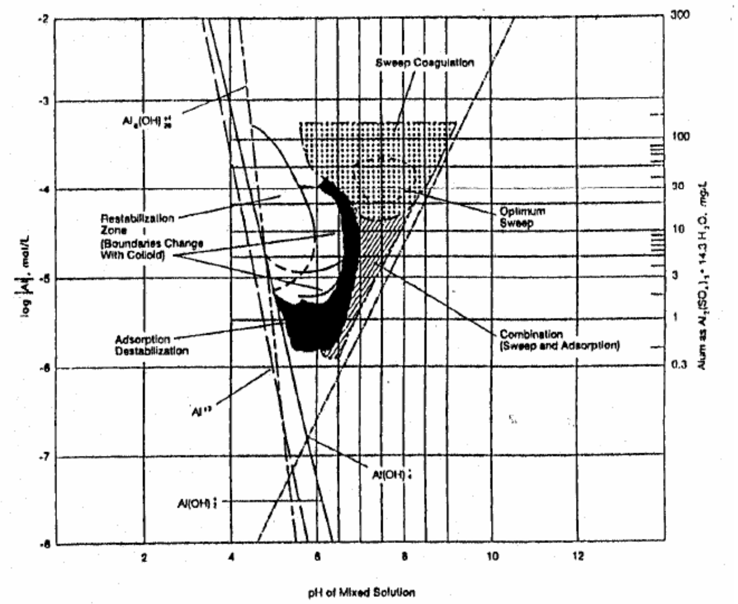

Figure 3 Diagram for design and control coagulation by alum

(Amirtharajah & Milks, 1982)

The coagulation dosage equivalent is presented in Table 4. The $Al_2(SO_4)_3$*$14H_2O$ and $Al_2(SO_4)_3$*$18H_2O$ of 10 mg/L equal to 0.9 and 0.8 mg/L in term of Al_2, respectively.

Table 4 Coagulant dosage equivalent of alum in term $Al_2(SO_4)$ and Al_3^{2+}

Dosage of alum (mg/L)	$Al_2(SO_4)_3$*$14H_2O$		$Al_2(SO_4)_3$*$18H_2O$	
	In term $Al_2(SO_4)_3$ (mg/L)	In term Al_2 (mg/L)	In term $Al_2(SO_4)_3$ (mg/L)	In term Al_2 (mg/L)
10	5.8	0.9	5.1	0.8
20	11.5	1.8	10.3	1.6
40	23.0	3.6	20.5	3.2
60	34.6	5.4	30.8	4.9
80	46.1	7.3	41.1	6.5
100	57.6	9.1	51.4	8.1
150	86.4	13.6	77.0	12.2
200	115.2	18.2	102.7	16.2
250	144.0	22.7	128.4	20.3

(Source: The calculation was done according to Hendricks; 2011)

2.5.2 Polyaluminium chloride (PACl) coagulant

PACl is the most popular coagulant for water treatment in Japan and Europe. PACl is prepared from aluminium as Al_2O_3 that react with HCl at high temperature in order to assemble to be $AlCl_3$. After that $AlCl_3$ react with base at high temperature and high pressure and it will become to aluminium polymer. When alum is added in solvents, alum will decrease concentration of Al_2O_3 (remain amount of Al_2O_3 about 10-11%). Sulfate is added to mix between 2 atoms of aluminium. The general formula of PACl is $Al_n(OH)_mCl_{3n-m}$. Figure 4 shows chemical structure of lapfloc PACl and alum (Hundt & O' Melia, 1988).

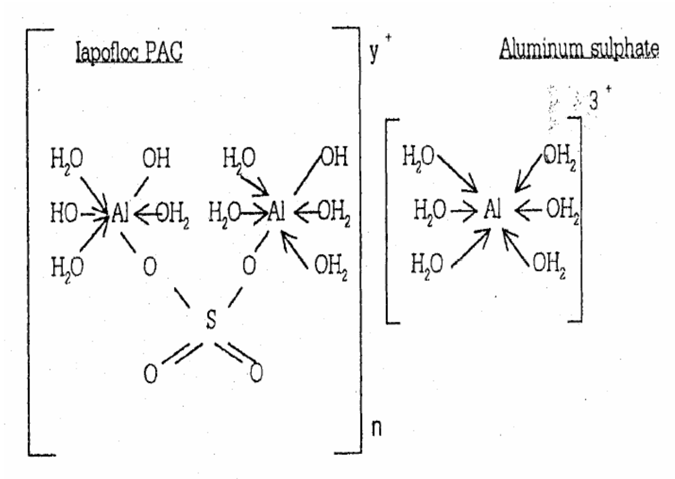

Figure 4 Chemical structure of lapfloc PACl and alum

(Hundt & O' Melia, 1988)

When PACl dissolves in water. Suddenly it will be hydrolyzed to more complex aluminium, $[Al1_3O_4(OH)_{24}]^{+7}$ or Al^{+13} . The assembly of aluminium depends on level of the assembly of base with aluminium solvent, type and concentration of base, concentration of aluminium chloride solvent and temperature. Amount of base and level of neutralization are the most important factor (Kaeding, 1992). The PACl dosage of 10 mg/L was equal to 2.6 mg/L in term of Al_2 (Table 5).

2.6 Adsorption

Adsorption on activated carbon is the most popular method for reduction of contaminant in water. Activated carbon is organic carbon that consists of powder activated carbon (PAC) and granular activated carbon (GAC). Adsorption is the adsorbent capability in attraction of molecule or colloid of adsorbate that attach with adsorbent in gas phase or liquid phase. The adsorption processes have 2 types including physical adsorption and chemical adsorption.

Physical adsorption

Physical adsorption can happen in multi-layers on adsorbent surface. It is the weak adsorption and no chemical bond but the attraction is Van der wals. It always occur in low temperature and low power in adsorption

Chemical adsorption

Chemical adsorption is strong adsorption because it occurs by the chemical bond between adsorbent and adsorbate. This mechanism depends on the type of adsorbate and surface of adsorbent after adsorption of molecule. This activity can occur in the monolayer

Table 5 Coagulant dosage equivalent of PACl in term $Al_2(OH)_3$and Al_3^{2+}

Dosage of PACl (mg/L)	In term $Al_2(OH)_3$ (mg/L)	In term Al_2 (mg/L)
10	5.0	2.6
20	9.9	5.1
40	19.9	10.2
60	29.8	15.3
80	39.7	20.4
100	49.7	25.5
150	74.5	38.3
200	99.4	51.1
250	124.2	63.8

(Source: The calculation was done according to Hendricks; 2011)

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2.7 DOM removal by coagulation process

The water from reservoir of the Tanggu WTP at northern China had the initial of turbidity of 5.12 NTU. The alum dosage of 100 mg/L at pH 5-6.5 could remove turbidity by 97% (Matilainen et al., 2010). The reclaimed water from treated industrial estate wastewater in the northern Thailand had the average of turbidity at 17.7 NTU. The alum dosage of 80 mg/L at uncontrolled pH could remove the maximum turbidity approximately 97% (C. Musikavong, Wattanachira, Marhaba, & Pavasant, 2005). For the treatment of pulp and paper mill wastewater in Malaysia, the wastewater had turbidity of 4,470 NTU. Under the optimal alum dosage of 1000 mg/L, turbidity reduction was found to be 99.8%. The optimal PACl dosage of 500 mg/L gave 99.9% reduction of turbidity (Ahmad, Wong, Teng, & Zuhari, 2008).

The raw water of a local reservoir in Singapore had the initial turbidity between 5.0 and 17.2 NTU. The 97% of turbidity could remove by alum dosage of 5 mg/L (Qin, Oo, Kekre, Knops, & Miler, 2006). The raw water of Sri-Trang reservoir in Hat Yai, Thailand had the UV-254 and DOC of 0.098 cm^{-1} and 4.3 mg/L, respectively. The optimal dosage of PACl at 20 mg/L could reduce UV-254 and DOC approximately 65 and 52% (Kueseng, Suksaroj, & Musikavong, 2011). The raw water from WTP in Turkey had the average of UV-254 and DOC of 0.0393 cm^{-1} and 3.5 mg/L. The optimal dosage of 80 mg/L of alum coagulation and a dosage of 80 mg/L of PACl coagulation reduced UV-254 by 69 and 58%, respectively. The 54% and 58% of DOC could be removed by 80 mg/L of alum coagulation and 80 mg/L of PACl coagulation, respectively (Ciner & Ozer, 2013). For the Danube river water source in Romania, the optimal a dosage of 75 mg/L of alum coagulation and a dosage of 30 mg/L of PACl coagulation reduced UV-254 to 75% and 95%, respectively (Pisol, 2011).

The reduction of organic matter and THMFP in reclaimed water from treated industrial estate wastewater in the northern Thailand by coagulation was studied. The average value of DOC and SUVA equaled 5.14 mg/L and 4.73 L/mg-m. DOC was reduced by alum and ferric chloride dosage of approximately 40 mg/L by 45 and 40%, respectively. SUVA was decreased by alum and ferric chloride dosage of approximately 20 mg/L by 80 and 35%, respectively (C. Musikavong et al., 2005)

The raw water located in U.S. and Canada had the average value of SUVA of 2.8 L/ mg-m. The 80 mg/L of alum could reduce SUVA approximately 42% (AWWA, 1993). The raw water of Hope Valley in South Australia used 20 mg/L of alum to reduce SUVA approximately 25%. The SUVA of raw water was 2.4 L/mg-m. The raw water of Myponga in South Australia had SUVA of 3.5 L/mg-m. They used 60 mg/L of alum to reduce SUVA by approximately 40% (Cook *et al*., 2009). DOM in raw water supply from reservoirs and canals as precursors to THMs formation was identified. Water samples were collected from two reservoirs, the U-Tapao canal (upstream and midstream) and the raw water supply in the rainy season and summer. In the reservoir and canal, aliphatic hydrocarbon and organic nitrogen were the major chemical. The optimal dosage of PACl coagulation was 40 mg/L at pH 7. It reduced UV-254 to 57% and DOC to 64% (C. Musikavong & Wattanachira, 2012). The coagulation for drinking water in USA was studied. DOC was reduced by 20 mg/L of PACl at pH 6.8 approximately 29% (Volk *et al*., 1999). The raw water from a local reservoir in Singapore had DOC between 3.27 and 7.45 mg/L. A dosage of 5 mg/L of alum at pH 5.8 was used to reduce DOC by approximately 45% in raw water in Singapore (Qin *et al*., 2005).

The surface raw water samples were collected from Harwood Reservoir. The average value of DON of water samples was 0.272 mg/L. The DON removal during water treatment by aluminum sulfate and cationic polymer coagulations was studied. The coagulation with aluminum sulfate removed equal or slightly lower amounts of DON when compared with DOC. The cationic polymer improved DON removal by an additional 15% to 20% over aluminum sulfate alone (Lee *et al*., 2006). Water samples were collected from Strickny located in Chicago, USA. Water sample had the value of DON between 1.1 and 1.2 mg/L. Effluent DON removal by enhanced coagulation and microfiltration were investigated. The coagulant dosages that achieved the maximum simultaneous removal were 1.5 Al(III)/initial DON-N. The percentages of DON reduction were 69% (Arnaldos & Pagila, 2010). A previous study investigated simultaneous color and DON removal from a sewage treatment plant effluent using alum coagulation of melanoidi. The initial value of DON equaled to 2.5 mg/L. An alum dose of 30 mg/L as aluminum was sufficient to reach maximum color removal at 75% and DON removal at 42% (Dwyer, Griffiths, & Lant, 2009).

2.8 DOM removal by enhanced coagulation with PAC

Removal of NOM in drinking water of Spain by adsorption and coagulation was investigated. The average value of DOC equaled to 5.0 mg/L. Maximum DOC removal of only coagulation treatment was 60%. Coagulation preceded by addition of PAC increased the removal of DOC up to 92% (Iriarte-Velasco, Chimeno-Alanis, Alvarez-Uriarte, & Gonzalez-Velasco, 2009). The Terkos Lake water in Turkey had average value of DOC of 4.41 mg/L. DBPs precursors was removed by enhanced coagulation and PAC adsorption. Enhanced coagulation using ferric chloride of 100 mg/L with PAC adsorption of 40 mg/L removed DOC to 76%. It was more effective than enhanced coagulation alone. The PAC adsorption kinetic had the contact time about 20-30 minutes for DOC adsorption to equilibrium. During in 30 minutes the low molecular weight was adsorbed to PAC (Uyak *et al*., 2006). However the high molecular weight of the NOM took much longer to diffuse and was adsorbed onto the carbon (Najm, Patania, J.G., & Krasner, 1994) The Western Australian WTP was investigated for enhanced coagulation using alum of 150 mg/L combined with PAC. It could remove NOM by 70% which led to reduce the formation of DBP by 80-95% (Kritiana *et al.*, 2011). The Tungkang River in Taiwan was investigated for the adsorption. The optimal alum coagulant for non purgeable dissolved organic carbon (NPOC) removal was 1-2 mg/L (approximately 40% reduction). The contact time for kinetic adsorption of 20 to 30 minutes was required. PAC dosage of 200 mg/L could remove the maximum NPOC by approximately 60% (Shen & Chung, 1998).

The water samples from wastewater treatment plant in USA had DON between 0.68-2.44 mg-N/L. The DON removal from wastewater effluent in USA by alum coagulation of 8 mg/L and PAC adsorption could be difficult. This is because wastewater effluent has SUVA that less than 2 L/mg-m (Chen, Kim, & Westerhoff, 2011). In 12 WTPs in Europe, the DON reduction by using combined process of powder activated carbon-ultrafiltration (PAC/UF) increased up to 45% (Tomaszewska & Mozia, 2002). Drinking water in China was surveyed. The combination of coagulation (10 mg/L of coagulant) and adsorption (1 g/L PAC) removed DON by approximately 82% from raw water of WTP in China (Liu, Gu, Yu, & Zhang, 2012). DON of 50-60% in wastewater was biodegradable during a activated sludge treatment. The advanced treatment of treated effluents achieved 72% of DON reduction (Parkin *et al*., 1981)

Drinking water supplies in Korea was investigated. The characteristic of source water had NDMA at 100 ng/L. Alum, ferric chloride and ferric sulfate coagulants could remove NDMA less than 10%.This is because NDMA on to particulate matter is minimal. At 10 mg/L PAC dose with a 4 h contact time, it could remove NDMA less than 5 % because of HPO interact between PAC and NDMA occurred. However longer time and high PAC dosage could remove NDMA approximately 50% (Chung et al., 2009). The effective of NDMA removal by PAC from wastewater effluents and wastewater influent in South Carolina was higher than that of surface water that not influenced by wastewater. Basic carbons (lower surface area) were higher removal of NDMA-FP than acidic carbons (higher surface area) (Sandi, 2014). The secondary effluent from wastewater treatment plant had NDMA-FP at 371 ng/L. Adsorptions of

NDMA precursors by PAC and GAC were examined. NDMA-FP was considered as a surrogate parameter for NDMA. PAC could reduce NDMA-FP by an approximately 37%-91%. GAC could reduce NDMA FP by an approximately 60%-90% (Hanigan et al., 2012).

Raw water supplies from U-tapao, Songkla province were surveyed. The initial value of DOC of water sample in rainy and summer season was 5.1 and 5.5 mg/L. The initial value of UV-254 of water sample in rainy and summer season equaled 0.414 and 0.159 cm^{-1}. In the rainy season, the 40 mg/L PACl and 80 mg/L PAC could remove UV-254 and DOC approximately 62 and 65%. In the summer season, the 40 mg/L PACl and 80 mg/L PAC could reduce UV-254 and DOC approximately 66 and 68% (Srimuang, Suksaroj, Suksaroj, & Musikavong, 2014). For the treatment of raw water supply from the Sri-Trang reservoir, Songkla province, 20 mg/L of PACl and 0.1 mg/L polymer combined with 10 mg/L PAC could reduce UV-254 and DOC by 74% and 71%, respectively. The UV-254 and DOC was 0.098 cm^{-1} and 4.3 mg/L (Kueseng et al., 2011). Water sample from a dam in Turkey was surveyed. The character of water sample had DOC at 2.48 mg/L. An alum of 80 mg/L combined with PAC and a dosage of 40 mg/L of PACl combined with PAC could reduce DOC approximately 50 and 50%(Kucukcongar & Sevimli, 2013).

The optimal condition of raw water supply in Sri-trang Resevior, Thailand for reduction of DOM was found at PACl 20 mg/L, PACl 20 mg/L and polymer 0.1 mg/L and PACl 20 mg/L with polymer 0.1 mg/L and PAC 10 mg/L, respectively. The initial value of DOC equaled to 4.3 mg/L. The results from this research showed that the coagulation could effectively remove more DOC of HPO than DOC of HPI. The PACl coagulation combined with polymer and PAC provided the highest level of DOC of HPI and DOC of HPO were 65% and 75%, respectively (Kueseng *et al*, 2011). A water treatment in Sweden used a enhanced coagulation and followed by adsorption with GAC. It could remove TOC and DOC by 80%. The fractionation of river and lake was showed that DOC of HPO was higher than DOC of HPI. Moreover DON is higher in HPI(Garcia, 2011) .

Raw water supplies from U-tapao, Songkla province were surveyed. The initial value of DOC water sample in rainy and summer season was 5.1 and 5.5 mg/L, respectively. In the rainy season, the coagulation with PACl reduced DOC of HPI and DOC of HPO at approximately 53% and 50%, respectively. The coagulation with PACl combined with PAC reduced DOC of HPI and DOC of HPO by approximately 63% and 58%, respectively. In the summer season, the coagulation with PACl reduced DOC of

HPI and DOC of HPO by 65% and 61%, respectively. The coagulation with PACl combined with PAC reduced DOC of HPI and DOC of HPO by 71% and 70%, respectively (Srimuang *et al*, 2014).

The water sample from Myponga Reservoir in Australia had turbidity, UV-254, DOC and SUVA at 1.95 NTU, 0.432 cm^{-1}, 11.7 mg/L and 3.7 L/mg-m, respectively. The magnetic ion exchange (MIEX) resin and 40 mg/L of PAC combined with 40 mg/L of alum could remove turbidity, UV-254, DOC and SUVA by approximately 93, 42, 92 and 79%, respectively (Fabris *et al*., 2007). In Australia, The feed water from the Myponga reservoir bloom had turbidity of 12-15 NTU, UV-254 of 0.469 cm^{-1}, DOC of 15.4 mg/L and SUVA of 3.05 L/mg-m. The aluminium sulfate of 4.4 mg/L combined with 20 mg/L PAC in membrane tank could reduce turbidity, UV-254, DOC and SUVA by approximately 87, 83, 63 and 53%, respectively (Dixon, Richard, Ho, Chow, & O’Neill, 2011)

CHAPTER 3

METHODOLOGY

3.1 Raw water sample

The Chao Phraya River is the main raw water source for producing tap water to serve the water consumers in Bangkok, Thailand. Raw water is pumped into a water canal that transports the water to 3 water treatment plants, namely the Samsen water treatment plant (WTP), the Thonburi WTP and the Bangkhen WTP. The Bangkhen WTP has a highest production capacity. A maximum capacity of 3,600,000 m^3 can be produced daily by the Bangkhen WTP to supply tap water to an approximate 6 million people.

The Tahjeen River is the main source of raw water supply of the Banglen WTP that located in Nakhonpathom province, Thailand. A maximum capacity of 440,000 m^3 of water supply can be served to an approximate 7 hundred thousand people. The water treatment process of the Bangkhen WTP and the Banglen WTP consists of coagulation, sedimentation, filtration, and chlorination. The alum and poly aluminum chloride (PACl) are used as coagulants. This work, therefore, selected alum and PACl as coagulants in experiments. The raw water supply of these 2 WTPs were considered as raw water supply samples for this research.

3.2 Sample collection and experimental procedure

Raw water supplies from the Bangkhen WTP and the Banglen WTP were collected one time. The water samples were collected on 30 September 2013 for the Bangkhen WTP. For the Banglen WTP, water samples were collected on 1 November 2013. Water samples for the analysis of the basic water quality such as alkalinity and turbidity and for the coagulation experiments were stored in a cold room at a controlled temperature of 4 ^{o}C until analysis. Samples for dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and *N*-nitrosodimethylamine formation potential (NDMA-FP) analyses were prepared by filtering through a Whatman GF/F (0.7 μm nominal pore size) filter that was pre-combusted at 550 ^{o}C for 2 h. These samples were stored in a cold room at a controlled temperature of 4 ^{o}C until analysis.

The experimental procedure was separated into 2 portions as can be seen in Figure 5. The first portion was the coagulation and adsorption experiments. Alum and PACl were used as coagulants in coagulation experiments. One optimal condition for coagulation was selected based on the reduction of DOC and DON. This coagulation condition at optimal condition then was used for 2 experiments: case (I) the coagulation combined with PAC adsorption and case (II) the coagulation and PAC adsorption. The second portion of raw water supply was analyzed for its ultraviolet adsorption at wavelength 254 nm (UV-254), DOC, specific ultraviolet adsorption (SUVA), ammonia (NH_3/NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), total dissolved nitrogen (TDN), DON, NDMA-FP. Raw water supplies were fractionated into hydrophobic organic fraction (HPO) and hydrophilic organic fraction (HPI). DOC, NH_3/NH_4^+, NO_2^-, NO_3^-, TDN and DON of HPO, and HPI were measured.

For the treated water, in case I, supernatants were collected after coagulation by PACl or alum combined with PAC after sedimentation time of 1 hour. In case II, supernatants after PACl or alum coagulation were collected. Thereafter, PAC was added into supernatant and stirred for conducting the adsorption experiment. The alkalinity, turbidity, UV-254, DOC, SUVA, NH_3/NH_4^+, NO_2^-, NO_3^-, TDN and DON of supernatant after coagulation (supernatant A), supernatant after coagulation combined with PAC (supernatant B) , and supernatant after coagulation and adsorption with PAC (supernatant C) were measured. NDMAFPs of raw water, supernatant A at optimal condition supernatant (turbidity < 1.2 NTU), supernatant B at optimal condition and supernatant C were analyzed. HPO and HPI of supernatant A at optimal condition, and supernatant B at optimal condition were measured for their DOC, NH_3/NH_4^+, NO_2^-, NO_3^-, TDN and DON. The results of the experiment in case II is showed in Appendix)

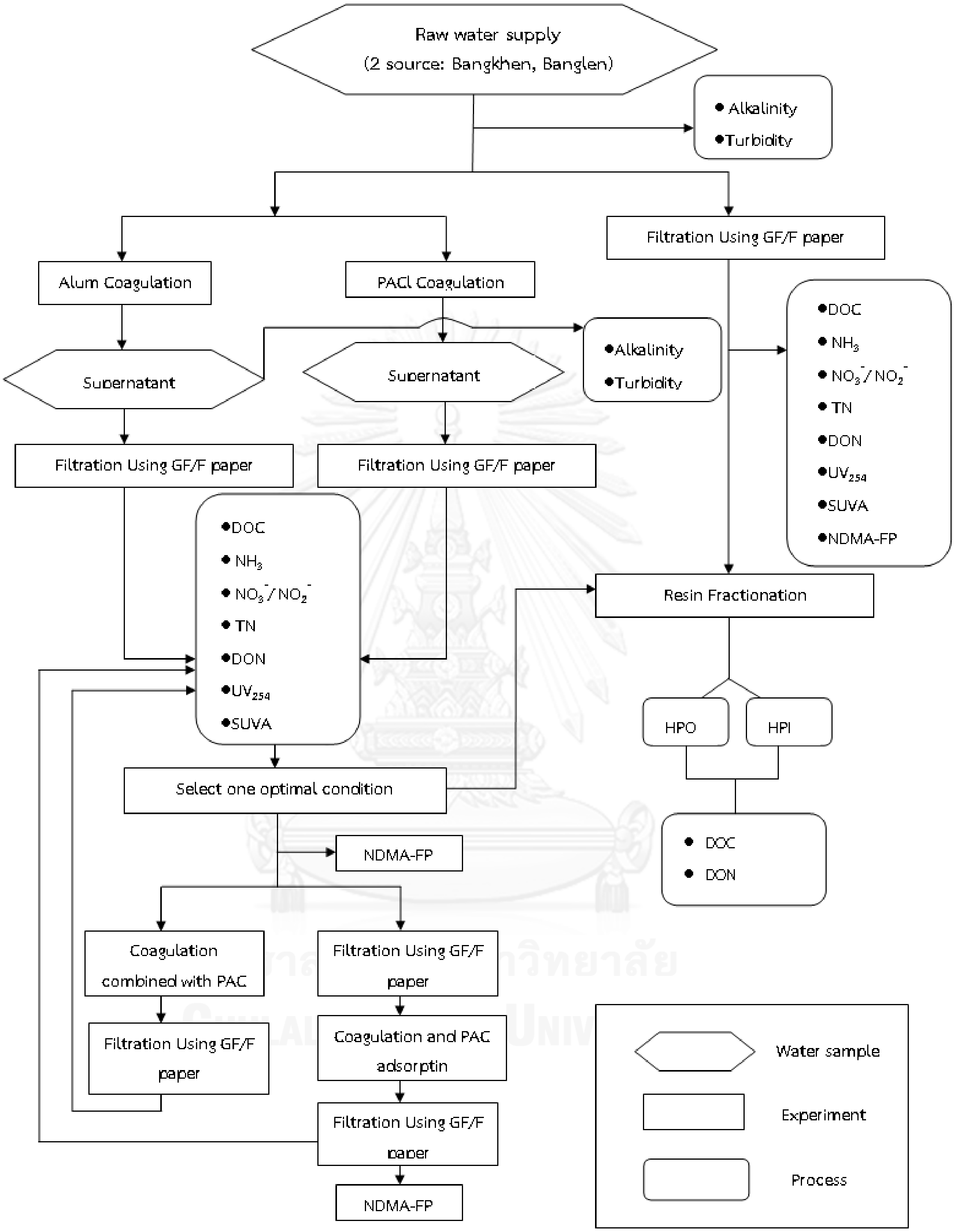

Figure 5 Research Framework

3.3 Resin fractionation procedure.

The fractionation experiment as shown in Figure 6 based on methods developed by Thurman *et al*., (1981) and Malcolm *et al*., (2003) was used in this study.

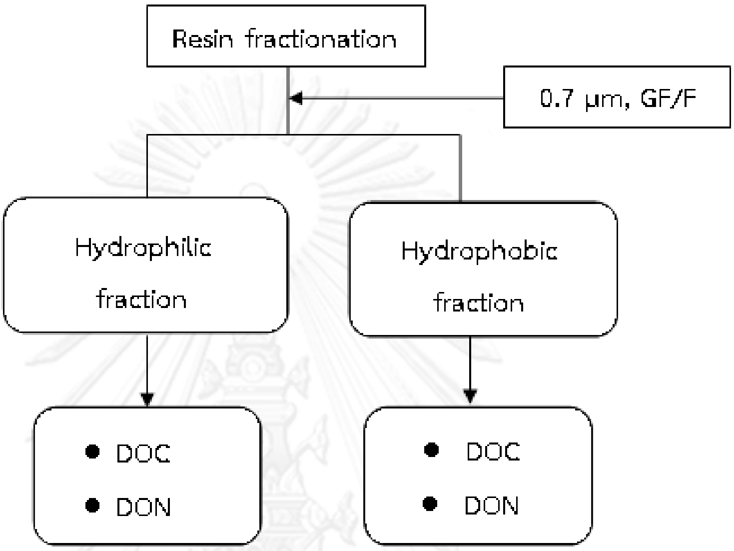

Figure 6 Fractionation procedure

3.3.1 DAX-8 resin preparation

The DAX-8 resin was refined by using 0.1 N NaOH and extracted by acetone for 24 hours. After that hexane and acetone were used for another 24 hours in the soxhlet extraction. The next step, the DAX-8 resin was washed by methanol and Milli-Q water. The refined DAX-8 resin was taken into columns in slurry of methanol. The packed resin was rinsed twice with 2.5 bed volume of 0.1 N NaOH and 0.1 N HCl and then with Mill-Q water until the conductivity and DOC of the effluent water was lower than 10 µs/cm and 0.2 mg/L, respectively (Thurman *et al*., 1981 and Malcolm *et al*., 2003).

3.3.2 Fractionation procedure

The pH of water sample was adjusted by H_2SO_4 to pH of 2 and then pumped into the DAX-8 resin column. DOC and DON was adsorbed on DAX-8 resin and eluted by base. Milli-Q water was replaced and discarded. The HPI was collected. The HPO was eluted with 0.25 bed volume of 0.1N NaOH and followed by 1.25 bed volume of 0.01 N NaOH. The pH of HPO and HPI was adjusted to neutral prior to being analyzed DOC and DON. HPO and HPI of raw water, supernatant at the optimal condition of coagulation, and the supernatant at optimal condition of coagulation combined with PAC was measured for their DOC, NH_3/NH_4^+, NO_2^-, NO_3^-, TN and DON.

3.4 Coagulation by jar test and adsorption

PACl and alum were used coagulants in the coagulation experiments. The variation of coagulant dosage from 10 to 250 mg/L was used. pH value was controlled at 7 by adding H_2SO_4 and NaOH 1.0 N . The alum and PACl was prepared by using a stock solution of the coagulants as shown in Table 6.

Table 6 Stock solution for dosage required.

Approximate dosage required, mg/L	Stock solution concentration, mg/L	1 mL added to 1 L sample equals
1-10 mg/l	1,000 mg/L	1 mg/L
10-50 mg/L	10,000 mg/L	10 mg/L
50-500 mg/L	100,000 mg/L	100 mg/L

PACl or alum was added in Mill-Q water in order to prepare a stock solution. Raw water of 1,000 mL was placed in breakers with stirring machine. The correct dosage of coagulant was added to each beaker. The jar test started stirring machine and operated at 100 rpm for 1 minute and reduced stirring speed to 30 rpm for 30 minute and stopped stirring for 60 minute. Allowed water samples to settle for 60 minutes. The supernatant was filtered through 0.7 µm, GF/F. It was pre-combusted at 550 ^{o}C. Water samples were analyzed for theirs DOC and DON. The optimal condition was selected from the best DOC and DON removal. The enhanced coagulation with PAC was performed under a coagulant dosage at optimal condition with variation of PAC dosages in order to determine the optimal PAC dosage. The supernatant at optimal condition of coagulation was used to conduct the adsorption experiment using one optimal PAC dosage from the previous experiment.

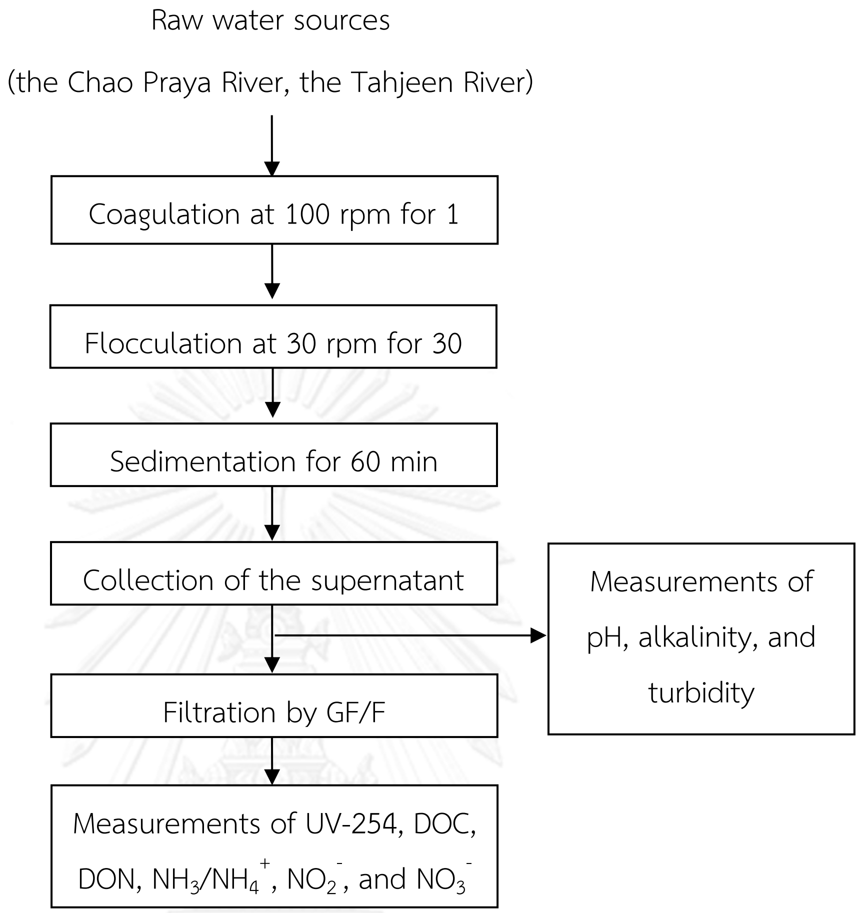

Figure 7 Jar test process

3.5 *N*-nitrosodimethylamine Formation Potential (NDMA FP) Analysis

- Water samples were collected and extracted in accordance with United State Environmental Protection Agency (US.EPA.) method EPA 521 solid phase extraction (US.EPA., 2004). All field samples must be dechlorinated with 80-100 mg of sodium thiosulfate per liter at time of collection. Sample stored in the lab must be held at 6°C and analyzed with 14 days after collection.

- N-nitrosodimethylamine ($NDMA_T$) is the total concentration of NDMA at anytime 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.

- NDMA-FP is the difference between the $NDMA_0$ and the $NDMA_7$. Figure 8 presents the formation potential test of a sample without free chlorine at the time of sampling. Figure 9 shows the formation potential test of a sample with free chlorine at the time of sampling.

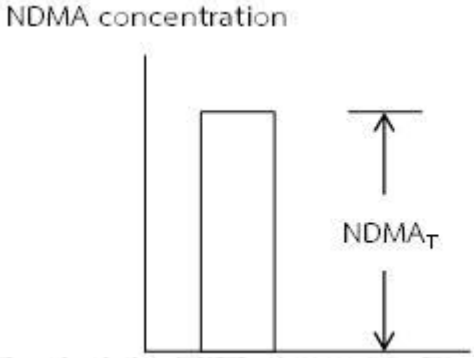

Figure 8 Definitions used in the formation potential test of a sample without free chlorine at the time of sampling

(Adapted from APHA, AWWA, and WPCF (1995))

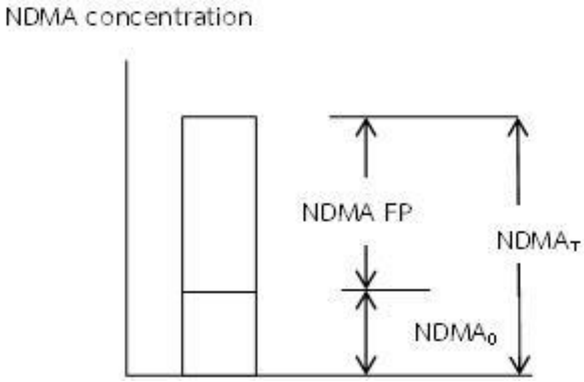

Figure 9 Definitions used in the formation potential test of a sample with free chlorine at the time of sampling

(Adapted from APHA, AWWA, and WPCF (1995))

The method of NDMA FP analysis is based on the THMFP analysis that was applied with the method developed by Mitch *et al.*, (2003) and Lee *et al.*, (2007).

3.5.1 NDMA Analysis

NDMA-FPs of raw water, supernatant at optimal condition of coagulation, and supernatant at optimal condition of enhanced coagulation with PAC was analyzed.

There were 3 analytical methods that were used to analyze NDMA and NDMAFP as summarized below:

The EPA Method 521 (US.EPA., 2004) that was used as the reference procedure was the first method for the NDMA analysis. It was modified to determine the NDMA in water samples by using 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). The condition for operating GC/NPD was presented in the following:

Inlet Condition

Mode: Splitless injections of 1 μL,

Injection port temperature: 220°C,

Initial temp: 40°C,

Pressure: 19.33 psi,

Split flow 60 mL/min,

Total flow: 64.8 mL/min

Gas type: Helium

Oven condition

The condition of temperature programs of oven adjusted for analyzing NDMA are shown in Table 7.

Table 7 temperature program for analyzing NDMA

Ramp	Rate (°C/min)	Temp (°C)	Time (min)	Remark
		40	0.00	Initial temp. 40°C
1	7	110	0.00	-
2	15	240	5.00	-

Detector condition

Temperature: 250°C,

Mode: Constant makes up flow: 30 mL/min,

Makeup Gas Type: Nitrogen

For development of the calibration curve, the external standard method was applied to make the calibration curve for this study. Standard solutions of each concentration for making the calibration curve was prepared in methylene chloride from the primary dilution standard solution or 200 mg/L stock standard solutions. The detection limited of GC/NPD was equal to 300 μg/L (4.02 μM). NDMA concentration of 400, 600, 800, and 1000 μg/L was prepared and injected to GC/NPD. The resulting calibration curve was shown in Appendix.

The free chlorine residual measurement was the second method**.** The pH of water samples was controlled at 7 ± 0.2 Chlorine and phosphate solutions were added into water samples. After that the adjusted water samples was incubated at 25±2 °C with 7 days reaction. After 7 days, water samples was analyzed for free chlorine residual according to Standard Method 4500-Cl G. (Colorimetric Method) (APHA, AWWA and WPCF, 1995).

The third method was for extraction of NDMA from the water sample. The NDMA extraction was performed using Resprep EPA 521 solid-phase extraction cartridges containing 2 grams of coconut activated carbon. in accordance with the EPA 521 method. 1000 mL of water sample was passed through a SPE cartridge. The cartridges were pre-conditioned with 3 mL methylene chloride, followed by 3 mL methanol and another 3 mL of methanol, respectively. 3 mL of reagent water was rinsed down the cartridges for 5 times. Then, water samples were passed through the cartridges at a flow rate of 10 mL/min under a vacuum condition. After sample extraction, air was drawn through the cartridge for 10 minutes. Finally, NDMA was eluted with methylene chloride and 1 mL of the extract was collected and preserved at -20 °C prior to injection into the GC/NPD. The extraction process was done in dark room in order to prevent the reaction of NDMA with the ultraviolet light.

When the solid-phase extraction cartridge was used, the percent recovery must be determined. Raw water supplies from a surface water source and DI water were used for determining the percent recovery of the extraction method in accordance with US.EPA. method EPA 521, The NDMA of 600, and 1000 ug/L were spiked into raw water supply and DI water samples. After that they were brought to perform the solid-phase extraction as described previously. For each water sample, the experiment was done in triplicates. After solid-phase extraction, NDMA in raw water supply and DI water were analyzed. The accuracy (percent recovery) and precision (RSD) of raw water supply were 55.4 percent and 11.9, respectively whereas that of DI water were 54.4 percent and 7,4, respectively. As stated previously, the detection limited of GC/NPD was 300 µg/L. By using the percent recovery of 55.4 percent and 1000 times for the concentrated of the sample, the detection limited of the methods therefore was 542 ng/L or 7.3 nM,

3.6 Analytical method and instrument

A pH meter was used to measure the pH of water samples and it was a direct measurement. Turbidity was measured by using a HACH 2100 turbidity meter. Water samples for analysis of NH_3/NH_4^+, NO_2^-, NO_3^- and TN was filtered by 0.7μm GF/F filter paper. Water samples for analysis of DOC and UV-254 was filtered by 0.7 μm GF/F filter paper, pre-combusted at 550 °C.

A titration technique was used to analyzed alkalinity in accordance with Standard Method 2320B (APHA, AWWA and WPCF, 1995). The Shimadzu TOC-V CSN/TOC Analyzer was used for measuring DOC in accordance with Standard Method 5310C: Combustion/non-dispersive infrared gas analysis Method (APHA, AWWA and WPCF, 1995). The TOC/TN Analyzer, multi N/C 3100, Analytic Jena AG, Germany, was used to analyze TN.

A DR 2700 Spectrophotometer was utilized to measure ammonia, nitrate and nitrite. Standard Method 8038, 8192, and 8507 (APHA, AWWA and WPCF, 1995) was used to analyze the ammonia, nitrate, and nitrite, respectively. A UV spectrophotometer was utilized to measure UV_{254} according to Standard Method 5910B: Ultraviolet Absorption Method (APHA, AWWA and WPCF, 1995). A colorimetric method (Standard method 4500-Cl G (APHA, AWWA and WPCF, 1995) was employed to analyzed free chlorine residual by Perkin-Elmer Model Lambda 25, UV/VIS spectrophotometer. At least duplicates of each measurement of DOC, DON and UV-254 were conducted.

The Formation of THMs and Other Disinfection By-Products and Liquid-Liquid Extraction Gas Chromatography Method (Standard method 5710 and 6232 B, respectively, APHA, AWWA and WPCF, 1995) and EPA method 521 was modified for analysis of NDMA-FP. The analytical instrument for NDMA analysis was Agilent 6890

Series with GC/NPD. The summary of analytical method, standard method and analytical instruments is shown in Table 8.

Table 8 Analytical method, standard method and analytical instruments.

Parameter	Analytical Method	Standard Method	Analytical instrument
pH	Direct Measurement	-	pH meter
Turbidity	Direct Measurement	-	HACH,2100 Turbidity meter
Alkalinity	Titration Method	Standard method 2320B	Titration
DOC	Combustion/non-dispersive infrared gas analysis Method	Standard method 5310C	Shimadzu TOC-V CSN/ TOC Analyzer
TN	Total bound Nitrogen (TNb) Method	-	TOC Analyzer, multi N/C 3100, Analytic Jena AG, Germany
NH_3/NH_4^+	Nessler Method	Method 8038	DR 2700 Spectrophotometer
NO_3^-	Cadmium Reduction Method	Method 8192	DR 2700 Spectrophotometer
NO_2^-	Diazotization Method	Method 8507	DR 2700 Spectrophotometer
UV-254	Ultraviolet Absorption Method	Standard method 5910B	UV Spectrophotometer
Free chlorine residual	Colorimetric Method	Standard method 4500-Cl G	Perkin-Elmer Model Lambda 25, UV/VIS spectrophotometer
$NDMA_0$/ $NDMA_7$	Formation of NDMA and Other Disinfection By-Products and Liquid-Liquid Extraction Gas Chromatography Method	US.EPA. method 5710 and 6232 B, EPA method 521 (US.EPA., 2004)	Agilent 6890 Series Gas Chromatography with NPD detector

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characteristics of the raw water supplies

Characteristics of the raw water supply of the Bangkhen WTP and the Banglen WTP are presented in **Table 9.** The pH of Bangkhen WTP and Banglen WTP closed to neutral. Alkalinities of 61 and 91 mg/L as $CaCO_3$ of raw water supplies of the Bangkhen WTP and Banglen WTP were detected, respectively. These values were suitable for coagulation. A slightly high turbidity of raw water of the Bangkhen WTP of 50 NTU was observed whereas a slightly low turbidity of 17 NTU was observed in raw water of the Banglen WTP.

The ultraviolet adsorption at wavelength 254 nm (UV-254), dissolved organic carbon (DOC), specific ultraviolet adsorption (SUVA) values of raw water of the Bangkhen WTP were 0.135 cm^{-1}, 4.2 mg/L and 3.2 L/mg-m, respectively. The UV_{254}, of 0.228 cm^{-1}, DOC of 7.3 mg/L and SUVA of 3.1 L/mg-m, were detected in raw water of the Banglen WTP, respectively. A characterization of the precursors to THM formation in the Bangkok water source was performed by Panyapinyopol, Marhaba, Kanokkantapong, and Pavasant (2005). A DOC concentration of about 4.8 mg/L was detected in the raw water of the Bangkhen WTP. The DOC in the raw water supply in this work was comparable to that of previous study. The SUVA value of raw water was higher than 3 L/mg-m. It could be stated that the nature of the DOM in the raw water supply allowed it to be easily removed by coagulation (Edzwald, 1993).

The concentrations of dissolved inorganic nitrogen (DIN) of raw water of the Bangkhen WTP were detected. The NH_3 concentration was 0.14 mg/L, The NO_2^- concentration was 0.006 mg/L.; and The NO_3^- concentration was 0.06 mg/L. The concentration of DON was found to be 0.24 mg-N/L. In the case of the Banglen WTP, the concentrations of DIN were detected by the NH_3 concentration of 0.48 mg/L; the NO_2^- concentration of 0.018 mg/L; and the NO_3^- concentration of 0.03 mg/L. The concentration of dissolved organic nitrogen (DON) was found to be 0.34 mg-N/L. Raw water supplies of the Bangkhen WTP and the Banglen WTP were contaminated with NDMA precursors. This is because DON was detected. This was indicating the need to find out a better way for removing DON from raw water supplies.

Table 9 Characteristics of raw water supplies of the Bangkhen WTP and Banglen WTP

Parameter	Bangkhen WTP	Banglen WTP
pH	7.3	7.3
Alkalinity (mg/L as $CaCO_3$)	61	91
Turbidity (NTU)	50	17
UV-254 (cm^{-1})	0.135	0.228
DOC (mg/L)	4.2	7.3
SUVA ($l\ mg^{-1}\ m^{-1}$)	3.2	3.1
NH_3/NH^+_4(mg/L)	0.14	0.48
NO_2^-(mg/L)	0.006	0.018
NO_3^-(mg/L)	0.06	0.03
DON(mg/L)	0.24	0.34
DOC/DON	18	21

The formation potential of N-DBPs in the disinfection process could be determined by the DOC/DON ratio (Doton *et al*., 2009). A high DOC/DON value has a much smaller propensity to form N-DBPs than a low DOC/DON value. DOC/DON of Bangkhen WTP and Banglen WTP were 18 and 21, respectively. According to these results, DOC/DON of the raw water of Banglen WTP was higher than that of Bangkhen WTP.

4.2 Coagulation experiments by alum and PACl

4.2.1 Turbidity removal by alum and PACl coagulation

Turbidity is used as a general indicator for determining the quality of a produced water supply. For the coagulation of raw water of the Bangkhen and Banglen WTP, residual turbidity and percentage of turbidity removal is presented in **Figure 10**. The alum dosage of 10 mg/L could reduce turbidity from 50 to 21 NTU, a reduction of 57%. Turbidity was gradually decreased from 21 to 2 NTU when the alum dosage was increased from 20 to 80 mg/L. An alum dosage of 100 mg/L could reduce turbidity to 1 NTU, a reduction of 98%. The PACl dosage of 20 mg/L could reduce turbidity from 50 to 0.4 NTU, a reduction of 99%. Any further increase in the PACl dosage (above 40 mg/L) did not provide better turbidity reduction. According to the drinking water standard of Thailand, turbidity must less than 5 NTU. The alum of 60 mg/L and PACl of 20 mg/L had the capacity to reduce the turbidity to meet standard.

The alum dosage of 10 mg/L could reduce turbidity in raw water of the Banglen WTP from 50 to 21 NTU, a reduction of 57%. Turbidity was gradually decreased from 17 to 6 NTU when the alum dosage was increased from 20 to 80 mg/L. The alum dosage of 100 mg/L could reduce turbidity to lower than 1 NTU, a reduction of 96 to 97%. The PACl dosage of 60 mg/L could reduce turbidity from 17 to 0.7 NTU, a reduction of 96%. The percentage of turbidity removal was not any different as a reduction 96 to 98 %, when the PACl dosage was increased from 80 to 100 mg/L. From this experiment, the alum dosage of 60 mg/L and PACl dosage of 10 mg/L could reduce turbidity in coagulated water to meet standard. The reduction of turbidity by PACl was better than that of alum in two raw water sources.

The turbidity of raw water comes from multiple factors such as amount of clay, silt, organic matter and inorganic matter. This could lead to the different in turbidity of water and the reduction of turbidity by the coagulation. The turbidity of raw water of the Bangkhen WTP was higher than that of the Banglen WTP. For the Bangkhen WTP, alum of 100 mg/L or PACl of 20 mg/L could reduce turbidity to lower than standard. In the case of the Banglen WTP, to reduce the turbidity to meet standard, alum of 80 mg/L or PACl of 60 mg/L were required. The best reduction of turbidity from raw water of the Bangkhen WTP and Banglen WTP could be obtained by using PACl of 20 and 60 mg/L, respectively. Considering the mechanism of turbidity reduction, there are two mechanisms involved in a turbidity reduction. The first one is a charge neutralization of negatively charge of colloidal particles by adsorption onto positively charge of coagulants species. The second one is a precipitation of colloids in term of $Al(OH)_3$ solids (Pertnisky and Edzwald et al., 2006).

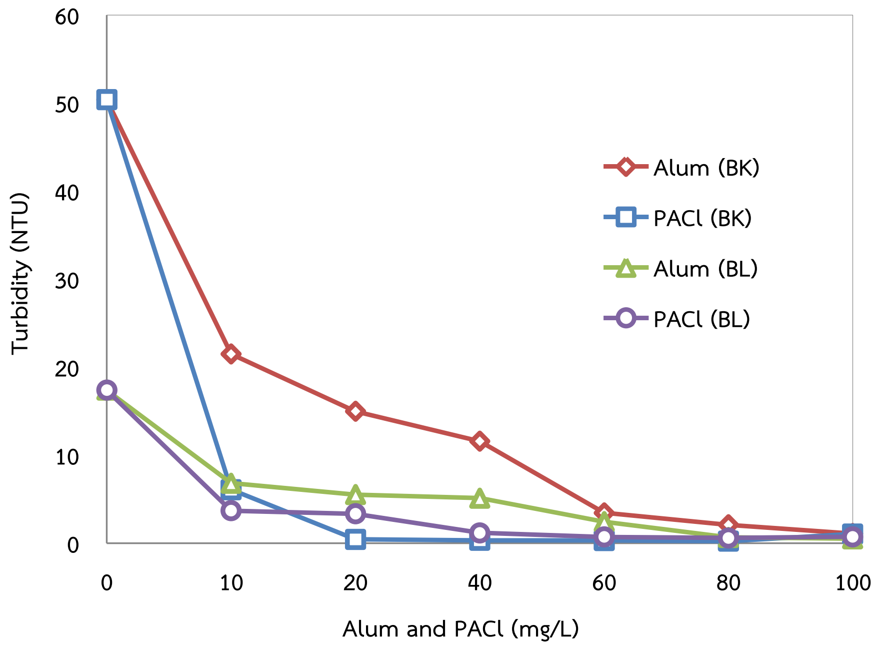

Figure 10 Residual turbidity after coagulation of raw water supply of the Bangkhen WTP and the Banglen WTP

The water from reservoir of the Tanggu WTP at northern China had the turbidity of 5.12 NTU. The alum dosage of 100 mg/L at pH 5-6.5 could remove turbidity by 97% (Matilainen *et al*., 2010). The reclaimed water from treated industrial estate wastewater in the northern Thailand had the average of turbidity at 17.7 NTU. The alum dosage of 80 mg/L at uncontrolled pH could remove the maximum turbidity approximately 97% (Musikavong *et al*., 2005). For the treatment of pulp and paper mill wastewater in Malaysia, the wastewater had turbidity of 4,470 NTU. Under the optimal alum dosage of 1000 mg/L, turbidity reduction was found to be 99.8%. The optimal PACl dosage of 500 mg/L gave 99.9% reduction of turbidity (Ahmad *et al*., 2008). The raw water of a local reservoir in Singapore had the turbidity between 5.0 and 17.2 NTU. The 97% of turbidity could be removed by alum dosage of 5 mg/L (Qin *et al*., 2006). In this work, the turbidity of raw water of the Bankhen WTP and Banglen WTP was 50.4 and 17.4 NTU. Under the optimal condition, the effective of alum and PACl coagulation could reduce turbidity by approximately 96-98%.

4.2.2 UV-254, DOC, SUVA and DON reduction by the alum and PACl coagulation of the Bangkhen WTP

UV-254 is parameter for identifying the aromatic content included humic and fulvic material in water (AWWA Research Foundation, 2002). As can be seen in **Figure 11.** For the Bangkhen WTP, the alum dosage of 80 mg/L could reduce UV-254 from 0.135 to 0.050 cm^{-1}, a reduction of 63%. UV-254 was slightly increased from 0.050 to 0.059 cm^{-1} when the alum dosage was increased from 80 to 100 mg/L. A PACl dosage of 10 mg/L gradually reduced UV-254. An increase in the PACl dosage from 10 to 80 mg/L gradually increased the reduction of UV-254. The UV-254 value was reduced from 0.079 cm^{-1} to 0.035 cm^{-1}. A PACl dosage of 80 mg/L provided the best reduction of UV-254 by 74%. This is because when the PACl dosage was increased from 80 to 100 mg/L, UV-254 was slightly increased from 0.035 to 0.046 cm^{-1}. The PACl coagulation provided the best performance capability on the reduction of UV-254 when compared with alum coagulation.

DOC is the parameter that represents the level of aromatic and aliphatic organic matter in the water. A reduction of the DOC, therefore, represents the reduction of both aromatic and aliphatic organic matter in water. With the alum coagulation of raw water of the Bangkhen WTP, DOC gradually decreased from 4.2 mg/L to 2.8 mg/L; an alum dosage of 80 mg/L provided the best reduction (approximately 33%). An increase in the alum dosage up to 100 mg/L resulted in slight increases in DOC (**Figure 11**). When PACl was used, DOC gradually decreased from 4.2 mg/L to 2.4 mg/L; a PACl dosage of 80 mg/L provided the best reduction (42%). When the amount of PACl was increased to 100 mg/L, a slight increase in DOC occurred. The PACl coagulation was more effective than alum coagulation in removing DOC. The best reduction of aliphatic and aromatic organic matter in the raw water supply of the Bangkhen WTP was obtained at a PACl dosage of 80 mg/L under a controlled pH of 7.

SUVA represents the ratio of aromatic organic matter to total organic matter in water. The reduciton of SUVA could provide better understanding on the removal of aromatic organic versus the removal of total organic matter. The SUVA value also could be used as an indicator to select the treatment process. Water that contain low SUVA value is not suitable for the coagulation process.

As can be seen in **Figure 11,** an alum dosage of 10 mg/L could slightly reduce SUVA from the raw water of the Bangkhen WTP. SUVA was decreased from 3.2 L/mg-m to 1.5 L/mg-m when the alum dosage was increased from 10 to 60 mg/L (approximately a 47 % reduction). Increasing the alum dosage up to 100 mg/L resulted in slight reductions in SUVA. The PACl dosage of 10 mg/L could slightly reduce SUVA. An increase in the PACl dosage from 20 to 80 mg/L gradually increased the reduction of SUVA. This is because SUVA values were reduced from 3.2 L/mg-m to 1.4 L/mg-m, A PACl dosage of 80 mg/L yielded the best reduction of SUVA by, 55%. The performance capability of the PACl coagulation on the reduction of SUVA was moderately higher than that of the alum coagulation.

DON is the primary NDMA precursor. The reduction of DON of Bangkhen WTP, therefore, could be used to represent the potential reduction of the formation of nitrosamine in a water supply. Considering alum coagulation, DON was decreased from 0.25 to 0.14 mg-N/L; an alum dosage of 80 mg/L provided the best result of DON reduction (approximately a 43% reduction). Increasing the alum dosage up to 100 mg/L did not increase DON reduction (**Figure 11**). When PACl was used, DON gradually decreased from 0.25 mg-N/L to 0.14 mg-N/L; a PACl dosage of 80 mg/L provided the best result of reduction of DON by 41%. Increasing the PACl dosage up to 100 mg/L did not increase the reduction of DON. The best removal of NDMA precursors in the raw water supply of the Bangkhen-WTP was obtained at a PACl and alum dosage of 80 mg/L under a controlled pH of 7. The comparison of coagulants dosages for removal contaminants from water should be done in term of the coagulant equivalent dosage. Alum and PACl contained Al that provided the positive charge for the coagulation mechanism. By determining the amount of aluminum ion in alum [$Al_2(SO_4)_3 18H_2O$] and PACl [$Al_2(OH)_3Cl_3$], 10 mg/L of PACl is equivalent to 32.5 mg/L of alum. It can be stated that by using the same amount of PACl and alum, PACl had high amount of positive charges for the coagulation mechanism. The best performance capability on DOC, UV-254, SUVA, and DON reductions could be obtained by using PACl in the coagulation when compared with alum.

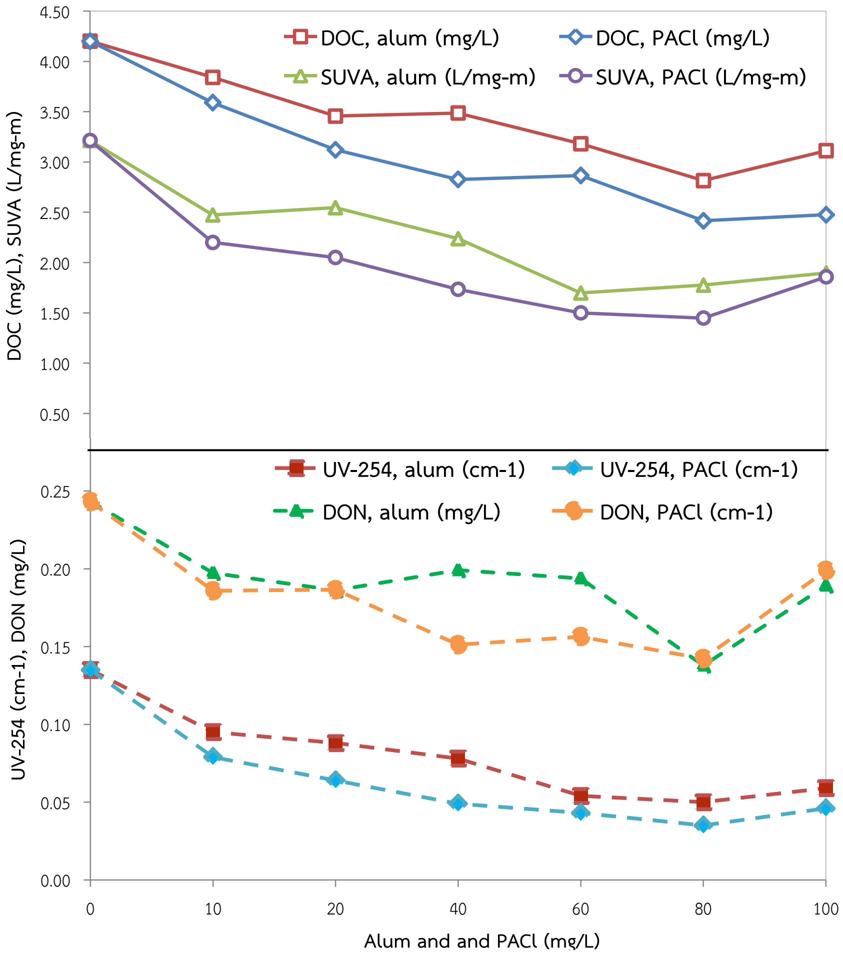

Figure 11 Residual UV-254, DON, DOC, and SUVA after coagulation of raw water supply of the Bangkhen WTP

4.2.3 UV-254, DOC, SUVA and DON reduction by the alum and PACl coagulation of the Banglen WTP

With an alum coagulation of raw water of the Banglen WTP, UV-254 gradually decreased from 0.228 cm^{-1} to 0.098 cm^{-1} by increasing alum dosage from 10 to 150 mg/L. Alum dosages of 200 and 250 mg/L provided the reduction of UV-254 of an approximately 57% (**Figure 12**). With PACl coagulation, UV-254 gradually decreased from 0.228 cm^{-1} to 0.081 cm^{-1}; when PACl dosage was increased from 10 to 150 mg/L. A PACl dosage of 150 mg/L provided the best reduction of UV-254 (approximately 64%). An increase in the PACl dosage up to 250 mg/L resulted in slight increase in UV-254.

DOC gradually decreased from 7.3 mg/L to 5.1 mg/L by increasing alum dosage from 10 to 250 mg/L. An alum dosage of 150 mg/L provided the best reduction of DOC (approximately 30%). An increase in the alum dosage up to 200 to 250 mg/L resulted in slight increas in DOC (**Figure 12**). For the PACl coagulation, DOC gradually decreased from 7.3 mg/L to 4.5 mg/L when PACl dosage was increased from 10 to 250 mg/L. A PACl dosage of 150 mg/L provided the best reduction of DOC (approximately 38%). An increase in the PACl dosage up to 250 mg/L resulted in a slight decreased in DOC. The PACl coagulation was more effective than alum coagulation in removing DOC. The best reduction of DOC removing of the Banglen WTP was obtained at a PACl dosage of 150 mg/L under a controlled pH of 7.

Figure 12 shows the result off SUVA of raw water of the Banglen WTP and percentage of SUVA reduction**.** SUVA was decreased from 3.1 L/mg-m to 1.9 L/mg-m when the alum dosage was increased from 10 to 250 mg/L (approximately a 38 % reduction). The PACl dosage of 10 mg/L slightly reduced SUVA. An increase in the PACl dosage from 20 to 150 mg/L gradually increased the reduction of SUVA value from 3.1 L/mg-m to 1.8 L/mg-m. A PACl dosage of 150 mg/L provided the best reduction of SUVA, 43%. A PACl of 150 mg/L had capacity to reduce SUVA higher than that of an alum of 250 mg/L.

DON was decreased from 0.34 to 0.17 mg-N/L when alum dosage was increased from 10 to 250 mg/L. An alum dosage of 250 mg/L provided the best result (approximately a 50% reduction). When PACl was used, DON gradually decreased from 0.34 mg-N/L to 0.17 mg-N/L, when PACl dosage was increased from 10 to 250 mg/L. A PACl dosage of 150 mg/L provided the best result, a reduction of DON of 51%. Increasing the PACl dosage up to 200 to 250 mg/L resulted in slightly increased DON levels. The capacity of DON reduction by PACl was higher than that of alum. The best removal of NDMA precursors in the raw water supply of the Banglen-WTP was obtained under a PACl dosage of 150 mg/L at a controlled pH of 7.

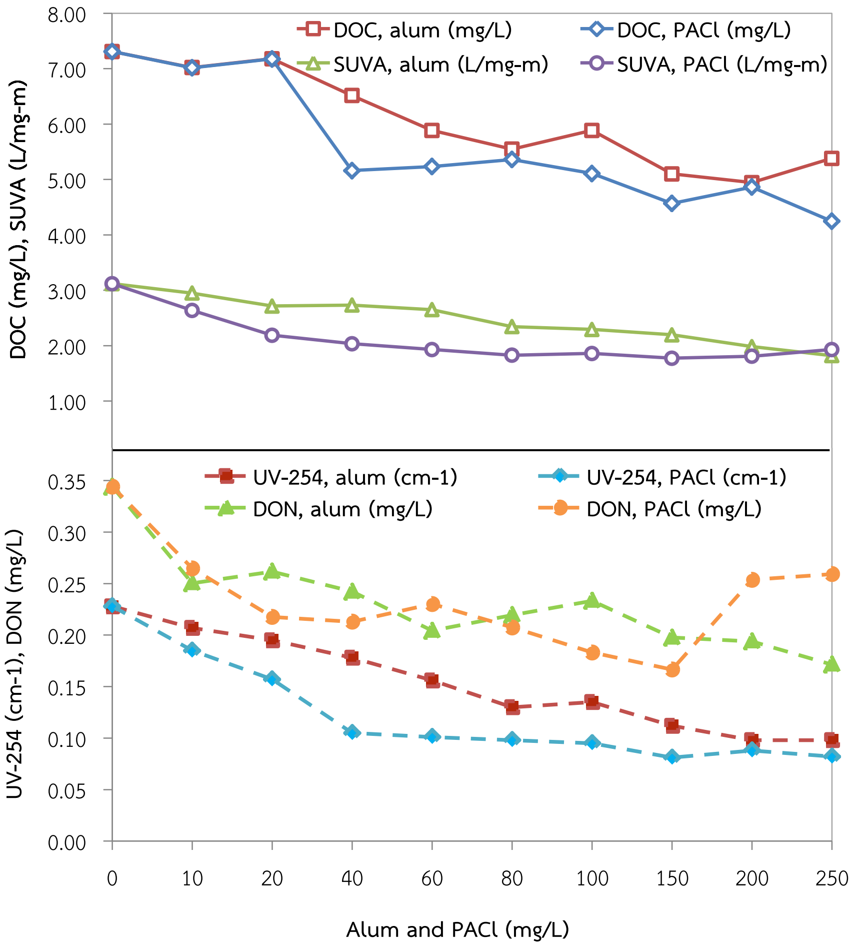

Figure 12 Residual UV-254, DON, DOC and SUVA after coagulation of raw water supply of the Banglen WTP

UV-254 measures aromatic that contain in the raw water. A low UV-254 means the less formation of chlorination by-products (Garcia *et al*., 2011). UV-254 of coagulated water at alum dosage of 80 mg/L and PACl dosage of 80 mg/L of the Bangkhen WTP were 0.050 cm^{-1} and 0.035 cm^{-1}, respectively. For the Banglen WTP, UV-254 of coagulated water at alum dosage of 150 mg/L and PACl dosage of 150 mg/L of Banglen WTP were 0.112 cm^{-1} and 0.081 cm^{-1}, respectively. From these results, it may imply that the UV-254 reduction by the PACl coagulation had the less chance in formation of chlorination by-products in both of water sources.

Water samples were collected from two reservoirs, the U-Tapao canal (upstream and midstream locations) and the raw water supply in the rainy season and summer. In the reservoir and canal, aliphatic hydrocarbon and organic nitrogen were the major chemical. The optimal point of PACl coagulation was a dosage of 40 mg/L at pH 7 that reduced UV-254 to 57% (Musikavong *et al*., 2013). For the treatment of raw water supply from the Sri-Trang reservoir, Songkla province, Thailand. The raw water supply had the UV-254 of 0.098 cm^{-1}. The optimal at 20 mg/L of PACl could reduce UV-254 approximately 65 % (Kueseng *et al*., 2011). The raw water from WTP in Turkey had the average of UV-254 of 0.0393 cm^{-1}. The optimal point of a dosage of 80 mg/L of alum coagulation and a dosage of 80 mg/L of PACl coagulation reduced UV-254 to 69% and 58%, respectively (Ciner & Ozer, 2013).

For Danube river water source in Romania, the optimal point of a dosage of 75 mg/L of alum coagulation and a dosage of 30 mg/L of PACl coagulation reduced UV-254 to 75% and 75%, respectively (Pisol, 2011). From this work, the Bangkhen WTP had the initial value of UV-254 of raw water of 0.135 cm^{-1}. The optimal condition of a dosage of 80 mg/L of PACl coagulation reduced UV-254 to 74%. The raw water of the Banglen WTP had the initial value of UV-254 of 0.228 cm^{-1}. The optimal condition of a dosage of 150 mg/L of PACl coagulation reduced DOC by 64%.

DOC represents the organic matter in raw water and is humic type (Hepplewhite, Newcombe, & Knappe, 2004). Under the optimal condition, the DOC in raw water of the Bangkhen WTP was reduced by 42% to the value of 2.4 mg/L. The DOC in raw water of the Banglen WTP was reduced by 38% to the values of 4,6 mg/L. It can be stated that the nature of DOM in raw water of the Bangkhen WTP was easily removed by that of the Banglen WTP when using the alum and PACl as coagulants.

NOM is removed by a combination of charge neutralization, entrapment, adsorption and complexation with coagulant metal ions into insoluble particle(Jarvis, Jefferson, & Parsons, 2004). The removal mechanism is different for specific types of NOM molecules. The different mechanism can be classified into three types: the mononuclear, medium polynuclear and precipitated/colloidal species (Duan *et al*., 2003). However a high ability to remove DOC is medium polymer or monomer species(Yan, Wang, Qu, Ni, & Chow, 2008).

The reduction of organic matter and THMFP in reclaimed water from treated industrial estate wastewater in the northern Thailand by coagulation was studied. The average value of DOC equal 5.14 mg/L. DOC were reduced by alum and ferric chloride dosage of approximately 40 mg/L by 45 and 40%, respectively (Musikavong *et al*., 2005). DOC was reduced by 20 mg/L of PACl at pH 6.8 approximately 29% for the drinking water in USA (Volk et al., 2000). The water sample from U-Tapao canal and the raw water supply in the rainy season and summer were studied. The optimal point of PACl coagulation was a dosage of 40 mg/L at pH 7 that reduced DOC to 64%

(Musikavong *et al*., 2013). The treatment of raw water supply from the Sri-Trang reservoir, Songkla province had DOC of 4.3 mg/L. The optimal at 20 mg/L dosage of PACl could reduce DOC by approximately 52% (Kueseng *et al*., 2011). The raw water from WTP in Turkey had the average DOC of 3.5 mg/L. The optimal point of a dosage of 80 mg/L of alum coagulation and a dosage of 80 mg/L of PACl coagulation reduced DOC to 54 and 58%, respectively (Ciner *et al*., 2013). From this research, the DOC of raw water of the Bangkhen WTP was 4.2 mg/L. The optimal condition of a dosage of 80 mg/L of PACl coagulation reduced DOC to 42%. The DOC of raw water of the Banglen WTP was 7.3 mg/L. The optimal condition of a dosage of 150 mg/L of PACl coagulation reduced DOC to 38%. This research used high amounts of coagulant when compared with the previous woks but the high percent reduction of DOM could be obtained. .

SUVA is a parameter that used for the measurement of aromatic content of NOM in relation in coagulation process. SUVA was lower than 2 L/mg-m that indicate the mostly organic matter of low molecular weight, hydrophilic and less reactive with chlorine. When SUVA between 2 and 4 L/mg-m it indicate a mixture of aquatic humic of NOM and combination of hydrophobic and hydrophilic substance of low and high molecular weight with more reactive with chlorine. The SUVA higher than 4 L/mg-m was showed mostly aquatic humics, high hydrophobicity and high molecular weight (Garcia *et al*., 2011). The residual SUVA of coagulated water at optimal point of the Bangkhen WTP was 1.4 mg/L. The residual SUVA of coagulated water at optimal point of the Banglen WTP was 1.8. The residual of SUVA of coagulated waters implied that the composition of NOM in coagulated water consisted of mostly non-humic substances, low molecular weight, hydrophilic and less reactive with chlorine.

The treated industrial estate wastewater in the northern Thailand had the average of SUVA equaled to 4.7 L/mg-m. SUVA was decreased by alum and ferric chloride dosage of approximately 20 mg/L by 80 and 35%, respectively (Musikavong *et al*., 2005). The raw water located in U.S. and Canada had the average value of SUVA of 2.8 L/ mg-m. The 80 mg/L of alum could reduce SUVA approximately 42% (AWWA Research Foundation, 1999). The raw water of Hope Valley in South Australia used 20 mg/L of alum to reduce SUVA by approximately 25% from by the initial SUVA of raw water of 2.4 L/mg-m. The raw water of Myponga in South Australia had SUVA of 3.5 L/mg-m. They used 60 mg/L of alum to reduce SUVA approximately 40% (Cook *et al*., 2009). For this research, the raw water of the Bangkhen WTP had the optimal condition at dosage of 80 mg/L of PACl coagulation. Under such condition, it could reduce SUVA to 55% from the SUVA value of 3.2 L/mg-m. The raw water of the Banglen WTP had the optimal condition at a dosage of 150 mg/L of PACl coagulation for reducing SUVA to 43% from the initial SUVA of 3.1 L/mg-m.

DON is the parameter that implies about the formation of nitrosamine, halonitromethanes, cyanogen-halides, haloacetroniles and other compounds. These N-CBPs formed when organic matter reacts with chlorine or chloramines. The formation potential of N-DBPs in the disinfection process could be determined by the DOC/DON ratio. A high DOC/DON value has a much smaller propensity to form N-DBPs than a low DOC/DON value (Dotson *et al*., 2009). DOC/DON of coagulated water at optimal of the Bangkhen WTP and the Banglen WTP were 17 and 33. These mean that the coagulated water at optimal point of the Banglen WTP had a much smaller propensity to form N-DBPs than that of the Bangkhen WTP.

The surface raw water samples were collected from Harwood Reservoir. The average value DON of water samples was 0.272 mg/L. Coagulation with aluminum sulfate removed equal or slightly lower amounts of DON. The cationic polymer improved DON removal by an additional 15% to 20% over aluminum sulfate alone (Lee *et al*., 2006). Water samples were collected from Strickny located in Chicago, USA. Water sample had the initial value of DON between 1.1-1.2 mg N/L. DON removal by enhanced coagulation and microfiltration could remove by approximately 69% (Arnaldos *et al*., 2010). A previous study investigated simultaneous color and DON removal from a sewage treatment plant effluent using alum coagulation of melanoidi. The DON equaled to 2.5 mg N/L. An alum dose of 30 mg/L as aluminum was sufficient to reach maximum color removal at 75% and DON removal at 42%(Dwyer et al., 2009). For this work, the Bangkhen WTP had the optimal coagulation condition at a dosage of 80 mg/L of PACl. It could reduce DON to 43%. The Banglen WTP had the optimal coagulation condition at a dosage of 150 mg/L PACl which could reduce DON to 50%. The reduction of DON by alum and PACl coagulation in this work was between 40 and 50% and was comparable to the result of DON reduction from the previous works.

For the experiment of enhanced coagulation, the optimal condition for each water source was selected from results of this section. Reductions of DOC and DON were the major indicators for selection of optimal condition. The best reduction of aliphatic and aromatic organic matter and NDMA precursors in the raw water supply of the Bangkhen WTP was obtained at a PACl dosage of 80 mg/L under a controlled pH of 7. The best reduction of DOC and DON in raw water supply of the Banglen WTP was obtained at a PACl dosage of 150 mg/L under a controlled pH of 7.

4.3 Characteristics of coagulated waters at the optimal condition

Characteristics of coagulated water at the optimal condition are presented in **Table 10**. pH of 7 was detected. This is because it was controlled during the coagulation. Alkalinity of 48 mg/L as $CaCO_3$ of coagulated water of the Bangkhen WTP at optimal condition was decreased from 61 mg/L as $CaCO_3$. For the coagulated water of Banglen WTP at optimal condition, alkalinity was decreased from 91 to 73 mg/L as $CaCO_3$. Turbidities of coagulated water of Bangkhen WTP of 0.24 NTU and of Banglen WTP of 0.75 NTU were lower than that of drinking water standard of Thailand of 5 NTU.

For the Bangkhen WTP, the UV-254, DOC, SUVA values of coagulated water of were 0.035 cm^{-1}, 2.8 mg/L and 1.2 L/mg-m, respectively. The percentage of UV-254, DOC and SUVA reduction at optimal condition were 74, 42 and 55 %, respectively. In the case of Banglen WTP, at optimal condition, UV-254 of 0.091 cm^{-1}, DOC of 4.5 mg/L, SUVA of 2.0 L/mg-m were found. The percentage of UV-254, DOC, and SUVA removal under optimal condition were 64, 38 and 43 %, respectively.

The NH_3, NO_2^-, and NO_3^- of coagulated water under the optimal condition of the Bangkhen WTP were 0.04, 0.005, 0.05 mg/l. respectively. The DON of 0.14 mg N/L was obtained in this water. For the coagulated water of the Banglen WTP under the optimal condition, The NH_3 of 0.16 mg/L, NO_2^- of 0.016 mg/L, and NO_3^- of 0.04 mg/L were detected. The DON of 0.17 mg N/L was obtained in this water.

According to study of Doton *et al*., (2009), the high DOC/DON ratio has a much smaller propensity to form N-DBPs than a low DOC/DON value. Under optimal condition, DOC/DON of Bangkhen WTP and Banglen WTP were 17 and 27, respectively. This could be indicated that after coagulation process the coagulated water of the Banglen WTP had high potential to create the N-DBPs than that of the Bangkhen WTP.

Table 10 Characteristics of coagulated water of the Bangkhen WTP and Banglen WTP at optimal condition

Parameter	**Coagulated water at optimal condition**	
	Bangkhen WTP[1]	Banglen[2]
pH	6.9	7.1
Alkalinity (mg/L as $CaCO_3$)	48	73
Turbidity (NTU)	0.24	0.35
UV-254 (m^{-1})	0.035	0.081
DOC (mg/L)	2.4	4.6
SUVA ($l\ mg^{-1}\ m^{-1}$)	1.4	1.8
NH_3/NH^+_4(mg/L)	0.04	0.16
NO_2^-(mg/L)	0.006	0.016
NO_3^-(mg/L)	0.06	0.04
DON(mg/L)	0.14	0.17
DOC/DON	17	33

[1] PACl dosage of 80 mg/L and pH 7, [2] PACl dosage of 150 mg/L and pH 7

4.4 Enhanced coagulation

4.4.1 Turbidity reduction by enhanced coagulation

The result of turbidity reduction by enhanced coagulation of the Bangkhen WTP is presented in **Figure 13**. PACl dosage of 80 mg/L with the powder activated carbon (PAC) dosage of 10 mg/L could reduce turbidity from 50 to 0.20 NTU, a reduction of 99.6%. Turbidity was decreased from 0.18 to 0.16 NTU when the PAC dosage was increased from 20 to 100 mg/L, a reduction of 33%.

The results of removal by enhanced coagulation of the Banglen WTP are showed in Figure 13. The PACl dosage of 150 mg/L with the PAC dosage of 10 mg/L could reduce turbidity from 17 to 0.64 NTU, a reduction of 96.2%. Turbidity was decreased from 0.59 to 0.56 NTU when the PAC dosage was increased from 20 to 250 mg/L.

Although the initial value of turbidity of two raw water sources was different but the results from enhanced coagulation combined with PAC were not significantly different and be very well in turbidity removal (approximately 96-99%).

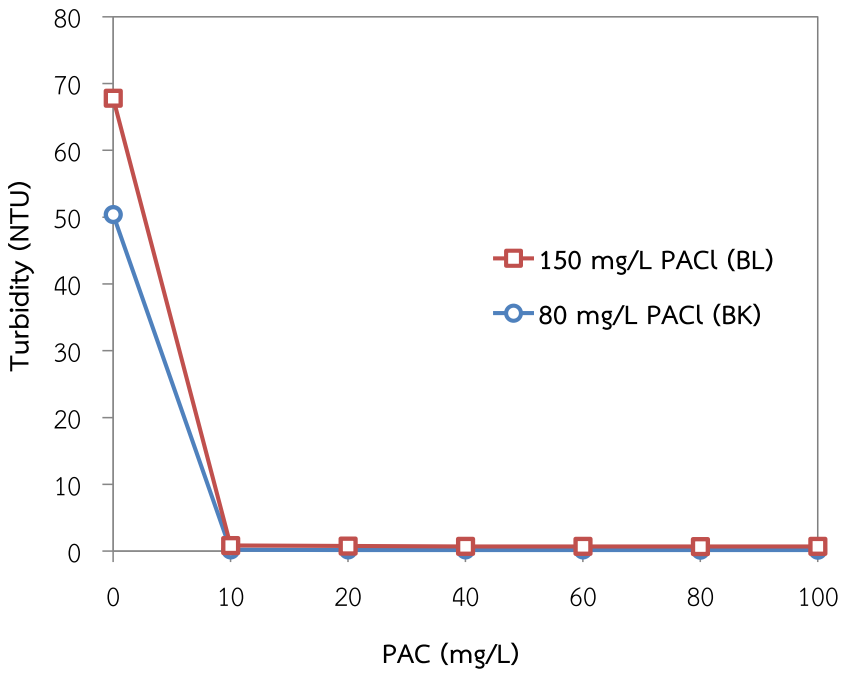

Figure 13 Residual turbidity of treated water by enhanced PACl coagulation with PAC of the Bangkhen WTP and the Banglen WTP

The water sample from Myponga Reservoir in Australia had turbidity at 1.95 NTU. The MIEX and 40 mg/L of PAC combine with 40 mg/L of alum could remove turbidity approximately 93% (Fabris *et al*., 2007). The feed water from the water of the Myponga reservoir had turbidity 12-15 NTU. The 4.4 mg/L aluminium sulfate and 20 mg/L PAC in membrane tank could reduce turbidity by an approximately 87% (Dixon *et al*., 2011). In this research, the turbidity of raw water from the Bankhen WTP and the Banglen WTP was 50.4 and 17.4 NTU, respectively. Turbidity reduction by enhanced coagulation combined with PAC in this work was success very well for removing turbidity (approximately 96-99%). According to the experiment in this work, the high amount of coagulants could help in combination of PAC to settle down.

4.4.2 UV-254, DOC, SUVA and DON reduction by enhanced PACl coagulation with PAC

For the Bangkhen WTP, the PACl dosage of 80 mg/L with the PAC dosage of 10 mg/L could reduce UV-254 from 0.135 to 0.015 cm^{-1}, a reduction of 89%. A PACl dosage of 80 mg/L combined with PAC dosage of 20 mg/L provided the best reduction (approximately 94%). An increase in the PAC dosage up to 100 mg/L did not increase in the UV-254 reduction (**Figure 14**). When the reduction of UV-254 by PACl of 80 mg/L was set as the baseline, the PACl of 80 mg/L with PAC of 20 mg/L provided the increasing in the UV-254 reduction by 17%.

A reduction of the DOC represents the reduction of both aromatic and aliphatic organic matter in water. For the Bangkhen WTP, the PACl dosage of 80 mg/L with the PAC dosage of 10 mg/L could reduce DOC from 4.2 to 1.3 mg/L, a reduction of 69%. A PACl dosage of 80 mg/L combined with PAC dosage of 20 mg/L provided the best reduction (approximately 77%). An increase in the PAC dosage up to 100 mg/L resulted in the slight decreases in DOC (**Figure 14**). When the reduction of DOC by PACl of 80 mg/L was set as the baseline, the PACl of 80 mg/L with PAC of 20 mg/L provided the increasing in DOC reduction by 17%

Figure 14 shows the result of enhanced PACl coagulation with PAC on SUVA of water from the Bangkhen WTP**.** A PACl dosage of 80 mg/L combined with PAC dosage of 10 mg/L could reduce SUVA from 3.2L/mg-m to 1.1 L/mg-m. A PACl dosage of 80 mg/L combined with PAC dosage of 20 mg/L provided the best reduction, 74%. SUVA was gradually increased from 0.83 L/mg-m to 0.86 L/mg-m when the PAC dosage was increased from 40 to 100 mg/L (approximately a 73 % reduction). SUVA lower than 2 L/mg-m indicate the organic matter of low molecular weight, hydrophilic, and less reactive with chlorine (Garcia *et al*., 2011). In this case, the additional of PAC of 20 mg/L increased the SUVA reduction by 38%.

DON was decreased from 0.24 mg-N/L to 0.12 mg-N/L when using a PACl dosage of 80 mg/L combined with a PAC dosage of 10 mg/L (**Figure 14)**. This provided the best result of a reduction of 49 %. Increasing the PAC dosage up to 100 mg/L resulted in no difference in DON levels. The best removal of NDMA precursors in the raw water of the Bangkhen-WTP was obtained at a PACl dosage of 80 mg/L combined with a PAC dosage of 20 mg/L at a controlled pH of 7 (approximately a 68% removal). The additional of PAC of 20 mg/L increased the DON reduction by 24%.

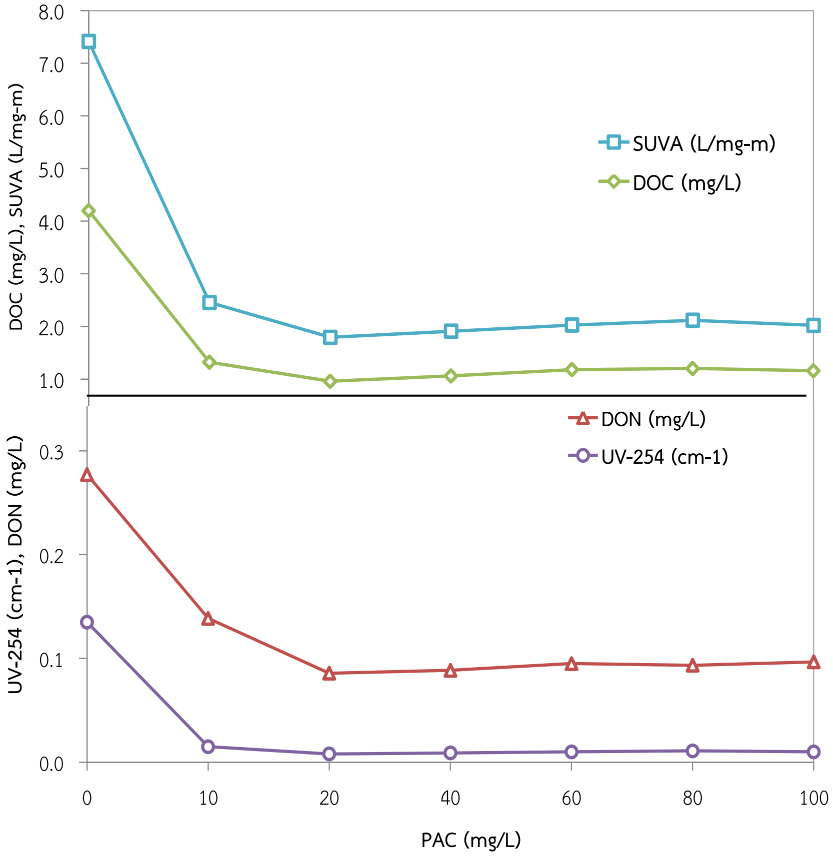

Figure 14 Residual UV-254, DON, DOC and SUVA of treated water by enhanced PACl coagulation with PAC of the Bangkhen WTP

For the Banglen WTP, the PACl dosage of 150 mg/L with the PAC dosage of 10 mg/L could reduce UV-254 from 0.228 to 0.025 cm^{-1}, a reduction of 89%. The PACl dosage of 150 mg/L combined with PAC dosage of 20 mg/L provided the first best reduction (approximately 95%). An increase in the PAC dosage up to 250 mg/L did not decrease UV-254 (**Figure 15**). When the reduction of UV-254 by PACl of 150 mg/L was set as the baseline, the PACl of 150 mg/L with PAC of 20 mg/L provided the increasing in UV-254 reduction of 9%.

The PACl dosage of 150 mg/L with the PAC dosage of 10 mg/L could reduce DOC from 7.3 to 1.4 mg/L, a reduction of 81%. The best reduction for DOC removing of the Banglen WTP was obtained at a PACl dosage of 150 mg/L combined with a PAC dosage of 20 mg/L under a controlled pH of 7, a reduction 85%. An increase in the PAC dosage up to 250 mg/L resulted did not increase in DOC reduction (**Figure 15**). The PACl of 150 mg/L with PAC of 20 mg/L provided the increasing in DOC reduction of 9% from the baseline.

Figure 15 shows the result of enhanced PACl coagulation with PAC on SUVA reduction. A PACl dosage of 150 mg/L combined with a PAC 10 mg/L reduced SUVA by 43%. An increase in the PACl dosage from 20 to 250 mg/L slightly increased the reduction of SUVA. This is because SUVA values were slightly reduced from 1.8 L/mg-m to 1.1 L/mg-m. A PACl dosage of 150 mg/L combined with a PAC 20 mg/L yielded the best reduction by 68%. It increased the SUVA reduction by 44% when compared with the utilization of PACl of 150 mg/L alone.

DON was decreased from 0.14 mg-N/L to 0.12 mg-N/L when using a PACl dosage of 150 mg/L combined with a PAC dosage of 20 mg/L (**Figure 15**). This provided the best result of a reduction of 65%. Increasing the PAC dosage up to 250 mg/L did not decrease DON levels. The best removal of NDMA precursors in the enhanced coagulation of raw water of the Banglen WTP was obtained by using a PACl dosage of 150 mg/L combined with a PAC dosage of 20 mg/L under controlled pH of 7 (approximately a 70% removal). Under such condition, it increased DON reduction from using PACl of 150 mg/L alone by 29%.

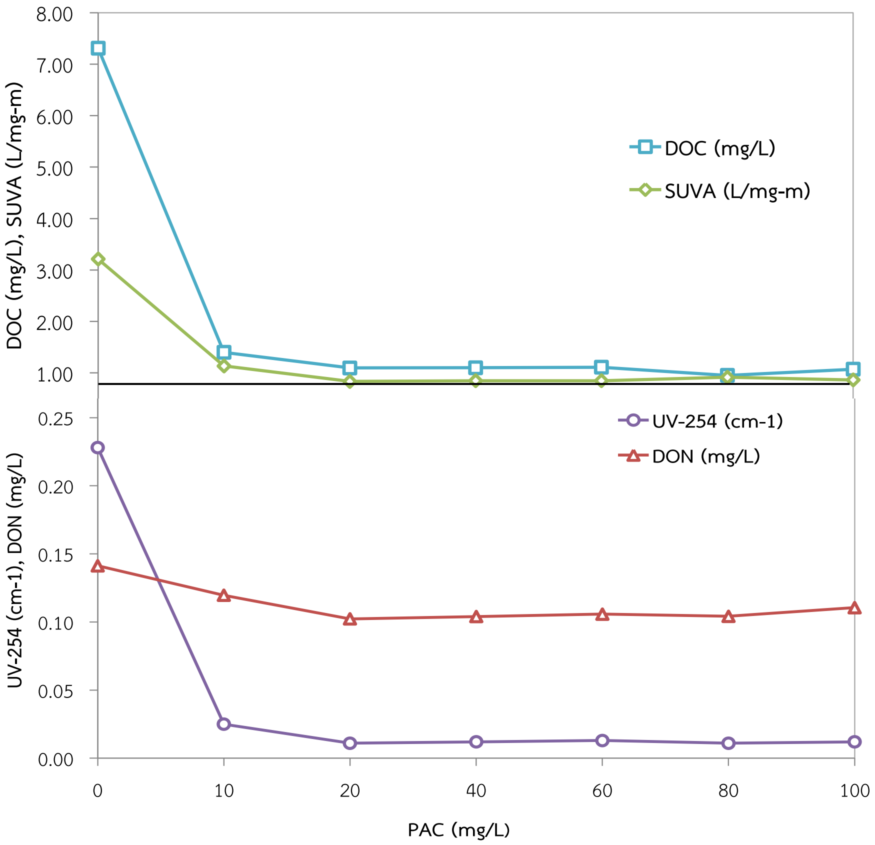

Figure 15 Residual UV-254, DON, DOC and SUVA of treated water by enhanced PACl coagulation with PAC of the Banglen WTP

UV-254 of coagulated water at optimal condition of enhanced coagulation for the Bangkhen WTP was 0.008 cm^{-1} and that of the Banglen WTP was 0.011 cm^{-1}. These meant that coagulated water of the Bangkhen WTP contained lower aromatic than that of the Banglen WTP. Moreover, coagulated water of the Bangkhen WTP had less opportunity in formation of chlorination by-products when compared with that of the Bangkhen WTP. The water sample from the Myponga Reservoir in Australia had UV-254 of 0.432 cm^{-1}. The MIEX and 40 mg/L of PAC combine with 40 mg/L of alum could remove UV-254 to 42% (Fabris *et al*., 2007). Raw water supplies from the U-tapao, Songkla province, Thailand had the initial value of UV-254 in rainy and summer season of 0.414 and 0.159 cm^{-1},respectively. In the rainy season, the 40 mg/L of PACl and 80 mg/L of PAC could reduce UV-254 approximately 62%. In the summer season, the 40 mg/L of PACl and 80 mg/L of PAC could reduce UV-254 approximately 66% (Srimuang *et al*., 2011).

The water from the water of the Myponga reservoir bloom had UV-254 of 0.469 cm^{-1}.The 4.4 mg/L of aluminum sulfate coagulation combined with 20 mg/L of PAC in membrane tank to reduce UV-254 by approximately 83 % (Dixon *et al*., 2011). The treatment of raw water supply from the Sri-Trang reservoir, Songkla province had the UV-254 equaled 0.098 cm^{-1}. The 20 mg/L of PACl and 0.1 mg/L polymer combined with 10 mg/L PAC could reduce UV-254 to 74% (Kueseng *et al*., 2011). In this research, UV-254 of raw water supply of the Bangkhen WTP was 0.135 cm^{-1}. The optimal condition of 80 mg/L of PACl combined with 20 mg/L of PAC reduce UV-254 by an approximately 94%. The raw water of the Banglen WTP had the initial value of UV-254 of 0.228 cm^{-1}. The optimal condition of 150 mg/L of PACl combined with 20 mg/L of PAC reduced UV-254 by approximately 95%. The percent reduction of UV-254 in this research was comparable to the previous work.

The residual DOC of coagulated water of the Bangkhen WTP at optimal condition by the enhanced coagulation was 1.2 mg/L, (an approximate 71% of DOC reduction). DOC of coagulated water of the Banglen WTP under optimal condition was 1.1 mg/L (an approximate 85% of DOC reduction). It can be stated that the optimal condition of enhanced coagulation of both the Bangkhen and Banglen WTP could successfully remove DOC. Coagulation can remove NOM that is processing high molecular weight. Negatively charged functional groups can engage in charge neutralization and adsorption onto floc particle. However, PAC is more effective for the adsorption of low molecular weight and uncharged NOM (Uyak *et al*., 2006) These mechanisms could be used to explain the successfully of DOC removal in this work.

The Terkos Lake water in Turkey had average DOC value of 4.41 mg/L. DBPs precursors removed by enhanced coagulation and PAC adsorption. Enhanced coagulation (using ferric chloride 100 mg/L) with PAC adsorption (40 mg/L) removed DOC to 76%. Enhanced coagulation with PAC was more effective than enhanced coagulation alone (Uyak *et al*., 2006).

The Western Australian WTP was investigated for enhanced coagulation (using alum 150 mg/L) combined with PAC. It could remove NOM by 70% which led to reduce the formation of DBP by 80-95% (Kritiana *et al.*, 2011). The Tungkang River in Taiwan was investigated for the adsorption. The contact time for kinetic adsorption of 20 to 30 min was required. A PAC dosage of 200 mg/L could remove the maximum NPDOC by approximately 60% (Shen *et al*, 1998).

The raw water from the Sri–Trang Reservoir, Songkla province, Thailand was coagulated and adsorbed by using 20 mg/L of PACl and 0.1 mg/L polymer combined with 10 mg/L PAC. Under such condition, it could reduce DOC up to 71% from the DOC of 4.3 mg/L (Kueseng *et al*., 2011). A water sample from a dam in Turkey had DOC of 2.48 mg/L. An alum dosage of 80 mg/L combined with PAC and a PACl dosage of 40 mg/L combined with PAC could reduce DOC by approximately 50% (Kucukcongar *et al*., 2013). The water sample from Myponga Reservoir in Australia had DOC of 11.7 mg/L .The MIEX and 40 mg/L of PAC combined with 40 mg/L of alum could reduce DOC by approximately 92% (Fabris *et al*., 2007). The Myponga reservoir bloom in Australia had DOC of 15.4 mg/L. The 4.4 mg/L of aluminium sulfate coagulation combined with 20 mg/L of PAC in membrane tank reduced DOC by approximately 64 % (Dixon *et al*., 2011).

DOCs of raw water supplies from the U-tapao, Songkla province in rainy and summer season were 5.1 and 5.5 mg/L, respectively. In the rainy season, the 40 mg/L of PACl and 80 mg/L of PAC could remove DOC by 65%. In the summer season, the 40 mg/L of PACl and 80 mg/L of PAC could remove DOC by 68% (Srimuang *et al*., 2011). In this work, the DOC of raw water of the Bangkhen WTP was 4.2 mg/L. The optimal condition of enhanced coagulation with PAC was at 80 mg/L of PACl combined with 20 mg/L of PAC. This condition could remove DOC by 77%. The DOC of raw water of the Banglen WTP of 7.3 mg/L was detected. The optimal condition of enhanced coagulation with PAC could be obtained at 150 mg/L of PACl combined with 20 mg/L of PAC. Under such condition, it could remove DOC by 85%. The obtained results from this study were corresponded well with the results of previous work.

The residual SUVA in treated water at optimal condition t of enhanced coagulation with PAC adsorption of the Bangkhen WTP was 0.83 mg/L. The SUVA of about 74% could be reduced by using the mentioned condition. For the Banglen WTP, the residual SUVA of treated water at optimal condition was 1.0 mg/L (an approximate, 68% of SUVA reduction). Residual SUVA values at optimal condition of both the Bangkhen and Bangkhen WTP were lower than 2 L/mg-m. It can be stated that the mostly organic matter of low molecular weight, hydrophilic and less reactive with chlorine contained in treated water. The water sample from Myponga Reservoir in Australia had SUVA of 3.7 L/mg-m. The MIEX and 40 mg/L of PAC combined with 40 mg/L of alum could remove SUVA by 79% (Fabris *et al*., 2007). SUVA of water from the Myponga reservoir bloom in Australia was 3.05 L/mg-m. The 4.4 mg/L aluminium sulfate and 20 mg/L of PAC in membrane tank could reduce SUVA by 53% (Dixon *et al*., 2013). In this research, the initial SUVA of raw water of the Bangkhen WTP was 3.2 L/mg-m. The optimal condition was at 80 mg/L of PACl combined with 20 mg/L of PAC. It could reduce SUVA by 75%. The initial SUVA of raw water from the Banglen WTP was 3.1 L/mg-m. The optimal condition could reduce SUVA by 68%. The results from this work was comparable well with previous works.

DON represents the trend to form N-DBPs in the disinfection step by observation from DOC/DON. A high DOC/DON value has a much smaller propensity to form N-DBPs than a low DOC/DON value (Dotson *et al*., 2009). DOC/DON of water at optimal condition of the Bangkhen WTP and the Banglen WTP were 17 and 33. DOC/DON of treated water by coagulation wih PAC at optimal condition of the Bangkhen and Banglenwater sources was 12 and 11, respectively. DOC/DON of coagulated water had a much smaller tendency to form N-DBPs than that of treated water This meant that PAC may increase the tendency to form N-DBPs.

The water samples from wastewater treatment plant in USA had DON between 0.68-2.44 mg-N/L. The DON removal from wastewater effluent by alum coagulation (8 mg/L) and PAC adsorption was uneasily, This is because wastewater effluent has SUVA less than 2 L/mg-m (Chen et al, 2011). In 12 WTPs in Europe, the DON reduction by using combined process of powder activated carbon-ultrafiltration (PAC/UF) increased up to 45% (Tomaszewska *et al*., 2002). . The combination of coagulation (10 mg/L of coagulant) and adsorption (1 g/L PAC) removed DON by approximately 82% from raw water of WTP in China (Liu *et al*., 2013). DON of 50-60% in wastewater was biodegradable in during an activated sludge treatment. The advanced treatment of treated effluents achieved 72% of DON reduction. In this study, the optimal condition at 80 mg/L of PACl combined with 20 mg/L of PAC. It could remove DON by 68% from the Bangkhen WTP. The initial DON of raw water of Banglen WTP was 0.34 mg N/L. The optimal condition of 150 mg/L of PACl combined with 20 mg/L of PAC removed DON by 70%. The percentage reduction of DON by enhanced coagulation with PAC in this work was comparable to the reduction of DON from the previous works.

4.5 Reduction of HPO and HPI by PACl coagulation and enhanced PACl coagulation with PAC

From **Figure 16**, DOCs of HPI of 2,2 mg/L and HPO of 2.0 mg/L were determined. When PACl was used in coagulation alone, DOCs of HPI and HPO were 1.5 and 1.1 mg/L, respectively. The PACl coagulation could remove DOCs of HPI and HPO by 31% and 47%, respectively. For enhanced coagulation, DOCs of HPI and HPO were 0.5 mg/L and 0.4 mg/L, respectively. Enhanced PACl coagulation with PAC could remove DOC of HPI and HPO by 75 and 80%, respectively. From this result, it showed that the percentage of reduction of HPO was higher than that of HPI in both of PACl coagulation and enhanced PACl coagulation with PAC. In addition, the addition of PAC could increase HPI and HPO reduction by 44 and 33%, respectively.

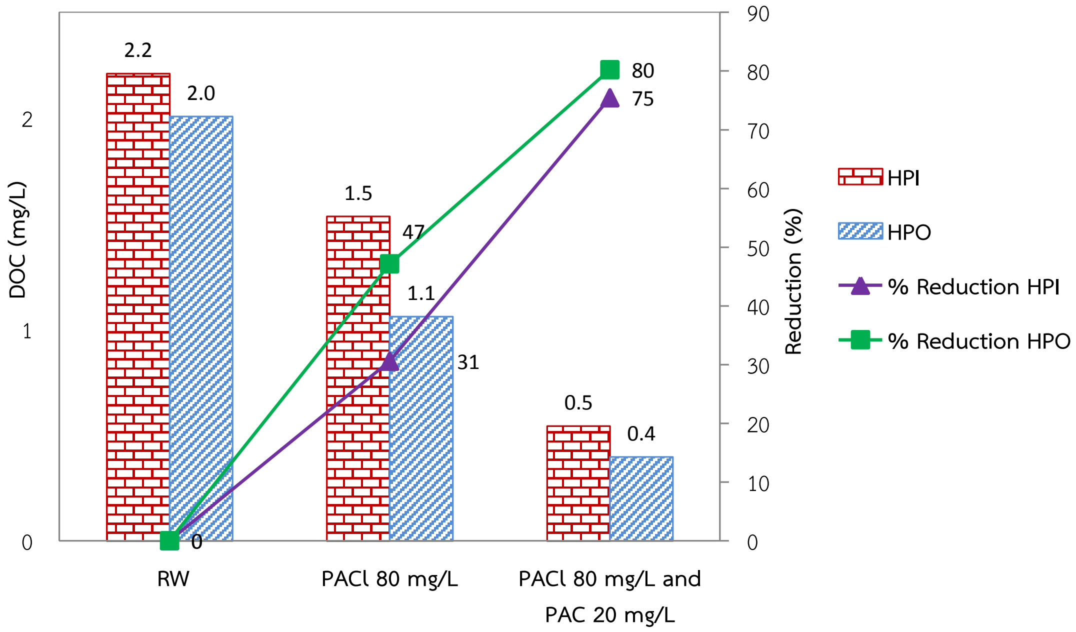

Figure 16 Reductions of DOC of HPI and HPO of Bangkhen WTP

From **Figure 17,** DOC of HPI and HPO in the raw water of the Banglen WTP were 3.9 and 3.7 mg/L, respectively. When PACl was used in coagulation alone, DOCs of HPI and HPO were 2.3 and 2.0 mg/L, respectively The PACl coagulation could remove DOCs of HPI and HPO by 42 and 45%, respectively. For enhanced coagulation, DOCs of HPI and HPO were 0.6 mg/L and 0.4 mg/L, respectively. Enhanced PACl coagulation with PAC could remove DOC of HPI and HPO by 83 and 89%, respectively. On this basis, the percent reduction of HPO was slightly higher than that of HPI in both of PACl coagulation and enhanced PACl coagulation with PAC. In addition, the addition of PAC could increase HPI and HPO reduction by 41 and 44%, respectively.

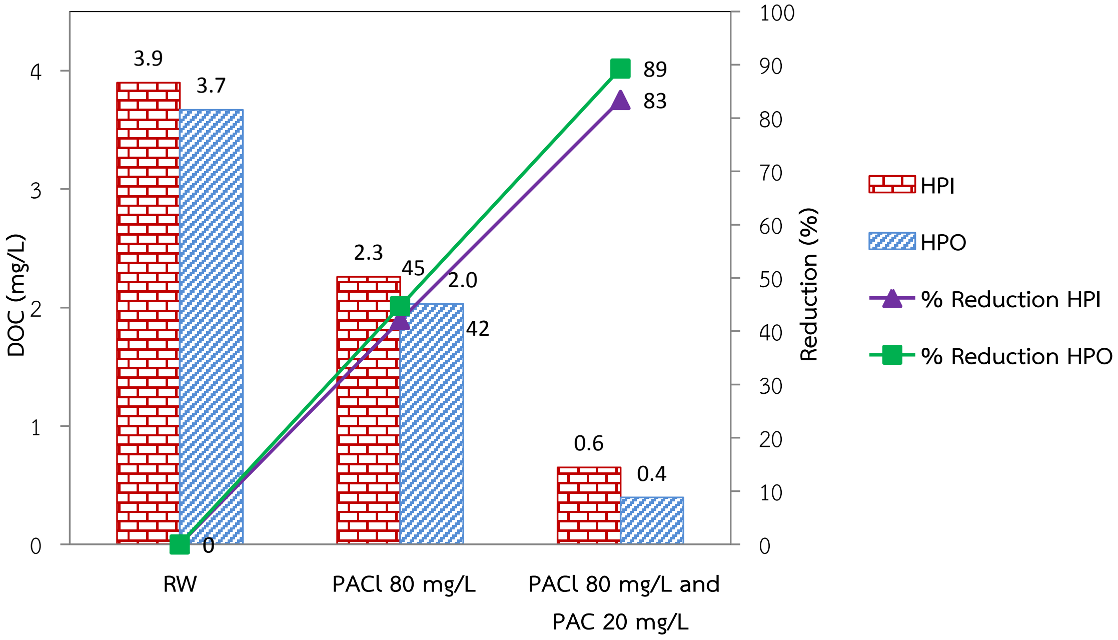

Figure 17 Reductions of DOC of HPI and HPO of Banglen WTP

From **Figure 16** and **Figure 17**, DOCs of HPO were removed more than DOCs of HPI in both of coagulation and enhanced coagulation process. HPO is high molecular weight and aromatic structure. The coagulation can remove easier HPO than HPI. HPI is surrounded by water and is limited from assembly of particles. The particles are eradicated in precipitation form in low level (AWWA, 1993).

The optimal condition of enhanced coagulation with PAC of raw water supply in the Sri-trang Resevior, Thailand was found at PACl of 20 mg/L with polymer of 0.1 mg/L and PAC of 10 mg/L. The result from this research showed that the coagulation could effectively remove more DOC of HPO than DOC of HPI. The PACl coagulation combined with polymer and PAC provided the highest level of DOC of HPI and DOC of HPO reduction at 65% and 75%, respectively (Kueseng *et al*, 2011).

A water treatment in Sweden used a enhanced coagulation and followed by adsorption with GAC. It could remove TOC and DOC by 80%. The fractionation of river and lake was showed that DOC of HPO was higher than DOC of HPI. Moreover DON is higher in HPI (Garcia *et al*, 2011). Raw water supplies from the U-tapao, Songkla province were surveyed. The DOC of water sample in rainy and summer season were 5.1 and 5.5 mg/L, respectively. In the rainy season, coagulation with PACl reduced DOC of HPI and DOC of HPO by 53% and 50%, respectively. The coagulation with PACl combined with PAC reduced DOC of HPI and DOC of HPO by approximately 63% and 58%, respectively. In the summer season, the coagulation with PACl reduced DOC of HPI and DOC of HPO by 65% and 61%, respectively. The coagulation with PACl combined with PAC reduced DOC of HPI and DOC of HPO by 71% and 70%, respectively (Srimuang *et al*, 2014). In this work, the PACl coagulation could remove DOCs of HPI and HPO of raw water of the Bangkhen WTP by 31% and 47%, respectively. The enhanced PACl coagulation with PAC could remove DOCs of HPI and HPO by 75 and 80%., respectively. For the Banglen WTP, the PACl coagulation could remove DOCs of HPI and HPO by 42 and 45%, respectively. The enhanced PACl coagulation with PAC could remove DOCs of HPI and HPO by 83 and 89%, respectively. Based on obtained results, DOC of HPO was removed more than DOC of HPI in both the Bangkhen and Banglen source water .

4.8 NDMA-FP

Table 11 and **Table 12** shows the result of NDMA-FP in raw water, coagulated water, coagulated water by PACl coagulation with PAC, treated water by PACl coagulation followed by adsorption, and coagulated water at turbidity less than 5 NTU of the Bangkhen WTP and the Banglen WTP. NDMA-FP of all water samples were lower than the detection limit of the methods of 542 ng/L or 7.3 nM. Therefore, it cannot be concluded that PACl coagulation, and enhanced PACl coagulation can remove NDMA-FP or not.

Table 11 NDMA-FP in raw water, coagulated water, coagulated water by PACl coagulation with PAC, treated water by PACl coagulation followed by adsorption, and coagulated water at turbidity less than 5 NTU of the Bangkhen WTP

Water sample	NDMA FP (ng/L)
BK RW	< 542
BK 80 PACl	< 542
BK 80 PACl +20 PAC (case I)	< 542
BK 80 PACl +20 PAC (case II)	< 542
BK 20 PACl (Turbidity < 5 NTU)	< 542
BK 60 Alum (Turbidity < 5 NTU)	< 542

Table 12 NDMA FP in raw water, coagulated water, coagulated water by PACl coagulation with PAC, treated water by PACl coagulation followed by adsorption, and coagulated water at turbidity less than 5 NTU of the Banglen WTP

Water sample	NDMA FP (ng/L)
BL RW	< 542
BL 80 PACl	<542
BL 80 PACl +20 PAC (case I)	< 542
BL 80 PACl +20 PAC (case II)	< 542
BL 10 PACl (Turbidity < 5 NTU)	< 542
BL 20 Alum (Turbidity < 5 NTU)	< 542

The drinking water supplies in Korea had NDMA of about 100 ng/L. Alum, ferric chloride and ferric sulfate coagulant could remove NDMA less than 10%. This is because the NDMA adsorption on to particulate matter is minimal. At 10 mg/L of PAC with a 4 hour contact time it could remove NDMA less than 5 %. However, the longer contact time and high PAC dosage could remove NDMA approximately by 50% (Chung *et al*, 2009). The NDMA removal by PAC from wastewater effluents and wastewater influent in South Carolina was higher than of from surface water. Basic carbons (lower surface area) were higher removal of NDMA-FP than acidic carbons (higher surface area) (Sandi *et al*, 2014). The secondary effluent from wastewater treatment plant had NDMA- FP of 371 ng/L. Adsorptions of NDMA precursors by PAC and GAC were examined. NDMA-FP was considered as a surrogate parameter for NDMA. PAC could reduce NDMA-FP by 37-91%. GAC could reduce NDMA-FP by 60-90% (Hanigan *et al*., 2012). In this research, NDMA-FP of all water samples was lower than the detection limit of the methods of 542 ng/L.

CHAPTER 5

CONCLUSION

The objective of this research was to remove *N*-nitrosodimethylamine (NDMA) precursor in raw water supplies of the Bangkhen water treatment plant (WTP) and the Banglen WTP by enhanced polyaluminium chloride (PACl) coagulation with PAC. The reduction of hydrophobic organic fraction (HPO) and hydrophilic organic fraction (HPI) were also determined in this work.

1. Turbidity, dissolved organic carbon (DOC), ultraviolet adsorption at wavelength 254 nm (UV-254), specific ultraviolet adsorption (SUVA), and dissolved organic nitrogen (DON) of raw water of the Bangkhen WTP were 61 NTU, 4.2 mg/L, 0.135 cm^{-1}, and 0.24 mg/L, respectively. Turbidity of 17 NTU, DOC of 7.3 mg/L, UV-254 of 0.228 cm^{-1}, SUVA of 3.1 L/mg-m, and DON of 0.34 mg/L were found in the raw water of the Banglen WTP

2. For raw water of the Bangkhen WTP, an alum dosage of 60 mg/L and PACl of 20 mg/L under controlled pH at 7 had the efficiency to reduce the turbidity to meet standard. For raw water of the Banglen WTP, the condition for reducing turbidity to meet standard could be found at alum dosage of 60 mg/L and PACl of 10 mg/L under controlled pH at 7.

3. The optimal condition of coagulation for DOC, UV-254, SUVA and DON reductions from the raw water of the Bangkhen WTP was at PACl dosage of 80 mg/L under a controlled pH of 7. It could reduce DOC, UV-254, SUVA, and DON by 74, 42, 55 and 41%, respectively. For the raw water of the Banglen WTP, the optimal condition of coagulation was at PACl dosage of 150 mg/L under a controlled pH of 7. It could reduce DOC, UV-254, SUVA, and DON by 64, 38, 43 and 52%, respectively.

4. The optimal condition of PACl coagulation followed by PAC adsorption for DOC, UV-254, SUVA and DON reductions from the raw water of the Bangkhen WTP was at PACl dosage of 80 mg/L combined with PAC of 20 mg/L under a controlled pH of 7. It could reduce DOC, UV-254, SUVA, and DON by 77, 94, 74 and 68%, respectively. For the raw water of the Banglen WTP, the optimal condition was at PACl dosage of 150 mg/L followed by PAC 20 mg/L under a controlled pH of 7. It could reduce DOC, UV-254, SUVA, and DON by 87, 95, 68 and 70%, respectively.

5. DOCs of HPI of 2,2 mg/L and HPO of 2.0 mg/L were determined in raw water of the Bangkhen WTP. DOC of HPI and HPO in the raw water of the Banglen WTP were 3.9 and 3.7 mg/L, respectively.

6. For the raw water of the Bangkhen WTP, the PACl coagulation could reduce DOC of HPO and HPI by 31 and 47%, respectively. The enhanced PACl coagulation with PAC could reduce DOC of HPO by 75% and DOC of HPI by 80%. For the raw water of the Banglen WTP, the PACl coagulation could reduce DOC of HPO by 42% and DOC of HPI by 45%. The enhanced PACl coagulation with PAC could reduce DOC of HPO and HPI by 83 and 89%, respectively.

7. NDMA-FP in raw waters, coagulated waters, coagulated water under enhanced coagulation of both the Bangkhen WTP and the Banglen WTP were not detectable under detection limit of 542 ng/L.

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APPENDIX

Table1: Dose, alkalinity,turbidity and percentage of turbidity removal of Bangkhen WTP (Coagulation)

Dose (ppm)	Alum			PACl		
	Residual alkalinity (mg/L as CaCO3)	Residual turbidity (NTU)	Percentage of turbidity removal	Residual alkalinity (mg/L as CaCO3)	Residual turbidity (NTU)	Percentage of turbidity removal
0	61.5	50.40	0	61.5	50.40	0
10	58	21.50	57	55	6.09	88
20	57	15.00	70	56	0.44	99
40	53	11.60	77	55	0.34	99
60	44	3.46	93	54	0.32	99
80	45	2.10	96	48	0.24	100
100	46	1.10	98	49	1.06	98

Table2: Dose,alkalinity,turbidity and percentage of turbidity removal of Banglen WTP (Coagulation)

Dose (ppm)	Alum			PACl		
	Residual alkalinity (mg/L as CaCO3)	Residual turbidity (NTU)	Percentage of turbidity removal	Residual alkalinity (mg/L as CaCO3)	Residual turbidity (NTU)	Percentage of turbidity removal
0	91	17.40	0	91	17.40	0
10	84	6.83	61	85	3.70	79
20	86	5.54	68	85	3.36	81
40	80	5.13	71	83	1.19	93
60	75	2.46	86	80	0.72	96
80	78	0.68	96	79	0.61	96
100	74	0.52	97	73	0.75	96
150	71	0.58	97	73	0.35	98
200	74	0.77	96	72	0.80	95
250	76	0.76	96	75	0.53	97

Table3: Dose, UV-254 and percentage of UV-254 reduction of Bangkhen WTP (Coagulation)

Dose(ppm)	Alum		PACl	
	UV-254 (cm-1)	Percentage of UV-254 reduction	UV-254 (cm-1)	Percentage of UV-254 reduction
0	0.135	0	0.135	0
10	0.095	30	0.079	41
20	0.088	35	0.064	53
40	0.078	42	0.049	64
60	0.054	60	0.043	68
80	0.05	63	0.035	74
100	0.059	56	0.046	66

Table4: Dose, UV-254 and percentage of UV-254 reduction of Banglen WTP (Coagulation)

Dose(ppm)	Alum		PACl	
	UV-254 (cm-1)	Percentage of UV-254 reduction	UV-254 (cm-1)	Percentage of UV-254 reduction
0	0.228	0	0.228	0
10	0.207	9	0.185	19
20	0.195	14	0.157	31
40	0.178	22	0.105	54
60	0.156	32	0.101	56
80	0.13	43	0.098	57
100	0.135	41	0.095	58
150	0.112	51	0.081	64
200	0.098	57	0.088	61
250	0.098	57	0.082	64

Table 5: Dose , DOC and percentage of DOC reduction of Bangkhen WTP (Coagulation)

Dose(ppm)	Alum		PACl	
	DOC (mg/L)	Percentage of DOC reduction	DOC (mg/L)	Percentage of DOC reduction
0	4.2	0	4.2	0
10	3.8	9	3.6	15
20	3.5	18	3.1	26
40	3.5	17	2.8	33
60	3.2	24	2.9	32
80	2.8	33	2.4	42
100	3.1	26	2.5	41

Table 6: Dose , DOC and percentage of DOC reduction of Banglen WTP(Coagulation)

Dose(ppm)	Alum		PACl	
	DOC (l mg-1 m-1)	Percentage of DOC reduction	DOC mg/L	Percentage of DOC reduction
0	7.3	0	7.3	0
10	7.0	4	7.0	4
20	7.2	2	7.2	2
40	6.5	11	5.2	29
60	5.9	19	5.2	28
80	5.5	24	5.4	27
100	5.9	19	5.1	30
150	5.1	30	4.6	38
200	4.9	32	4.9	33
250	5.4	26	4.2	42

Table 7: Dose , SUVA and percentage of SUVA reduction of Bangkhen WTP (Coagulation)

Dose(ppm)	Alum		PACl	
	SUVA	Percentage of	SUVA	Percentage of
	l mg-1 m-1	SUVA reduction	mg/L	SUVA reduction
0	3.2	0	3.2	0
10	2.5	23	2.2	32
20	2.5	21	2.1	36
40	2.2	30	1.7	46
60	1.7	47	1.5	53
80	1.8	45	1.4	55
100	1.9	41	1.9	42

Table 8: Dose , SUVA and percentage of SUVA reduction of Banglen WTP (Coagulation)

Dose(ppm)	Alum		PACl	
	SUVA	Percentage of	SUVA	Percentage of
	l mg-1 m-1	SUVA reduction	l mg-1 m-1	SUVA reduction
0	3.1	0	3.1	0
10	2.9	5	2.6	15
20	2.7	13	2.2	30
40	2.7	12	2.0	35
60	2.7	15	1.9	38
80	2.3	25	1.8	41
100	2.3	26	1.9	40
150	2.2	30	1.8	43
200	2.0	36	1.8	42
250	1.8	42	1.9	38

Table 9 : Dose, NH_3/NH_4^+, NO_3-, NO_2^- and DON of Bangkhen WTP (Coagulation)

Dose (ppm)	Alum					PACl				
	NH_3/NH_4^+ (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	DON (mg/L)	Percentage of DON reduction	NH_3/NH_4^+ (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	DON (mg/L)	Percentage of DON reduction
0	0.14	0.06	0.006	0.24	0	0.14	0.06	0.006	0.24	0
10	0.07	0.03	0.004	0.20	19	0.07	0.08	0.005	0.19	24
20	0.07	0.04	0.007	0.19	23	0.06	0.05	0.005	0.19	23
40	0.03	0.04	0.007	0.20	18	0.04	0.06	0.006	0.15	38
60	0.08	0.07	0.005	0.19	20	0.04	0.05	0.005	0.16	36
80	0.04	0.07	0.007	0.14	43	0.04	0.06	0.006	0.14	41
100	0.08	0.06	0.005	0.19	22	0.03	0.04	0.005	0.20	18

Table 10: Dose, NH_3/NH_4^+, NO_3^-, NO_2^- and DON of Banglen WTP (Coagulation)

Dose (ppm)	Alum					PACl				
	NH_3/NH_4^+ (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	DON (mg/L)	Percentage of DON reduction	NH_3/NH_4^+ (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	DON (mg/L)	Percentage of DON reduction
0	0.48	0.03	0.018	0.34	0	0.48	0.03	0.018	0.34	0
10	0.23	0.03	0.010	0.25	27	0.19	0.01	0.013	0.26	23
20	0.16	0.03	0.011	0.26	24	0.23	0.05	0.015	0.22	37
40	0.16	0.03	0.011	0.24	30	0.26	0.04	0.014	0.21	38
60	0.2	0.03	0.010	0.20	41	0.29	0.04	0.011	0.23	33
80	0.15	0.03	0.010	0.22	36	0.23	0.06	0.016	0.21	40
100	0.18	0.03	0.007	0.23	32	0.14	0.06	0.014	0.18	47
150	0.19	0.03	0.008	0.20	43	0.16	0.04	0.016	0.17	52
200	0.17	0.03	0.006	0.19	44	0.14	0.04	0.010	0.25	26
250	0.15	0.05	0.010	0.17	50	0.17	0.04	0.008	0.26	25

Table 11: DOC, DON and DOC/DON of Bangkhen WTP (Coagulation)

Dose (ppm)	Alum			PACl		
	DOC	DON	DOC/DON	DOC	DON	DOC/DON
0	4.20	0.24	18	4.20	0.24	18
10	3.84	0.20	19	3.59	0.19	19
20	3.46	0.19	18	3.12	0.19	16
40	3.49	0.20	17	2.83	0.15	19
60	3.18	0.19	17	2.87	0.16	18
80	2.82	0.14	20	2.42	0.14	17
100	3.11	0.19	16	2.48	0.20	12

Table 12: DOC, DON and DOC/DON of Banglen WTP (Coagulation)

Dose (ppm)	Alum			PACl		
	DOC	DON	DOC/DON	DOC	DON	DOC/DON
0	7.31	0.34	22	7.31	0.34	22
10	7.02	0.25	28	7.02	0.26	27
20	7.18	0.26	28	7.18	0.22	33
40	6.52	0.33	20	5.16	0.21	25
60	5.89	0.204	29	5.23	0.18	29
80	5.55	0.22	25	5.36	0.15	36
100	5.89	0.23	26	5.11	0.15	34
150	5.10	0.198	26	4.57	0.14	33
200	4.94	0.19	26	4.86	0.25	19
250	5.38	0.17	32	4.25	0.26	16

Table 13: Dose,alkalinity,turbidity and percentage of turbidity removal of Bangkhen WTP (Enhanced coagulation)

PAC (ppm)	80 mg/L PACl		
	Residual alkalinity (mg/L as CaCO3)	Residual turbidity (NTU)	Percentage of turbidity removal
0	61.5	50.40	0
10	50	0.20	100
20	55	0.18	100
40	60	0.18	100
60	60	0.17	100
80	60	0.16	100
100	60	0.16	100

Table 14: Dose, alkalinity, turbidity and percentage of turbidity removal of Banglen WTP (Enhanced coagulation)

PAC (ppm)	150 mg/L PACl		
	Residual alkalinity (mg/L as CaCO3)	Residual turbidity (NTU)	Percentage of turbidity removal
0	91	17.40	0
10	75	0.64	96
20	80	0.59	97
40	85	0.53	97
60	85	0.54	97
80	85	0.54	97
100	85	0.56	97
150	85	0.52	97
200	85	0.55	97
250	85	0.56	97

Table15: Dose, UV-254 and percentage of UV-254 reduction of Bangkhen WTP (Enhanced coagulation)

PAC (ppm)	80 mg/L PACl	
	UV-254 (cm-1)	Percentage of UV-254 reduction
0	0.135	0
10	0.015	89
20	0.008	94
40	0.009	93
60	0.010	93
80	0.011	92
100	0.010	93

Table16: Dose, UV-254 and percentage of UV-254 reduction of Banglen WTP (Enhanced coagulation)

PAC (ppm)	150 mg/L PACl	
	UV-254 (cm-1)	Percentage of UV-254 reduction
0	0.228	0
10	0.025	89
20	0.011	95
40	0.012	95
60	0.013	94
80	0.011	95
100	0.012	95
150	0.012	95
200	0.010	96
250	0.012	95

Table 17: Dose , DOC and percentage of DOC reduction of Bangkhen WTP (Enhanced coagulation)

PAC (ppm)	80 mg/L PACl	
	DOC (mg/L)	Percentage of DOC reduction
0	4.2	0
10	1.3	69
20	1.0	77
40	1.1	75
60	1.2	72
80	1.2	71
100	1.2	72

Table 18: Dose , DOC and percentage of DOC reduction of Banglen WTP (Enhanced coagulation)

PAC (ppm)	150 mg/L PACl	
	DOC (l mg-1 m-1)	Percentage of DOC reduction
0	7.3	0
10	1.4	81
20	1.1	85
40	1.1	85
60	1.1	85
80	1.0	87
100	1.1	85
150	1.1	85
200	0.9	88
250	1.1	85

Table 19: Dose , SUVA and percentage of SUVA reduction of Bangkhen WTP (Enhanced coagulation)

PAC (ppm)	80 (mg/L) PACl	
	SUVA l mg-1 m-1	Percentage of SUVA reduction
0	3.21	0
10	1.14	65
20	0.83	74
40	0.85	74
60	0.85	74
80	0.92	71
100	0.86	73

Table 20: Dose , SUVA and percentage of SUVA reduction of Banglen WTP (Enhanced coagulation)

PAC (ppm)	150 (mg/L) PACl	
	SUVA l mg-1 m-1	Percentage of SUVA reduction
0	3.12	0
10	1.79	43
20	1.00	68
40	1.09	65
60	1.17	62
80	1.15	63
100	1.12	64
150	1.12	64
200	1.13	64
250	1.13	64

Table 21: Dose,NH_3, NH_4^+,NO_3^-,NO_2^- and DON of Bangkhen WTP (Enhanced coagulation)

PAC (ppm)	80 mg/L PACl				
	NH_3/NH_4^+ (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	DON (mg/L)	Percentage of DON reduction
0	0.14	0.06	0.006	0.24	0
10	0.03	0.08	0.004	0.12	49
20	0.02	0.09	0.001	0.08	68
40	0.01	0.01	0.006	0.08	67
60	0.01	0.01	0.004	0.09	65
80	0.02	0.01	0.004	0.08	66
100	0.03	0.10	0.004	0.09	64

Table 22 : Dose, NH_3/NH_4^+, NO_3-, NO_2^- and DON of Banglen WTP (Enhanced coagulation)

Dose (ppm)	150 mg/l PACl				
	NH_3/NH_4^+ (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	DON (mg/L)	Percentage of DON reduction
0	0.48	0.03	0.018	0.34	0
10	0.13	0.01	0.003	0.12	65
20	0.09	0.03	0.003	0.10	70
40	0.09	0.01	0.005	0.10	69
60	0.08	0.01	0.004	0.11	69
80	0.07	0.03	0.003	0.10	69
100	0.06	0.01	0.003	0.11	67
150	0.07	0.01	0.004	0.10	70
200	0.05	0.03	0.006	0.11	68
250	0.01	0.05	0.004	0.11	69

Table 23: DOC, DON and DOC/DON of Bangkhen WTP (Enhanced Coagulation)

Dose (ppm)	DOC	DON	DOC/DON
0	4.2	0.24	18
10	1.3	0.12	11
20	1.0	0.08	12
40	1.1	0.08	13
60	1.2	0.09	14
80	1.2	0.08	15
100	1.2	0.09	13

Table 24: DOC, DON and DOC/DON of Bangkhen WTP (Enhanced Coagulation)

Dose (ppm)	DOC	DON	DOC/DON
0	7.3	0.34	21
10	1.4	0.12	12
20	1.1	0.10	11
40	1.1	0.10	11
60	1.1	0.11	10
80	1.0	0.10	9
100	1.1	0.11	10
150	1.1	0.10	10
200	0.9	0.11	8
250	1.1	0.11	10

Table 25 : NH_3/NH_4^+, NO_3^-, NO_2^- and DON of fractionation of Bangkhen WTP

Sample	NH_3/NH_4^+	NO_3^-	NO_2^-	DON
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
HPI BK RW	0.08	0.10	0.004	0.32
HPI BK 80 PACl	0.14	0.13	0.005	0.37
HPI BK 80 PACl+ 20 PAC	0.08	0.11	0.004	0.38
HPO BK RW	0.01	0.01	0.003	0.18
HPO BK 80 PACl	0.01	0.01	0.002	0.16
HPO BK 80 PACl + 20 PAC	0.01	0.01	0.002	0.12

Table 26 : NH_3/NH_4^+, NO_3^-, NO_2^- and DON of fractionation of Banglen WTP

Sample	NH_3/NH_4^+	NO_3^-	NO_2^-	DON
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
HPI BL RW	0.26	0.07	0.004	0.40
HPI BL 150 PACl	0.11	0.09	0.004	0.31
HPI BL 150 PACl+ 20 PAC	0.07	0.07	0.002	0.26
HPO BL RW	0.05	0.01	0.003	0.22
HPO BL 150 PACl	0.00	0.00	0.002	0.18
HPO BL 150 PACl + 20 PAC	0.02	0.01	0.003	0.11

T

Table 27: DOC, DON and DOC/DON of HPI and HPO of Bangkhen WTP

Sample	DOC	DON	DOC/DON
HPI BK RW	2.2	0.32	6.9
HPI BK 80 PACl	1.4	0.37	3.9
HPI BK 80 PACl+ 20 PAC	0.5	0.38	1.4
HPO BK RW	2.0	0.18	11.1
HPO BK 80 PACl	1.1	0.16	6.6
HPO BK 80 PACl + 20 PAC	0.4	0.12	3.4

Table 28: DOC, DON and DOC/DON of HPI and HPO of Banglen WTP

Sample	DOC	DON	DOC/DON
HPI BL RW	3.9	0.40	9.8
HPI BL 80 PACl	2.2	0.31	7.2
HPI BL 80 PACl+ 20 PAC	0.6	0.26	2.2
HPO BL RW	3.7	0.22	16.8
HPO BL 80 PACl	1.8	0.18	10.3
HPO BL 80 PACl + 20 PAC	0.4	0.11	3.4

The fractional distribution of DOC and DON in raw water, coagulated water and enhanced coagulated water of Bangkhen WTP and Banglen WTP

Table 29 and **Table 30** show the mass balance of DOC and DON in raw water, coagulated water and enhanced coagulated water of Bangkhen WTP. The tolerance ranges of mass balance fractionation were between 10 to 15 percent (Day *et al*., 1991) and between 8 to 12 percent (Croue *et al*., 1993). The percentage of difference is determined by subtracting of DOC or DON mass after fractionation from DOC or DON mass before fractionation. The percentage of DOC difference in raw water, coagulated water and enhanced coagulated water were 0,-7 and 2, respectively. The percentage of DON difference in raw water, coagulated water and enhanced coagulated water were -110,-281 and -521, respectively. From this results show both of surplus and negative case. For surplus cases, it may come from the resins that adsorb organic substance during cleaning process. After that organic substances were eluted in the elution process. Negative cases, it may come from some organic matters absorbed on the resin. The percentage of DON difference was negative due to the first measurement of DON in raw water was slightly low when passed the column of fractionation it could be contaminated from inorganic compound. Moreover the instrument may determine the results be error.

Table 29 Mass balance of DOC in raw water, coagulated water and enhanced coagulated water of the Bangkhen WTP

Water samples	Parameters	Fractionation				
		HPI[1]	HPO[2]	HPI+ HPO	Total[3]	percentage of diff [4]
BK RW	DOC (mg/L)	2.2	2.0	4.2	4.2	0
	DOC (mg)	4.4	4.0	8.4	8.4	0
BK 80 PACl	DOC (mg/L)	1.5	1.1	2.6	2.4	-7
	DOC (mg)	3.1	2.1	5.2	4.8	-7
BK 80 PACl +20 PAC	DOC (mg/L)	0.5	0.4	4.9	1.0	2
	DOC (mg)	1.1	0.8	1.9	1.9	2

[1]HPI= Hydrophilic fraction, [2]HPO = Hydrophobic fraction, [3]Total of DOC before fractionation, [4]percentage of difference = (Total-(HPI+HPO))/Total)*10

Table 30 Mass balance of DON in raw water, coagulation and enhanced coagulation of the Bangkhen WTP

Water samples	Parameters	Fractionation				
		HPI[1]	HPO[2]	HPI+ HPO	Total[3]	percentage of diff [4]
BK RW	DON (mg/L)	0.32	0.18	0.50	0.24	-110
	DON (mg)	0.64	0.36	1.01	0.48	-110
BK 80 PACl	DON (mg/L)	0.37	0.16	0.53	0.14	-281
	DON (mg)	0.75	0.32	1.07	0.28	-281
BK 80 PACl +20 PAC	DON (mg/L)	0.38	0.12	0.50	0.08	-521
	DON (mg)	0.76	0.23	0.99	0.16	-521

[1] HPI= Hydrophilic fraction, [2] HPO = Hydrophobic fraction, [3] Total of DOC before fractionation, [4] percentage of difference = (Total-(HPI+HPO))/Total)*100

Table 31 and **Table 32** show the mass balance of DOC and DON in raw water, coagulated water and enhanced coagulated water of Banglen WTP. The percentage of DOC difference in raw water, coagulated water and enhanced coagulated water were -3, 6 and 5, respectively. The percentage of DON difference in raw water, coagulated water and enhanced coagulated water were -81,-247 and -272, respectively. From this results show both of surplus and negative case. The reason from these results was same as mention in term of Bangkhen WTP.

Table 31 Mass balance of DOC in raw water, coagulation and enhanced coagulation of the Bangklen WTP

Water samples	Parameters	Fractionation				
		HPI[1]	HPO[2]	HPI+ HPO	Total[3]	percentage of diff[4]
BL RW	DOC (mg/L)	3.9	3.7	7.6	7.3	-3
	DOC (mg)	7.8	7.3	15.1	14.6	-3
BL 150 PACl	DOC (mg/L)	2.3	2.0	4.3	4.6	6
	DOC (mg)	4.5	4.1	8.6	9.1	6
BL 150 PACl +20 PAC	DOC (mg/L)	0.6	0.4	1.0	1.1	5
	DOC (mg)	1.3	0.8	2.1	2.2	5

[1]HPI= Hydrophilic fraction, [2]HPO = Hydrophobic fraction, [3]Total of DOC before fractionation, [4]percentage of difference = (Total-(HPI+HPO))/Total)*100

Table 32 Mass balance of DON in raw water, coagulation and enhanced coagulation of the Banglen WTP

Water samples	Parameters	Fractionation				
		HPI[1]	HPO[2]	HPI+ HPO	Total[3]	percentage of diff[4]
BL RW	DON (mg/L)	0.40	0.22	0.62	0.34	-81
	DON (mg)	0.80	0.44	1.23	0.68	-81
BL 150 PACl	DON (mg/L)	0.31	0.18	0.49	0.14	-247
	DON (mg)	0.62	0.34	0.97	0.28	-247
BL 150 PACl +20 PAC	DON (mg/L)	0.26	0.11	0.37	0.10	-272
	DON (mg)	0.52	0.23	0.75	0.20	-272

[1]HPI= Hydrophilic fraction, [2]HPO = Hydrophobic fraction, [3]Total of DOC before fractionation, [4]percentage of difference = (Total-(HPI+HPO))/Total)*100

The percentage of HPI and HPO

Percentage of HPI and HPO are shown in **Figure 1.** HPI of from raw water, coagulated water and coagulated water of enhanced coagulation by PAC of the Bangkhen WTP were 52, 59 and 58 %, respectively. For HPO, raw water, coagulated water and coagulated water of enhanced coagulation by PAC were 48, 41 and 42%, respectively. HPI was the major DOM fraction in raw water and coagulated water of the Bangkhen WTP. It can be implied that water samples of Bangkhen WTP composed of non-humic substance more than humic substance.

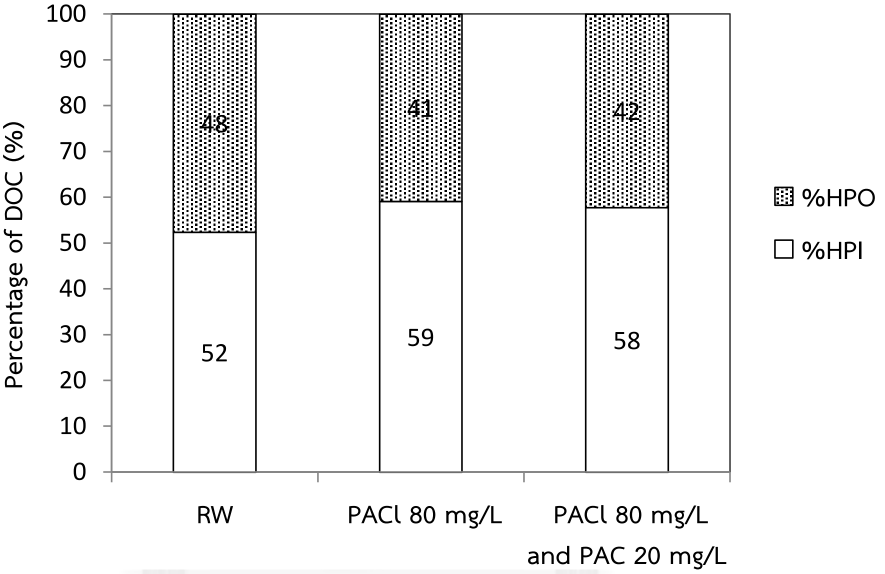


Figure 1 Percentages of HPI and HPO of water samples of the Bangkhen WTP

Percentages of HPI and HPO of water samples of the Banglen WTP are shown in **Figure 2.** HPI of raw water, coagulated water and coagulated water by enhanced PACl coagulation with PAC were 52, 53 and 62 %, respectively. For HPO, raw water, coagulated water and coagulated water by enhanced PACl coagulation with PAC were 48, 47 and 38%, respectively. HPI was the major DOM fraction in water samples of the Banglen WTP.

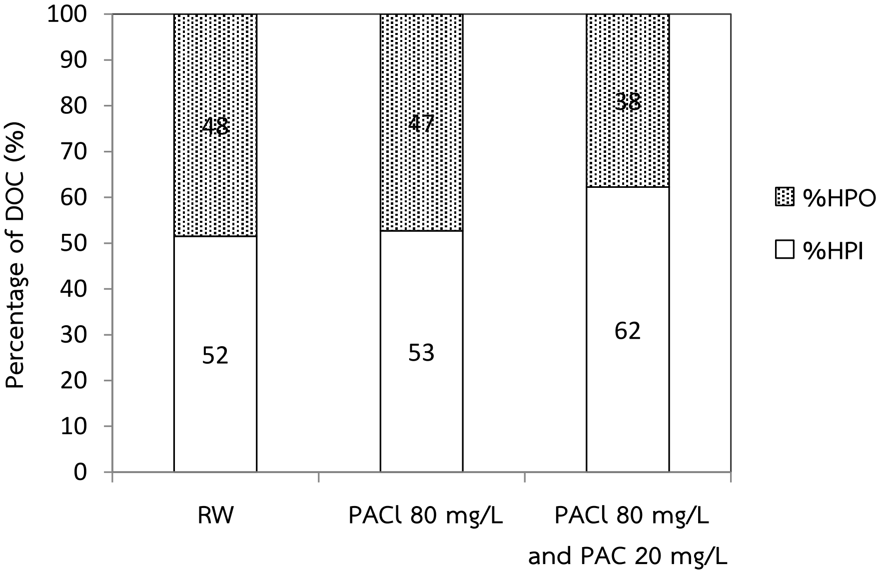


Figure 2 Percentages of HPI and HPO of water samples of the Banglen WTP

Comparison the reduction of NDMA precursors between enhanced PACl coagulation with PAC and PACl coagulation followed by PAC adsorption

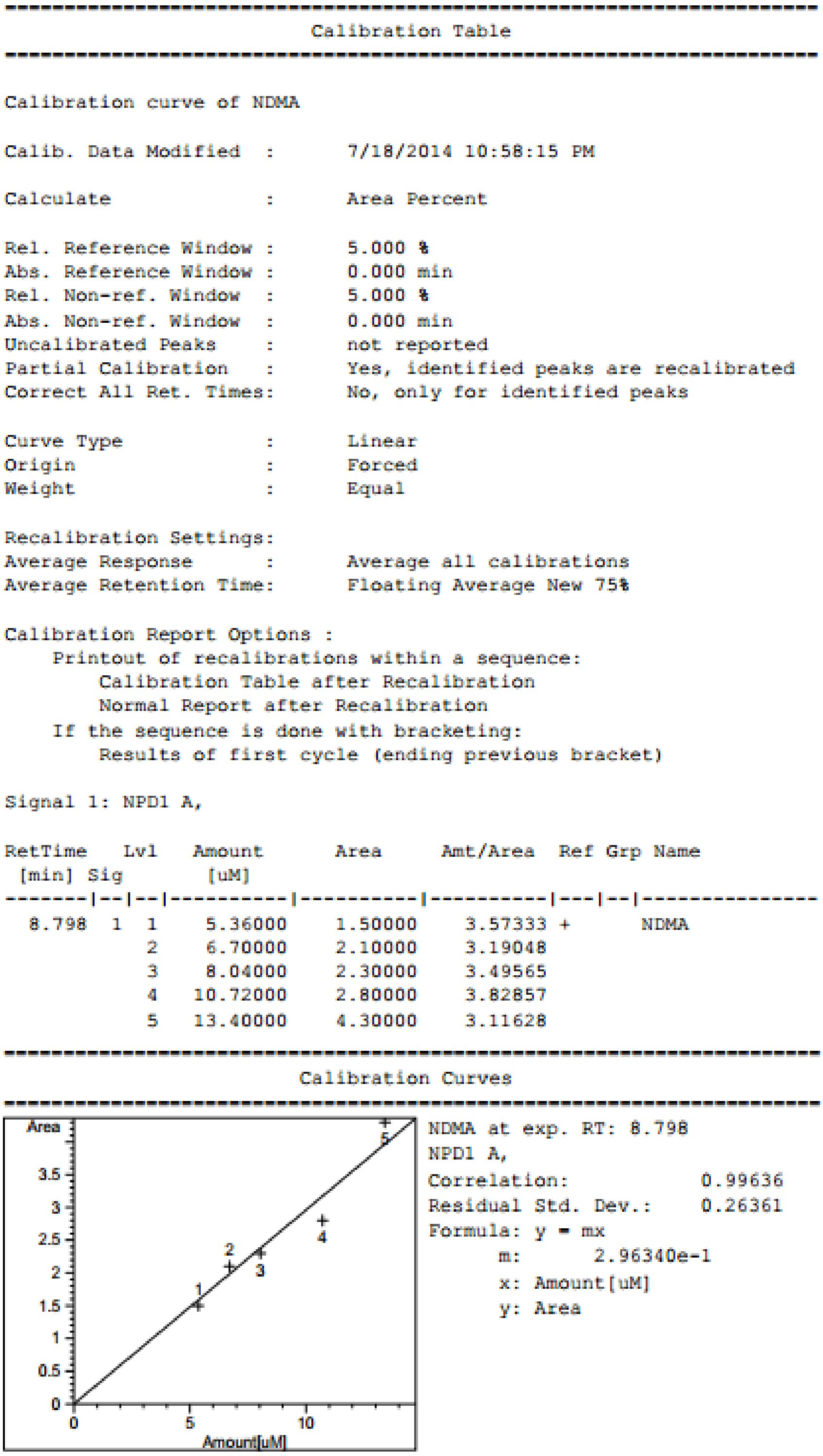
As can be seen from Table 33. Percent reductions of UV-254 , DOC, and DON by using PACl coagulation combined with PAC were comparable to that of PACl coagulation followed by PAC adsorption for water samples from both the Bangkhen WTP and the Banglen WTP. However, the percent reduction of SUVA by using PACl coagulation combined with PAC was slightly higher than that of PACl coagulation followed by PAC adsorption. It can be stated that the water treatment plant could applied the PAC during coagulation. There is no need to develop the new adsorption unit in the plant. However, they should concern about the solid loading rate of clarify and the filtration rate of filtration system.

Table 33 Percent reduction of NDMA precursors by enhanced PACl coagulation with PAC and PACl coagulation followed by PAC adsorption

Parameters	**Percent reduction (%)**			
	The Bangkhen WTP		**The Banglen WTP**	
	PACl combined with PAC[1]	PACl followed by PAC[2]	PACl combined with PAC[3]	PACl followed by PAC[4]
UV-254	94	92	95	95
DOC	77	79	85	87
SUVA	75	59	68	58
DON	68	54	70	69

[1] PACl of 80 mg/L combined with PAC of 20 mg/L at pH 7, [2] PACl of 150 mg/L combined with PAC of 20 mg/L at pH 7, [3] PACl of 80 mg/L followed by adsorption with PAC of 20 mg/L at pH 7, [4] PACl of 150 mg/L followed by adsorption with PAC of 20 mg/L at pH 7

Figure 3 NDMA calibration curve



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=====================================================================
                          Calibration Table
=====================================================================

Calibration curve of NDMA

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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%

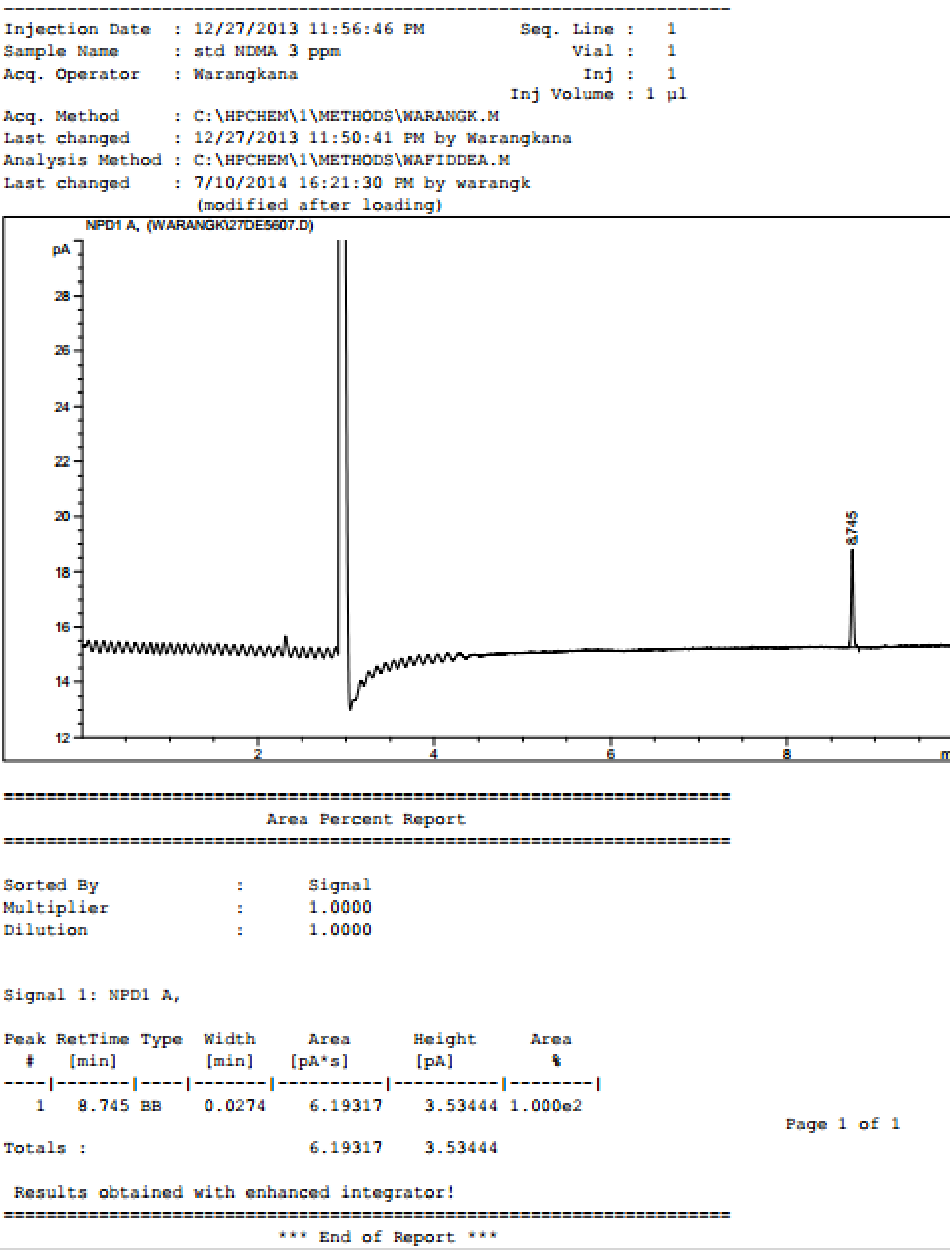
Calibration Report Options :
    Printout of recalibrations within a sequence:
        Calibration Table after Recalibration
        Normal Report after Recalibration
    If the sequence is done with bracketing:
        Results of first cycle (ending previous bracket)

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
```

Figure 4 NDMA standard 3 PPM



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Injection Date  : 12/27/2013 11:56:46 PM         Seq. Line :    1
Sample Name     : std NDMA 3 ppm                      Vial :    1
Acq. Operator   : Warangkana                           Inj :    1
                                               Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\WARANGK.M
Last changed    : 12/27/2013 11:50:41 PM by Warangkana
Analysis Method : C:\HPCHEM\1\METHODS\WAFIDDEA.M
Last changed    : 7/10/2014 16:21:30 PM by warangk
                  (modified after loading)
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=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: NPD1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   8.745 BB    0.0274    6.19317    3.53444 1.000e2

Totals :                     6.19317    3.53444

 Results obtained with enhanced integrator!
=====================================================================
                          *** End of Report ***
```

Page 1 of 1

VITA

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