



**Characterization and Reduction of Fractionated Dissolved Organic Matter in
Raw Water Supply from U-Tapao Canal by Enhanced Coagulation**

Kanjane Srimuang

**A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of
Master of Engineering in Environmental Engineering
Prince of Songkla University**

2011

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Thesis Title Characterization and Reduction of Fractionated Dissolved Organic Matter in Raw Water Supply from U-Tapao Canal by Enhanced Coagulation

Author Ms. Kanjane Srimuang

Major Program Environmental Engineering

Major Advisor:

.....
 (Asst. Prof. Dr. Charongpun Musikavong)

Co-advisors:

.....
 (Asst. Prof. Dr. Chaisri Suksaroj)

.....
 (Asst. Prof. Dr. Thunwadee Suksaroj)

Examining Committee:

.....Chairperson
 (Assoc. Prof. Dr. Udomphon Puetpaiboon)

.....
 (Assoc. Prof. Dr. Surapong Wattanachira)

.....
 (Asst. Prof. Dr. Lupong Kaewsichan)

.....
 (Asst. Prof. Dr. Charongpun Musikavong)

.....
 (Asst. Prof. Dr. Chaisri Suksaroj)

The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment of the requirements for the Master of Engineering Degree in Environmental Engineering

.....
 (Prof. Dr. Amornrat Pongdara)
 Dean of Graduate School

ชื่อวิทยานิพนธ์	การจำแนกลักษณะและการลดกลุ่มสารอินทรีย์ละลายน้ำในน้ำดิบประปาจากคลองอู่ตะเภาโดยการเพิ่มประสิทธิภาพการโคแอกกูเลชัน
ผู้เขียน	นางสาวกาญจณีย์ ศรีเมือง
สาขาวิชา	วิศวกรรมสิ่งแวดล้อม
ปีการศึกษา	2553

บทคัดย่อ

การศึกษานี้มีวัตถุประสงค์เพื่อศึกษาการกำจัดสารอินทรีย์ละลายน้ำและการลดศักยภาพการก่อตัวของสารไตรฮาโลมีเทนในน้ำดิบประปาจากคลองอู่ตะเภา อ.หาดใหญ่ จ.สงขลา ด้วยกระบวนการเพิ่มประสิทธิภาพการโคแอกกูเลชันโดยทำการทดลองโคแอกกูเลชันด้วย Polyaluminium chloride (PACl) และเพิ่มประสิทธิภาพการโคแอกกูเลชันด้วย PACl โดยใช้ Cationic polymer และ Powder activated carbon (PAC) ที่สภาวะควบคุมพีเอชเท่ากับ 7 เพื่อวิเคราะห์ดัชนีตัวแทนสารอินทรีย์ได้แก่ Ultraviolet absorption ที่ความยาวคลื่น 254 nm (UV-254), Dissolved Organic Carbon (DOC) และ Trihalomethane Formation Potential (THMFP) และศึกษาลักษณะสารอินทรีย์โดยใช้เทคนิค Fluorescent Excitation-Emission Matrix (FEEM) และ Fourier Transformed Infrared Spectroscopy (FTIR) จากผลการศึกษาพบว่าน้ำดิบฤดูฝนมีค่า UV-254, DOC และ THMFP เท่ากับ 0.414 cm^{-1} , 5.1 mg/L และ 729 $\mu\text{g/L}$ ตามลำดับ ส่วนน้ำดิบฤดูแล้งมีค่า UV-254, DOC และ THMFP เท่ากับ 0.159 cm^{-1} , 5.5 mg/L และ 509 $\mu\text{g/L}$ ตามลำดับ และเมื่อนำน้ำดิบมาผ่านกระบวนการแฟรกชันโดยใช้เรซินชนิด DAX-8 และ XAD-4 เพื่อแยกสารอินทรีย์ออกเป็นกลุ่ม hydrophobic (HPO) transphilic (TPI) และ hydrophilic (HPI) พบว่าน้ำดิบฤดูฝนมีสารอินทรีย์กลุ่ม HPO 42 % TPI 27 % และ HPI 31% ตามลำดับ ส่วนน้ำดิบฤดูแล้งมีสารอินทรีย์กลุ่ม HPO 44 % TPI 23 % และ HPI 33 % ตามลำดับ การกำจัดสารอินทรีย์ โดยกระบวนการโคแอกกูเลชันพบว่าการใช้ PACl 40 mg/L ร่วมกับ polymer 1 mg/L และ PAC 80 mg/L มีประสิทธิภาพการกำจัดสารอินทรีย์ในน้ำดิบได้ดีที่สุด โดยสามารถลดค่า DOC และ UV-254 ได้ 84 % และ 69% ตามลำดับ และที่สภาวะดังกล่าวสามารถกำจัดสารอินทรีย์กลุ่ม Aliphatic C-H ที่ 2924 cm^{-1} และ Alcoholic compounds ที่ 1096-1033 cm^{-1} ได้ดี ส่วนการวิเคราะห์ลักษณะกลุ่มของสารอินทรีย์ด้วยเทคนิค FEEM ในน้ำดิบประปาตรวจพบสารอินทรีย์กลุ่ม humic และ fulvic acid-like substance และ tryptophan-like substance สารอินทรีย์กลุ่ม humic และ fulvic acid-like substances ถูกกำจัดได้ดีกว่าสารอินทรีย์กลุ่ม tryptophan-like substances โดยกระบวนการโคแอกกูเลชัน และเมื่อนำน้ำตัวอย่างหลังผ่านกระบวนการโคแอกกูเลชันที่สภาวะเหมาะสมมาผ่านกระบวนการแฟรกชันพบว่าการใช้ PACl 40 mg/L ร่วมกับ polymer 1 mg/L และ PAC 80 mg/L กำจัดค่า DOC และลดศักยภาพการก่อตัวของสารไตรฮาโลมีเทนของสารอินทรีย์ทั้ง 3 กลุ่มได้ดี ในทุกตัวอย่างน้ำที่นำมาวิเคราะห์ ไตรฮาโลมีเทนมีค่าคลอโรฟอร์มมากกว่า 80% ของสัดส่วนสารประกอบ THMs ทั้งหมด และจากการเปรียบเทียบค่าความเข้มข้นของสาร THMs ในตัวอย่างน้ำหลังจากผ่านกระบวนการทดลองต่างๆ กับค่ามาตรฐานของ U.S. Environmental Protection Agency (USEPA) และ World Health Organization (WHO) พบว่าการใช้ PACl 40 mg/L ร่วมกับ polymer 1 mg/L และ PAC 80 mg/L สามารถลด THMs ให้มีค่าน้อยกว่าค่าสูงสุดที่มาตรฐานกำหนดที่ 80 $\mu\text{g/L}$

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Author	Miss Kanjane Srimuang
Major Program	Environmental Engineering
Academic Year	2010

ABSTRACT

This study aims to investigate the dissolved organic matter (DOM) removal and the reduction of trihalomethane formation potential (THMFP) from raw water supply collected from U-Tapao Canal, Hat Yai, Songkhla in rainy season and summer by enhanced coagulation. The coagulation experiments were conducted using the polyaluminium chloride (PACl) as a coagulant and the enhanced coagulation by adding cationic polymer and powder activated carbon (PAC) was determined. The pH of all experiments was controlled at 7. The DOM was measured in terms of ultraviolet absorption at a wavelength 254 nm (UV-254), dissolved organic carbon (DOC), THMFP, fluorescent excitation-emission matrix (FEEM) and fourier transformed infrared spectroscopy (FTIR). The UV-254, DOC, THMFP of raw water in rainy season were 0.414 cm^{-1} , 5.1 mg/L, and 729 $\mu\text{g/L}$, respectively, whereas that of summer were 0.159 cm^{-1} , 5.5 mg/L, and 509 $\mu\text{g/L}$, respectively. The DOM in water samples was fractionated by DAX-8 and XAD-4 resin into hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fractions. HPO of 42%, TPI of 27%, and HPI of 31 % was determined in rainy season and HPI, TPI, and HPO of 44%, 23%, and 33% was determined in summer. The optimal conditions for DOM removal arranged in an order of high efficiency were PACl 40 mg/L combined with polymer 1 mg/L and PAC 80 mg/L yielded the maximum DOM reduction efficiency in terms of DOC and UV-254 removal at 84% and 69%, respectively. At that condition, it could remove aliphatic C-H at 2924 cm^{-1} and alcoholic compounds at $1096\text{-}1033 \text{ cm}^{-1}$ effectively. The FEEM analysis found humic and fulvic acid-like substances and tryptophan-like substances existed in raw water supply. Coagulation process could remove humic and fulvic acid-like substances better than tryptophan-like substances. Considering, the fractionation of all treated water samples in all experiments, PACl 40 mg/L combined with polymer 1 mg/L and PAC 80 mg/L could remove DOC and THMFP of all organic fractions. The trihalomethane analysis indicated that all water samples contained chloroform more than 80% of total THMs. Comparison of result with U.S. Environmental Protection Agency (USEPA) and World Health Organization (WHO) standard limit showed that the use of PACl 40 mg/L combined with polymer 1 mg/L and PAC 80 mg/L could remove THMs to a level lower than $80\mu\text{g/L}$ standard limit.

ACKNOWLEDGEMENTS

I would like to express my appreciation to my advisor, Assistant Professor Dr. Charongpun Musikavong, for his valuable guidance, inspiration, utmost help, encouragement and advice through out the research. He has shown me how to conduct myself in a professional manner and has prepared me to handle all aspects of faculty life. Not only has he been there to guide me through my education endeavors as a mentor, he has been there as a friend. None of this would have been possible without him, and for this, I am forever grateful. Special respect and thanks are also extended to Assistant Professor Dr. Chisri Suksaroj, Assistant Professor Dr.Thunwadee Suksaroj for valuable suggestions and guidance as co- advisor.

I would like to thank my committee members: Assistant Professor Dr. Lupong Kaewsichan, Associate Professor Dr. Udomphon Puetpaiboon, and Associate Professor Dr.Suraphong Wattanachira.

I would like to thankful to the Department of Civil Engineering of Songkla University Graduate School for financial support.

I would like to sincerely thank the National Research Center for Environmental and Hazardous Waste Management (NRC-EHWM), Chiang Mai University for the analysis sample.

Finally, I would not have been possible without the support of my family and friends. Thank you for standing by me, listening to my complaints, and lending a helping hand when possible. You were truly the inspiration that I needed to succeed.

Kanjane Srimuang

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ABBREVIATIONS AND SYMBOLS

$\mu\text{g/L}$	Microgram per liter
μm	Micrometer
$\mu\text{s/cm}$	Microsemen per centimeter
Al	Aluminium
BDCM or CHBrCl_2	Bromodichloromethane
CatPAM	Cationic polymer
cm	Centimeter
COM	Colloidal organic matter
CPEM	Cationic polyacrylamide
DADMC	Polydiallyl dimethy ammonium chloride
DBCM or CHBr_2Cl	Dibromochloromethane
DBPs	Disinfection by-products
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOC_{HPI}	Dissolved organic carbon of hydrophilic
DOC_{HPO}	Dissolved organic carbon of hydrophobic
DOC_{TPI}	Dissolved organic carbon of transphilic
DOM	Dissolved organic matter
DPD	N, N-diethyl-p-phenylenediamine
ECD	Electron capture detector
Em	Emission wavelength
Ex	Excitation wavelength
FeCl_3	Ferric chloride
FEEM	Fluorescent excitation-emission matrix
FEEM_{HPI}	Fluorescent excitation-emission matrix of hydrophilic
FEEM_{HPO}	Fluorescent excitation-emission matrix of hydrophobic
FEEM_{TPI}	Fluorescent excitation-emission matrix of transphilic

FTIR	Fourier Transformed Infrared Spectroscopy
g/cm^3	Gram per cubic centimeter
GAC	Granular activated carbon
GC	Gas chromatography
GV	Guideline values
HAAs	Haloacetic acids
HANs	Haloacetonitriles
HPI	Hydrophilic
HPO	Hydrophobic
L/mg-m	Liter per milligram-meter
LD50	Lethal dose 50%
MCLG	Maximum contaminant level goals
MCLs	Maximum contaminant levels
MW	Molecular weight
mg/hr	Milligram per hour
mg/kg	Miligram per kilogram
mg/L	Miligram per liter
mg/L as CaCO_3	Miligram per liter as calcium carbonate
mg/mg DOC	Milligram per milligram dissolved organic carbon
mM Al	Millimole of aluminium
mm Hg	Millimeter of mercury
N.D.	Not detected
nm	Nanometer
nm/min	Nanometer per minute
NOM	Natural organic matter
NTU	Nepheo turbidity unit
O_2^-	Super oxide
O_3	Ozone
$^\circ\text{C}$	Degree celsius

OH ⁰	Hydroxyl radical
PAC	Powder activated carbon
PACl	Polyaluminium chloride
POM	Particulate organic matter
QSU	Quinine sulfate unit
R ²	Regression
SS	Suspended solids
SUVA	Specific ultraviolet absorption
TBM or CHBr ₃	Tribromomethane or bromoform
TCM or CHCl ₃	Trichloromethane or chloroform
THMFP	Trihalomethane formation potential
THMFP _{HPI}	Total trihalomethane formation potential of hydrophilic
THMFP _{HPO}	Total trihalomethane formation potential of hydrophobic
THMs	Trihalomethanes
TPI	Transphilic
TTHM	Total trihalomethane
TTHM ₀	Total trihalomethanes
TTHMFP	Total trihalomethane formation potential
TTHM _T	Total trihalomethanes
USEPA	United states environmental protection agency
UV-254	Ultraviolet absorbance at wavelength-254 nm
WHO	World health organization
w/w	Weight per weight

CHAPTER I

INTRODUCTION

1.1 Motivation

In general, water supply process utilizes coagulation, flocculation, sedimentation, and filtration to produce water supply and it can be distributed through the water supply network. Moreover, during the disinfection process with chlorine or chlorinated compounds, the organic matter could potentially be converted to harmful disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs). THMs are identified as potential adverse health agents for which U.S. Environmental Protection Agency (USEPA) proposed the drinking water standard under the Disinfectants/Disinfection By-Products (D/DBP) Rule with a THMs Maximum Contaminant Level (MCL) of 0.08 mg/L for Stage 1 and 0.04 mg/L for Stage 2. (Liang and Singer, 2003; Hassan, 2006).

Natural organic matter (NOM) is a heterogeneous mixture of aliphatic and aromatic polymers (Stedmon *et al.*, 2003) and can be operationally divided into hydrophobic, transphilic and hydrophilic fractions. Hydrophobic fraction primarily consists of humic and fulvic acids. Humic acid is described as being soluble in dilute alkaline media and will participate upon acidification; whereas fulvic acid will remain in the solution at a low pH (Kanokkantapong *et al.*, 2006). According to Thurman and Malcolm (1981), aquatic organic substances are derived from soil and plants and comprise up to one-half the DOC in water. Hydrophilic and transphilic fractions are those comprised of carbohydrates with low molecular weight, proteins, and amino acids (Marhaba *et al.*, 2003). Considering, NOM surrogate parameters in term of DOM quantity, DOC is generally used to quantify the level of DOM in water. Absorption of ultraviolet at wavelengths 254 nm (UV-254), specific ultraviolet absorbance (SUVA), which is defined as the ultraviolet (UV) absorbance at 254 nm divided by DOC concentration expressed in $\text{Lmg}^{-1}\text{-m}^{-1}$, have shown to be a good indicator of aromatic content. In the case of NOM characteristic, fourier transform infrared (FTIR) and fluorescent excitation emission matrix (FEEM) are commonly used to identify nature and abundance of structure units in DOM molecule. FTIR can be utilized to

characterize the putative origin of DOM in water. (Liang and Singer, 2003; Yang *et al.*, 2008) (Hua and Reckhow, 2007). FEEM have since been utilized to provide a more specific fingerprint of the organic matter (OM) contained within the source water (Yang *et al.*, 2008).

The successful technique that was commonly employed to reduce the level of the DBPs was to reduce the level of DOM prior to it being chlorination. The coagulation processes were conducted using the polyaluminium chloride (PACl) as a coagulant and the enhanced coagulation, such as pH adjustment, adding cationic polymer and powder activated carbon (PAC) could be an effective method for organic matter removal in the raw water under the optimal dosage of coagulant and pH (Cheng *et al.*, 1995; Dennett *et al.*, 1996; and Marhaba and Pipada, 2000). In addition, enhanced coagulation technique could be employed to improve THMs precursors removal (Bolto *et al.*, 1999; and Bolto *et al.*, 2002).

U-Tapao Canal, located in Hatyai is used as source water to produce water supply for utility in the area of Songkhla, Thailand. This raw water is to a considerable extent contaminated with domestic wastewater, industrial wastewater, pesticides and other organic matters. These organic matters therefore can react with chlorine in the water treatment process to form THMs. Under this situation, THMs as a suspected human carcinogen may directly affect consumers. Therefore, there is a need to study the removal of dissolved organic matters by coagulation with PACl, polymer, and powder activated carbon (PAC), and to identify the nature of NOM in raw water from the U-Tapao Canal, and to analyze the formation of carcinogens of NOM fraction.

1.2 Objectives

1. To determine the quantification of hydrophobic, transphilic, and hydrophilic organic fractions in raw water supply from U-Tapao Canal.
2. To evaluate the formation potential of THM of hydrophobic, transphilic, and hydrophilic fractions in raw water supply.
3. To study the reduction of hydrophobic, transphilic, and hydrophilic fractions in raw water supply by enhanced coagulation processes.
4. To identify the organic compounds of hydrophilic, transphilic, and hydrophobic fractions in raw water and coagulated water.

1.3 Scopes of This Work

1. Raw water supply samples were collected from U-Tapao Canal, Hat Yai, Songkhla province, Thailand
2. The jar-test experiments were conducted to obtain an optimal condition for dissolved organic matter (DOM) removal.
3. DOM in raw water and coagulated water were fractionated into three fractions that consist of hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fractions by using a series of Supelite DAX-8 and Amberlite XAD-4 resin.
4. FTIR analysis was used to characterize the nature DOM and DOM fractions.

1.4 Advantages of This Work

1. To know the physical and chemical properties of raw water from U-Tapao Canal.
2. To know and characterize the organic matter and the formation of THM compounds.
3. To be a guideline for assessment and removal of organic matter in water.

CHARTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Dissolved Organic Matter

Dissolved organic matter (DOM) defined as the complex matrix of organic material present in natural waters, affects significantly many aspects of water treatment. DOM even though present in a tiny quantity, can react with chlorine during chlorination to form halogenated disinfection by-products (DBPs) which are all classified as carcinogenic substances. DOM consists of humic substances, amino acids, sugars, aliphatic acids, and a large number of organic molecules (Marhaba and Pu, 2000). Humic substances include humic and fulvic acids; while non-humic substances include hydrophilic acids, proteins, carbohydrates, carboxylic acids, amino acids, and hydrocarbons (Thurman, 1985; Amy and Chadik 1983). DOM can be separated into humic and non-humic fraction. The humic fraction has a more hydrophobic character than the non-humic fraction. The humic fraction consists of humic and fulvic acids. The non-humic consists of hydrophilic acids, proteins, amino acids and carbohydrate. However, in terms of their chemical properties and implication for water supply, the humic substance is the most important (Owen *et al.*, 1995). DOM which consists of humic and fulvic acid (aquatic humic), cause natural color, is the most important (Edzwald, 1993).

DOM plays a role in many aspects of fresh water. DOM is capable of forming complexes with metals such as iron. It can serve as a substrate for microbial growth and can exert significant oxidant demand, thereby interfering with both oxidation and disinfection during drinking water treatment. Depending on the concentration and type of DOM, the acidity of water can also be affected. DOM serves as the organic precursor. DBP formation was influenced by water quality (e.g., TOC, pH, temperature) and treatment conditions (e.g., disinfectant dose, contact time, removal of DOM before the point of disinfectant application, prior addition of disinfectant).

Non-humic substances, such as algae and their extra cellular products have been shown to be precursors to trihalomethane (THMs) (Morris and Baum, 1978; Oliver and Shindler, 1980).

Oliver and Shindler (1980) observed faster reaction kinetics between chlorine and algae than between chlorine and aquatic humic materials. Their results suggest that algae in surface waters may be a major contributor to THM production. Humic acids have generally been found to be more reactive with chlorine than fulvic acids. There is also evidence that the humic fraction produces greater concentrations of haloacetic acid (HAAs) and THMs than the non-humic fraction.

Humic acid are thought to be complex aromatic macromolecules with amino acid, amino sugars, peptides, aliphatic compounds involved in linkages between the aromatic groups. The hypothetical structure for humic acid suggested by Stevenson (1982) is shown to contain free and bond phenolic OH group, quinone structure, nitrogen and oxygen as bridge units and carboxylic groups variously placed on aromatic ring (Figure 2.1)

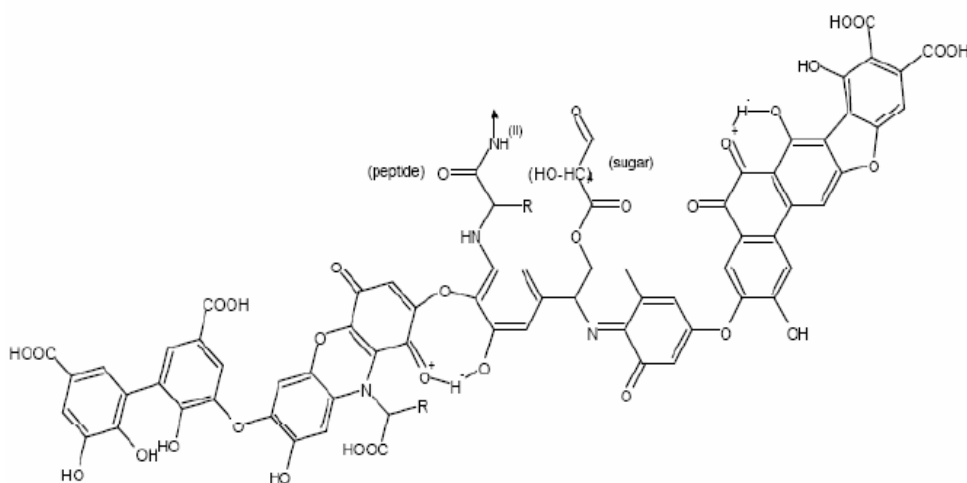


Figure 2.1 Suggested structure of humic acid (Stevenson, 1982)

The hypothetical structure of fulvic acid suggested by Kubibicki and Apitz (1999) contain both aromatic and aliphatic structure extensively substituted with oxygen-containing functional group. The humic acid structure shows that the humic acids are highly aromatic and contains more carboxylic and phenolic functional groups compared to the fulvic acid. These humic and fulvic acids play a central role in both pollutant chemistry and the biogeochemistry of natural waters and soils (Cabaniss *et al.*, 2000).

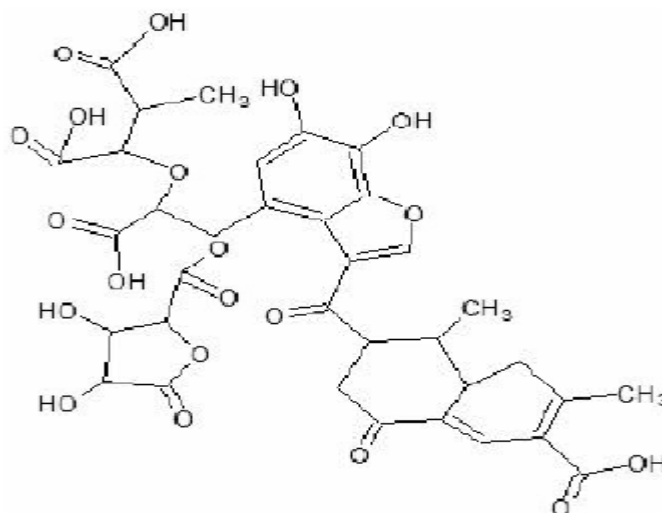


Figure 2.2 Fulvic acid structures (Kubibicki and Apitz, 1999)

Although the humic substances are classified complex, they can be conveniently classified into these components:

- Humic acid: the fraction of humic substance that is not soluble in water under acidic conditions ($\text{pH} < 2$) but is soluble at higher pH.
- Fulvic acid: the fraction of the humic substance that is soluble in water under all pH.
- Humin, black color, is a non-soluble part in any condition in the fraction of humic substances.

2.2 Fractionation

NOM is a heterogeneous mixture comprised of humic and fulvic acids, lignins, carbohydrates, and proteins of various sizes and molecular weight (Hua and Reckhow, 2008). Isolation techniques have been developed to characterize NOM and separate organic matter based on the polarity of the organic compounds. Since no absorbent can isolate the entire group of organics present in given water sample, improvements on these techniques have quantitatively isolated NOM fractions through adsorption to various resins. Leenheer (1981) proposed the use

DAX-8 resin to isolate the hydrophobic and hydrophilic acid fractions. However, due to the concentration of inorganic salts in the water and the difficulty of separating these salts from the hydrophilic organics, a large portion of the DOC remained unattainable (Aiken *et al.*, 1992). Expanding on the techniques of Thurman and Malcolm, (1981); Aiken *et al.*, (1992) used a two column apparatus that utilized both DAX-8 and XAD-4 resins which isolated the humic and fulvic acids of the hydrophobic fraction as well as a portion of the hydrophilic acid fraction while maintaining the operational definition of the organics. More recently, the operational characteristics of the organic fractions have been redefined to hydrophobic acid (non-polar organics which adsorb onto DAX-8 resin), transphilic acid (intermediate polarity which adsorb onto XAD-4 resin), and the remaining effluent consisting of the hydrophilic, or polar, fraction which did not adsorb (Croue *et al.*, 1999; Liang and Singer, 2003).

While it can be concluded that humic substances play an important role in the formation of DBP, chlorination of NOM isolates have resulted in conflicting reports from various researchers (Liang and Singer, 2003). Marhaba and Van (2000) isolated water from the Passaic River in New Jersey and found it to be comprised of over 50 percent hydrophilic acid. DBP formation potential tests yielded THM and HAA concentrations of 69 and 4 percent, respectively, of the total DBP formation within the hydrophilic acids fraction. Similarly, the hydrophobic acid fraction comprised 6 and 26 percent of the THM and HAA formation, respectively. Meanwhile, Liang and Singer (2003) reported that while research by Hua and Reckhow, (2007) displayed similar trends to that of Marhaba and Van (2000) for low humic waters, their results showed the hydrophobic fraction as being the primary contributor to THM and HAA formation.

Malcom and MacCarthy (1992) successfully isolated more than 85 percent of dissolved organic solutes from soil and sediment river water using XAD-8 and XAD-4 resins. These authors also noted that approximately 65 percent of the DOC was first removed on XAD-8 resin and then an additional 20% of the DOC was removed on XAD-4 resin and of the 65 percent of the solutes removed on XAD-8 resin, 40 percent were fulvic, 16 percent were humic acid, and 9 percent were hydrophobic neutrals. Aiken *et al.*, (1992) removed on the overall 83 percent DOM, with the majority of fractionation isolated on the XAD-8 resin (23 to 58 percent) than on XAD-4 resin (7 to 25 percent) while Martin-Mousset *et al.*, (1997) found a DOM recovery of between 55 to 75%. The review of the fractionation method for isolation of DOM in water sources in Table 2.1

Table 2.1 Review of fractionation method for isolation of DOM in water sources.

Water source	Resin	Fraction	Reference
Moorabool, Hope Valley, and Wanneroo (Australia)	XAD-4, DAX-8, and IRA-958	Very HPOA 34-80%, slightly HPOA 9-21%, HPI charged fraction 9-33%, and HPIN 1-15%	Bolto <i>et al.</i> ,1999
Da Cha creek, Taichung,Taiwan (DOC 2 mg/L)	DAX-4 and DAX-7	HPO substance 43%, HPIA 41%, and non-acid hydrophilic 16%	Chang <i>et al.</i> ,2001
Nakdong River, Korea (DOC 3.71 mg/L)	XAD-4 and XAD-8	HPO, Transphilic, and HPI	Lee <i>et al.</i> , 2002
South Platte River, Colorado, USA (DOC 2.6 mg/L)	XAD-4, XAD-8, and MSC-1H	HPOA, HPON, Transphilic acids, Transphilic neutral, and HPI	Croue <i>et al.</i> ,2003
Mosina Water Intake (TOC 3.8-6.5 mg/L)	XAD-4, XAD-8, AGMP-50, and Duolite A7	Humic acids 19%, HPOA 54%, HPOB traces, HPON 12%, HPIA 7%, HPIB 5%, and HPIN 3%	Swietlik <i>et al.</i> ,2004
Saguaro Lake, Mexico	XAD-4, DAX-8	HPO22%, TPI 10%, and HPI 31%	Mash <i>et al.</i> ,2004
Sein-Aval wastewater treatment plant,Paris	XAD-4, DAX-8	HPO35%, TPI 20%, and HPI 45%	Benoit <i>et al.</i> ,2008
Bitumen roof runoff,Berlin	XAD-4, DAX-8	HPO65%, TPI 18%, and HPI 17%	Ropru and Martin.,2008
Waste effluent,USA	XAD-4, DAX-8	HPO29%, TPI 35%, and HPI 36%	Park <i>et al.</i> ,2008
Glane River, France	XAD-4, DAX-8	HPO65.5%, TPI 13%, HPI 16% and HA5%	Labanowski and Feuillade.,2009

2.3 Surrogate Parameter for NOM

To describe the characteristic of NOM, surrogate parameters must be used because no single analytical technique is capable of measuring the widely varied characteristic of NOM. Commonly used NOM surrogates include dissolved organic carbon (DOC) ultraviolet absorbance at wavelength-254 nm (UV-254) fluorescent excitation-emission matrix (FEEM) and trihalomethane formation potential (THMFP). Moreover, THMFP removals are also present to highlight any difference between TOC and THMFP removals (USEPA, 1999)

It was not practical to analyze each individual chemical compound in NOM; consequently, NOM was evaluated in term of surrogate parameters as follow;

2.3.1 Dissolved Organic Carbon (DOC)

Dissolved organic carbons are defined as the fraction of TOC that passes through a 0.22 μm filter paper. DOC is independent of the oxidation state of the organic matter. Organic carbon in natural water can be composed in two fractions, particulate organic carbon (POC) and dissolved organic carbon (DOC). In surface water, between 50 and 60% of humic substances is DOC (Thurman, 1985)

2.3.2 UV absorbance at wavelength 254-nm (UV-254)

UV absorbance at a wavelength of 254 nm was first used as a surrogate parameter for the estimation of non-purgable organic carbon concentrations of raw water (Edzwald *et al.*, 1985). More specifically, this measurement was normalized to the total organic carbon (TOC) concentration and denoted as SUVA (specific ultra-violet absorbance). Researchers have since used this parameter as a measure of the aromatic content of NOM and to predict the formation potential of DBP (Edzwald *et al.*, 1985; Liang and Singer, 2003). Westerhoff *et al.* (2001) confirmed the percent aromaticity as measured by SUVA through carbon-13 nuclear magnetic resonance (NMR); yet found poor correlations to their activity of the NOM with chlorine. This information suggests that while UV can characterize the organic content of the water, it is a weak indicator of NOM reactivity derived from various sources.

2.3.3 Specific Ultraviolet Absorbance (SUVA)

A useful indicator of NOM character is Specific Ultraviolet Absorbance (SUVA). SUVA, is defined as the ultraviolet absorbance (UVA) of a given samples determined at a wavelength of 254 nm and divided by the dissolved organic carbon (DOC) concentration of the solution (expressed in L/mg-m). The SUVA index has been shown the well correlation with the aromatic content of NOM. The more aromatic the NOM the more hydrophobic it will be leading to water with a higher SUVA. Edzwald and Tobiason (1999) defined guidelines for SUVA and showed a good correlation between value and the nature of the organic material (as shown in Table 2.2).

Table 2.2 Guidelines for the nature of NOM (Edzwald and Tobiason, 1999)

SUVA	Composition
> 4	Mostly aquatic NOM. High hydrophobicity, high molecular weight
2-4	Mixture of aquatic NOM and other NOM. Mixture of hydrophobic
< 2	Mostly non-humic substances. Low hydrophobicity. Low molecular weight

Cho *et al.*, (2002) reported that the prediction equation for NOM rejection can be developed in terms of the SUVA parameters and or humic content. Correlation between NOM rejection and SUVA was found to be higher than between NOM reject and molecular weight suggesting that electrostatic repulsion are more important than size exclusion for NOM rejection.

2.3.4 Trihalomethane Formation Potential (THMFP)

THMFP determines the potential of DOM to form THMs under relatively extreme chlorination conditions. THMFP is defined as the difference between the concentration of THMs after the collected sample has been subjected to chlorination (Term-THM) and the concentration of THMs at the time of sampling (Inst-THM). The recommended (Standard Methods, 1995) chlorination conditions for THMFP tests include an incubation time of seven days with a free chlorine residual of 3 to 5 mg/L at the end of the incubation period. The recommended incubation

temperature is $25 \pm 2^\circ\text{C}$ and the recommended pH is 7.0 ± 0.2 with phosphate buffer. The definition terms of THMFP are described as follows:

Total trihalomethanes (TTHMs) are the sum of all four compounds concentration, which include chloroform, bromoform, dichlorobromomethane and dibromochloromethane.

TTHM_0 is the total THMs concentration at the time of the sampling. It can range from non-detectable to several hundred micrograms per liter if the sample has been chlorinated.

TTHM_7 is the total concentration of all four THMs compounds that are formed when the sample is incubated at $25 \pm 2^\circ\text{C}$ in the presence of excess free chlorine over a 7-day reaction time under the recommended chlorination conditions for THMFP (Standard Methods, 1995).

THMFP or ΔTHMFP is the difference between the final TTHM_T concentration and the initial TTHM_0 concentration as shown in Figure 2.3 and 2.4, respectively. THMFP determinations provide a worst-case scenario of the concentration of THMs that may be formed.

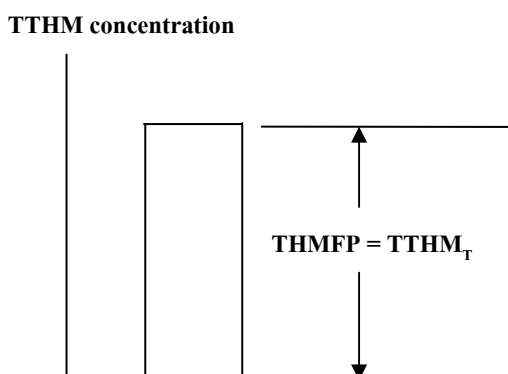


Figure 2.3 Definition used in the formation potential test of a sample without free chlorine at the time of sampling.

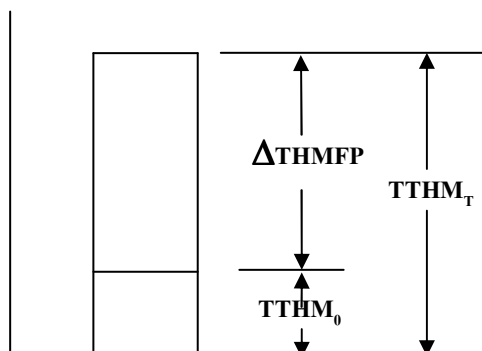


Figure 2.4 Definition used in the formation potential test, of a sample with free chlorine at the time of sampling

Chemllam and Kraner (2001) investigated the formation and speciation of DBPs result from chlorination of nanofilter permeates obtained from various source water locations and membrane types, and reported that CHCl_2Br that contains 1 mol Br/mol THM peaked at 12 $\mu\text{mol}/\text{mmol Br}^-/\text{DOC}$ compare to CHClBr_2 that contains 2 mol Br/mol THM and peaked at approximately twice the Br^-/DOC at 25 $\mu\text{mol}/\text{mmol}$.

2.4 Fluorescent Excitation-Emission Matrix (FEEM)

Fluorescence spectroscopy is an optical technique used to characterize DOM (Roccaro *et al.*, 2009). This procedure entails the absorption of light by a molecule which excites an electron and promotes it to an unoccupied orbital. As the molecule relaxes, it returns to the lowest sublevel via relaxation and internal conversion. The emission wavelength is then determined by the difference in energy between the single state and the ground state (Stedmon *et al.*, 2003).

2.4.1 FEEM of DOM in Water Sources and Wastewater

FEEM can provide information on the putative origin of fluorescent organic matter of DOM in water. Stedmon and Markager (2005a) reported a peak at $290\text{-}310\text{nm}_{\text{Ex}}/370\text{-}410\text{nm}_{\text{Em}}$ in freshwater that has been encouraged to produce algae by manipulation of nutrient level. Sirivedhin and Dallbauman, (2004) reported that fluorescent spectroscopy to investigate the water sample and the ground water. The FEEM peaks of tryptophan-like, tyrosine-like and fulvic-like substances were at $275\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$, and $275\text{nm}_{\text{Ex}}/305\text{ nm}_{\text{Em}}$ and $340\text{nm}_{\text{Ex}}/425\text{nm}_{\text{Em}}$,

respectively. Coble (1996) utilized high-resolution fluorescent spectroscopy to characterize the DOM in water samples from a wide variety of freshwater, coastal and marine environments. The fluorescent signals of humic-like, tyrosine-like, and tryptophan-like were observed. The fluorescent peak positions of the major fluorescent component in bulk seawater were as follows: tyrosine-like and protein-like ($275\text{nm}_{\text{Ex}}/310\text{nm}_{\text{Em}}$), tryptophan-like and protein-like ($275\text{nm}_{\text{Ex}}/340\text{nm}_{\text{Em}}$), humic-like ($260\text{nm}_{\text{Ex}}/380\text{-}460\text{nm}_{\text{Em}}$), marine humic-like ($312\text{nm}_{\text{Ex}}/380\text{-}420\text{nm}_{\text{Em}}$) and humic-like ($250\text{nm}_{\text{Ex}}/420\text{-}480\text{nm}_{\text{Em}}$). Khan *et al.*, (2005) also reported the location of fluorescent peaks of DOM in the Lake Biwa watershed of fulvic acid was found at $300\text{-}395\text{nm}_{\text{Ex}}/406\text{-}490\text{nm}_{\text{Em}}$. Gone *et al.*, (2009) utilized FEEM to characterize fluorescent organic matter in Agbo reservoir. The location of fluorescent peaks of tryptophan-like, humic and fulvic acid were found at $230\text{-}240\text{ nm}_{\text{Ex}}/350\text{-}400\text{nm}_{\text{Em}}$, $240\text{-}250\text{ nm}_{\text{Ex}}/450\text{-}450\text{nm}_{\text{Em}}$ and $330\text{-}340\text{ nm}_{\text{Ex}}/440\text{-}450\text{nm}_{\text{Em}}$, respectively.

Baker, (2001); Baker and Inverarity, (2004); Hudson *et al.*, (2008) utilized fluorescent as an alternative to existing water quality parameters commonly employed in the monitoring of river pollution and wastewater treatment processes. Janhom *et al.*, (2009) demonstrated characteristic of brewery wastewater with spectrofluorometry analysis. The fluorescent peaks at $230\text{ nm}_{\text{Ex}}/315\text{ nm}_{\text{Em}}$ (peak A), $275\text{nm}_{\text{Ex}}/315\text{ nm}_{\text{Em}}$ (peaks B), $230\text{nm}_{\text{Ex}}/365\text{ nm}_{\text{Em}}$ (peak C), $280\text{ nm}_{\text{Ex}}/365\text{ nm}_{\text{Em}}$ (peaks D), $290\text{nm}_{\text{Ex}}/400\text{nm}_{\text{Em}}$ (peaks E), $335\text{-}355\text{ nm}_{\text{Ex}}/405\text{-}465\text{ nm}_{\text{Em}}$ (peaks F), $255\text{ nm}_{\text{Ex}}/455\text{ nm}_{\text{Em}}$ (peaks G), and $500\text{ nm}_{\text{Ex}}/525\text{ nm}_{\text{Em}}$ (peaks H). Peak A, B, C and D were associated with tyrosine-like and tryptophan-like substances, respectively whilst each individual peak E, F and G was associated with humic and fulvic acid like substances.

Swietlk *et al.*, (2004) used application of fluorescent spectroscopy in the studies of natural organic matter fractions before and after a treatment process in the reaction with chlorine dioxide and ozone. FEEM analysis detected strong broad peaks of humic and fulvic acid-like at $250\text{-}265\text{ nm}_{\text{Ex}}/422\text{-}452\text{ nm}_{\text{Em}}$ and $300\text{-}336\text{ nm}_{\text{Ex}}/414\text{-}446\text{ nm}_{\text{Em}}$. Baker and Curry, (2004) utilized fluorescent spectroscopy for monitoring the removal of leachates from landfill. The FEEM peaks of protein tryptophan-like and fulvic-like substances were at $275\text{-}280\text{nm}_{\text{Ex}}/350\text{-}360\text{nm}_{\text{Em}}$, and $320\text{-}340\text{nm}_{\text{Ex}}/400\text{-}440\text{ nm}_{\text{Em}}$, respectively. Chen *et al.* (2003) divided excitation and emission boundaries into five regions based largely upon supporting literature. Fluorescent peaks have

been associated with humic-like, tyrosine-like, tryptophan-like, and phenol-like organic compounds. In general, fluorescent peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) are related to simple aromatic proteins such as tyrosine (Regions I and II). Fluorescent peaks at intermediate excitation wavelengths (250-280 nm) and shorter emission wavelengths (<380 nm) are related to soluble microbial byproduct-like material (Region IV). Fluorescent peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) are related to humic acid-like organics (Region V). For fulvic acids, fluorescent peaks with minimum excitation wavelengths of 250 nm indicated shoulders of fluorescent peaks located at shorter excitation wavelengths. Therefore, fluorescent peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Region III).

There are some studies that developed the relationship between the fluorescent intensity of outstanding peaks and DOM surrogates parameters such as DOC and THMFP. Marhaba and Kochar, (2000) utilize fluorescence signatures to quantify NOM for use in the prediction of DBP formation. Recent studies have shown the use of fluorescence spectroscopy to assess NOM reactivity. Previous researchers have used peak intensity excitation-emission pairs, as well as the emission band at its half intensity for a specified excitation wavelength (Fabbricino and Korshin, 2004) and correlated these measurements to DBP formation (Roccaro *et al.*, 2009). Baker, (2001); Hudson *et al.*, (2008) studied investigating the relationship between humic and fulvic like fluorescent at $320-340\text{nm}_{\text{Ex}}/410-430\text{nm}_{\text{Em}}$, $370-390/460-480\text{nm}_{\text{Em}}$ and BOD. The moderate correlations ($R^2=0.72-0.77$) were found. Table 2.3 the presents summary of offered mapping of FEEM regions and fluorescent DOM.

Table 2.3 Summary of the offered mapping of FEEM regions and fluorescent DOM.

Substances	Excitation (nm) /Emission (nm)	Source	References
Tryptophan-like proposed	275/340	Bulk seawater	Coble, 1996
	265-280/300-370	Groundwater from Sutherland, Scotland, Derbyshire, England, Dordogne, France, Wiltshire, England	Baker and Genty, 1999
	278-279/340-353	Discharge from sewage treatment plants, England	Baker, 2001
	278/353	Natural water and wastewater, USA	Her <i>et al.</i> , 2003
	280/320	Lake water, Japan	Komatsu <i>et al.</i> , 2005
	280/340	Industrial wastewater, Spain	Marhuenda-Egea <i>et al.</i> , 2007
	240/355 and 280/355	Industrial estate wastewater, Thailand	Musikavong <i>et al.</i> , 2007
	230/365 and 285/365	Brewery wastewater, Thailand	Janhom <i>et al.</i> , 2009
	235-240/340-355	Quyung municipal wastewater treatment plant (WWTP) of Shanghai, China	Wang <i>et al.</i> , 2009
Fulvic acids	350/450	Suwannee river, peat and soil standards, IHSS	Marhaba and kochar, 2000
	245/445 and 320/443	Suwannee river fulvic acid (SRFA,with lower MW and high aromaticity)	Her <i>et al.</i> , 2003
	255/455 and 320/450	Suwannee river fulvic acid (1S101F), IHSS	Sierra <i>et al.</i> , 2005
	250/438	Industrial wastewater, Spain	Marhuenda-Egea <i>et al.</i> , 2007
	330/410	Industrial estate wastewater, Thailand	Musikavong <i>et al.</i> , 2007
	335-355	Brewery wastewater, Thailand	Janhom <i>et al.</i> , 2009

Table 2.3 Summary of the offered mapping of FEEM regions and fluorescent DOM.

Substances	Excitation(nm) /Emission (nm)	Source	References
Humic acids	250/450	Suwannee river, peat and soil standards, IHSS	Marhaba and kochar, 2000
	235-255/453-465	Commercially available humic acid, Wako Pure Chemical Industries Ltd.	Nakajima <i>et al.</i> , 2002
	261/457 and 325/452	Suwannee river humic acid (SRFA, with lower MW and high aromaticity)	Her <i>et al.</i> , 2003
	260/485 and 330/470	Suwannee river humic acid (1S101F), IHSS	Sierra <i>et al.</i> , 2005
	335/436	Industrial wastewater, Spain	Marhuenda-Egea <i>et al.</i> , 2007
	275/300	Industrial estate wastewater, Thailand	Musikavong <i>et al.</i> , 2007
	255/455 and 500/525	Brewery wastewater, Thailand	Janhom <i>et al.</i> , 2009
	305-315/405-415	Quyung municipal wastewater treatment plant (WWTP) of Shanghai, China	Wang <i>et al.</i> , 2009
Fulvic acid and humic acid-like proposed	290-340/395-430	Groundwater from Sutherland, Scotland, Derbyshire, England, Dordogne, France, Wiltshire, England	Baker and Genty, 1999
	230/440 and 330/440	Hawaiian river water	Coble <i>et al.</i> , 1993
	260/380-460 and 350/420-480	Bulk seawater	Coble, 1996
	337/423	Natural water and wastewater, USA	Her <i>et al.</i> , 2003
	320-360/400-470	Landfill leachates, England	Baker and Curry, 2004
	235/435 and 320/430	Lake water	Komatsu <i>et al.</i> , 2005

2.5 Fourier Transforms Infrared (FTIR)

The FTIR spectroscopy is mostly used for the identification of functional groups and the determination of their relative distribution. FTIR spectroscopy subjects a compound to infrared radiation in the 4000-400 cm^{-1} range. Although this radiation is weak, it does supply sufficient energy for bonds in the molecule to vibrate by stretching or bending. The atom of molecule can be considered as linked by springs that are set in motion by the application of energy. As the molecule is subjected to the individual wavelengths in the 4000-400 cm^{-1} range, it absorbs only those processing exactly the energy required to cause a particular vibration.

IR spectroscopy has been widely used for gross characterization of DOM and can provide valuable information on the structural and functional properties of DOM molecule (Chen *et al.*, 2002). Peuravuori *et al.*, (2005) used infrared spectroscopy for gross characterization of humic-type constituents. It can provide valuable information on the structural and functional properties of NOM, e.g. oxygen-containing functional groups, occurrence of protein and carbohydrate moieties and relative proportions of aromatic versus aliphatic moieties. Kanokkantapong *et al.*, (2006) demonstrated the FTIR analyses of the pre and post chlorinated water samples. It provided a better understanding of the possible functional group associated with the formation of HAAs, which could potentially be carboxylic acids, aromatic amide, amino acids and ketone. Spectrum of amino showed that there existed a combination of carboxylate (COO^- stretching near 1600 and 1400 cm^{-1}) and primary amine salt (N-H stretching in the middle range of 3300-2600 cm^{-1} and N-H bending at 1610-1500 cm^{-1} in pre-HAAFP samples and these groups were dramatically decreased in the post-HAAFP.

Her *et al.*, (2008) studied identification of potential NOM foulants in groundwater for nanofiltration (NF) membrane fouling in California, USA. The result shown FTIR spectra of GW1 and GW3 samples are compared with Suwannee River (SRNOM, International Humic Substance Society, USA). The peak near 3440 cm^{-1} is indicative of OH and NH stretching. The peak at 1731 cm^{-1} is indicative of carboxylic acid. The peak at 1637 cm^{-1} is a typical peak of amine group and C=O combined with aromatic ring. The peak of C-O bond was alcohol and ether

in polysaccharide at 1066 cm^{-1} . The peaks at 680 cm^{-1} and 655 cm^{-1} are possibly various forms of ionic sulfate which are found with GW3 (Figure 2.5).

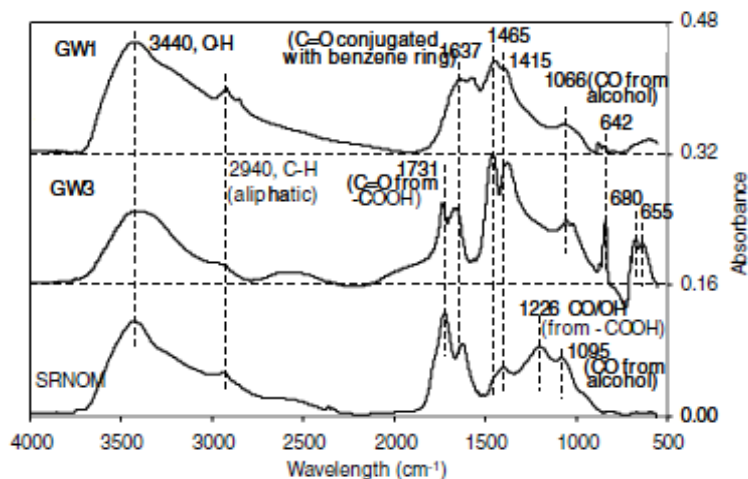


Figure 2.5 FTIR spectra of GW1, GW3 and SRNOM.

Zularisam *et al.*, (2006) used ATR-FTIR to determine the functional groups of certain unknown foulants, which correspond to their vibration energy of atomic bonds. Different functional groups absorb energy at different specific wavelengths that later can be translated into an intensity response. Frequent absorption band as shown in Table 2.4. Zularisam *et al.*, (2007) proposed that the FTIR spectra of NOM from Ulu Pontian river at wavenumber are primary and secondary amides (1646 cm^{-1} , 1640 cm^{-1} , 1630 cm^{-1} , and 1576 cm^{-1}), alcohol (1040 cm^{-1}), ethers and esters (1240 cm^{-1} , 1372 cm^{-1} , 1462 cm^{-1}). Whereas Bekok Dam reservoir at mentioned wavenumber are carboxylic group (1720 cm^{-1}), N-H amide II (1550 cm^{-1} and 1568 cm^{-1}), ethers and esters (1215 cm^{-1}). (Figure 2.6 and 2.7).

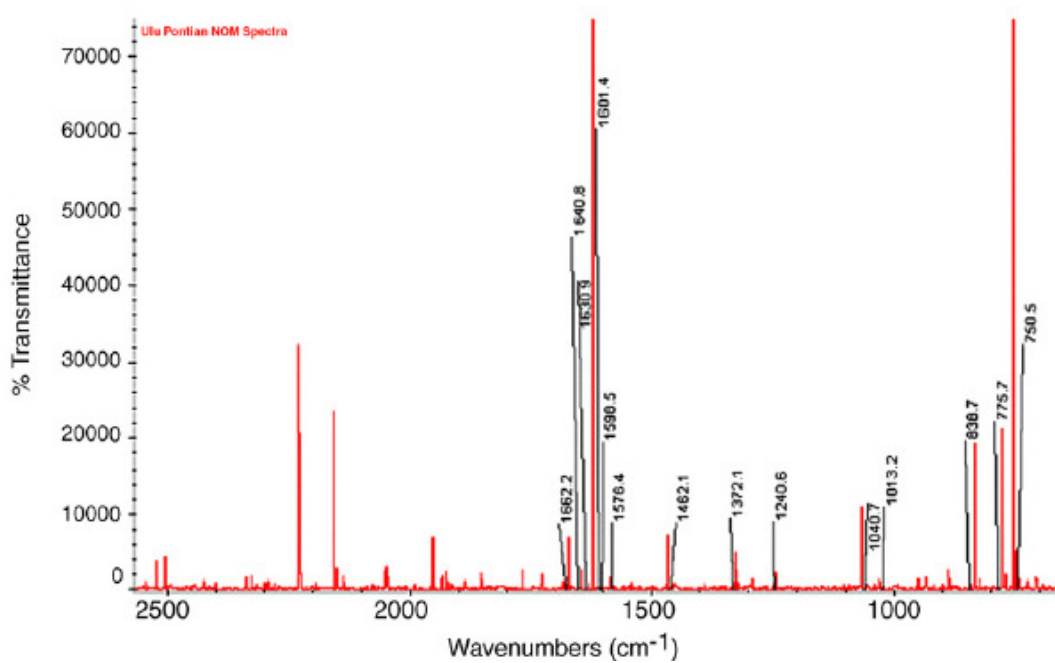


Figure 2.6 FTIR spectra of NOM from Ulu Pontian River.

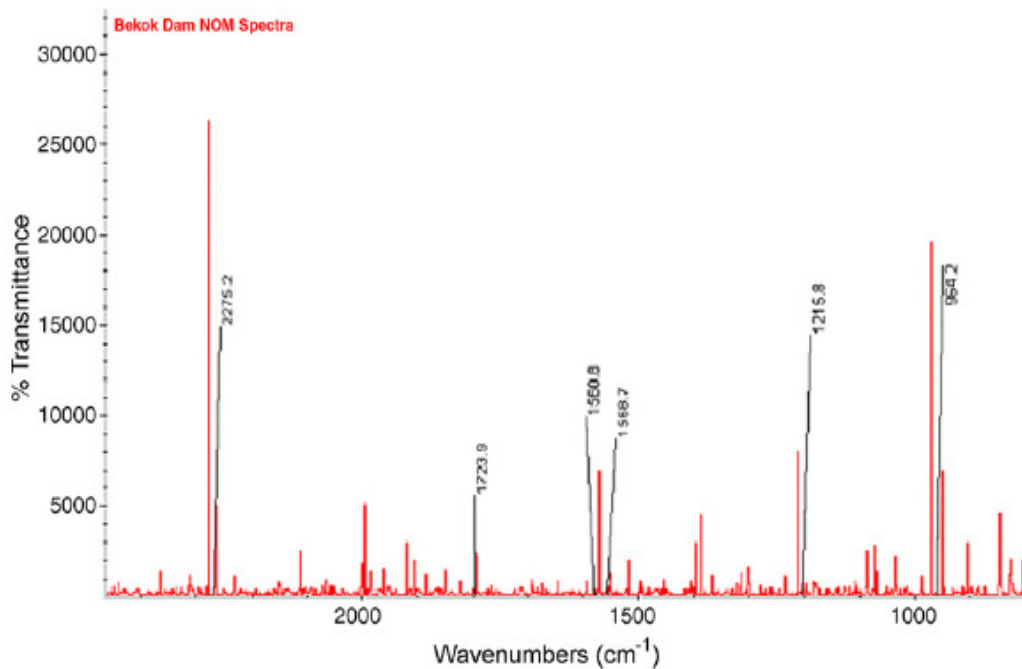


Figure 2.7 FTIR spectra of NOM from Bekok Dam reservoir.

Table 2.4 Common IR spectra for humic substances, polysaccharides and proteins

Bands (cm ⁻¹)	functional groups
Humic substance	
3400-3300	O-H stretching N-H stretching
2940-2900	Aliphatic C-H stretching
1725-1720	Carboxylic acids
1660-1630	C=O stretching of amide group
1620-1600	Aromatic C=C
1590-1517	COO ⁻ , N-H
1460-1450	Aliphatic C-H
1400-1390	OH deformation, C-O stretching of phenolic
1280-1200	C-O stretching, OH deformation of COOH
1170-950	C-O stretching of polysaccharide
Polysaccharides	
3400	Alcohol (1,2,3,Ar)
2940	Alkane
1480	Alkane
1370	1370 (starch)
1170	Tertiary alcohol
1120	Secondary alcohol
1040	Aliphatic ether
1000	Primary alcohol
775	Ethyl
Proteins group	
3300	Alcohol
1640	Alkane in aromatic
1540	Mono substituted amide
1100	Ether

Source: Zularisam *et al.*, (2007)

When FTIR spectra was use to measure the DOM fractions present in the secondary effluent from the Wanchang Wastewater Treatment Plant (Harbin, china), by the Xue *et al.*, (2008), the organic fractions HPO-A,HPO-N,TPI-A, and TPI-N were characterized by aliphatic C-H ($2950-2850\text{ cm}^{-1}$, 1450 cm^{-1} and 1390 cm^{-1}), aromatic C=C (1600 cm^{-1}), C=O ($1640-1585\text{ cm}^{-1}$), and C-O ($1280-1137\text{ cm}^{-1}$ and $1090-1040\text{ cm}^{-1}$) peaks. The aliphatic C-H band was more pronounced for HPO-N and TPI-N than HPO-A and TPI-A. The aromatic C=C peaks was more prominent in HPO-A than in the other, which showed the highest adsorption intensity in the FTIR spectra of HPO-A. This observation corresponded well with the studies of Benoit *et al.*, (2008) that was found C=O stretching of amide groups ($1670-1650\text{ cm}^{-1}$), N-H bending vibration of amide groups ($1570-1550\text{ cm}^{-1}$), carboxylic C=O ($2850-2500\text{ cm}^{-1}$ and 1700 cm^{-1}) and alcohol C-O ($1090-1040\text{ cm}^{-1}$).

Xue *et al.*, (2008) investigated the behavior and characteristics of dissolved organic matter (DOM) during soil aquifer treatment (SAT). The functional groups found C=O peak at $1730-1710\text{ cm}^{-1}$, O-H peak at about 1400 cm^{-1} , C-O peak at $1250-1150\text{ cm}^{-1}$, aliphatic C-H, C-H₂,C-H₃ stretching peak at $2950-2850\text{ cm}^{-1}$ and C=O stretching of amide groups peaks at $1660-1666\text{ cm}^{-1}$. Shirra *et al.*, (2008) identified functional groups on granular activated carbon (GAC) as pretreatment to reverse osmosis (RO) of membrane bioreactor (MBR). The peaks at wavenumbers 3360 cm^{-1} (N-H stretch) and 1610 cm^{-1} (N-H bend and N-C=O stretch) are of primary amine and N-acetyl amino sugars, respectively, and the peak at 1410 cm^{-1} (C-N stretch) is of secondary and tertiary amines, representing proteins. The peaks at wavenumber 1050 cm^{-1} (C-O-C stretch) and 1160 cm^{-1} (COH stretch) indicated carbohydrates (representing polysaccharides). Fulvic and humic acids spectra indicated bands at about 1720 , 1650 , 1500 , 1210 , 1160 , 1100 cm^{-1} . A fairly broad at 1700 cm^{-1} was due to a carbonyl stretch in carboxylic acids and a small band at 1650 cm^{-1} implies the presence of benzophenones. The benzene ring in aromatic compounds, normally, absorbs (stretching) at $1630-1430\text{ cm}^{-1}$. The band at 1200 cm^{-1} and 1100 cm^{-1} indicated C-O stretching and the presence of secondary alcohol (Samios *et al.*, 2005). The FTIR spectra of DOM of humic and fulvic acid substances was obtained from literature data in Table 2.5.

Table 2.5 Summary of the FTIR spectra of DOM, fulvic acid and humic acid substances that obtained from literature data.

Wavenumber (cm ⁻¹)			Assignment
DOM	Fulvic acid	Humic acid substances	
3670-3300	3400	3670 – 3300	OH group
3100-3000	-	3077-3030	Aromatic C-H stretching
2950-2850	2919	2950-2850	Aliphatic C-H,CH ₂ ,CH ₃ stretching
-	-	2850-2500	Carboxyl ate ion
1730-1710	1717	1725-1640	C=O stretching of carboxylic , Aldehydes and ketones and ester
1670-1650	-	-	C=O stretching of amide groups (amide-1)
-	1589	1640-1585	C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinones
1620-1590	1606	-	Aromatic C=C vibration
1570-1550	-	-	N-H bending vibration of amide groups (amide-2)
-	-	1515	C=C stretching vibration of benzene, pyridines
1465-1440	-	1440	Aliphatic C-H deformation
1420-1400	-	1400-1390	O-H bending vibration of carboxylic groups, C-O stretching of alcohol
1380-1370	1399	-	C-H deformation of C-H ₃ groups
-	-	1390-1322	Salts of carboxylic acids
1300-1000	1217	1280-1137	C-O stretching of ester, ethers, phenol and alcohol
-	-	1090-1040	C-O stretching of alcoholic compounds
910-730	919-744	-	C-H bending vibration of aromatic rings
800-600	-	880-750	Hydrogen-bonded OH stretching vibration carboxylic groups

Source: Peuravuori *et al.*, (2005)

Her *et al.*, (2008)

Zularisam *et al.*, (2006)

Xue *et al.*, (2008).

2.6 Disinfections and Disinfection By-Products (DBPs)

Disinfection is used to eliminate pathogenic microorganisms in drinking water and also sewage effluent. Pathogens presented in water supplies are extremely harmful and can cause disease in humans. For drinking water, disinfection is an important step to ensure that water is safe to drink. Moreover, a certain level of disinfectant should remain in the finished water to prevent the re-growth of micro-organisms in the distribution system.

2.6.1 Disinfectants

Disinfection can be achieved with many chemical disinfectants such as ozone, ultraviolet (UV) radiation, potassium permanganate, chlorine dioxide, and chlorine. Each method has its own advantages and disadvantages as briefly discussed below.

2.6.1.1 Ozone

Ozone is the most effective oxidant and disinfectant. It is formed by passing air through high voltage electrical discharge field where O_2 is converted to O_3 . As a very strong oxidant, ozone requires shorter contact time and lower dose than most other disinfectants. However, as ozone is unstable, it is required that ozone be generated on-site which means that every facility must have an ozone generator. In addition, ozone cannot remain long enough in the water distribution system and therefore this poses the problems on the re-growth of the microorganisms.

2.6.1.2 Ultraviolet radiation

Ultraviolet (UV) radiation is generated by a specific lamp. When the radiation penetrates the cell wall of an organism, the cell's genetic material is interrupted and the cell is incapable of further reproducing. UV light is an effective disinfectant particularly in destroying bacteria and viruses. The efficiency depends on the contact time. However, it cannot provide a disinfecting role in the water distribution system. UV radiation is unsuitable for water with high levels of suspended solids, color, turbidity, or soluble organic matter because these materials can absorb and obstruct the UV radiation which leads to a lower disinfection performance.

2.6.1.3 Chlorine dioxide

Chlorine dioxide (ClO_2) is a very effective disinfectant for odor and taste control but it has to be generated onsite because chlorine dioxide is an unstable gas. This gas was reported to produce only few DBPs of concern (Richardson *et al.*, 1994) which are chlorite and chlorate (Marhaba and Washington, 1998). There is no significant formation of THMs and it does not react with bromide to form brominated by-products.

2.6.1.4 Chlorine

At atmospheric pressure, chlorine gas is toxic, yellow-green in color, and forms liquid at high pressure. Chlorine is most widely used in the disinfection process because it is very effective in removing almost all microbial pathogens. It is appropriate as both primary and secondary disinfectants. Moreover, the most important advantage that chlorine still commonly using is it can maintain as a residual disinfectant in the water supply distribution system.

2.6.2 Disinfection By-Products

Only some of disinfection by-products (DBPs) have been examined for their toxicological effects but most have been found to exhibit carcinogenic potential. The formation of DBPs depends on the type of precursors in the water and also on the types of disinfectants.

2.6.2.1 Ozone disinfection by-products

Ozone will not produce chlorinated by-products such as THMs, HAAs, and HANs but it may form a variety of oxidation by-products in the presence of organic matter (Marhaba and Washington, 1998). However, if the waters containing bromide ion are ozonated, brominated species DBPs can form.

2.6.2.2 Ultraviolet radiation disinfection by-products

It is possible to obtain oxidative by-products in the high pressure UV systems. UV DBPs may form due to the production of OH radicals when the water is in contact with UV radiation. However, conventional UV does not appear to form any DBPs of current concerns (Marhaba and Washington, 1998).

2.6.2.3 Chlorine disinfection by-products

Chlorine DBPs are formed when free chlorine (hypochlorous acid: HOCl) added to water reacts with the organic matter presented in water. THMs were often found to be the most dominant DBPs, followed by HAAs (Krasner *et al.*, 1989; Marhaba and Van, 1999; Owen *et al.*, 1995; and Grenier *et al.*, 1992). THMs and HAAs were identified as potential adverse health effect agents. The generalized equation describing the formation of chlorine halogenated DBPs is shown in Equation (2.1) (Marhaba and Washington, 1998):



2.6.3 Trihalomethane (THMs)

Trihalomethanes (THMs) have been found to be the most widespread organic contaminants in drinking water. THMs are part of a group of organic chemicals that contain one carbon atom, one hydrogen atom and three halogen atoms. The most common of these halogen atoms responsible for trihalomethane formation in water are bromine and chlorine (Rook, 1977). Table 2.6 gives the chemical formulae of the four most common trihalomethanes, which are formed during chlorination. These are chloroform, bromodichloromethane, dibromochloromethane and bromoform.

Table 2.6 Chemical formulas of the four most common trihalomethanes

Individual, DBPs	Structure	Individual, DBPs	Structure
Trichloromethane or Chloroform (CHCl ₃ or TCM)	$\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}-\text{H} \\ \\ \text{Cl} \end{array}$	Tribromomethane or Bromoform (CHBr ₃ or TBM)	$\begin{array}{c} \text{Br} \\ \\ \text{Br}-\text{C}-\text{H} \\ \\ \text{Br} \end{array}$
Bromodichloromethane (CHBrCl ₂ or BDCM)	$\begin{array}{c} \text{Cl} \\ \\ \text{Br}-\text{C}-\text{H} \\ \\ \text{Cl} \end{array}$	Dibromochloromethane (CHBr ₂ Cl or DBCM)	$\begin{array}{c} \text{Br} \\ \\ \text{Cl}-\text{C}-\text{H} \\ \\ \text{Br} \end{array}$

Source: Rook, (1977).

2.6.4 Factors Influencing THM Formation

Numerous factors affect the formation of THMs during water treatment process. Variations in THMs formation reactions include the concentration of the precursor material, chlorine concentration, contact time, temperature, pH and turbidity as follow:

2.6.4.1 Chlorine Dosage

Chlorine dosage is another factor affecting the concentration of THMs formed. The THMs level rises with increasing chlorine dose (Kavanaugh *et al.*, 1980). A linear relationship between chlorine consumption and THMs production were found with an order of reaction greater than or equal to unity. The concentration of chloroform was about 150 µg/L in a sample dosed with 20 mg/L of chlorine (Trussell and Umphres 1978). Natural Environmental Board (1984) illustrated the relationship between chloroform level in water distribution system and chlorination rate. The chloroform level increased from 20 to 220µg/L after chlorine dose was varied from 4 to 30 mg/L. The highest levels of chloroform were found at chlorine dosage of 22 mg/L.

2.6.4.2 Precursor Concentration

Nature organic matter (NOM) is considered to contain many of the precursors that affect THM formation. NOM consists of a mixture of humic substances such as humic and fulvic and non-humic material. The amount of NOM leads to increase the concentration of THMs. The relationship has led to the use of dissolved organic matter measurement as surrogate parameter for estimating the extent of THM formation (IPCS, 2000)

2.6.4.3 Water Temperature

The formation of THMs increases with temperature (AWWARF 1991, Siddiqui and Amy, 1993). The impact of temperature on THMs was strongest at longer contact time (Carlson and Hardy, 1998)

2.6.4.4 pH

Natural Environmental Board (1984) tested the effect of pH on chloroform production at constant temperature, TOC and chlorine dosage and found that chloroform concentration decreased as pH decreased

2.6.4.5 Contact Time

THM concentrations increase as the reaction time increase. After chlorine addition, there is a period of rapid THM formation for the initial few hours, followed by a decline in the rate of THM formation, suggesting fast and slow NOM reactive sites.

2.6.5 Toxicity of THMs

THMs induce toxicity in the liver and kidneys of the rodents exposed to doses of about 0.5 mmol/kg of body weight. The THMs have little reproductive and development toxicity, but bromodichloromethane has been shown to reduce sperm motility in rats consuming 39 mg/kg of body weight per day in drinking water. Like chloroform, bromodichloromethane, when administered in corn oil, induces cancer in the liver and kidneys after lifetime exposures to high doses. Unlike chloroform, bromodichloromethane, dibromochloromethane and bromoform induce tumors of the large intestine in rats exposed by corn oil gavage. Bromodichloromethane induces tumors at all three target sites and at lower doses than the other THMs (ICPS, 2000). (as shown in Table 2.7).

Potential risk to human health from possible carcinogenic properties of the halogenated compounds found in chlorinated drinking water was also investigated (WHO, 1984); Theiss *et al.*, (1977) reports the maximum concentration limit of total THMs below 100 µg/L in drinking water supply.

The U.S. EPA has issued the Disinfectants/ Disinfection By-Products (D/DBP) rule reduced the MCL for TTHMs to 80µg/L for Stage1D/DBP and 40µg/L for Stage 2 (USEPA, 2003).

Table 2.7 Toxicity of THMs compound

THMs compound	Effect to Health
Chloroform	Effect to central nervous system , tumors and cancer in livers, kidneys and large intestine.
Bromodichloromethane	Effect to tumors and cancer in livers, kidneys
Dibromochloromethane	Effect to central nervous system, tumors in livers kidneys
Bromoform	Effect to central nervous system and cancer in livers, kidneys and large intestine.

Sources: USEPA (1999); IPCS (2000)

2.6.6 Criterion of THMs

The WHO index for additive toxicity, IWHO, for THMs is an overall guideline value to estimate the toxic (developmental and non-carcinogenic) risk associated with chlorinated drinking water. The IWHO value should be ≤ 1 for compliance with WHO guidelines and is calculated in Equation (2.2)

$$\frac{C_{\text{bromoform}}}{GV_{\text{bromoform}}} + \frac{C_{\text{DBCM}}}{GV_{\text{DBCM}}} + \frac{C_{\text{BDCM}}}{GV_{\text{BDCM}}} + \frac{C_{\text{chloroform}}}{GV_{\text{chloroform}}} \leq 1 \quad (2-2)$$

Where C is the surveyed concentration of each THM, and GV is the WHO guideline value. WHO, (2004) have been established separately at 200 mg/L for TCM, 100 mg/L for each of TBM and DBCM, and 60 mg/L for BDCM.

2.7 Removal of THMs Precursor

2.7.1 Coagulation and Flocculation

Coagulation and flocculation consists of adding a floc-forming chemical reagent to a water or wastewater to enmesh or combine with non-settleable colloidal solids and slow settling suspended solids to produce a rapid-settling floc (Reynolds and Richards, 1996). Coagulation is the addition and rapid mixing of a coagulant, which will cause destabilization of the colloidal and fine suspended solids, and then the initial agglomeration of the destabilized particles. Flocculation

is the gentle agitation or slow stirring to aggregate the destabilized particles and form a rapid-settling floc. The floc is subsequently removed by sedimentation or filtration.

2.7.2 Adsorption PAC

Adsorption with activated carbon several organic compounds could be well adsorbed on the surface of activated carbon (AC). Granular activated carbon (GAC) and powder activated carbon (PAC) are often used in drinking water treatment for the removal of organic, odor, taste, and color. Activated carbon can remove organic precursors effectively with an adequately long contact time provided the adsorption capacity is high.

2.8 Mechanisms of Coagulation

Particle destabilization can be achieved through four mechanisms: (1) double layer compression, (2) adsorption and charge neutralization, (3) enmeshment in a precipitate, and (4) adsorption and antiparticle bridging (Benefield *et al.*, 1982). Coagulation is the processes by which the charge on particles is destroyed. In this sense, double layer compression and charge neutralization are considered coagulation, while enmeshment and bridging are classified as flocculation (Benefield *et al.*, 1982).

2.8.1 Double Layer Compression

Double layer compression involves electrostatic repulsion. It occurs when counter ions is added as coagulant. Surrounding the negatively charged colloidal particle is an inner fixed layer and outer diffused layer of counter ions. The concentration of counter ions is highest at the particle surface and decreases to that of the bulk solution at the outer boundary of the diffused layer. Destabilization of particles by counter ions causes the diffused layer to compress around the particles. Compression of the diffused layer decreases the electrostatic repulsive forces between the similar colloidal particles and the zeta potential is mitigated. Thus, the attractive forces (van der waals forces) can dominate to bind particles together.

2.8.2 Charge Neutralization

Charge neutralization occurs when a charged particle is destabilized by coagulant ions. As the coagulant dissociates in water, hydrolysis reactions produce positively charged metal

hydroxide ions that adsorbed to the surface of the negative particles. The charge on the colloidal particle is reduced to a level where the colloidal are destabilized.

2.8.3 Sweep Coagulation

Sweep coagulation involves the formation of a solid precipitate. In sweep coagulation, physical interaction occurs between the voluminous metal hydroxide precipitates and the raw water colloids. The negative colloids are enmeshed in the precipitates.

2.8.4 Inter-particle Bridging

Destabilized particles can be aggregated by bridging with a polymer. Interparticulate bridging entails the interaction between the polymer and the reactive groups on the destabilized particles. When a polymer with high molecular weight comes into contact with a colloidal particle, some of the reactive groups in the polymer adsorb at the particle surface and leaving other portions of the molecule extending into the solution (AWWA, 1990).

2.9 Coagulants

2.9.1 Polyaluminium chloride (PACl)

These compounds have the general formula $(Al_n(OH)_mCl_{(3n-m)})_x$ and have a polymeric structure, totally soluble in water. The length of the polymerized chain, molecular weight and number of ionic charges is determined by the degree of polymerization. On hydrolysis, various mono- and polymeric species are formed, with $[Al_{13}O_4(OH)_{24}]^{+7}$ being a particularly important cation. A less predominant species is $[Al_8O_4(OH)_{20}]^{+4}$. An important property of polyaluminium coagulants is their basicity. This is the ratio of hydroxyl to aluminum ions in the hydrated complex and in general, the higher the basicity, the lower will be the consumption of alkalinity in the treatment process and hence impact on pH.

2.9.2 Polymer

Polyelectrolyte is a polymer that having ionizable groups, usually one or more per repeat unit (Vorchheimer, 1981). Monomers are polymerized to form polyelectrolyte with high molecular weight and high charge densities. The complexity of the polyelectrolyte is based on the numerous structures including linear, cross-linked and branched chains, and the variation in the

manufacturing processes. The advantage of polyelectrolyte is the removal of turbidity with much less floc compared with conventional coagulant. (Carn and Parker, 1985).

Polyelectrolyte can be classified as anionic (negative charge), cationic (positive charge) or nonionic (neutral). The cationic polyelectrolytes are often referred as primary coagulants while anionic and nonionic polyelectrolytes are referred to either as coagulant aids or flocculants (Letterman and Pero, 1990).

Particle destabilization and aggregation with polyelectrolyte can be divided into three general categories: charge neutralization, polymer bridge formation, and combination of charge neutralization and polymer bridge formation (Metcalf and Eddy, 2003). For the first category, cationic polyelectrolyte acts as primary coagulants to lower or neutralize the negative charged particles in water. The polyelectrolyte must be adsorbed to the particle for proper charge neutralization. The second type of polyelectrolyte action is inter-particle bridging. Anionic and nonionic polymers that have high molecular weight and appreciable length are able to attach at a number of adsorption sites of particle surface.

2.10 The ability of coagulants used to remove THMs precursor

THMs precursor removal by from natural waters by chemical coagulation (PACl, Polymer and PAC) has been reported in a limited basis. (as shown in Table2.8)

Table 2.8 Review of coagulation condition

Water source	Condition	%Removal	Reference
Synthetic water, reservoir	Polyaluminium chloride 60 mg/L with Copolymer acrylamide/trimethylaminoethyl acrylate and nonionicpolyacrylamide 0.5-1mg/L	20% lindane removal, 65% <i>p,p</i> -DDT removal, more than 70% aldrin removal etc.	Lee <i>et al.</i> , 1998
Salerno Southern Italy	Optimum dose PACl 20 mg/L pH 6	84, 50 and 65 % removal of turbidity DOC and THMFP, respectively	Rizzo <i>et al.</i> , 2005
Bakio Northern Spain ,reservoir	Alum combine with 40 mg/L PACl at pH 6	31, 60 and 64 % of DOC,UV-254 and THMFP reduction, respectively	Velasco <i>et al.</i> , 2007
Kitami Japan, river	Polyaluminium chloride 30 mg/L	94% and 65% removal of turbidity and humic acid, respectively	Nagare, <i>et al.</i> , 2008
Pearl Southern China, river	PACl 0.05, 0.10, 0.15, 0.20, 0.45 and 0.50 mM Al at pH 5.5-7, Optimum dose PACl concentration 0.50 mM Al at pH 7	20 and 35 % removal of DOC and UV-254, respectively	Yan, <i>et al.</i> , 2007

Table 2.8 Review of coagulation condition

Water source	Condition	%Removal	Reference
Biscayne Aquifer, Edisto River, Mississippi River, Jame River, Ilwaco Reservoir, Daytona Beach Aquifer, and Scioto River (USA)	Four cationic polymers at 15-20 mg/L	27-65% THMFP reduction	Amy and Chadik, 1983
Moorabool river, Hope Valley (reservoir/long river), and Wanneroo (groundwater)	DADMAC 5-8 mg/L, CatPAM 7-8 mg/L, CPMA (cationic polymethacrylate) 7-8 mg/L, and alum 30-60 mg/L	%UV removal; 35-70%, 31-69%, 50-75%, and 69-88%, respectively	Bolto <i>et al.</i> , 1999
Pan-Hsing water treatment plant (Taiwan) and humic acid	Optimum dose at 2 mg/L and 10 mg/L DADMAC, respectively	69% and 82% chloroform removal, respectively	Chang <i>et al.</i> , 1999
Bell Bay: Tasmania, Hope Valley: South Australia, and Wanneroo: Western Australia	DADMAC 5-8 mg/L, Cationic polymethacrylate 7-8 mg/L and alum 30-60 mg/L	>40%, > 50%, and >60% UV removal, respectively	Bolto <i>et al.</i> , 2002
Synthetic source water (Humic acid)	- Alum 60 mg/L combine with 10 mg/L DADMAC - Alum 20-60 mg/L with CatPAM and Nonionic PAM 2-10 mg/L	- 90% TOC removal of Humic acid - Less than 10% Humic acid removal	Chang <i>et al.</i> , 2005

Table 2.8 Review of coagulation condition

Water source	Condition	%Removal	Reference
Myponga Australia reservoir	Alum combine with PAC, Optimum dose PAC pH 5.5-7	79 and 90% of Turbidity and NOM removal, , respectively	Ho and Newcombe., 2005
Terkos Lake Istanbul, river	Ferric chloride 80 mg/L with PAC 40 mg/L	70, 76 and 36 % of DOC,UV-254 and SUVA removal, respectively	Uyak <i>et al.</i> , 2007
Tampa Bay USA, water supply treatment	PAC 20 mg/L pH at 7	- 90% Non-humic acid - Less than 10% Humic acid	Huang <i>et al.</i> , 2008
Guangzhou PR China, water supply treatment	Adsorption humic < 300 and > 17,000 Da	50 % of UV-254 removal	Zhao <i>et al.</i> , 2009

CHAPTER III

METHODOLOGY

3.1 Water Source

The U-Tapao Canal, it has capacity of about $2,160 \times 10^3$ cubic meter. It is the main source of raw water supply for four cities in Songkhla. The canal flows in the direction from south to north through communities, industries and agricultural areas. Nowadays, approximately 100,000-150,000 m^3/day of water supply is produced using raw water from U-Tapao Canal as shown in Figure 3.1. Raw water from U-Tapao Basin (UTM 661975 772906), Songkhla province, Thailand was selected to be the raw water supply for the water treatment plant in Hat Yai. It is also the water sample in this study.



Figure 3.1 Pumping Station of Hat Yai, Songkhla, province, Thailand

3.2 Sample Collection and Preservation

The raw water supply was collected from U-Tapao Canal at pumping station of Hat Yai water treatment plant. Water samples were collected two times in October 2009 represented the nature of dissolved organic matter (DOM) in rainy season whereas that of in April 2010 represented the nature of DOM in summer and stored in a cold room with a temperature controlled at $4\text{ }^{\circ}\text{C}$.

3.3 Procedure

3.3.1 Experimental Procedure

The experimental procedure is briefly shown in the following steps and is conclusively described in the diagram in Figure 3.2

1. The water samples were measured for pH, temperature, alkalinity, dissolved oxygen (DO), suspended solids (SS), and turbidity. For measurements of DOM surrogate parameters, water samples were filtered through a pre combusted (550 °C for 2 h) Whatman GF/F (nominal pore size 0.7 µm). Filtered water samples were analyzed for ultraviolet absorbance at 254 nm (UV-254), dissolved organic carbon (DOC), trihalomethane formation potential (THMFP). Fluorescent excitation-emission matrix (FEEM), and fourier transform infrared (FTIR) were analyzed in order to identify nature of DOM.
2. Subsequently, resin adsorption procedures were used to fractionate five liters of the filtered water into three DOM including hydrophobic (HPO), transphilic (TPI), and hydrophilic (HPI) fractions. The three DOM fractions were analyzed for their UV-254, DOC, SUVA, THMFP, FTIR and FEEM.
3. Coagulation experiment, it will be described in section 3.3.2
4. Coagulated water at the optimal condition were analyzed for their turbidity, alkalinity, UV-254, DOC, SUVA, THMFP, FTIR and FEEM.
5. The filtered coagulated water at optimal condition was then fractionated into three fractions. The three DOM fractions were analyzed for their UV-254, DOC, SUVA, THMFP, FTIR and FEEM.

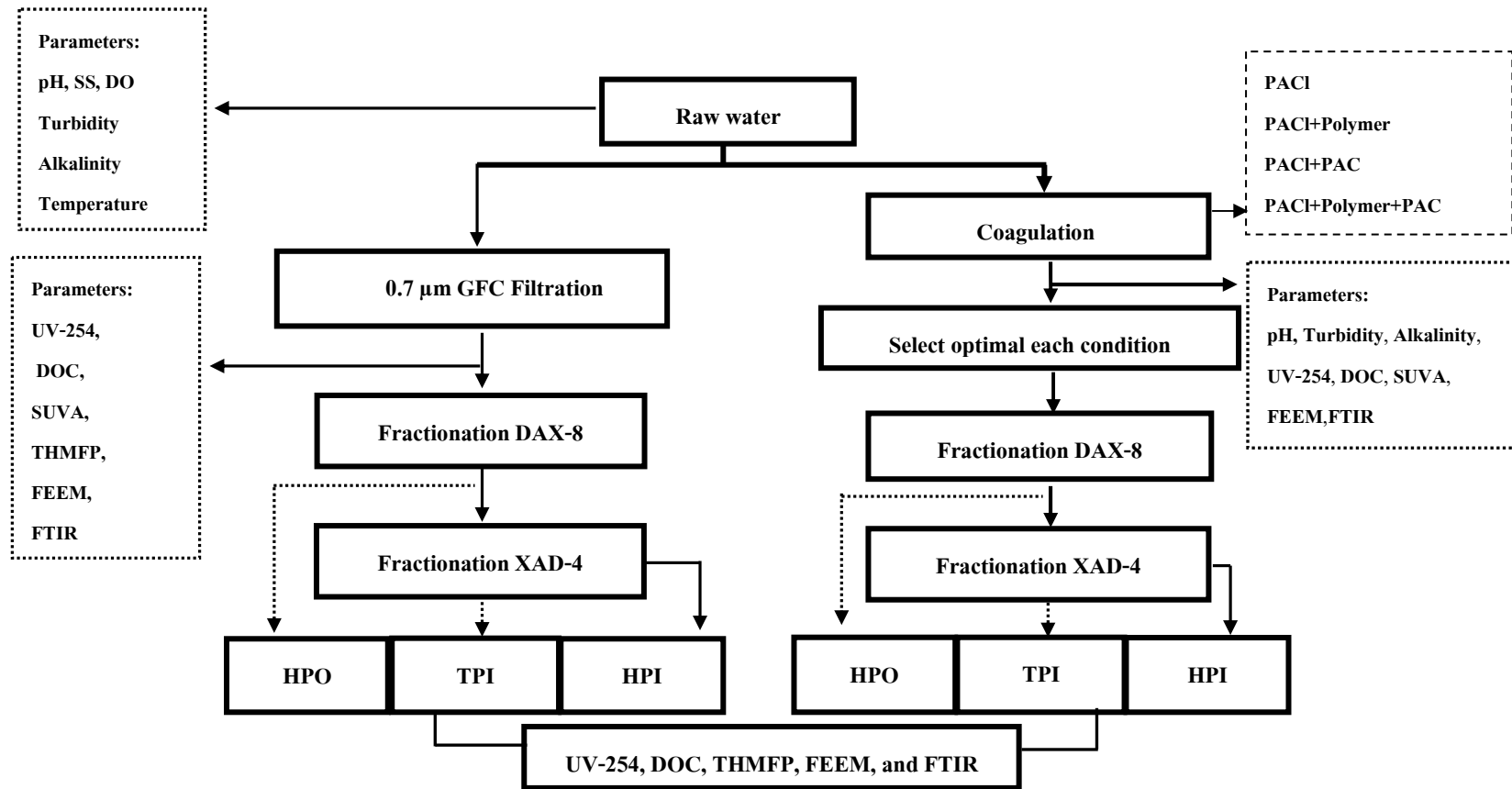


Figure 3.2 experimental procedure diagrams

3.3.1.1 Resin Fractionation Procedure

The resin fraction procedures were used to fractionate five liters of filtered water into three DOM fractions; including the hydrophobic (HPO), transphilic (TPI), and hydrophilic (HPI) fractions. The three DOM fractions were analyzed for their UV-254, DOC, THMFP, FEEM and FTIR. Leenheer (1981) fractionated DOM in the water samples by using a series of resins (DAX-8 and XAD-4). The specifications of the resins are described as follows:

DAX-8:

- Nonionic resin (SUPELCO)
- 60% porosity
- 40-60 mesh
- 160 square meter per dry gram

XAD-4:

- Nonionic resin (AMBERLITE)
- Macro-reticular cross linked aromatic polymer
- 50% porosity
- Moisture holding capacity 54-60%
- Harmonic mean size 0.49-0.69 mm
- Surface area 750m²/g

3.3.1.2 Resin Preparation

DAX-8

- Refine the resin with 0.1 N NaOH for 24 h.
- Rinse the resin with Milli-Q water to remove NaOH
- Purify the resin acetone for 24 h in a set of soxhlet extraction apparatus
- Purify the resin hexane for 24 h in a set of soxhlet extraction apparatus
- Rinse the resin with methanol until the effluent is free of hexane

- Transfer the purified resin into the column with glass wool packed at the bottom as supported in slurry of methanol. It must be noted that glass wool used in the experiment was purified by a set of soxhlet extraction apparatus for 24 h prior to its being packed into the column
- Rinse the packed column with more than 2.5 bed volume(BV) of 0.1 N NaOH, followed with 0.1 HCl and Milli-Q water respectively, until the DOC and conductivity of the effluent water is less than 0.1 mg/L and 10 μ s/cm, respectively

XAD-4

- Purify the resin methanol for 24 h in a set of soxhlet extraction apparatus
- Transfer the purified resin into the column with glass wool packed at the bottom as supported in slurry of methanol.
- Rinse the packed column with more than 2 bed volume (BV) of 0.1N NaOH, followed with 0.1 and 0.01HCl and Milli-Q water respectively, until the DOC and conductivity of the effluent water is less than 0.1 mg/L and 10 μ s/cm, respectively

3.3.1.2 Fractionation Procedure

Resin adsorption procedure was employed to fractionate five liters, which were adjusted pH 7 ± 2 of filtered water sample into three DOM fractions; including hydrophobic (HPO), transphilic (TPI), and hydrophilic (HPI) fractions by using a series of DAX-8 resin (Leenheer, 1981) and XAD-4, a weak anion exchange resin, respectively (Marhaba *et al.*, 2003). Method for isolating HPO and TPI fraction of DOC are described elsewhere (Quanrud *et al* 2003). Briefly, organics were extracted and fractionated using DAX-8/XAD-4 resin chromatography following established methods (Aiken *et al.*, 1992). Samples were acidified pH 2 and passed through two columns in containing DAX-8 and XAD-4 resin. After all Samples were run through the columns, each column was separately back eluted with 0.1 N NaOH. The eluted from DAX-8 is defined as HPO and

eluted from XAD-4 as defined TPI. The diagram of the resin fractionation procedure is presented in Figure 3.3

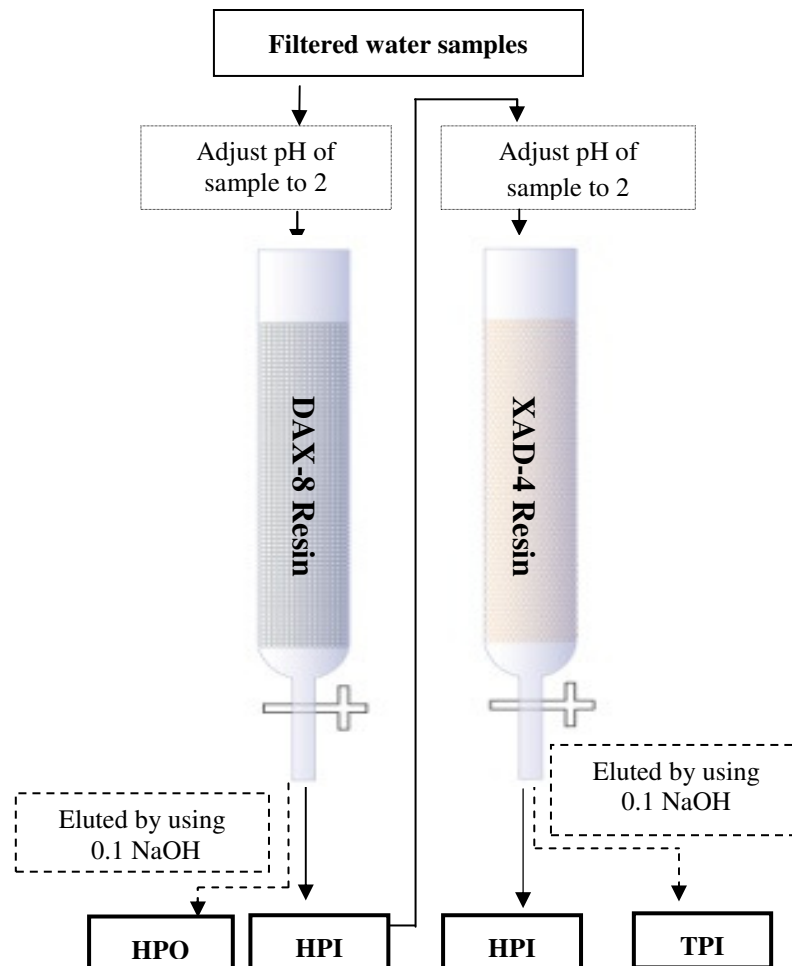


Figure 3.3 Resin fractionation procedures

3.3.2 Coagulation Experiment

3.3.2.1 Jar-Test Apparatus and Process

Since many factors influence coagulation and complex reaction involved, the coagulant dosage required for coagulation of particular water normally is determined from the experiment. The experimental jar-test apparatus, as shown in Figure 3.4, it was used for such a purpose in this study and the jar-test procedure is briefly described as follow:

- 1) Using a multistage stirrer apparatus, simultaneous tests were conducted on a series of samples covering a range of coagulant concentration. On the addition of the coagulant, the samples were rapidly mixed with 100 rpm for 1 minute, followed by slow mixing with 30 rpm for 30 minutes.
- 2) The samples were then allowed to stand for 1 hour for settlement, after which turbidity, alkalinity, UV-254, DOC and SUVA of filtered supernatant was measured and the lowest coagulant dose giving adequate removal noted.
- 3) Using the same concentration of coagulant, a second similar set of test was also performed on pH-adjusted sample to determine the optimum condition coagulation.

The picture of multistage jar-test apparatus are show as follow.

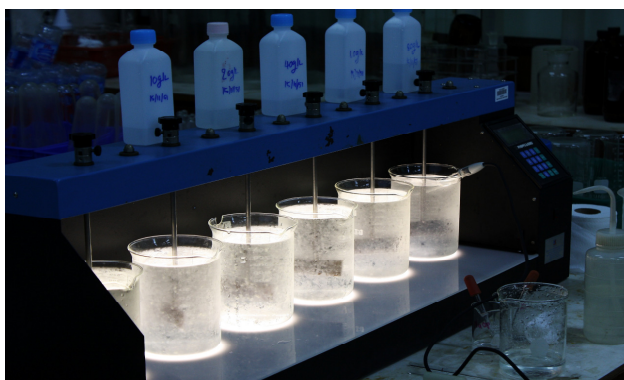


Figure 3.4 The experimental jar-test apparatus

3.3.2.2 Jar-Test Condition

The jar-test procedure as stated previously were experimented under the condition of coagulation as depicted in Table 3.1

Table 3.1 The experimental jar-test condition

Coagulant	Coagulant Dosage (mg/L)	pH
1) PACl	0, 10, 20, 30,40, 50	controlled pH at 7
2) PACl+Polymer	PACl 40 mg/L (optimal condition 1) and polymer 0.2, 0.4, 0.6, 0.8 and 1 mg/L	controlled pH at 7
3) PACl+PAC	PACl 40 mg/L (optimal condition 1) and PAC 10, 20, 40, 60, 80 mg/L	controlled pH at 7
4) PACl+ Polymer+PAC	PACl 40 mg/L combined with polymer 1 mg/L and PAC 80 mg/L	controlled pH at 7

1) Polyaluminium chloride (PACl)

PACl specification: % Al=12; Basicity: 80%; Working solutions were prepared daily by diluting the above PACl with distilled water (1:1000) depending on the dose required.

2) Polyelectrolyte or Polymer

Polymers used in this experiment were cationic polyacrylamide (MR FLOC[®] 5000).

3) Powder activated carbon (PAC)

PAC used in this experiment was typically in powder (95-100% pass through a 100-mesh sieve). (HRO M325-60CARBOKARN).

3.4 Spectrofluorometry Analysis

3.4.1 Sample Preparation

The filtered raw water and coagulated water were adjusted to a pH of about 7 ± 0.2 . In the case of the DOM fractions, concentrated HPO, TPI and HPI fractions from the resin fractionation process were diluted with Milli-Q water to their original DOC, which was calculated by using the mass balance from the resin fractionation results. The three DOM fractions were then adjusted to a pH of about 7 ± 0.2 .

3.4.2 Quinine Sulfate Standard

The quinine sulfate $[(C_{20}H_{24}N_2O_2)_2H_2SO_4 \cdot 2H_2O]$ solution was used to check the stability of spectrofluorometry. The calibration curve was regularly established using 5 points of quinine sulfate in 0.1 M H_2SO_4 . 10 quinine sulfate units (QSU) are equivalent to the fluorescent spectra of 10 $\mu\text{g/L}$ of quinine sulfate solution at 450 nm with an excitation wavelength of 345 nm (Kasuga *et al.* 2003).

3.4.3 Spectrofluorometer Operating Conditions

A JASCO FP-6200 spectrofluorometer was used to measure the FEEM of all water samples in this study using the following operating conditions:

Measurement Mode: Emission

Band with excitation: 5 nm

Band with emission: 5 nm

Response: Medium

Sensitivity: High

Scanning speed: 2000 nm/min

Excitation wavelength: Start at 220 nm, end at 600 nm

Emission wavelength: Start at 220 nm, end at 600 nm

Excitation wavelength interval: 5 nm

Emission wavelength interval: 1 nm

3.4.4 FEEM Measurement Procedure

- Check the Raman Test Photometric Stability. The value should be less than $\pm 1\%$ / hour.
- Measure the fluorescent intensity of the quinine sulfate solution of 10 QSU at 450 nm with an excitation wavelength of 345 nm.
- Measure the FEEM of the Milli-Q water.
- Measure the FEEM of the water samples
- Subtract the FEEM of the water samples with the FEEM of the Milli-Q water.
- Convert the fluorescent intensity of the subtracted FEEM of the water samples into QSU unit.
- Eliminate the influence of the primary and secondary scatter fluorescence and highlight the target peak by discarding the FEEM data when the excitation wavelength (Ex) \geq emission wavelength (Em) or $Ex \times 2 \leq Em$ (Komatsu *et al.* 2005)
- Remove the Rayleigh and Raman scattering peaks at $Em \pm 10-15nm$ of each Ex (Zepp *et al.* 2004) (Figure 3.6)

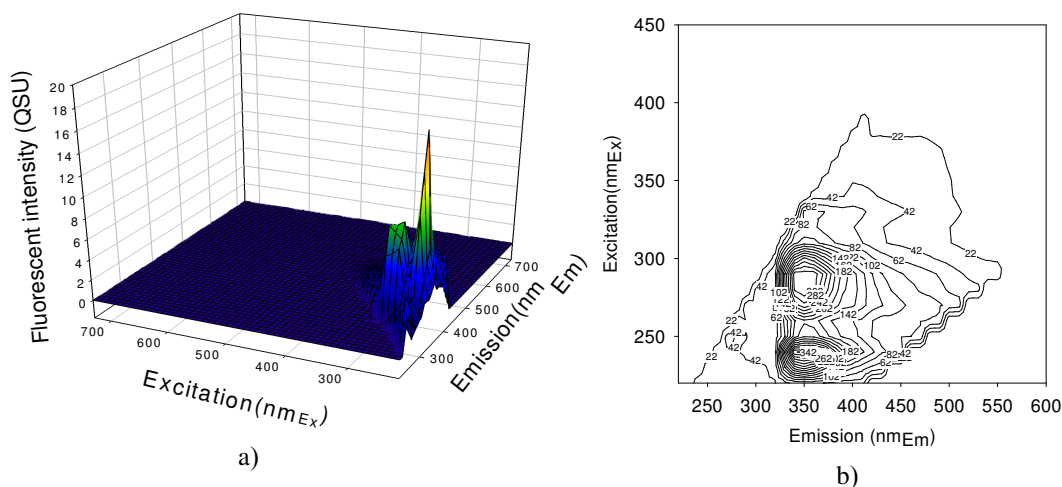


Figure 3.6 FEEM of sample (a) 3D (b) contour from program Sigma plot

3.5 FTIR Analysis

The filtered raw water and coagulated water were poured in special glass bottles that were resistant to the freeze-drying unit. Concentrated HPO, TPI and HPI after elution process of all water samples were put in the glass bottles. Then all samples were placed in a pre-freeze at -20°C for at least 12 h. They were placed in freeze-drying unit at -57°C and 0.004 bars for at least 24 h to produce a uniform powder for determining organic compound using a FTIR spectrometer

A few milligram of uniform powder of all the water samples were placed in pellets were made using 1 mg of uniform powder combined with 150 mg of potassium bromide (KBr) and were analyzed by using Jasco FTIR 460 plus. Spectra were obtained at wavelength from 4000 to 400 cm^{-1} .

3.6 Analytical Method and Instrument

3.6.1 pH

pH was directly measured by pH meter HACH Sessions 1 with an accuracy of ± 0.01 pH unit. The unit was daily calibrated with buffer solutions at pH 4, 7, and 9.

3.6.2 Turbidity

The HACH Turbidity meter Model 2100 was used to measure turbidity.

3.6.3 Alkalinity

Alkalinity was measured in accordance with Standard Method 2320 B.

3.6.4 Suspended solids

Suspended solid was measured in accordance with Standard method 2540 D.

3.5.5 Dissolved oxygen

Dissolved oxygen was measured in accordance with Standard method 4500 C.

3.6.6 UV-254

UV-254 was analyzed in accordance with Standard Method 5910B (Standard Methods, 1995) using a spectrophotometer spectronic Genesys 10 UV at 254 nm with matched quartz cells that provided a path length of 10 mm. At least two replications of each measurement of the UV-254 analysis were performed. All fractionated samples were adjusted to pH 7 by NaOH or H₂SO₄ prior to the measurement.

3.6.7 DOC

DOCs were analyzed in accordance with Standard Method 5310D (Standard Method, 1995) using a TOC analyzer (O.I. analytical, College Station, Texas, USA). Milli-Q water (ELGA, Lane End, High Wycombe, UK) was used on every sample to clean the system. At least two replications of each measurement of the DOC analysis were performed.

3.6.8 Specific ultraviolet absorption (SUVA)

Specific UV absorbance (SUVA) (L/mg-m) was calculated as the ratio of UV absorbance at 254 nm to DOC value in mg/L

3.6.9 FTIR

FTIR were analysis, filtered water samples were pre-freeze at -20 °C for at least 12 h. They were placed in freeze-drying unit at -57°C and 0.004 bars for at least 24 h to produce a uniform powder for determining organic compound using a FTIR

spectrometer. For FTIR analysis, pellets were made using 1 mg of uniform powder combined with 150 mg of potassium bromide (KBr) and were analyzed by using Jasco FTIR 460 plus. Spectra were obtained at wavelength from 4000 to 400 cm^{-1} .

3.6.10 THMFP

THMFP measurements were carried out according to Standard Method 5710B (Standard Method, 1995). The neutralized solution was buffered by a phosphate solution before incubation at 25 ± 2 °C in amber bottles with PTFE liners. At the end of the 7-day reaction period, samples should have a remaining free chlorine residual of between 3 and 5 mg/L. The residual chlorine was measured according to the procedures mentioned in Standard Method 4500-Cl G, the *N,N*-dechloro-*p*-phenylenediamine colorimetric method. The level of chlorine was then represented by the light absorbance at 515 nm using a spectrophotometer spectronic unicam Genesys 10 UV with matched quartz cells that provided a path length of 10 mm. THMs were extracted with pentane in accordance with Standard Method 6232B (Standard Method, 1995). Agilent Gas Chromatography-6890 with an electron capture detector (ECD) (Agilent technologies Inc., Wilmington, Delaware, USA) and chromatographic column (J&W Science DB-624, DE, USA) with 0.2-mm X 25 m 1.12 μm film was used to analyze THMs under the following operating conditions (Table 3.2)

Table 3.2 Method condition analyze THMs

Manufacture name/model	HP 6890 GC
Inlet conditions	Mode: Split Initial temp: 225 °C Pressure: 31.14 psi Split ratio: 10:1 Split flow: 96.4 mL/min Total flow: 108.7 mL/min Gas type: Helium
Column	HP-5 5% phenyl Methyl Siloxane Length: 30 m Diameter: 320 µm Film thickness: 0.25 µm Mode: constant flow Initial flow: 9.6 mL/min Init pressure: 31.15 psi
Detector	ECD Temperature: 300 °C Mode: Constant make up flow Make up flow: 60.0 mL/min Make up Gas type: Nitrogen
Injection temperature	225 °C
Initial temperature	60 °C initial time 1.00 min
Temperature program	10 °C/minute to 100 °C 1 minute 10 °C/minute to 130 °C 1 minute 10 °C/minute to 180 °C 1 minute
Final time duration	16 minute

At least two replications of each measurement for the THMFP analysis were performed and Milli-Q water was used for all dilutions, sample and chemical preparations, and final glassware cleaning. A summary of the analytical methods and instruments used in this study is illustrated in Table 3.3.

Table 3.3 Analytical methods and instruments

Parameter	Analytical method	Standard	Analytical Instrument
pH	Direct measurement	-	pH meter HACH Sessions 1
Turbidity	Direct measurement	-	HACH, 2100 Turbidity Meter
Alkalinity	Titration Method	Standard method 2320B*	-
Dissolved oxygen	Azide modification	Standard method 4500 C*	-
Suspended solid	Total suspended solids dried at 103-105 °C	Standard method 2540 D*	
Temperature	Direct measurement	-	Horiba Thermometer, Model D-13E
UV-254	Ultraviolet Absorption Method	Standard method 5910 B*	spectrophotometer spectronic unicam Genesys 10 UV
DOC	Wet Oxidation Method	Standard method 5310C*	O.I. analytical 1010 TOC Analyzer
Free chlorine residual	Colorimetric Method	Standard method 4500-Cl G*	spectrophotometer spectronic unicam Genesys 10 UV
THMFP	Formation of Trihalomethane and Other Disinfection By-Products and Liquid-Liquid Extraction Gas Chromatography Method	Standard method 5710 and 6232B*	Agilent 6890 Series Gas Chromatography with ECD detector
FEEM analysis	-	-	JASCO FP-6200 spectrofluorometer
FTIR	-	-	Jasco FTIR 460 plus

(*Standard Methods, 1995)

CHAPTER IV

CHARACTERIZATION AND REDUCTION OF TRIHAROMETHANE FORMATION POTENTIAL BY ENHANCED COAGULATION

4.1 Introduction and Objective

Often, raw water supply is reported to contain organic matter concerned, since, the organic matter could potentially be converted to harmful disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Rook, 1977; Marhaba and Washington, 1998). The formation of chlorinated DBPs depends on many factors such as chlorine dosage and contact time, turbidity, temperature, and, quantity of DOM. Among these parameters, quantity and characteristic of DOM are the most important factors. Quantity of DOM can be measured by using DOM surrogate parameters including dissolved organic carbon (DOC), ultraviolet absorbance at wavelength 254 nm (UV-254) and trihalomethane formation potential (THMFP). Whereas three dimensional florescent spectroscopy analysis by a fluorescent excitation-emission matrix (FEEM) (Khan *et al.*, 2005; Gone *et al.*, 2009; Hudson *et al.*, 2008; Baker, 2001; Baker and Inverarity, 2004; Janhom *et al.*, 2009, Baker and Curry, 2004; Swietlk *et al.*, 2004; Chen *et al.*, 2003; Sirivedhin and Dallbauman, 2004; Stedmon and Markager, 2005a; Roccaro *et al.*, 2009) and fourier transform infrared (FTIR) are commonly used to characterize nature of DOM (Chen *et al.*, 2002; Peuravuori *et al.*, 2005; Kanokkantapong *et al.*, 2006; Her *et al.*, 2008; Zularisam *et al.*, 2007; Xue *et al.*, 2008).

The successful technique that was commonly employed to reduce the level of the DBPs was to reduce the level of DOM prior to it being chlorination. The coagulation processes were conducted using the polyaluminium chloride (PACl) as a coagulant and the enhanced coagulation, such as pH adjustment, adding cationic polymer and powder activated carbon (PAC) could be an effective method for organic matter removal in the raw water under the optimal dosage of coagulant and pH (Cheng *et al.*, 1995; Marhaba and Pipada, 2000). In addition, enhanced coagulation technique could be employed to improve THMs precursors removal (Bolto *et al.*, 1999; and Bolto *et al.*, 2002).

U-Tapao Canal is the raw water source to produce water supply for utility in the area of Songkhla, Thailand. It is also the main source of raw water supply for four cities in Songkhla. Nowadays, approximately 100,000-150,000 m³/day of water supply is produced using raw water from U-Tapao Canal. These raw waters are considerable extent contaminated with domestic wastewater, industrial wastewater and pesticides and other organic matters. These organic matters therefore can react with chlorine to form THMs. Under this situation, THMs as a suspected human carcinogen may directly affect consumers. Therefore, there is a need to determine the optimal condition for reducing DOC, UV-254 and THMFP by polyaluminium chloride (PACl) coagulation and the enhanced PACl coagulation by using polymer and powder activated carbon (PAC), and to identify the nature of DOM by FEEM and FTIR technique for better understanding on reactivity of DOM on THMs

4.2 Material and Methods

4.2.1 Sample Collection and Experiment Procedure

The raw water was collected from U-Tapao Canal at pumping station of Hat Yai water treatment plant. Water samples were collected two times in October 2009 represented the nature of DOM in rainy season whereas that of in April 2010 represented the nature of DOM in summer. The water samples were measured for pH, temperature, alkalinity, dissolved oxygen (DO), suspended solids (SS), and turbidity. For measurements of DOM surrogate parameters, water samples were filtered through a pre combusted (550 °C for 2 h) Whatman GF/F (nominal pore size 0.22 µm). Filtered water samples were analyzed for ultraviolet absorbance at 254 nm (UV-254), dissolved organic carbon (DOC), trihalomethane formation potential (THMFP). Fluorescent excitation-emission matrix (FEEM), and fourier transform infrared (FTIR) were analyzed in order to identify nature of DOM.

The raw waters supply samples were used to perform the coagulation experiment using Jar-Test apparatus. The jar-test procedures as stated previously were experimented under the condition of coagulation as depicted in Table 4.1. Coagulated waters were measured for their DOC, UV-254, FEEM, FTIR, and THMFP. Details of the coagulation experiment and analytical

methods for analyzing UV-254, DOC, FEEM, FTIR and THMFP are presented in Chapter III, section 3.5 and 3.6.

Table 4.1 The experimental jar-test condition

Coagulant	Coagulant Dosage (mg/L)	pH
1) PACl	0, 10, 20, 30,40, 50	controlled pH at 7
2) PACl+Polymer	PACl 40 mg/L (optimal condition 1) and polymer 0.2,0.4,0.6,0.8and1mg/L	controlled pH at 7
3) PACl+PAC	PACl 40 mg/L (optimal condition 1) and PAC 10, 20, 40, 60, 80 mg/L	controlled pH at 7
4) PACl+ Polymer+PAC	PACl 40 mg/L combined with polymer 1 mg/L and PAC 80 mg/L	controlled pH at 7

4.3 Results and Discussions

4.3.1 Characteristics of Raw Waters Supply

The general water quality and DOM surrogate parameter of raw water supply from pumping station at U-Tapao Canal in rainy season and summer were showed in Table 4.2. The pH values of raw water supply from both seasons were close to neutral. It can be stated that pH of raw water supply is suitable for coagulation. A relatively low alkalinity ranged between 22 and 24 mg/L as CaCO_3 were observed. Since, alkalinity must be destroyed in the reaction with coagulant to produce floc. But to prevent pH drop by alkalinity consuming during coagulation flocculation process, the additional alkalinity in case of low alkalinity raw water is more required. The turbidity of raw water from both seasons was higher than 5 NTU, they were not adequately clear enough to allow for direct utilization as potable water. The traditional treatment process, which commonly consists of coagulation, sedimentation, and filtration, is necessary in this case for removing turbidity and suspended solids prior to utilization produced water as potable water.

For rainy season, the values of DOC, UV-254, SUVA and THMFP of raw water were 5.1 mg/L, 0.414 cm^{-1} , 8.1 L/mg-m and $729 \mu\text{g/L}$, respectively. Whereas that of summer, the values of DOC, UV-254, SUVA and THMFP of raw water were 5.5 mg/L, 0.159 cm^{-1} , 2.8 L/mg-m and $509 \mu\text{g/L}$, respectively. On this basis, the highest UV-254 absorbance was observed in rainy season.

UV-254 is used to provide information of aromatic hydrocarbon, the level of UV absorbance depends upon the level of aromatic hydrocarbon in the water. In case of high aromatic content in water high value of UV absorbance are obtained.

The DOC values of raw water supply of rainy season and summer almost same. DOC is used to represent both aromatic and aliphatic hydrocarbons in water. The highest SUVA value the ratio of UV-254/DOC of water was observed in rainy season. SUVA has been found to be good predictor of the carbon aromaticity content of NOM and THMs formation in water (Liang and Singer, 2003). Reckhow *et al.*, (1990) found that DPBs formation increases with the increased activated aromatic content of NOM. Similarly, the highest THMFP concentration of 729 $\mu\text{g/L}$ was detected in rainy season, due to the highest UV-254 content of water.

Thai meteorological department, the South East, (2008) reported that rainfall amount during the time collection in rainy season was approximately 35 to 90 mm (heavy rain), the possibility that rain water flowing into the U-Tapao Canal was high quantity. It may also leach the aromatic DOM from non-point source to the canal in rainy season.

Table 4.2 DOM characteristics in raw water.

Parameter	Raw water supply	
	Rainy Season	Summer
pH	6.9	7.4
Temperature ($^{\circ}\text{C}$)	28.5	32
Alkalinity (mg/L as CaCO_3)	22	24
DO (mg/L)	6.5	6.0
Suspended solid (mg/L)	64	13.6
Turbidity (NTU)	24.4	22.8
DOC (mg/L)	5.1	5.5
UV-254 (cm^{-1})	0.414	0.159
SUVA (L/mg-m)	8.1	2.8
THMFP($\mu\text{g/L}$)	729	509

The THMFP of raw water obtained in this study were compared with other raw water sources in Thailand (as shown in Table 4.3). It was found that the THMFP values of raw water in

this study were considerably higher than those of other raw water sources in Thailand. Based on this finding the DOM in the raw water must be more effectively removed by the coagulation processes.

The U.S. EPA has issued the Disinfectants/ Disinfection By-Products (D/DBP) rule reduced the MCL for THMs to 80 $\mu\text{g/L}$ for Stage 1 D/DBP and 40 $\mu\text{g/L}$ for Stage 2 (USEPA, 2003). The World Health has set the health related guideline values (GV) at 200 $\mu\text{g/L}$ for CHCl_3 , 100 $\mu\text{g/L}$ for each of CHClBr_2 and CHBr_3 , and 60 $\mu\text{g/L}$ for CHCl_2Br (WHO, 2004). In water samples of rainy season and summer that the detected species of THM were CHCl_3 , CHCl_2Br , and CHClBr_2 . For rainy season, the concentrations of THMs detected in chlorinated water sample during study were 608 $\mu\text{g/L}$ for CHCl_3 , 80 $\mu\text{g/L}$ for CHCl_2Br , 39 $\mu\text{g/L}$ for CHClBr_2 , respectively. Whereas that of summer, the concentrations of THMs were 420 $\mu\text{g/L}$ for CHCl_3 , 56 $\mu\text{g/L}$ for CHCl_2Br , 32 $\mu\text{g/L}$ for CHClBr_2 , respectively. Considering the presence of THM species, it was found that CHCl_3 was the major THM species in raw water in this study. These relevantly corresponded to the result by Inthanuchit (2009). They found that CHCl_3 82 percent, CHCl_3 was the dominant THM compound in raw water from U-Tapao Canal. Teksoy *et al.*, (2008) report that percent of CHCl_3 -FP for 73 percent in raw water, it was major THMFP species found in raw water of Doganci Dam in Turkey.

Table 4.3 THMFP and THMs species in raw water of this study compared with the values from other raw water supply sources in Thailand.

Water Source	Sampling Times	THMFP ($\mu\text{g L}^{-1}$)	CHCl_3 -FP ($\mu\text{g L}^{-1}$)	CHBrCl_2 -FP ($\mu\text{g L}^{-1}$)	CHBr_2Cl -FP ($\mu\text{g L}^{-1}$)	CHBr_3 -FP ($\mu\text{g L}^{-1}$)
The Chao Phraya River Bangkok, Thailand (Panyapinyopol <i>et al.</i> , 2005)	August 2003	313	262 (84%) ¹	43.8 (14%)	6.9 (2%)	ND
Aung-Keaw Reservoir, Chiang Mai, Thailand (Homklin, 2004)	November 2004	403	372 (92%)	20.3 (5%)	11.1 (3%)	ND
Mae-Kuang Reservoir, Chiang Mai, Thailand (Homklin, 2004)	December 2004	236	214 (90%)	15.4 (7%)	6.9 (3%)	ND
Mae-Sa River, Chiang Mai, Thailand (Homklin, 2004)	February 2005	113	94 (83%)	11.7 (10%)	7.0 (7%)	ND
Mae-Hae Reservoir (Pumpaisanchai, 2005)	November 2004	482	462 (95%)	20 (5%)	ND	ND
Bhumibol Dam Reservoir, Tak, Thailand (Panyapinyopol <i>et al.</i> , 2005)	April 2005	318	292 (92%)	25.6 (8%)	ND	ND
Ping River Chiang Mai, Thailand (Chimongkol, 2008)	November 2008	239	223 (93%)	14 (6%)	2 (0.8%)	ND
Raw water from U-Tapao Canal of this study in rainy season.	October 2009	729	608 (83%)	80 (11%)	39 (6%)	ND
Raw water from U-Tapao Canal of this study in summer.	April 2010	508	420 (82%)	56 (13%)	32 (5%)	ND

Remark: ¹() = percent distribution and ND = Not detected

4.3.2 Reduction of DOC and UV-254 by Enhanced Coagulation

Based on the results in Figure 4.1 and Table 4.4, for rainy season, about 5.1 mg/L of DOC in raw water was promptly reduced to 2.2 mg/L by 40 mg/L of PACl dosage. At this condition, the removal of 57 percent of DOC from the supernatant was observed. DOC reduced from 5.1 mg/L to 1.9 mg/L, approximately 63 percent by PACl 40 mg/L combined with polymer 1 mg/L at pH 7 (Figure 4.2). From this point, it was could remove DOC slightly higher than that

PACl only. DOC decreased from 5.1 mg/L to 2.04 mg/L, approximately 65 percent by PACl 40 mg/L combined with PAC 1 mg/L at controlled pH of 7 (Figure 4.3). While the PACl 40 mg/L combined with polymer 1 and PAC 80 mg/L could remove DOC by approximately 83 percent as shown in Figure 4.4.

In case of UV-254 reduction in rainy season, UV-254 decreased from 0.414 cm^{-1} to 0.200 cm^{-1} , approximately 52 percent, by PACl coagulation of 40 mg/L at a controlled pH 7. UV-254 decreased from 0.414 cm^{-1} to 0.113 cm^{-1} , approximately 53 percent by PACl 40 mg/L combined with polymer 1 mg/L at controlled pH of 7. UV-254 decreased from 0.414 cm^{-1} to 0.159 cm^{-1} , approximately 62 percent by PACl 40 mg/L combined with PAC 1 mg/L at controlled pH of 7. UV-254 decreased from 0.414 cm^{-1} to 0.128 cm^{-1} , approximately 53 percent by PACl 40 mg/L combined with polymer 1 mg/L and PAC 80 mg/L at controlled pH of 7. (Figure 4.5 to 4.8)

Whereas that for summer, DOC decreased from 5.5 mg/L to 2.2 mg/L, respectively by PACl coagulation at 40 mg/L and pH 7 (Figure 4.1 and Table 4.4). This condition can remove about 59 percent of DOC. DOC decreased from 5.5 mg/L to 1.9 mg/L, approximately 63 percent by PACl 40 mg/L combined with polymer 1 mg/L at controlled pH of 7. DOC decreased from 5.5 mg/L to 1.7 mg/L, approximately 65 percent by PACl 40 mg/L combined with PAC 80 mg/L at controlled pH of 7. High efficiency of PACl 40 mg/L combined with polymer 1 and PAC 80 mg/L for DOC removal was also observed for raw water.

In case of UV-254 reduction, UV-254 decreased from 0.155 cm^{-1} to 0.075 cm^{-1} , approximately 52 percent, by PACl coagulation of 40 mg/L at a controlled pH 7. UV-254 decreased from 0.155 cm^{-1} to 0.059 cm^{-1} , approximately 62 percent by PACl 40 mg/L combined with polymer 1 mg/L at controlled pH of 7. UV-254 decreased from 0.155 cm^{-1} to 0.053 cm^{-1} , approximately 66 percent by PACl 40 mg/L combined with PAC 80 mg/L at controlled pH of 7. UV-254 decreased from 0.155 cm^{-1} to 0.046 cm^{-1} , approximately 70 percent by PACl 40 mg/L combined with polymer 1 mg/L and PAC 80 mg/L at controlled pH of 7 (Table 4.5).

According to the report of USEPA (1999), the value of DOC in raw water of about $>4 - 8 \text{ mg/L}$ and alkalinity $0-60 \text{ mg/L as CaCO}_3$, were required for a 40 percent reduction in DOC. Water samples from U-Tapao Canal have the DOC and alkalinities that fall into this range. DOC

reduction at optimal condition could be achieved at more than 40 percent. Therefore, in this study organic matter in raw water was removed. These observations were corresponded to the report by Uriarte *et al.*, (2010). The polyaluminium coagulation at 40 mg/L at pH 6 could remove 64.2, 59.7 and 30.9 percent of THMFP, UV-254, and DOC, respectively. Inthanuchit (2009) report that the optimal condition of coagulation in raw water for rainy season and summer, were observed at dosage of 40 mg/L combined with polymer 1mg /L and PAC 80 mg/L with a pH of 7.

The mechanism of PACl coagulation for removing DOM in raw water was the charge neutralization. From the previously studied of AWWA (1993), it was found that PACl coagulation reduced humic like (aromatic hydrocarbon) 50 percent of water samples from Ohio River Water (ORW), Lake Gaillard Water (LGW), Mississippi River Water (MRW), Paaanic River Water (PRW), Salt River Project Water (SRPW) and Florida groundwater (FGW) by PACl coagulation

The mechanism of polymer coagulation was the interparticulate bridging entails the interaction between the polymer and the reactive groups on the destabilized particles. When a polymer with high molecular weight comes into contact with a colloidal particle, some of the reactive groups in the polymer adsorb at the particle surface and leaving other portions of the molecule extending into the solution (AWWA, 1990). By comparing with AWWA (1993), it was found that reduction of humic like (aromatic hydrocarbon) 50 to 60 percent of water samples from State Project Water and Colorado River Water (SPW and CRW), SRPW, ORW, Harwood's Mill Reservoir (HMR) by PACl combined with polymer coagulation.

Powder activated carbon is used for removal of low molecular weight and taste-odor causing materials in raw water (Uyak *et al.*, 2007). It can also remove organic precursors effectively with an adequately long contact time that provided the high adsorption capacity.

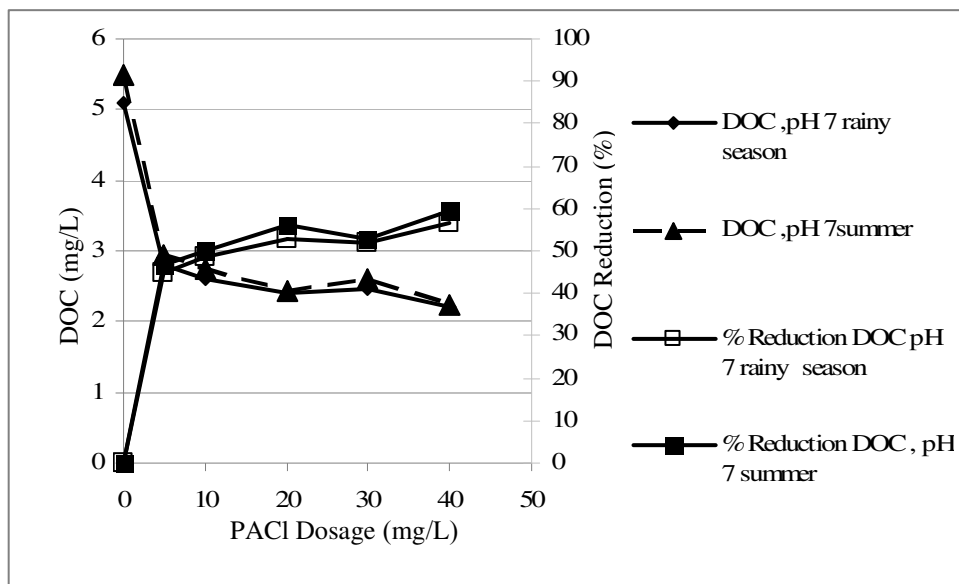


Figure 4.1 Residual DOC and Percent DOC reduction as a function of PACl dosage and controlled pH at 7

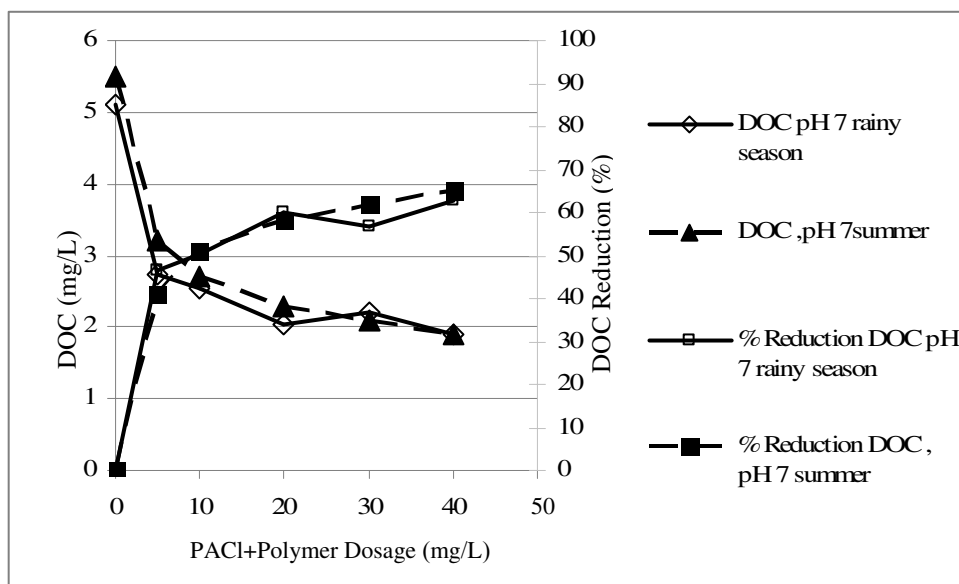


Figure 4.2 Residual DOC and Percent DOC reduction by PACl 40 mg/L and variation of polymer dosage and controlled pH at 7

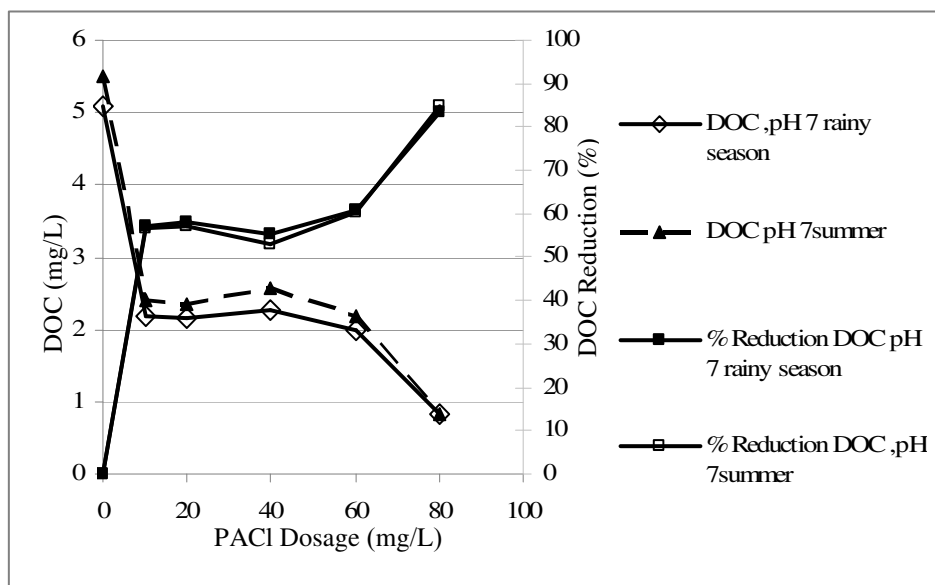


Figure 4.3 Residual DOC and Percent DOC reduction by PACl 40 mg/L and variation of PAC dosage and controlled pH at 7

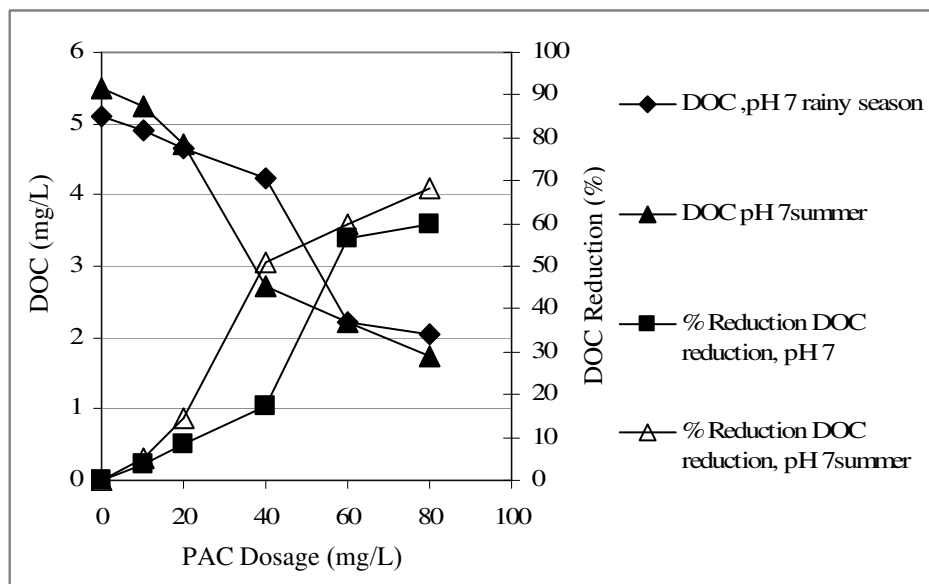


Figure 4.4 Residual DOC and Percent DOC reduction by PACl 40 mg/L combined with polymer and PAC at controlled pH of 7

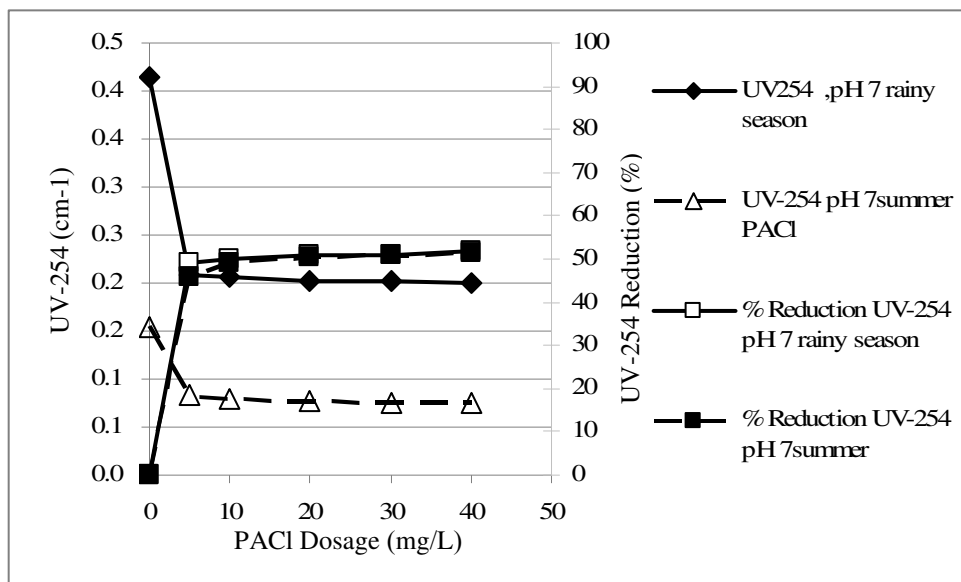


Figure 4.5 Residual UV-254 and Percent UV-254 reduction as a function of PACl dosage and controlled pH at 7.

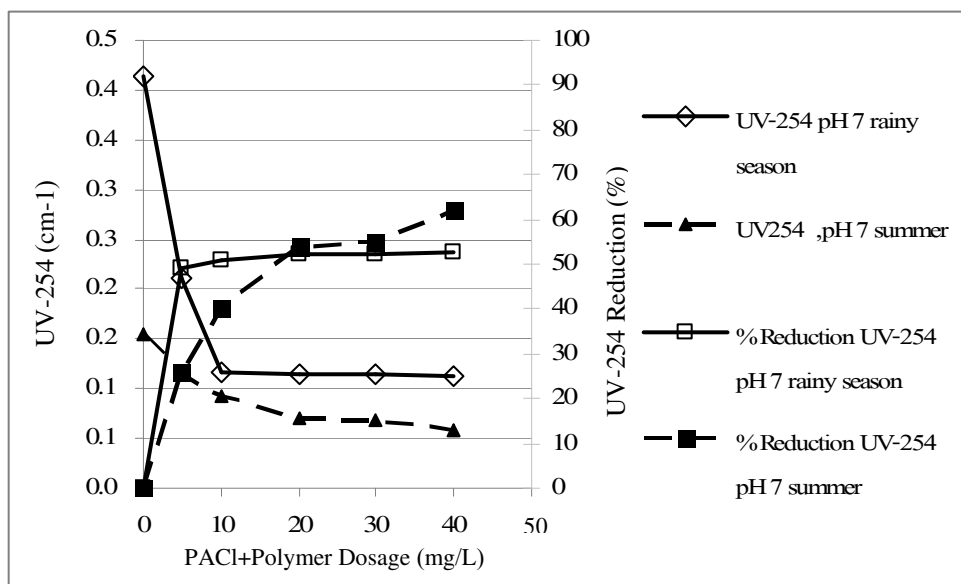


Figure 4.6 Residual UV-254 and Percent UV-254 reduction by f PACl 40 mg/L variation of polymer dosage and controlled pH at 7.

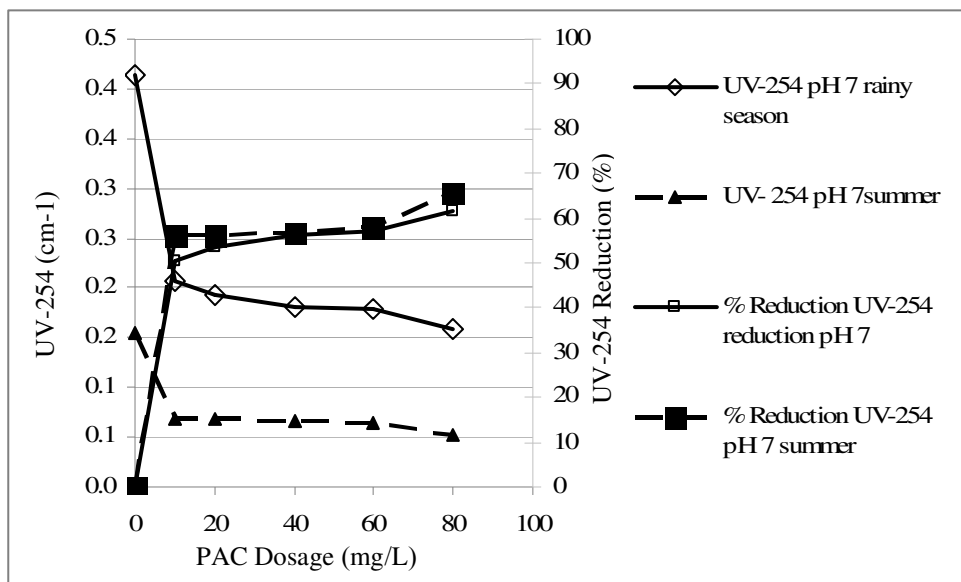


Figure 4.7 Residual UV-254 and Percent UV-254 reduction by f PACI 40 mg/L variation of PAC dosage and controlled pH at 7.

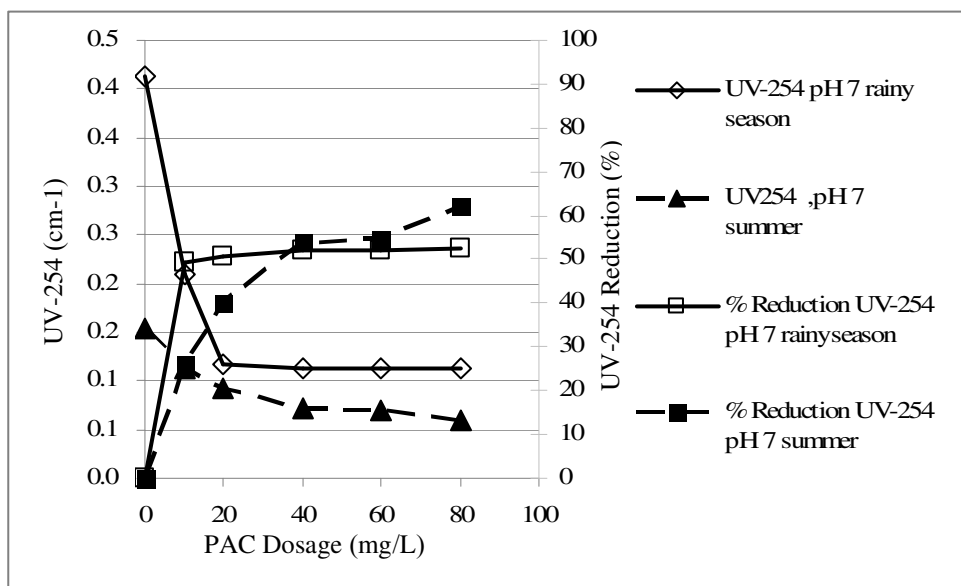


Figure 4.8 Residual DUV-254 and Percent UV-254 reduction by PACI 40 mg/L combined with Polymer and PAC at controlled pH of 7

Considering the DOC and UV-254 values, DOC is commonly used as the primary surrogates of DOM. It consists of both humic and non-humic like. Humic-like include aromatic hydrocarbon; while non-humic like include aliphatic hydrocarbons (Thurman, 1985; Amy, 1993). UV-254 includes aromatic compounds. The summary of UV-254 and DOC reduction by coagulation process are as followed; PACl, PACl combined with polymer, PACl combined with PAC, and PACl combined with polymer and PAC are showed in Table 4.4 and 4.5.

Table 4.4 Reduction efficiency and increasing in reduction efficiency by enhanced coagulation on the DOC and UV-254 in rainy season.

Coagulant	Optimal condition	Reduction efficiency		Increasing in reduction efficiency	
		UV-254	DOC	UV-254	DOC
(1) PACl	40 mg/L	52	57	-	-
(2) PACl + Polymer	PACl 40 mg/L and polymer 1mg/L	53	63	1	6
(3) PACl + PAC	PACl 40 mg/L and PAC80 mg/L	62	65	10	8
(4) PACl + Polymer + PAC	PACl 40 mg/L combined with Polymer 1mg/L and PAC80 mg/L	69	83	17	26

Table 4.5 Reduction efficiency and increasing in reduction efficiency by enhanced coagulation on the DOC and UV-254 in summer.

Coagulant	Optimal condition	Reduction efficiency		Increasing in reduction efficiency	
		UV-254	DOC	UV-254	DOC
(1) PACl	40 mg/L	52	59	-	-
(2) PACl + Polymer	PACl 40 mg/L and polymer 1mg/L	62	65	10	6
(3) PACl + PAC	PACl 40 mg/L and PAC80 mg/L	66	68	14	9
(4) PACl + Polymer + PAC	PACl 40 mg/L combined with Polymer 1mg/L and PAC80 mg/L	70	85	18	26

4.3.3 Classification of DOM in Raw Water and Coagulated water

FEEM result of raw water supply from this study is demonstrated in Figure 4.9. For raw water in rainy season, a total of three fluorescent peaks were detected; strong broad peaks of tryptophan-like at $230\text{-}235\text{nm}_{\text{Ex}}/340\text{-}350\text{nm}_{\text{Em}}$ (Peak A) and $280\text{-}285\text{nm}_{\text{Ex}}/340\text{-}350\text{nm}_{\text{Em}}$ (Peak B) and humic and fulvic acid-like peaks at $265\text{nm}_{\text{Ex}}/450\text{nm}_{\text{Em}}$ (Peak C). For the summer, only strong broad peaks of tryptophan-like at Peak A and Peak B were detected. This broad peak could blind the humic peaks. Consequently, tryptophan-likes substances and humic-like should be the major fluorescent DOM in raw water from U-Tapao Canal. It must be noted that in general, tryptophan-like substances did not detected in natural water sources, it normally found in the wastewater (Lee and Ahn.,2004; Musikavong *et al.*, 2007). On this basis, it is possible that contaminant from the domestic wastewater, industrial wastewater, sewage or farms pollutions could be the suspicious sources, which discharge DOM to U-Tapao Canal (Musikavong *et al.*, 2007).

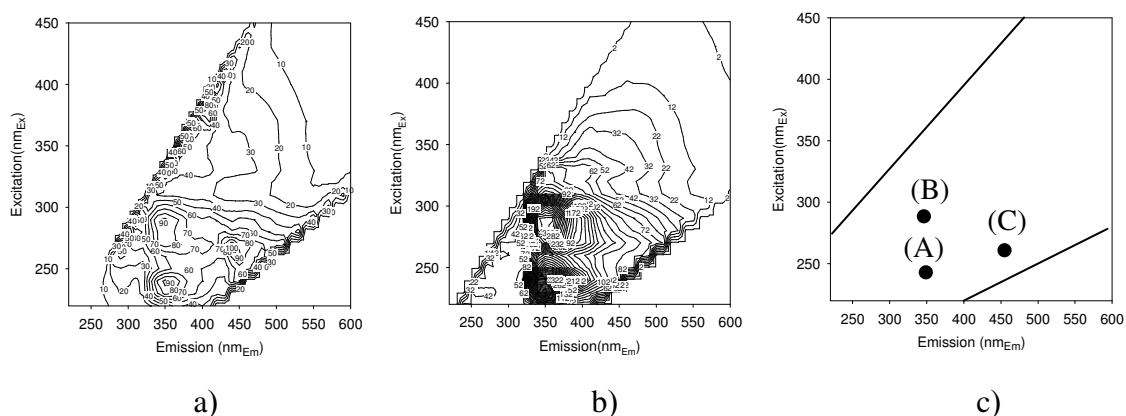


Figure 4.9 FEEMs of signatures of raw water supply in rainy season (a), raw water supply in summer (b) and summary of fluorescent peak position (c), (contour interval in QSU unit).

With more detailed consideration, the fluorescent intensities at each of the fluorescent peaks could be utilized for determining the quantity of each fluorescent organic matter in water. A summation of the fluorescent intensities of all outstanding fluorescent peaks in a FEEM has been proposed to determine the quantity of the total fluorescent organic matter in water (in QSU). In addition, the reduction of each fluorescent organic matter was also evaluated by the reduction of the fluorescent intensity of each peak. The reduction of the total fluorescent organic matter by

coagulation process was evaluated by the reduction of the summation of the fluorescent intensities of overall outstanding peaks.

Samples of FEEM result coagulated water are demonstrated in Figure 4.10. By considering coagulated water in rainy season and summer, a total of three fluorescent peaks were detected; strong broad peaks of tryptophan-like at $230\text{-}235\text{nm}_{\text{EX}}/340\text{-}350\text{nm}_{\text{EM}}$ (Peak A) and $280\text{-}285\text{nm}_{\text{EX}}/340\text{-}350\text{nm}_{\text{EM}}$, (Peak B) and humic and fulvic acid-like peaks at $265\text{nm}_{\text{EX}}/450\text{nm}_{\text{EM}}$ (Peak C).

In general, fluorescent peaks at intermediate excitation wavelengths (250-280 nm) and shorter emission wavelengths (<380 nm) are related to soluble microbial byproduct-like material (Chen *et al.*, 2003). Peaks in the range of Ex/Em 240-260nm/380-480 nm as well as of Ex/Em 320-350 nm/400-480 nm are associated with humic-like substances (Baker *et al.*, 2007).

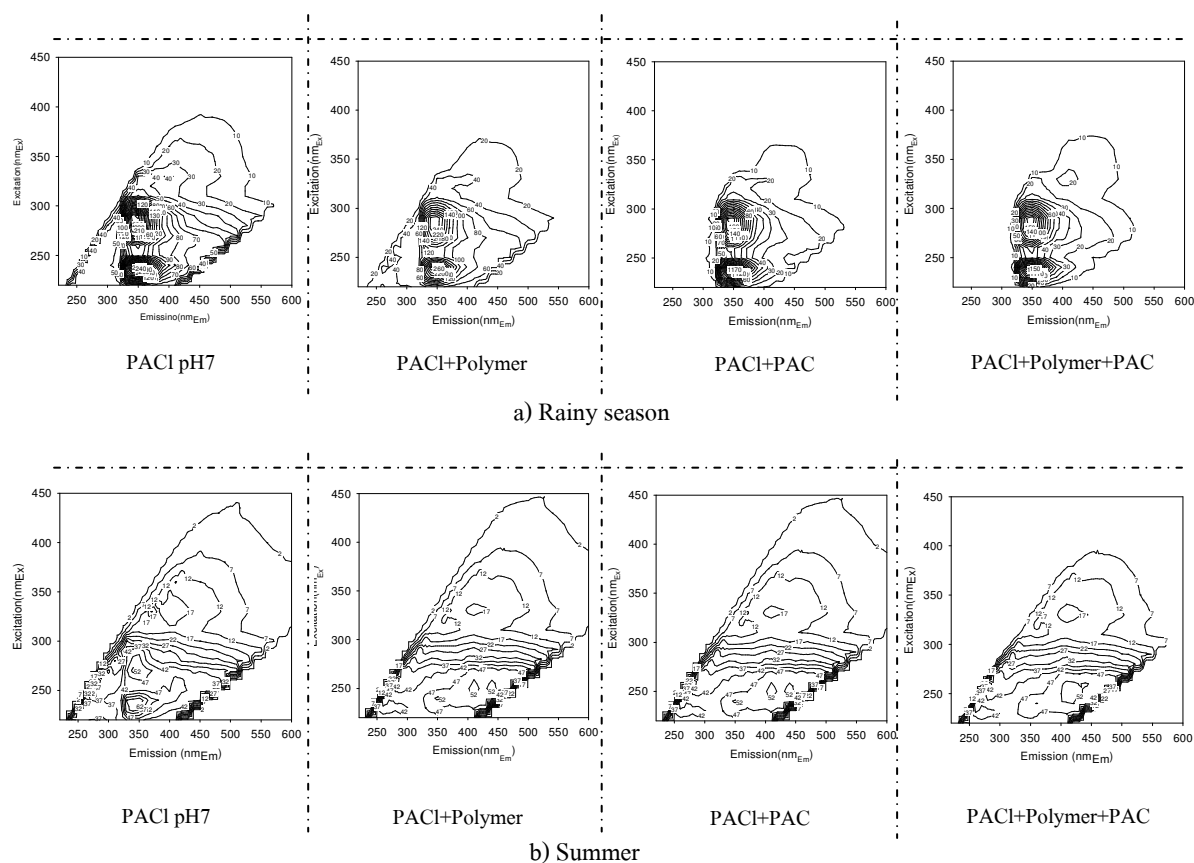


Figure 4.10 Samples of the patterns of FEEMs (contour interval of 4 QSU) of coagulated water in rainy season a) and summer b)

Fluorescent organic matter of each FEEM peak could be defined as follows: peaks A and B are tryptophan-like substances and peaks C is humic and fulvic acid-like substances. Average values of the fluorescent intensities at each of the fluorescent peaks and average values of the summation of the fluorescent intensities of the three outstanding peaks in the FEEMs of raw water and coagulated water by enhanced coagulation are illustrated in Figure 4.11 and 4.12.

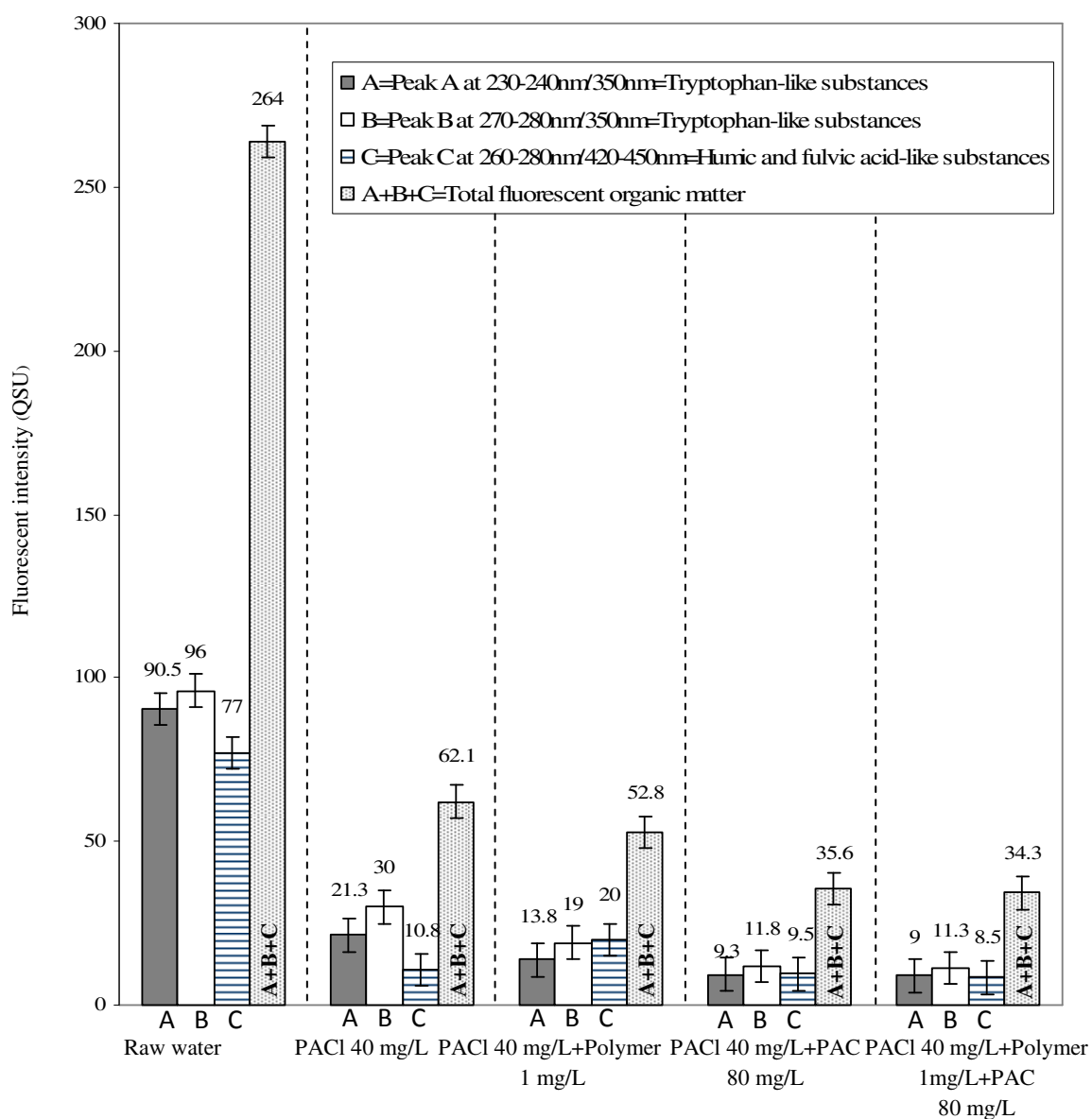


Figure 4.11 Fluorescent intensity of raw water and coagulated water by enhanced coagulation in rainy season

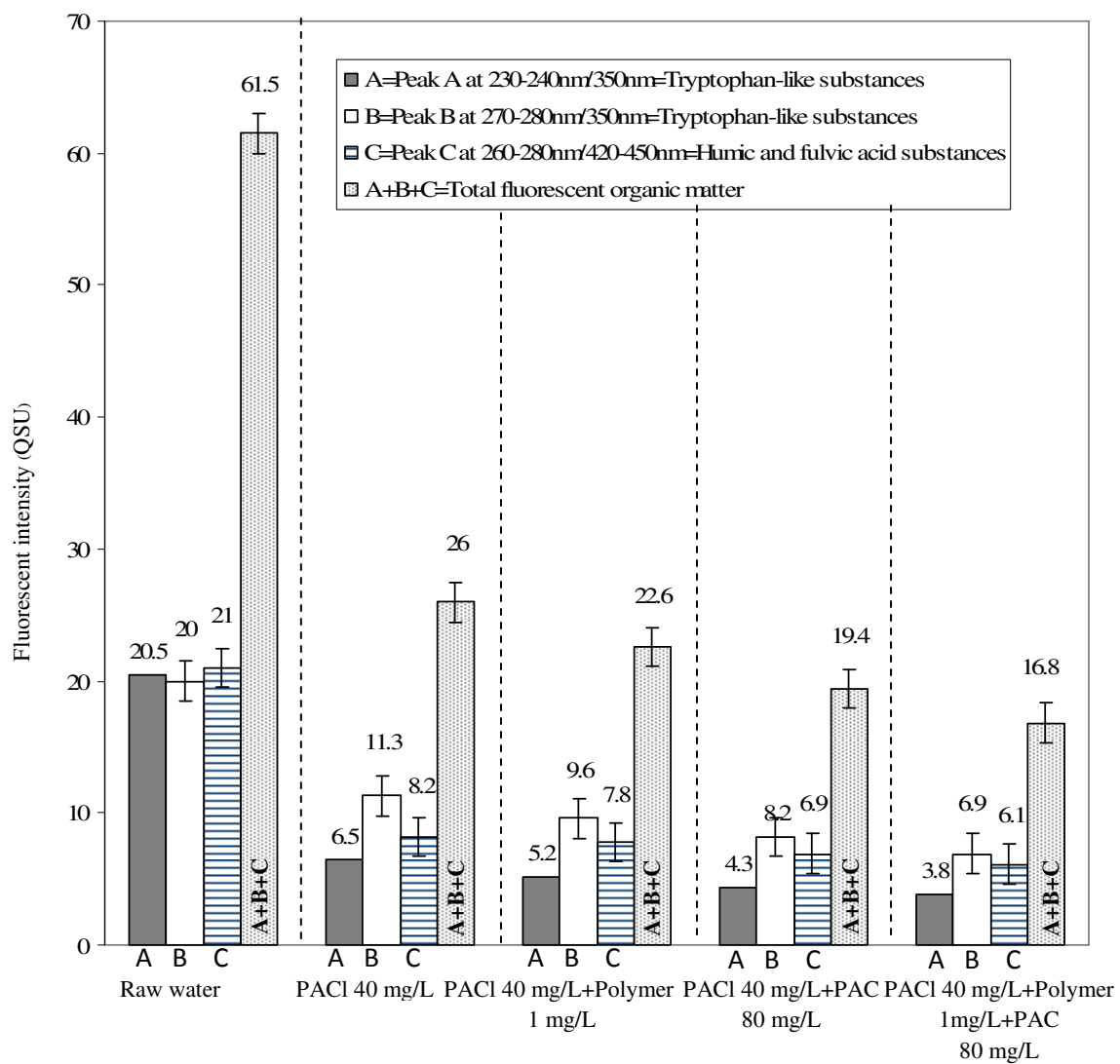


Figure 4.12 Fluorescent intensity of raw water and coagulated water by enhanced coagulation in summer

Table 4.6. Fluorescent intensity at peak positions and their reduction efficiency by enhanced coagulation

Water samples	Fluorescent intensity (QSU)				Reduction efficiency				Increasing in reduction efficiency			
	Peak A ¹	Peak B ²	Peak C ³	Total (A+B+C)	Peak A ¹	Peak B ²	Peak C ³	Total (A+B+C)	Peak A ¹	Peak B ²	Peak C ³	Total (A+B+C)
Raw water in rainy season	90.5	96	77	264	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
(1) PACl	21.3	30	10.8	62.1	76	69	85	76	N.D.	N.D.	N.D.	N.D.
(2) PACl+Polymer	13.8	19	20.0	52.8	84	80	74	80	8	11	N.D.	4
(3) PACl+PAC	9.3	11.8	9.5	30.6	89	84	87	88	13	15	2	12
(4) PACl+Polymer+PAC	9.0	11.3	8.5	28.8	90	88	89	89	14	19	4	13
Raw water in summer	20.5	20	21	61.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
(1) PACl	6.5	11.3	8.2	26	68	44	61	58	N.D.	N.D.	N.D.	N.D.
(2) PACl+Polymer	5.2	9.6	7.8	22.6	75	52	63	63	7	8	2	5
(3) PACl+PAC	4.3	8.2	6.9	19.4	79	59	67	68	11	15	6	10
(4) PACl+Polymer+PAC	3.8	6.9	6.1	16.8	81	66	71	73	13	22	10	15

Remark: 1= Tryptophan like substances (230-240nm_{Ex}/350nm_{Em})

2= Tryptophan like substances (270-280nm_{Ex}/350nm_{Em})

3= Humic and fulvic acid like substances (260-280nm_{Ex}/420-450nm_{Em})

N.D. =Not detected

() = Reduction of DOC values

The reduction efficiency and increasing in reduction efficiency by enhanced coagulation of the fluorescent intensity of each peak and overall peaks by are presented in Figure 4.5 and Table 4.6. The result shows that in case of coagulated water by PACl, the tryptophan-like substances at peaks A and B were reduced by 76 and 69 percent, respectively, and humic-like substances at peaks C was reduced by 85 percent. PACl combined with polymer could reduce tryptophan-like substances at peak A and B by 84 and 80 percent respectively, and it could reduce humic-like substances at peaks C by 74 percent. PACl combined with PAC could reduce the tryptophan-like substances at peak A and B by 89 and 84 percent, respectively, and humic-like substances at peaks C was reduced by 87 percent. PACl combined with polymer and PAC could reduce the tryptophan-like substances at peak A and B by 90 and 88 percent, respectively, and humic-like substances at peaks C was reduced by 89 percent. The PACl combined with polymer and PAC yields the highest DOM reduction efficiency the tryptophan-like substances and humic-like substances.

For the reduction of tryptophan-like substances in summer by PACl coagulation, the tryptophan-like substances at peaks A and B were reduced by 68 and 44 percent, respectively. PACl combined with polymer slightly reduced the tryptophan-like substances at peak B. PACl combined with PAC reduced the tryptophan-like substances at peaks A and B by 79 and 59 percent, respectively. In the case of the reduction of humic and fulvic acid-like substances by PACl coagulation, the humic and fulvic acid-like substances at peaks, C was slightly reduced by 61 percent; PACl combined with polymer could reduce the humic and fulvic acid-like substances at peaks C by 63 percent. PACl combined with PAC could reduce the humic and fulvic acid-like substances at peak C by 67 percent, while PACl combined with polymer and PAC yield the highest efficiency on the humic and fulvic acid-like substances reduction at peak C by 71 percent.

Based on the FEEM results, it can be stated that the coagulation could remove tryptophan-like substances more slightly than humic and fulvic acid-like substances. This observation corresponded well with the study of USEPA (1999), which reported that the fluorescent intensities of humic-like fluorescent peaks were significantly reduced by coagulation. The summation of fluorescent intensities of peaks A, B, and C was utilized to represent the total fluorescent organic matter in the water which was mainly included of tryptophan-like, and humic

and fulvic acid-like substances. For rainy season, PACl coagulation, total fluorescent organic matter was reduced by 76 percent. PACl combined with polymer could reduce total fluorescent organic matter by 80 percent, PACl combined with PAC could reduce total fluorescent organic matter by 88 percent, while the PACl combined with polymer and PAC could reduce the total fluorescent organic matter by 89 percent. Whereas that of summer, PACl coagulation, total fluorescent organic matter was reduced by 58 percent. PACl combined with polymer could reduce total fluorescent organic matter by 63 percent, PACl combined with PAC could reduce total fluorescent organic matter by 68 percent, while the PACl combined with polymer and PAC could reduce the total fluorescent organic matter by 73 percent.

In the case of overall increasing reduction efficiency in rainy season, PACl combined with polymer, PACl combined with PAC, PACl combined with polymer and PAC could reduce total fluorescent organic matter by 4, 12, and 13 percent, respectively, whereas that of summer, the value of total fluorescent organic matter was reduced by 5, 10, and 15 percent, respectively.

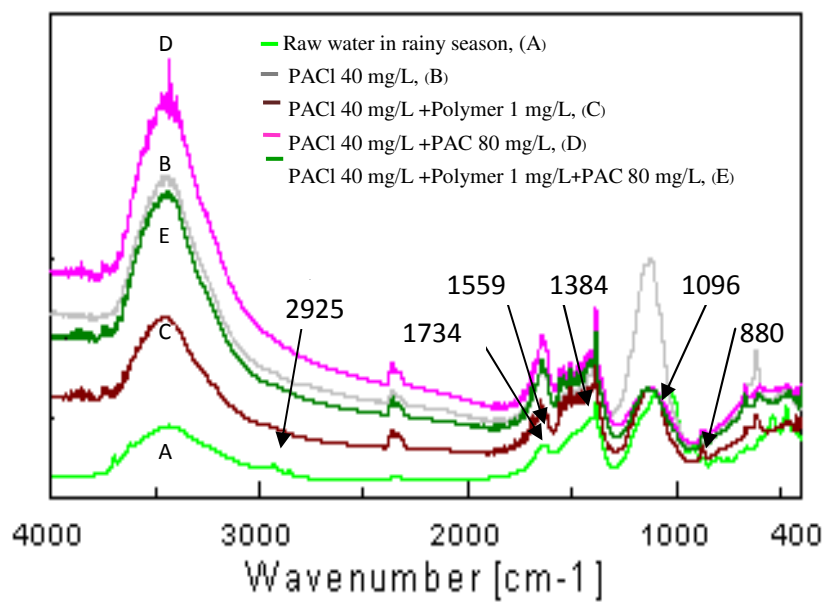
FTIR spectroscopy was employed in order to identify functional group of DOM in raw water and coagulated water in rainy season and summer. Many researchers utilized FTIR to determine functional group of DOM in groundwater (Her *et al.*, 2008), reservoir water (Zularisam *et al.*, 2007), river water (Kanokkantapong *et al.*, 20006; Zularisam *et al.*, 2007; Kim and Yu, 2005) and wastewater (Xue *et al.*, 2008; Benoit *et al.*, 2008). The functional group of DOM water samples was comparing to the FTIR results of the studies of Aiken *et al.*, 1985; Sposito, 1989; Davis *et al.* 1999; Barber *et al.*, 2001; Lin *et al.*, 2001, Musikavong and Wattanachira, 2010). In case of raw water in rainy season and summer, the carboxylic C=C was illustrated at band of 1734-1684 cm^{-1} , cyclic and acyclic compounds, ketones, and quinones contents were indicated by C=O peaks between 1635-1589 cm^{-1} , the bands in range of 1516-1506 cm^{-1} were attributed to the aliphatic C-H deformation. The phenolic OH was illustrated by the strong peaks at 1404-1384 cm^{-1} . Carboxylic group was also indicated by O-H peaks between 871-825 cm^{-1} were detected. However aliphatic C-H, C-H₂, C-H₃ were illustrated the peak at 2925 cm^{-1} . The bands at peaks 1096 -1033 cm^{-1} was indicated by C-O of alcoholic compound and the bands at peaks 667 – 518 cm^{-1} was indicated by COOH. They were detected only in raw water in rainy season.

CCH₃ of methyl ester and C-O of esters, ethers, and phenol were identified by peak at 1456-1404 cm⁻¹ and 1141 cm⁻¹. They were detected in raw water in summer.

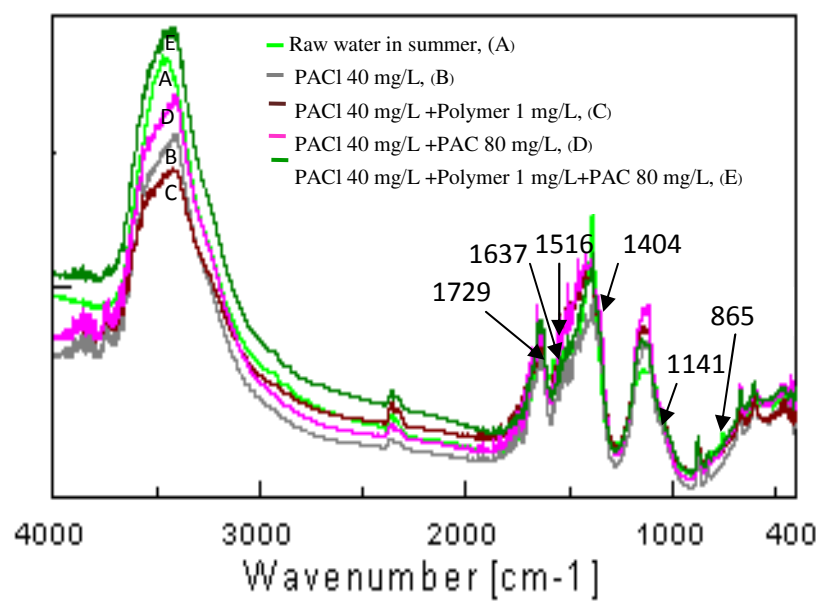
After treatment, for all experiment at optimal conditions, it was obtained that the peak near 3440 cm⁻¹ is indicative of OH and NH stretching. The peak at 1731 cm⁻¹ is indicative of carboxylic acid. The peak at 1637 cm⁻¹ is a typical peak of amine group and C=O combined with aromatic ring. The peak of C-O bond from alcohol and ether in polysaccharide at 1066 cm⁻¹. Considering the removal of DOM, the peak at 2925 cm⁻¹ is that indicative of aliphatic C-H, C-H₂, C-H₃. The peak at 1096 cm⁻¹ is that a typical peak of alcoholic compounds, and the peak at 1384 cm⁻¹ is that indicative of C-H deformation of CH₃ could be easily removed by enhanced coagulation. For C=O of carboxylic acids, amide group, could be partially removed by enhanced coagulation, therefore, they could potentially react with chlorine to form THMs. These relevantly corresponded to the result by Verma *et al.*, (2010). They reported that coagulated water by polyaluminium chloride could remove esters was that illustrated by peak at 1310-1250 cm⁻¹ and the bands at peaks 800-400 cm⁻¹ was that indicated by CH bending vibration of aromatic rings. The summary of the FTIR spectra of raw water and coagulated water in rainy season and summer are presented shown in Table 4.7.

Table 4.7 Summary of the FTIR spectra of raw water and coagulated water

Water Samples	Rainy season		Summer	
	Functional group	Reduction	Functional group	Reduction
Raw water	Aliphatic C-H, CH ₂ , CH ₃ carboxylic Aromatic C=C amide groups benzene, pyridines alcoholic compounds carboxylic groups		carboxylic ketones and quinones benzene, pyridines Aliphatic C-H alcohol ester, ethers, phenol carboxylic groups	
PACl 40 mg/L	carboxylic Aromatic C=C amide groups ester, ethers, phenol benzene, pyridines alcoholic compounds	Aliphatic C-H, CH ₂ , CH ₃ alcoholic compounds carboxylic groups	carboxylic ketones and quinones benzene, pyridines Aliphatic C-H alcohol ester, ethers, phenol carboxylic groups	Aliphatic C-H carboxylic groups
PACl 40 mg/L+ Polymer 1 mg/L	carboxylic Aromatic C=C amide groups ester, ethers, phenol benzene, pyridines alcoholic compounds	Aliphatic CH, CH ₂ , CH ₃ alcoholic compounds carboxylic groups	carboxylic ketones and quinones benzene, pyridines Aliphatic C-H alcohol ester, ethers, phenol carboxylic groups	Aliphatic C-H carboxylic groups
PACl 40 mg/L+ PAC 80 mg/L	carboxylic Aromatic C=C amide groups ester, ethers, phenol benzene, pyridines alcoholic compounds	Aliphatic CH, CH ₂ , CH ₃ alcoholic compounds carboxylic groups	carboxylic ketones and quinones benzene, pyridines Aliphatic C-H alcohol ester, ethers, phenol carboxylic groups	Aliphatic C-H carboxylic groups
PACl 40 mg/L+ Polymer 1 mg/L+ PAC 80 mg/L	carboxylic Aromatic C=C amide groups ester, ethers, phenol benzene, pyridines alcoholic compounds 667-518	Aliphatic CH, CH ₂ , CH ₃ alcoholic compounds carboxylic groups	carboxylic ketones and quinones benzene, pyridines Aliphatic C-H alcohol ester, ethers, phenol carboxylic groups	Aliphatic C-H benzene, pyridines carboxylic groups



a)



b)

Figure 4.13 FTIR spectra of raw water and coagulated water in a) rainy season and b) summer

4.3.4 Reduction of Trihalomethanes Formation Potential by Enhanced Coagulation

As can be seen from Figure 4.14 to 4.15, THMFP value of raw water in rainy season and summer was 729 μ g/L and 509 μ g/L, respectively. While THMFP of 359 μ g/L and 248 μ g/L was observed from coagulated water by PACl at dosage of 40 mg/L at controlled pH of 7, at this condition, it could reduce THMFP in raw water in rainy season and summer by 46 and 51 percent, respectively.

THMFP of 318 μ g/L and 213 μ g/L was observed from coagulated water by PACl and polymer at dosage of 40 mg/L and 1 mg/L at controlled pH of 7, at this condition, it could reduce THMFP in raw water in rainy season and summer by 56 and 58 percent, respectively.

THMFP of 241 μ g/L and 193 μ g/L was observed from coagulated water by PACl and PAC at dosage of 40 mg/L and 80 mg/L at controlled pH of 7, at this condition, it could reduce THMFP in raw water in rainy season and summer by 67 and 62 percent, respectively.

THMFP of 139 μ g/L and 103 μ g/L was observed from coagulated water by PACl and polymer and PAC at dosage of 40 mg/L and 1 mg/L and 80 mg/L at controlled pH of 7, on this basis, it could reduce THMFP in raw water in rainy season and summer by 80 and 79 percent, respectively.

Chloroform, dichlorobromomethane, and dibromochloromethane were the THMFP species observed in this study. However, chloroform was the major THMFP species while dichlorobromomethane and dibromochloromethane were found in minority. Based on the obtained results, the use of 40 mg/L of PACl combined with 1 mg/L of polymer and 80 mg/L of PAC could reduce THMFP and THM species. It could reduce the THMFP by 80 and 79 percent for rainy season and summer, respectively. CHCl_3 , was reduced by 80 percent, it was the major THM species that was reduced. According to the report of the WHO (2004) which the Metropolitan Waterworks Authority used this report as a water quality standard for tap water in Thailand, the maximum acceptable levels for CHCl_3 and CHCl_2Br are 200 μ g/L and 60 μ g/L, respectively. From these results, it can be stated that the THMFP values of coagulated water by PACl combined with polymer and PAC in this study met the WHO standard and also the standard of Thailand Metropolitan Waterworks Authority.

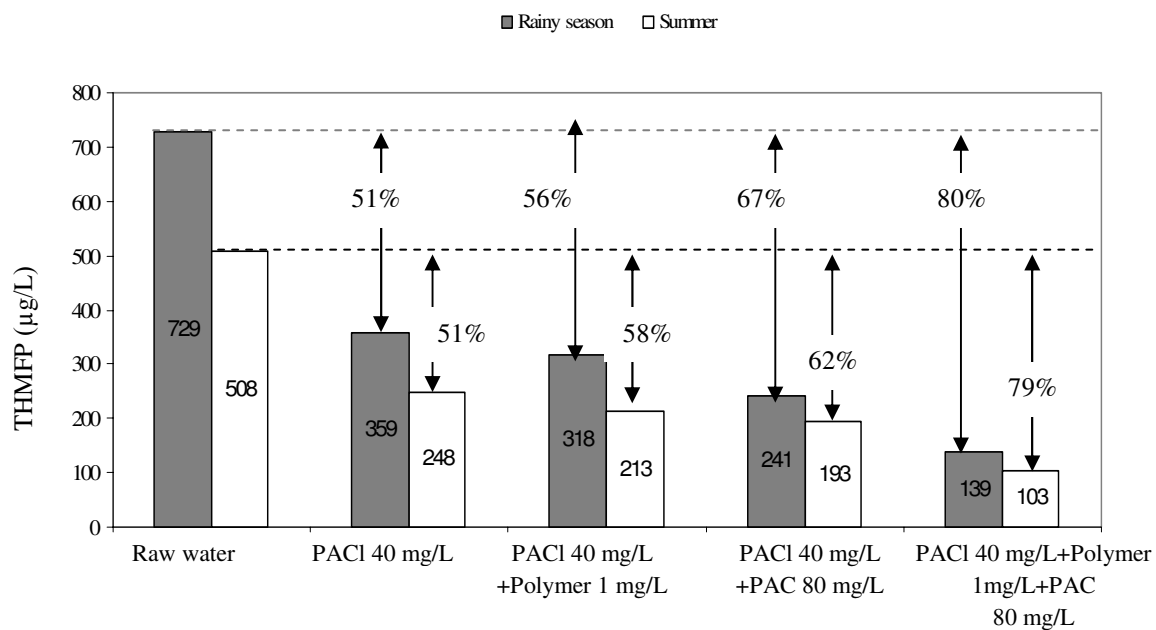


Figure 4.14 Reduction of THMFP by coagulation in rainy season and summer

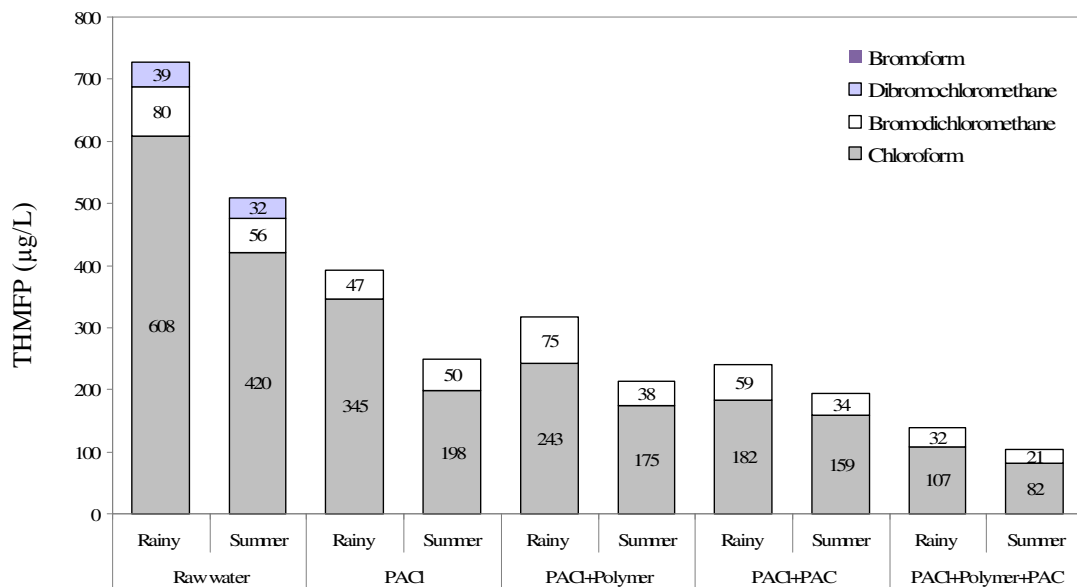


Figure 4.15 THMFP of raw water and coagulated water in rainy season and

4.3.5 Specific THMFP

The specific THMFP was the ratio between THMFP and DOC of each water sample. Specific THMFP provides an indication of the potential of the organic carbon in water to react with chlorine to form THMs. As can be seen from Figure 4.16, which presents the specific THMFP of raw water, the specific THMFP of raw water was lower than the specific THMFP of coagulated water. Therefore, it can be stated that water samples after the coagulation process were slightly more reactive with chlorine to form THMs.

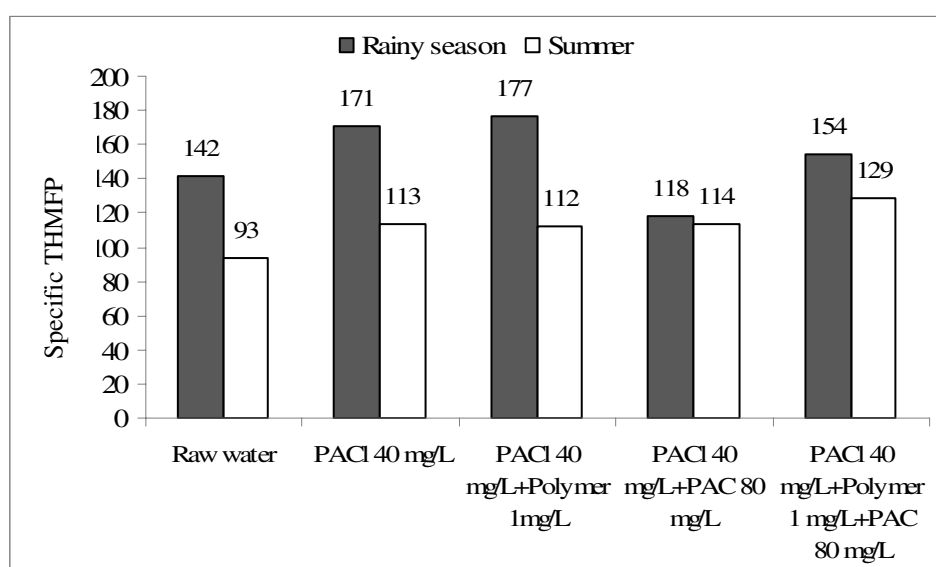


Figure 4.16 Specific THMFP of raw water and coagulated water in rainy season and summer

4.3.6 Concluding Remark

The use of 40 mg/L of PACl combined with 1 mg/L of polymer and 80 mg/L of PAC yielded the highest DOM reduction efficiency in terms of DOC, UV-254 and THMFP for both season. The FEEM analysis in rainy season and summer found humic and fulvic acid- like substances peaks ($265\text{nm}_{\text{Ex}}/450\text{nm}_{\text{Em}}$) and tryptophan-like substances ($230\text{-}235\text{nm}_{\text{Ex}}/340\text{-}350\text{nm}_{\text{Em}}$ and $280\text{-}285\text{nm}_{\text{Ex}}/340\text{-}350\text{nm}_{\text{Em}}$) existed in raw water supply sample. After coagulation, in rainy season that the use of 40 mg/L of PACl combined with 1 mg/L of polymer and 80 mg/L of PAC could remove humic and fulvic acid-like and tryptophan-like, approximately 85 and 89 percent, respectively. For summer coagulated water that the use of 40 mg/L of PACl combined with 1

mg/L of polymer and 80 mg/L of PAC could remove humic and fulvic acid and tryptophan-like, approximately 85 and 74 percent respectively. The FTIR analysis found functional groups including aliphatic C-H, C-H₂, C-H₃ at 2924 cm⁻¹, carboxylic acids at 1734-1700 cm⁻¹, amide group at 1684-1635 cm⁻¹, aromatic C=C at 1627-1576 cm⁻¹, CH₃ group at 1385 cm⁻¹, and alcoholic compounds at 1096-1033 cm⁻¹. PACl coagulation combined with polymer and PAC at optimal condition could remove aliphatic C-H at 2924 cm⁻¹ and alcoholic compounds at 1096-1033 cm⁻¹ effectively. THMFP value of raw water in rainy season and summer was 729µg/L and 509µg/L, respectively. While that of THMFP of 359µg/L and 248µg/L was observed from coagulated water with PACl at dosage of 40 mg/L at controlled pH of 7. In this condition, it could reduce THMFP in raw water in rainy season and summer by 46 and 51 percent, respectively. PACl and polymer coagulation could reduce THMFP in raw water in rainy season and summer by 56 and 58 percent, respectively. PACl and PAC coagulation could reduce THMFP in raw water in rainy season and summer by 67 and 62 percent, respectively. PACl combined with polymer and PAC coagulation could reduce THMFP in raw water in rainy season and summer by 80 and 79 percent, respectively.

CHAPTER V

CHARACTERIZATION AND REDUCTION OF DOM FRACTIONS IN RAW WATER AND COAGULATED WATER

5.1 Introduction and Objective

Dissolved organic matter (DOM) in natural waters is of particular concern because DOM can react with chlorine during chlorination to form disinfection by-products (DBPs) could potentially be carcinogenic such as haloacetic acids (HAAs) and trihalomethanes (THMs)(Rook,1977;Marhaba and Washington, 1998). The formation of DBPs is based on the quantity and characteristic of DOM. The quantity of DOM surrogate parameters including dissolved organic carbon (DOC), ultraviolet absorption at wavelength 254 nm (UV-254), and trihalomethane formation potential (THMFP). The characteristic of DOM is identified by using resin fractionation, fluorescent excitation emission (FEEM), and fourier transform infrared (FTIR) technique. Resin fractionation has been employed in order to provide a better understanding of the characteristics of the DOM in the water. The resin fraction can separate the DOM into specific organic groups based on their physical and chemical properties. DOM in the water sample is separated into three DOM fractions; namely the hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fractions by using a series of DAX-8 and XAD-4 resins. Each fraction has difference ability to form DBPs. The hydrophobic fractions represent almost 50 percent of DOC with larger molecular weight (MW). The hydrophilic fraction composes of 25-40 percent of DOC with lower MW and operationally defined as non-humic fraction. The transphilic fraction comprises approximately 25 percent of DOC in natural water but with MW in between hydrophobic and hydrophilic fractions (Zularisam *et al.*, 2007). Each DOM fraction is analyzed for their UV-254, DOC, THMFP, FEEM and FTIR in order to gain better understanding on THMs formation. The FEEM are associated with humic-like substance, tryptophan-like substance, and tyrosine-like substance. FTIR spectrum has been used to qualitatively determined functional groups. As previously mentioned in chapter IV, the PACl coagulation could remove efficiency DOM, the enhanced coagulation could increase the DOM reduction quantity efficiency. However, the information on hydrophobic, transphilic, and hydrophilic reduction in

U-Tapao water source is limited. The aim of this chapter, therefore, is to determine the characteristics of the DOM fractions in raw water supply from U-Tapao Canal, Hat Yai, Songkla and their coagulated water by enhanced coagulation. The THMFP and specific THMFP values of each individual DOM fraction of each water sample were determined. Finally, DOM fractions, THMFP and specific THMFP results could be used to facilitate the control and removal of DOM and DBPs.

5.2 Material and Methods

5.2.1 Sample Collection and Experiment Procedure

The raw water was collected from U-Tapao Canal at pumping station of Hat Yai water treatment plant. Water samples were collected two times in October 2009 represented the nature of DOM in rainy season whereas that of in April 2010 represented the nature of DOM in summer. Water samples were filtered through a pre-combusted (550 °C for 2 h) Whatman \square F/F filter (nominal pore size 0.7 μ m) and measured for DOC, UV-254, SUVA, FEEM, FTIR, and THMFP. Raw water was used to conduct coagulation at condition as shown in Table 5.1. The coagulated water was measured for their DOC, UV-254, SUVA, FEEM, FTIR, and THMFP. The resin adsorption procedure (Thurman and Malcolm, 1981, Aiken *et al.*, 1992) was used to fractionate five liters of the filtered raw water and coagulated water into the following three DOM fractions: HPO, TPI and HPI. The each organic fraction of all water samples were then analyzed for their UV-254, SUVA, DOC, FEEM, FTIR, and THMFP values. Details of the resin fractionation procedure and analytical methods for analyzing UV-254, DOC, FEEM, FTIR, and THMFP are presented in Chapter III, Section 3.6.

Table 5.1 The experimental jar-test condition

Coagulant	Coagulant Dosage (mg/L)	pH
1) PACl	40 mg/L	pH at 7
2) PACl+Polymer	PACl 40 mg/L and polymer 1mg/L	pH at 7
3) PACl+PAC	PACl 40 mg/L and PAC 80 mg/L	pH at 7
4) PACl+Polymer+PAC	PACl 40 mg/L combined with polymer 1mg/L and PAC 80 mg/L	pH at 7

5.3 Results and Discussions

5.3.1 Characteristics of DOM fractions in Raw Water

DOM in raw water was fractionated into hydrophilic, transphilic, and hydrophobic fractions by DAX-8 and XAD-4 resin. The mass balances of DOC and the value of DOC in rainy season and summer are represented in Table 5.2. The percent difference between the summation of the DOC of the three fractions and DOC of the unfractionated in raw water were 5.8 percent and 5.5 percent for rainy season and summer, respectively. The tolerance range of fractionation mass balance was between 10-15 percent and 8-12 percent as found by Day *et al.*, (1991); Marhaba *et al.*, (2000). The loss of DOC mass may occur during the elution process. According to the previous reports by Day *et al.*, (1991); Marhaba *et al.*, (2000), the hydrophilic fractions in almost all natural waters studied were higher than the hydrophobic fractions. Typically, the range of the hydrophilic fraction in natural waters was between 53 and 70 percent by weight of DOC.

Table 5.2 Characteristics of DOM fraction in raw water in rainy season and summer.

DOC (mg/L)	DOM fractions				Unfractionated water	% Diff
	HPO	TPI	HPI	HPO+TPI+HPI		
Rainy season	2.0	1.3	1.5	4.8	5.1	5.8
Summer	2.3	1.2	1.7	5.2	5.5	5.5

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

The DOC mass distribution of the raw water obtained in this study was compared with other water source (as shown in Table 5.3). It was found that the HPO was the major DOM fractions in water samples from many sources (the DOC of HPO was approximately 40-55 %). In addition, HPO was also found to be the major DOM fractions in raw water from U-Tapao Canal. The percent DOC distribution of HPO, TPI, and HPI were approximately 43, 26, and 32 percent respectively.

Table 5.3 The DOC mass distribution of the raw water in this study was compared with other water source

Water Source	DOC of raw water (mg/L)	%DOM fractions by DOC values			References
		HPO	TPI	HPI	
		Ground water (W1), (California,USA)	4.94	71	
Yffiniac River (Paris)	8.42	50	25	25	Lee <i>et al.</i> ,2004
Marne River (Paris)	2.7	50	22	28	Lee <i>et al.</i> ,2004
Cazau Lake (Paris)	4.99	39	25	35	Lee <i>et al.</i> ,2004
Bultiere Reservoir (Paris)	6.86	44	26	31	Lee <i>et al.</i> ,2004
Lake Ijssel water	4.32	55	20	25	Kennedy <i>et al.</i> ,2005
Bartlett Lake	N.A.	40	13	27	Mash <i>et al.</i> ,2004
Raw water from this study (rainy season)	5.1	42	27	31	-
Raw water from this study (summer)	5.5	44	23	33	-

5.3.2 Characteristics of DOM Fractions in Coagulated Water

Hydrophobic, transphilic and hydrophilic organic were accounted for 35-45 percent, 20-28 percent and 33-39 percent of total DOC, respectively. Based on the obtained results in Table 5.4 and Figure 5.1, it was found that HPO was the major DOM fractions in the coagulated water by PACl 40 mg/L in rainy season and summer (the DOC of HPO was approximately 48 and 45 by weight of the total DOC respectively). Coagulated water by PACl 40 mg/L combined with polymer 1 mg/L and PACl 40 mg/L combined with PAC 80 mg/L, HPO was also obtained as the major DOM fractions. Interestingly, coagulated water by PACl 40 mg/L combined with polymer 1 mg/ and PAC 80 mg/L, HPO and HPI were obtained as the major DOM fractions. This may have been due to the fact that coagulation processes may easily remove HPO and difficulty in removing HPI. Therefore, percent HPI was increased.

For conclusion, the coagulated water, which DOC of about 2 mg/L, HPO was the major DOM fractions, whereas the coagulated water which has low DOC of about 0.9 mg/L, HPI was major DOM fractions.

Table 5.4 The summary of DOC mass distribution of the raw water and coagulated water in rainy season and summer

Water Source	DOC of coagulated water (mg/L)	%DOM fractions by DOC values		
		HPO	TPI	HPI
Raw water supply in rainy season	5.1	42	27	31
PACl 40 mg/L	2.2	48	19	33
PACl 40 mg/L combined with polymer 1 mg/L	1.9	44	22	33
PACl 40 mg/L combined with PAC mg/L	2.0	45	26	29
PACl 40 mg/L combined with polymer 1 mg/ and PAC 80 mg/L	0.9	31	31	38
Raw water supply in summer	5.5	44	23	33
PACl 40 mg/L	2.2	45	25	30
PACl 40 mg/L combined with polymer 1 mg/L	1.9	39	28	33
PACl 40 mg/L combined with PAC mg/L	1.7	42	27	31
PACl 40 mg/L combined with polymer 1 mg/ and PAC 80 mg/L	0.8	35	26	39

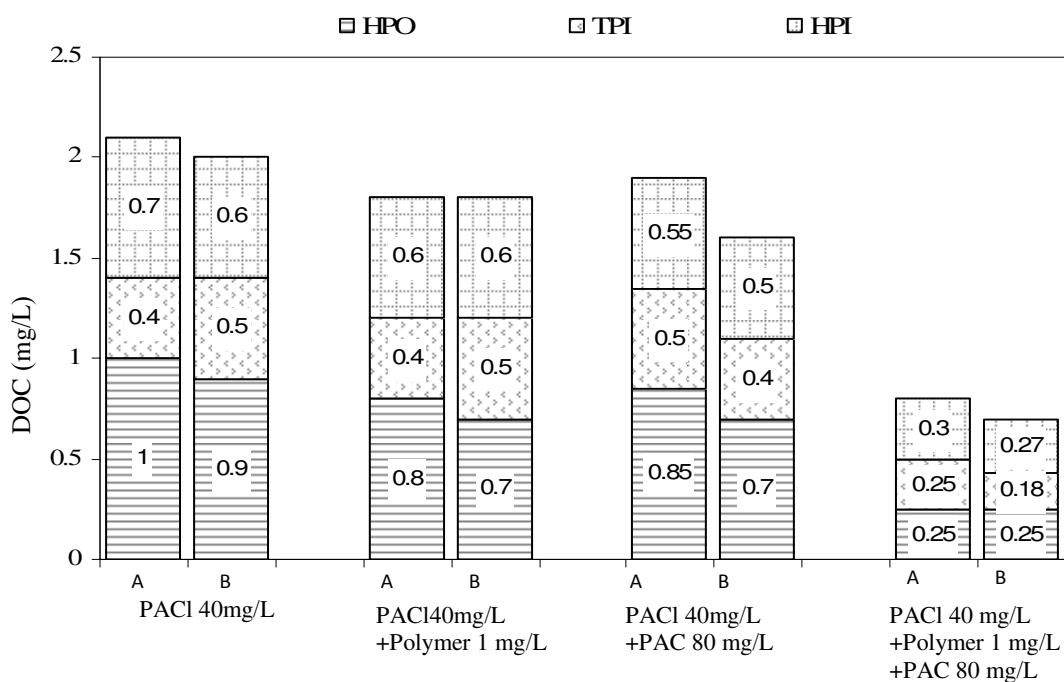


Figure 5.1 Mass balance of DOM in coagulated water in rainy season (A) and summer (B)

5.3.3 Reduction of DOC and THMFP of DOM Fractions

As can be seen in Figure 5.2 and Table 5.5, the use of 40 mg/L of PACl could remove DOC from raw water by about 57 percent in terms of DOC concentration in rainy season. Hydrophobic and transphilic fraction were removed about 60 and 63 percent, respectively whereas about 53 percent of the hydrophilic fraction was removed. The use of 40 mg/L of PACl combined with 1 mg/L of polymer could remove hydrophobic fraction, transphilic fraction, and hydrophilic fraction by 65, 69, and 60 percent, respectively. The use of 40 mg/L of PACl combined with 80 mg/L of PAC could remove hydrophobic fraction, transphilic fraction, and hydrophilic fraction by 68, 70, and 63 percent, respectively. The use of 40 mg/L of PACl combined with 1 mg/L of polymer and the use of 80 mg/L of PAC could remove hydrophobic fraction, transphilic fraction, and hydrophilic fraction by 88, 81 and 80 percent, respectively.

For summer, the use of 40 mg/L of PACl could remove DOC from raw water by about 60 percent in terms of DOC concentration. More detailed consideration of results from the raw water show that 53 percent of the hydrophilic fraction was removed while about 63 and 60 percent of the transphilic and hydrophobic fraction were removed, respectively. The use of 40 mg/L of PACl combined with 1 mg/L of polymer could remove hydrophobic fraction, transphilic fraction, and hydrophilic fraction by 69, 58, and 65 percent, respectively. The use of 40 mg/L of PACl combined with 80 mg/L of PAC could remove DOC in raw water by about 82 percent. 80 and 81 percent of the hydrophilic and transphilic fraction were removed whereas the hydrophobic fraction was reduced by about 80 percent. The use of 40 mg/L of PACl combined with 1 mg/L of polymer and the use of 80 mg/L of PAC could remove hydrophobic fraction, transphilic fraction, and hydrophilic fraction by 89, 85 and 85 percent, respectively (as shown in Figure 5.3 and Table 5.3). From the obtained results, it is notified that the hydrophobic and transphilic fraction could be easily removed by PACl coagulation and enhanced coagulation, while the hydrophilic fraction was slightly difficult to remove by PACl coagulation. The use of 40 mg/L of PACl combined with 1 mg/L of polymer and 80 mg/L of PAC yielded highest for removal of DOM fraction.

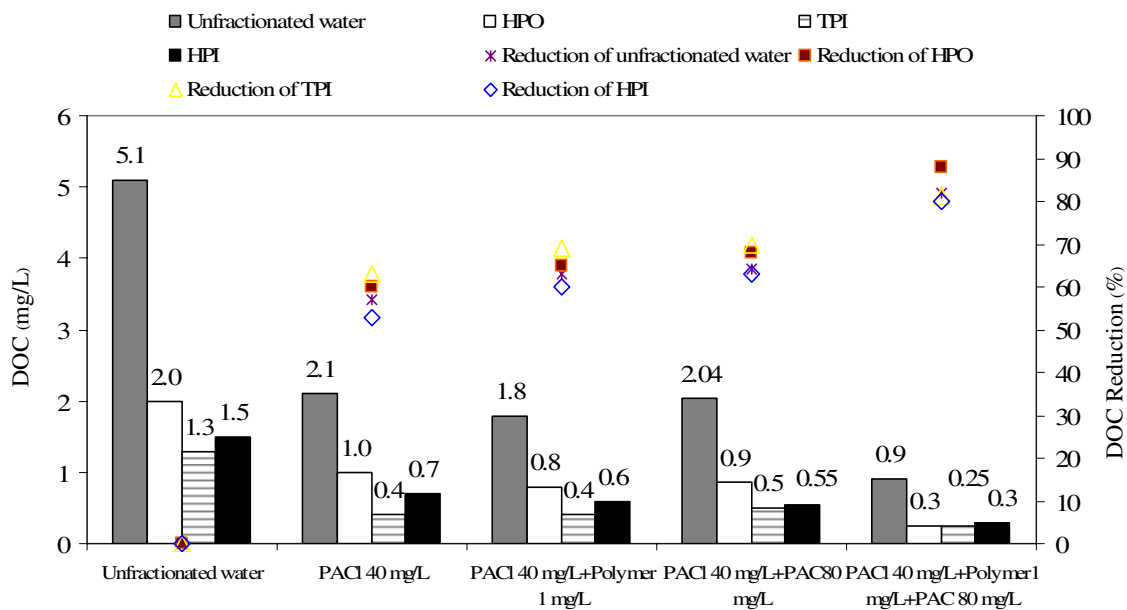


Figure 5.2. Residual DOC, DOC percent reduction and accumulations of percent DOC reduction of unfractionated and fraction water in winter season by enhanced coagulation

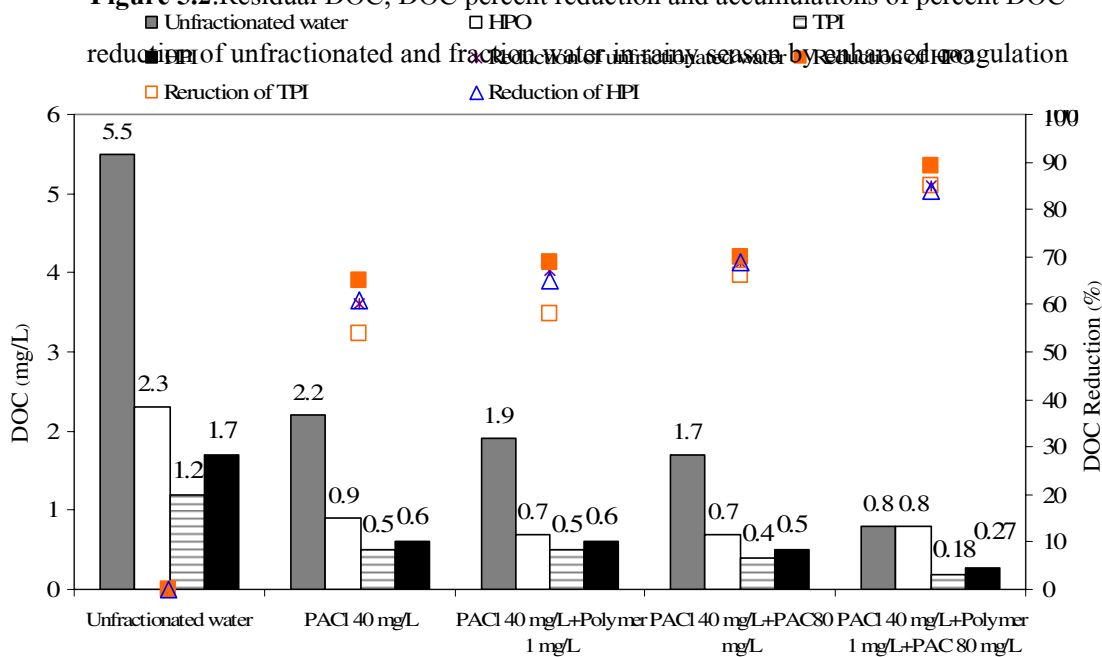


Figure 5.3. Residual DOC, DOC percent reduction and accumulations of percent DOC reduction of unfractionated and fraction water in summer by enhanced coagulation

From previous study, the overall DOC removal was still dominated by the hydrophobic fraction followed by the transphilic and hydrophilic fractions (Zularisam *et al.*, 2007). Both the hydrophobic and transphilic fractions had been widely reported to have greater MW (Lee *et al.*,

2005) or higher relative molecular mass than the hydrophilic fraction by previous researchers (Cho *et al.*, 2000). On the other hand, the hydrophobic and transphilic fractions have more complex molecular structures (aromatic) than the hydrophilic fraction (aliphatic structure).

The reduction efficiency and increasing in reduction efficiency by enhanced coagulation of the water samples on the DOC as shown in Table 5.4. The result shown that the use of 40 mg/L of PACl combined with 1 mg/L of polymer and the use of 80 mg/L of PAC in rainy season could increase the DOM reduction efficiency of hydrophobic, transphilic, and hydrophilic fraction by 38, 18, and 27 percent respectively. Whereas that of summer, the values of DOM reduction efficiency of hydrophobic, transphilic, and hydrophilic fraction by 28, 28, and 20 percent respectively.

According to the studies by Marhaba and Pipada, 2000; Marhaba and Yan, 2000; Tan *et al.*, 2005; Kim *et al.*, 2006; Ji *et al.*, (2008) reported that coagulation reduced humic substances (hydrophobic) and high molecular weight organic matters better than non-humic substances (hydrophilic) and low molecular weight organic matters. Similarly, in this study, hydrophobic fractions in raw waters were removed more easily than hydrophilic and transphilic fractions by enhanced coagulation at optimal condition in rainy season and summer.

Table 5.5 Reduction efficiency and increasing in reduction efficiency of the water samples on DOC

Water sample	Reduction efficiency				Increasing in reduction efficiency by enhanced coagulation			
	Unfractionated	HPO	TPI	HPI	Unfractionated	HPO	TPI	HPI
Raw water in rainy season								
(1) PACl 40 mg/L	57	60	63	57	-	-	-	-
(2) PACl 40 mg/L +Polymer 1mg/L	63	65	69	63	6	15	6	7
(3) PACl 40 mg/L+PAC 80mg/L	64	68	70	64	7	18	7	10
(4) PACl 40 mg/L +Polymer 1mg/L +PAC 80 mg/L	82	88	81	82	25	38	18	27

Raw water in summer								
(1) PACl 40 mg/L	60	65	54	60	-	-	-	-
(2) PACl 40 mg/L +Polymer 1mg/L	67	69	58	67	7	8	1	1
(3) PACl 40 mg/L+PAC 80 mg/L	69	70	66	69	9	9	9	5
(4) PACl 40 mg/L +Polymer 1mg/L +PAC8 0 mg/L	85	89	85	85	25	28	28	20

Based on the obtained results in Figure 5.4 and 5.5 and Table 5.6, THMFP created from DOM in raw water were 729 and 508 $\mu\text{g/L}$ in rainy season and summer, respectively, THMFP values of hydrophobic, transphilic, and hydrophilic fractions of raw water in rainy season were 256, 132, and 308 $\mu\text{g/L}$ respectively, whereas that of about 201, 97, and 210 $\mu\text{g/L}$ of raw water in summer were found. HPI was the major fractions that contributed THM formation, corresponding to 44 and 41 percent of total THMFP in raw water rainy season and summer, respectively.

For rainy season, THMFP of 138, 96, and 142 $\mu\text{g/L}$ were observed from hydrophobic, transphilic, and hydrophilic fractions of coagulated water by PACl 40 mg/L, respectively. The optimal condition could remove 55, 27, and 46 percent of THMFP of hydrophobic, transphilic, and hydrophilic fractions, respectively. The use of 40 mg/L of PACl combined with 1 mg/L of polymer could remove 62, 33, and 56 percent of THMFP of hydrophobic, transphilic, and hydrophilic fractions, respectively. THMFP of 112, 89, and 117 $\mu\text{g/L}$ were observed from hydrophobic, transphilic, and hydrophilic fractions. The use of 40 mg/L of PACl combined with 80 mg/L of PAC could remove 73, 49, and 64 percent of THMFP of hydrophobic, transphilic, and hydrophilic fractions, respectively. THMFP of 82, 67, and 92 $\mu\text{g/L}$ were observed from hydrophobic, transphilic, and hydrophilic fractions. The use of 40 mg/L of PACl combined with 1 mg/L of polymer and the use of 80 mg/L of PAC could remove 88, 67, and 77 percent of THMFP of hydrophobic, transphilic, and hydrophilic fractions, respectively. THMFP of 37, 43, and 59 $\mu\text{g/L}$ were observed from hydrophobic, transphilic, and hydrophilic fractions as shown in Figure 5.6.

For summer, THMFP values of hydrophobic, transphilic and hydrophilic fractions of coagulated water by PACl 40 mg/L is present in Figure 5.7. This optimal condition could remove 56, 40, and 52 percent of THMFP of hydrophobic, transphilic and hydrophilic fractions, respectively. The use of 40 mg/L of PACl combined with 1 mg/L of polymer could remove 64, 47, and 57 percent of THMFP of hydrophobic, transphilic and hydrophilic fractions, respectively. THMFP of 76, 51, and 86 $\mu\text{g/L}$ were observed from hydrophobic, transphilic and hydrophilic fractions. The use of 40 mg/L of PACl combined with 80 mg/L of PAC could remove 67, 47, and 64 percent of THMFP of hydrophobic, transphilic and hydrophilic fractions, respectively. THMFP of 69, 51, and 73 $\mu\text{g/L}$ were observed from hydrophobic, transphilic and hydrophilic fractions. The use of 40 mg/L of PACl combined with 1 mg/L of polymer and the use of 80 mg/L

of PAC could remove 89, 66, and 77 percent of THMFP of hydrophobic, transphilic and hydrophilic fractions, respectively. THMFP of 23, 33, and 47 $\mu\text{g/L}$ were observed from hydrophobic, transphilic and hydrophilic fractions, respectively.

THMFP values of hydrophilic fractions in each organic fraction were higher than THMFP values of hydrophobic and transphilic fractions. After coagulation, THMFP of hydrophobic fractions was reduced more than the THMFP of hydrophilic and transphilic fractions. Interestingly, THMFP of transphilic fraction was difficult to remove by enhanced coagulation, this may be due to the high value of THMs in water supply. Due to the reduction in complexity of organic matter in fractionated water, the creation of THMFP in fractionated water was higher than the creation of THMFP in raw water and coagulated water. According to studies by Singer, (1999), transphilic and hydrophilic fractions can give higher THM and HAA yield on chlorination than the hydrophobic fraction.

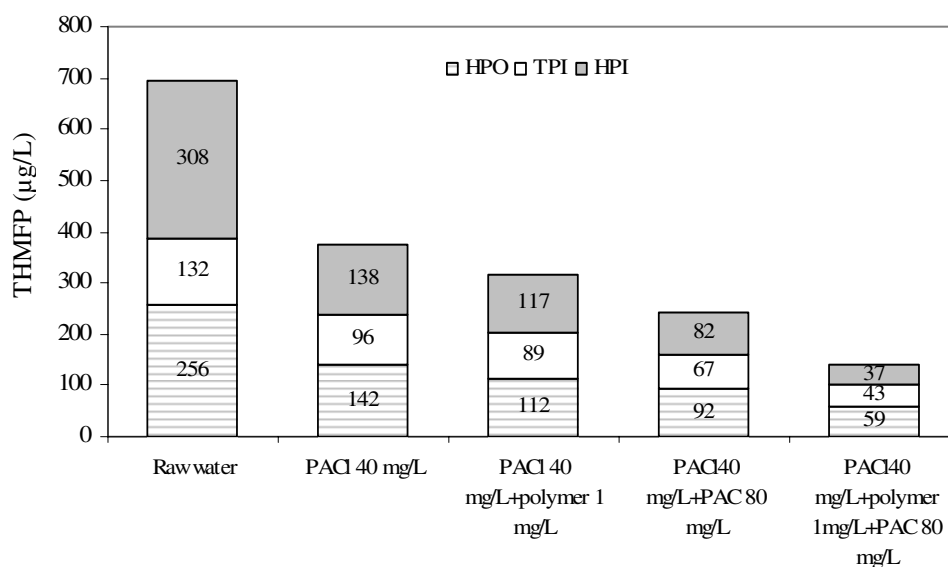


Figure 5.4 THMFP of raw water and coagulated water and THMFP of DOM fractions in rainy season

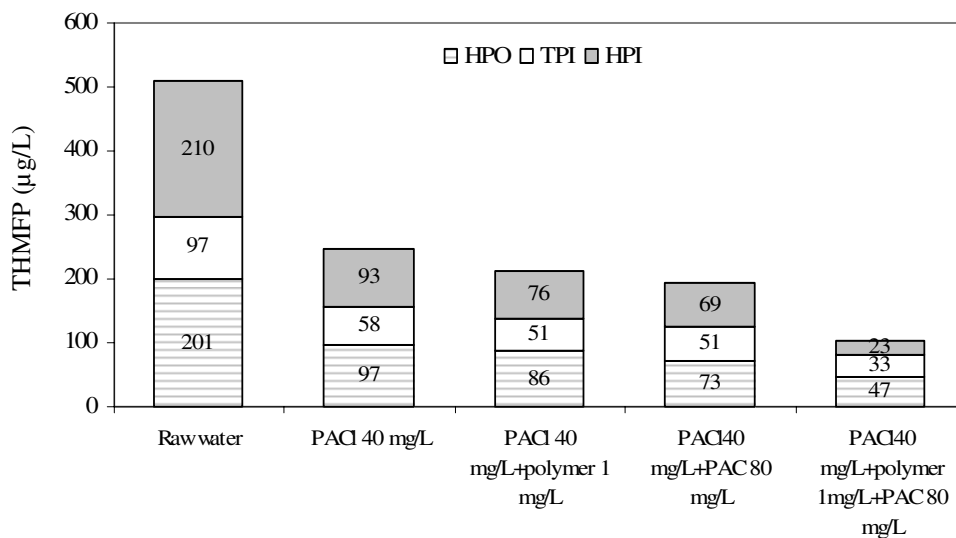


Figure 5.5 THMFP of raw water and coagulated water and THMFP of DOM fractions in summer

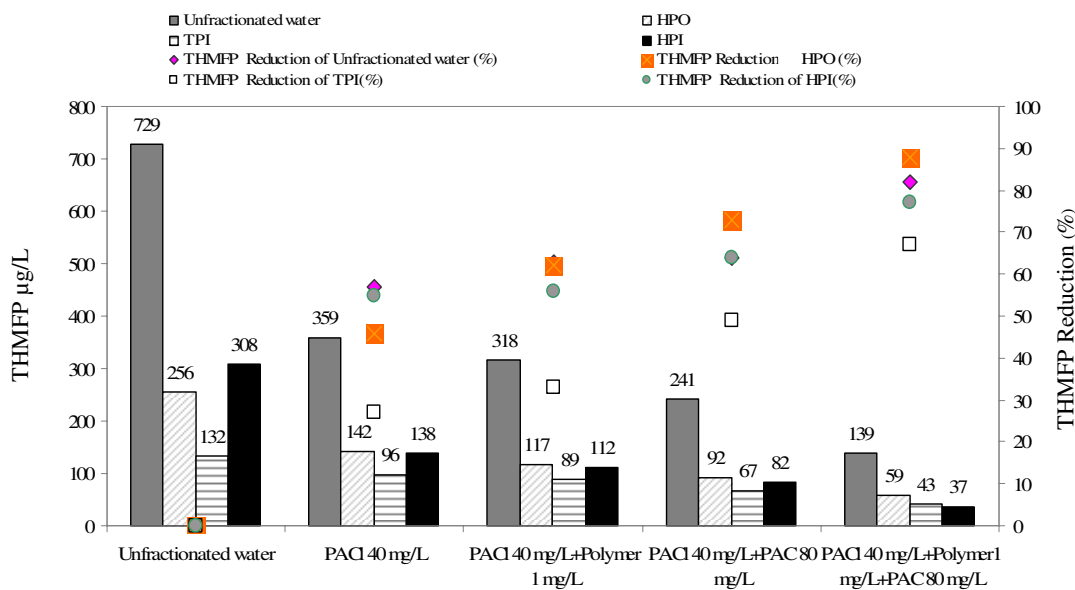


Figure 5.6 THMFP percent reduction and accumulations of percent THMFP reduction of unfractionated and fraction water in rainy season by enhanced coagulation

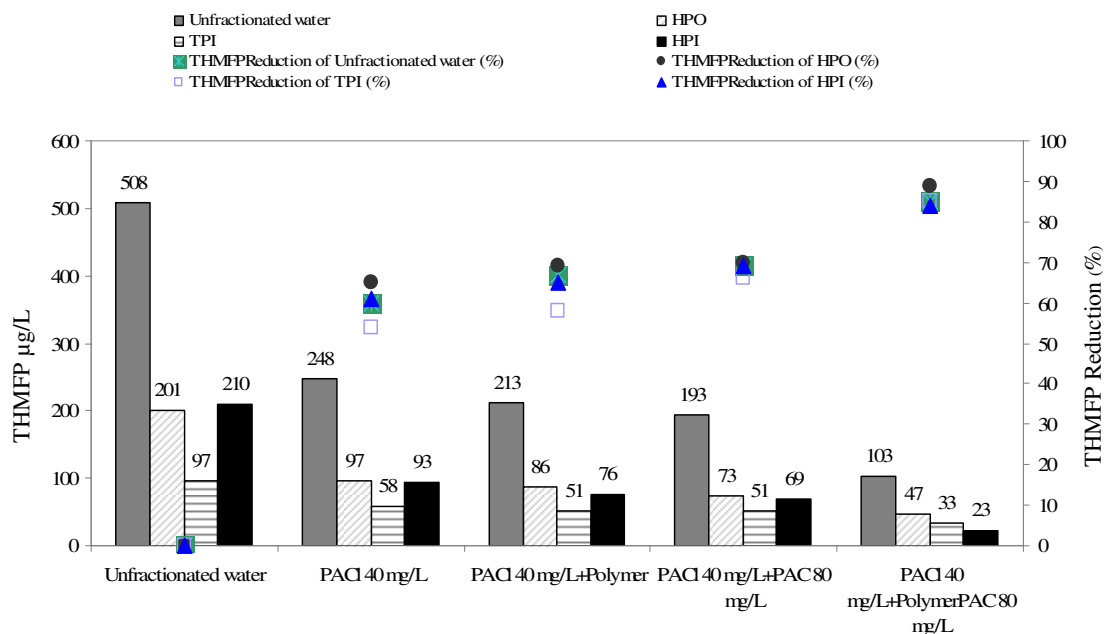


Figure 5.7 THMFP percent reduction and accumulations of percent THMFP reduction of unfractionated and fraction water in summer by enhanced coagulation

Based on the results in Table 5.6, PACI coagulation could remove THMFP of hydrophobic and hydrophilic fractions close to 50 percent. However, it could reduce THMFP of transphilic fractions. Enhanced coagulation by polymer slightly increases the THMFP reduction of DOM fraction. Enhanced coagulation by PAC moderately increases the THMFP reduction of DOM fraction. Enhanced coagulation by adding polymer and PAC yielded the maximum THMFP reduction efficiency for both season.

Table 5.6 Reduction efficiency and increasing in reduction efficiency of the water samples on THMFP

Water sample	Reduction efficiency				Increasing in reduction efficiency by enhanced coagulation			
	Unfractionated	HPO	TPI	HPI	Unfractionated	HPO	TPI	HPI
Raw water in rainy season								
(1) PACl 40 mg/l	51	46	27	55	-	-	-	-
(2) PACl 40 mg/l +Polymer 1 mg/L	56	62	33	56	5	7	6	6
(3) PACl 40 mg/l+PAC 80 mg/L	67	73	49	64	16	18	22	20
(4) PACl 40 mg/l +Polymer 1mg/L +PAC 80 mg/L	81	88	67	77	30	33	40	33
Raw water in summer								
(1) PACl 40 mg/l	51	56	40	52	-	-	-	-
(2) PACl 40 mg/l +Polymer 1 mg/L	58	64	47	57	7	8	7	5
(3) PACl 40 mg/l+PAC 80 mg/L	62	67	47	64	11	11	7	12
(4) PACl 40 mg/l +Polymer 1mg/L +PAC 80 mg/L	78	89	66	77	27	33	26	25

5.3.4 THMs Species

THMs are the by-products of water chlorination. During the chlorination process, commonly used for disinfection, chlorine can react with humic substances in the natural organic matter form (NOM) to form THMs. THMs are part of a group of organic chemicals that contain one carbon atom, one hydrogen atom and three halogen atoms. The most common of these halogen atoms responsible for trihalomethanes formation in water are bromine and chlorine (Rook, 1977). The THMs that actually occur in water supply include chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloroform (CHBr_2Cl) and bromoform (CHBr_3). WHO (2004) reported that the maximum acceptable levels for CHCl_3 , CHCl_2Br and CHClBr_2 are 200, 60, and 100 $\mu\text{g/L}$, respectively. The U.S. EPA has issued the Disinfectants/ Disinfection By-Products (D/DBP) rule reduced the MCL for TTHMs to 80 $\mu\text{g/L}$ for Stage 1 D/DBP and 40 $\mu\text{g/L}$ for Stage 2 (USEPA, 2003). In terms of toxicity, CHCl_2Br is therefore more hazardous than CHCl_3 . However, CHCl_3 was present at much higher concentrations than the other THM species, and therefore it was considered to carry a higher level of human-health concern.

The THMFP and THM species of each DOM fraction for raw water and coagulated water in rainy season and summer obtained are illustrated in Figure 5.10 to 5.11, respectively. Percent distributions of CHCl_3 -FP, CHCl_2Br -FP, CHClBr_2 -FP and CHBr_3 -FP in the raw water and coagulated water of DOM fraction in rainy season and summer are depicted in Figure 5.13 to 5.14, respectively. The TTHMFP value of 729 was observed in rainy season. It was from the CHCl_3 -FP of 608 $\mu\text{g/L}$, CHCl_2Br -FP of 80 $\mu\text{g/L}$ and CHClBr_2 -FP of 39 $\mu\text{g/L}$. While that of summer THMFP value was 508 $\mu\text{g/L}$. It was from the CHCl_3 -FP of 420 $\mu\text{g/L}$, CHCl_2Br -FP of 56 $\mu\text{g/L}$ and CHClBr_2 -FP of 32 $\mu\text{g/L}$. CHCl_3 , therefore, was the major THMs species in the raw water and made up about 83 percent of the total THMFP. These results are similar to reported results from Teksoy *et al.*, (2008). It was found that at about 82 percent, CHCl_3 was the predominant THM compound of raw water from Doganci Dam.

For rainy season, the optimal conditions of PACl coagulation could be used to reduce THMFP 50 percent; the THMFP of 392 $\mu\text{g/L}$ was detected and it composed of CHCl_3 -FP of 345 $\mu\text{g/L}$ and CHCl_2Br -FP of 47 $\mu\text{g/L}$, respectively. The enhanced coagulation by adding cationic polymer could be used to reduce THMFP 56 percent; the THMFP of 318 $\mu\text{g/L}$ was detected and it

composed of CHCl_3 -FP of $263\mu\text{g/L}$ and CHCl_2Br -FP of $55\mu\text{g/L}$. The enhanced coagulation by adding cationic polymer and PAC could be used to reduce THMFP 81 percent; the THMFP of $139\mu\text{g/L}$ was detected and it composed of CHCl_3 -FP of $107\mu\text{g/L}$ and CHCl_2Br -FP of $32\mu\text{g/L}$, respectively. Whereas that of summer the optimal conditions of PACl coagulation could be used to reduce THMFP 52 percent; the THMFP of $248\mu\text{g/L}$ was detected and it composed of CHCl_3 -FP of $198\mu\text{g/L}$ and CHCl_2Br -FP of $50\mu\text{g/L}$, respectively. The enhanced coagulation by adding cationic polymer could be used to reduce 58 percent; the THMFP of $213\mu\text{g/L}$ was detected and it composed of CHCl_3 -FP of $175\mu\text{g/L}$ and CHCl_2Br -FP of $38\mu\text{g/L}$. The enhanced coagulation by adding cationic polymer and PAC could be used to reduce THMFP 79 percent; the THMFP of $108\mu\text{g/L}$ was detected and it composed of CHCl_3 -FP of $82\mu\text{g/L}$ and CHCl_2Br -FP of $21\mu\text{g/L}$, respectively.

THMs guideline value of fractionated water in rainy season of coagulated water by PACl, the enhanced coagulation by adding cationic polymer, the enhanced coagulation by adding cationic PAC, the enhanced coagulation by adding cationic polymer and PAC approximately of 3.1, 2.4, 1.9, 1.8, and 0.8 was found, respectively. Whereas that of summer THMs guideline value of fractionated water of coagulated water by PACl, the enhanced coagulation by adding cationic polymer, the enhanced coagulation by adding cationic PAC, the enhanced coagulation by adding cationic polymer and PAC approximately of 1.4, 1.4, 1.2, 1.1, 0.4 was detected, respectively.

Finally the conclusion, the enhance coagulation by adding cationic polymer and PAC successfully reducing THMFP and THMs species in rainy season and summer. When comparing the criterion of THMs, it was found that THMs guideline value approximately 0.8 and 0.4 was lower than WHO standard, respectively (as shown in Figure 5.9).

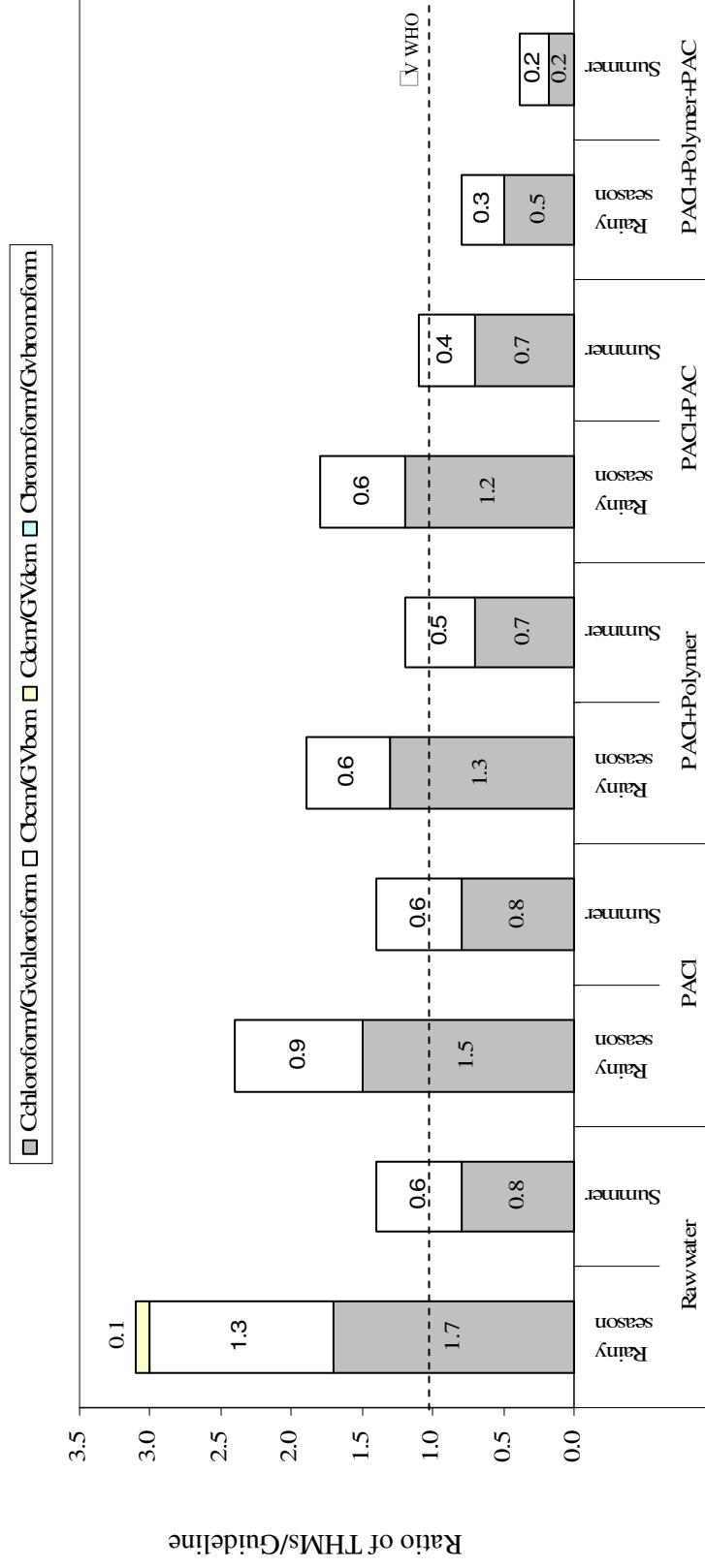


Figure 5.9 THMs/WHO guideline of fractionated water in rainy season and summer

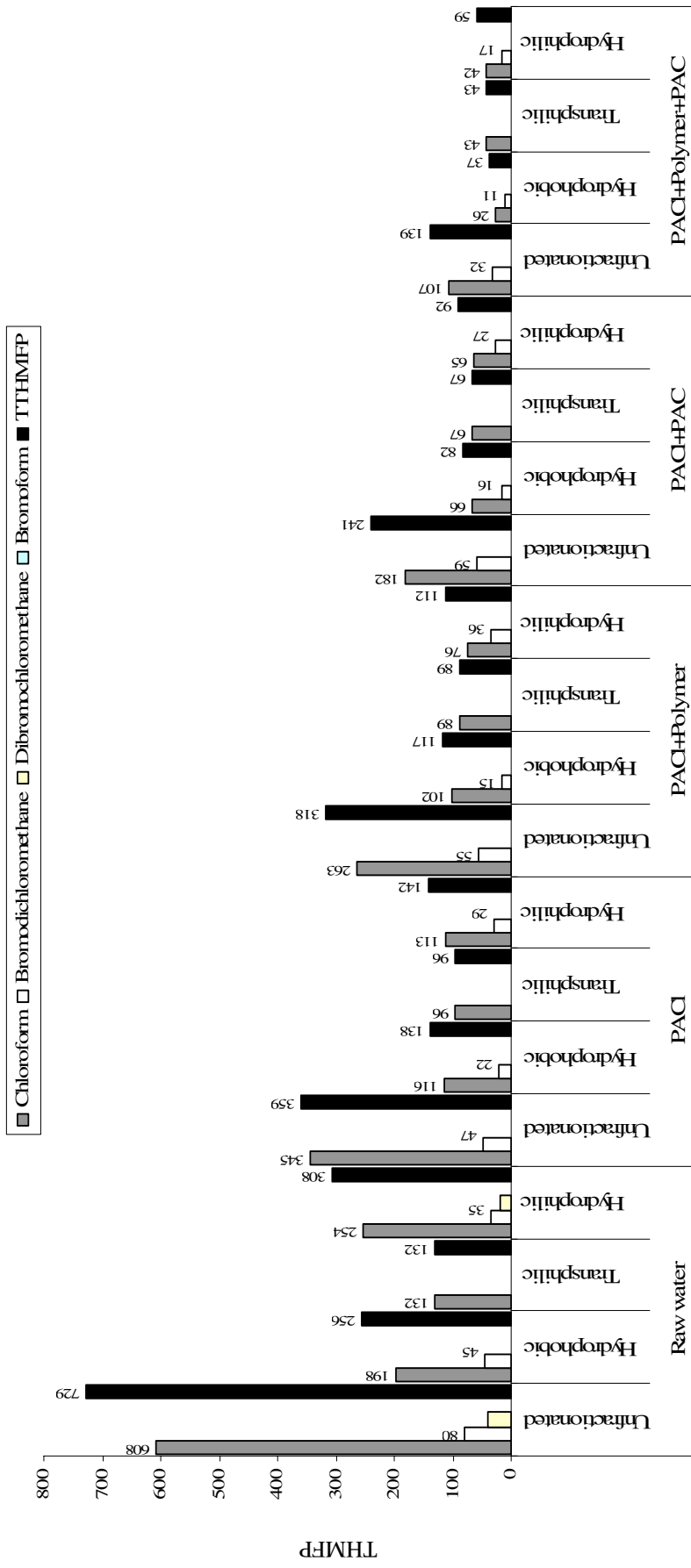


Figure 5.10 THMFP, CHCl₃-FP, CHCl₂Br-FP, CHClBr₂-FP and CHBr₃-FP value of unfractionated and fractionated water in rainy season

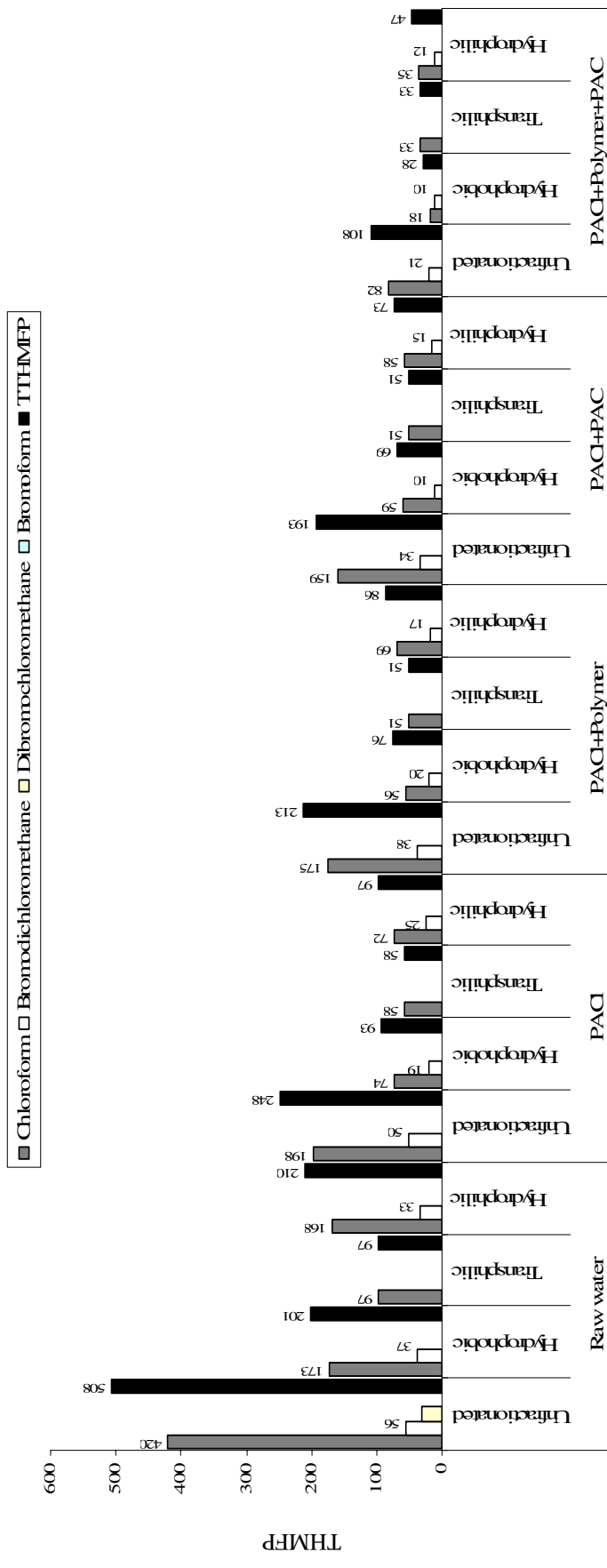


Figure 5.11 THMFP, CHCl₃-FP, CHCl₂Br-FP, CHClBr₂-FP and CHBr₃-FP value of unfractionated and fractionated water in summer

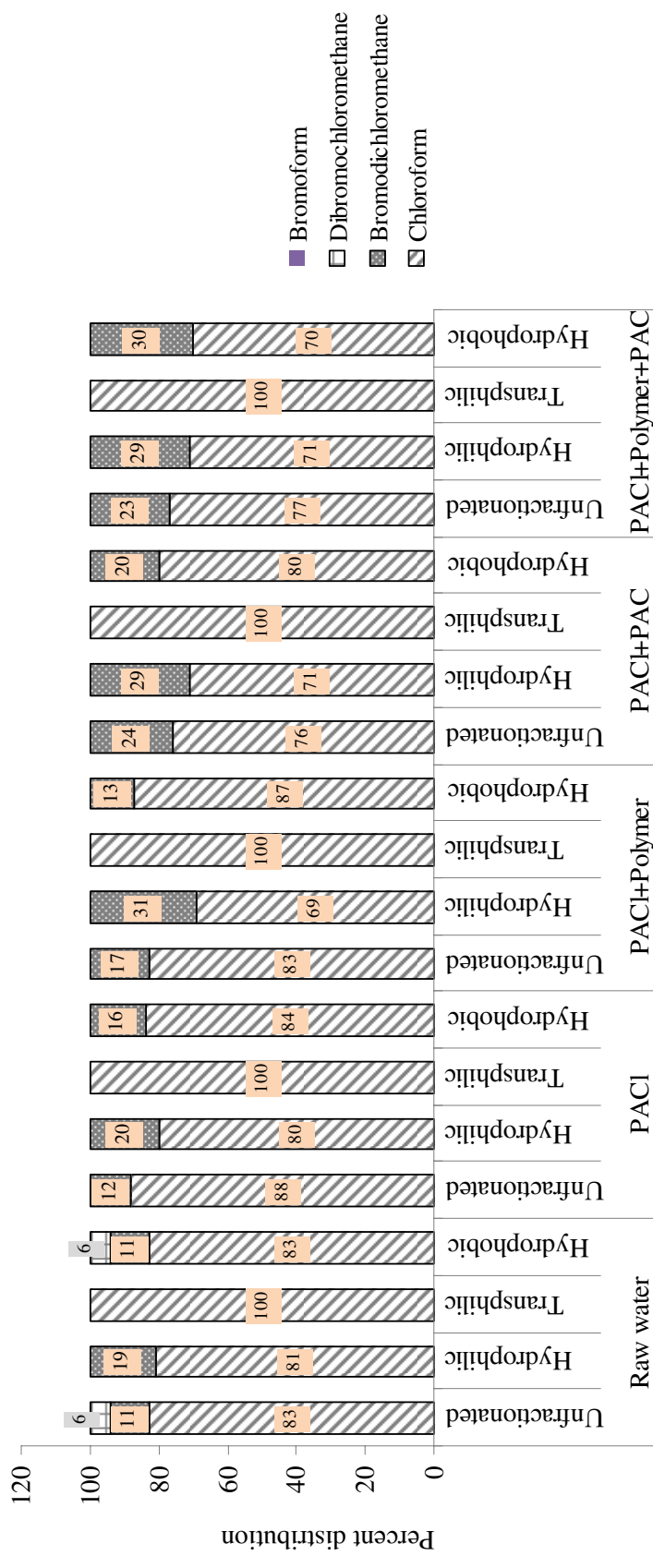


Figure 5.12 Percent distribution of CHCl₃-FP, CHCl₂Br-FP, CHClBr₂-FP and CHBr₃-FP of unfractionated and fractionated water in rainy season.

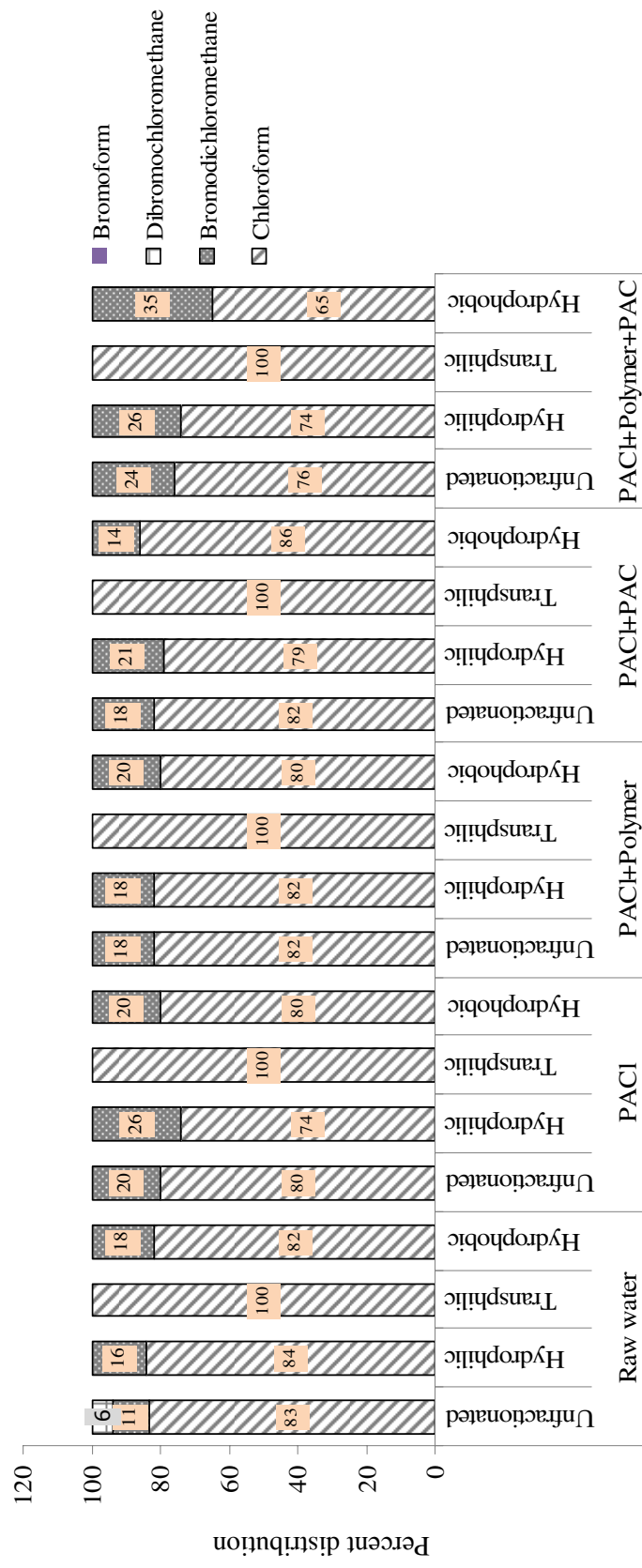


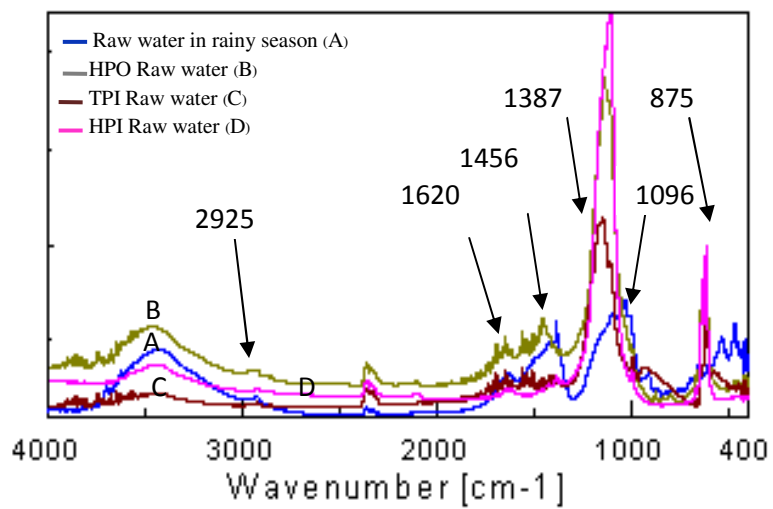
Figure 5.13 Percent distribution of CHCl_3 -FP, CHCl_2Br -FP, CHClBr_2 -FP and CHBr_3 -FP of unfractionated and fractionated water in summer.

5.3.5 FTIR of DOM Fraction

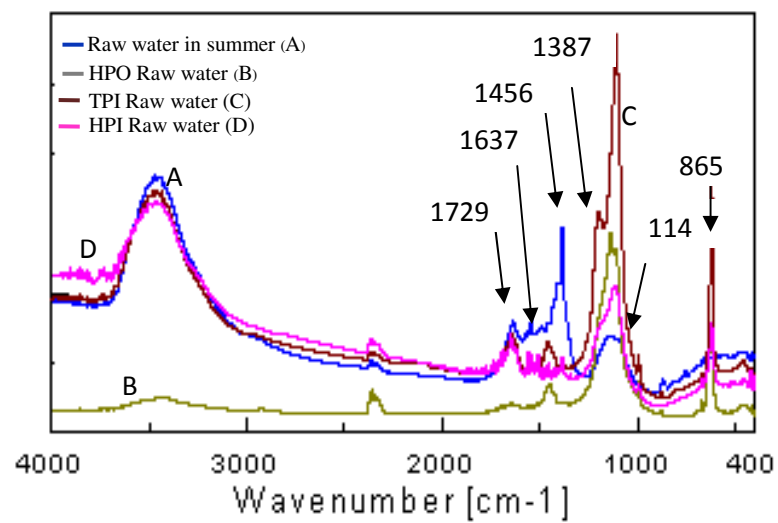
The FTIR spectra of DOM fraction of raw water and coagulated water in rainy season and summer is shown in Figure 5.14 and Table 5.7, whereas that of coagulated water of each enhanced coagulation condition are presented Figure 5.15 to 5.18. By comparing the FTIR results of the studies of Aiken *et al.*, (1985), Sposito, (1989) and Barber *et al.*, (2001), it was found that in case of raw water, the carboxylic C=O was illustrated at band of 1734-1684 cm^{-1} , cyclic and acyclic compounds, ketones, and quinones contents were indicated by C=O peaks between 1635-1589 cm^{-1} . The bands in range of 1516-1506 cm^{-1} were attributed to the aliphatic C-H deformation. The phenolic OH was illustrated by the strong peaks at 1404-1384 cm^{-1} , carboxylic group was also indicated by O-H peaks between 871-825 cm^{-1} were detected in rainy season and summer. The band at around 2925 cm^{-1} was attributed to aliphatic C-H, C-H₂, C-H₃. The peaks at 1096 -1033 cm^{-1} was attributed to C-O of alcoholic compound. The peak at around 667 – 518 cm^{-1} was attributed to COOH, they were detected only in water in rainy seasons. While, CCH₃ of methyl ester and C-O of esters, ethers, and phenol were identified by peak at 1456-1404 cm^{-1} and 1141 cm^{-1} , respectively, for raw water in summer. Considering the removal of DOM, aliphatic C-H, C-H₂, C-H₃, C-O of alcoholic compounds and C-H deformation of CH₃ could be easily removed by enhanced coagulation.

In case of fractionated water, HPO has absorption bands at 1620-1594 cm^{-1} that illustrated aromatic C=C, and the aromatic C-H was that illustrated at band of 875-832 cm^{-1} . This corresponded aromatic associated to typical hydrophobic characteristic of humic substance. The aromatic C=C peak was more prominent in HPO than the other, which exhibited the highest adsorption intensity in the FTIR spectra of HPO. On the contrary, it was the peak at 1456 cm^{-1} that displayed the highest adsorption intensity in the FTIR spectra of TPI. These results suggested that HPO had greater aromatic C=C content while TPI had greater aliphatic C-H content, consistent with our previous observations that HPO was the most abundant in aromatic structures as revealed by UV analysis. HPI fractions showed a peak of 1720, 1540, 1640 cm^{-1} which illustrated COOH and C=O. This associated with carboxylic groups. It showed a peak wavenumber at 1040 cm^{-1} , which corresponded to C-O bonds of alcohols or ether associated to

hydrophilic character materials. HPI fraction shows more complicated absorption bands at low wavenumbers due to halogenated compounds or some other hydrophilic organic compounds. Moreover, all three fractions showed weak peaks for C-O at $1350-1000\text{ cm}^{-1}$ of particular interest. It was the significant peaks of amide-I at $1674-1652\text{ cm}^{-1}$ and amide-II at $1576-1556\text{ cm}^{-1}$ in the TPI fraction (indicating amide such as amino sugar, which corresponded carboxylic groups associated to typical hydrophilic characteristic of tryptophan substance). Although HPO contained amide-I and amide-II peaks appeared minor peak, the small peak around $1429-1404\text{ cm}^{-1}$ due to carboxylic group or alcohols was visible in the HPO fraction but not in the spectra of the others. These relevantly corresponded to the report result by Zhang *et al.*, (2008). three hydrophobic were similar in spectra with four distinctive adsorption bands $1670-1700\text{ cm}^{-1}$ indicating carboxylate salt COO^- at $1600-1650\text{ cm}^{-1}$ suggesting aromatic C=C or aldehydes and ketone groups C=O at $1400-1450\text{ cm}^{-1}$ attributed to aliphatic structures and $900-1200\text{ cm}^{-1}$ largely due to carbohydrates C-C or alkyl group (C-O). The summary of the FTIR spectra of DOM fractions of raw water and coagulated water in rainy season and summer are presented shown in Table 5.8.

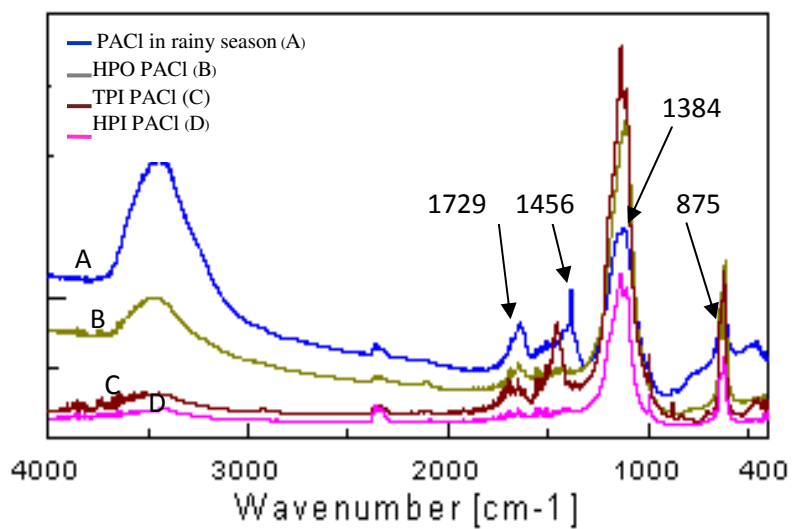


a)

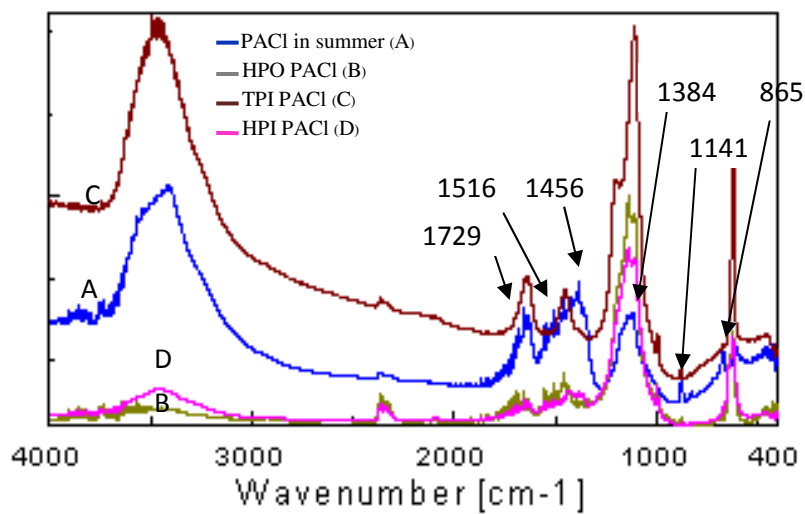


b)

Figure 5.14 FTIR spectra of DOM fraction in raw water in a) rainy season b) summer



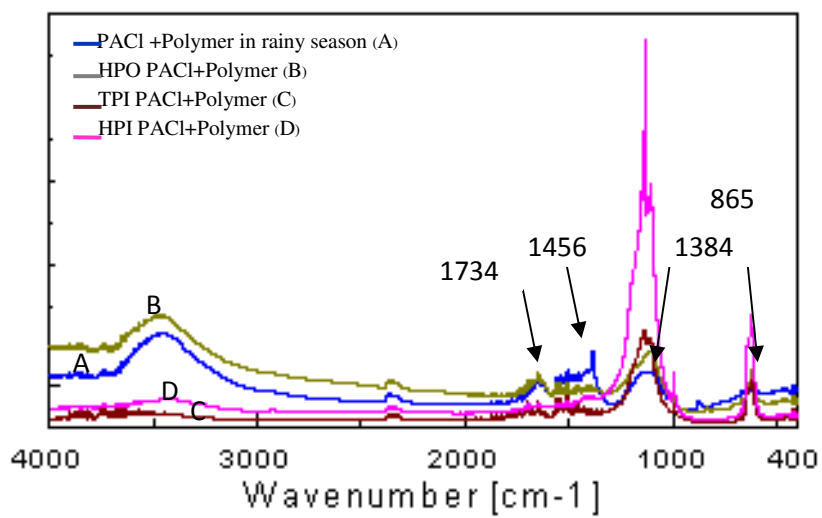
a)



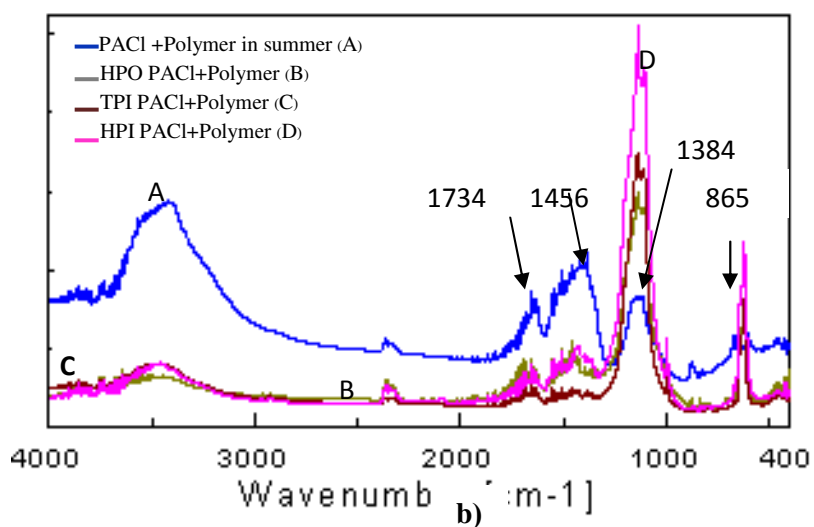
b)

Figure 5.15 FTIR spectra of DOM fraction in coagulated water with PACI in a) rainy season

b) summer

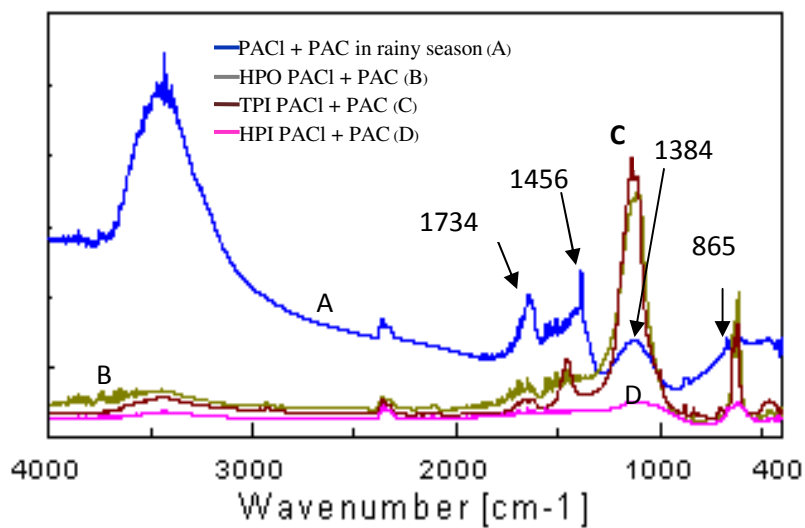


a)

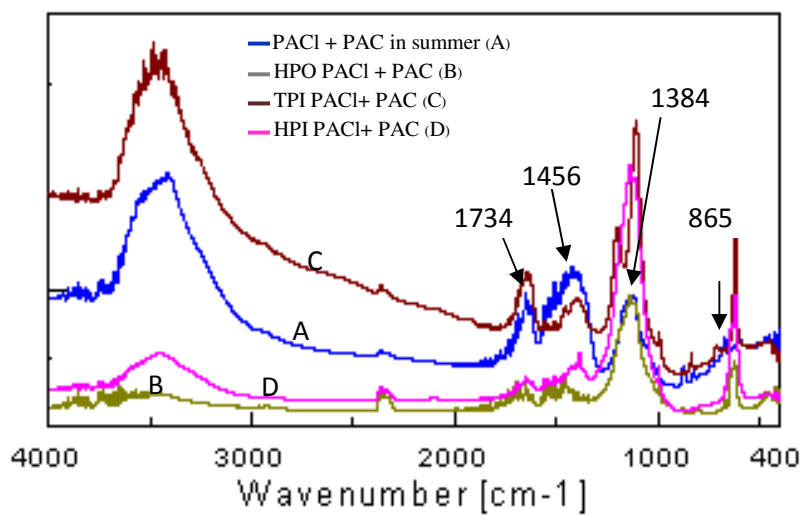


b)

Figure 5.16 FTIR spectra of DOM fraction in coagulated water with PACl combined with Polymer in a) rainy season b) summer



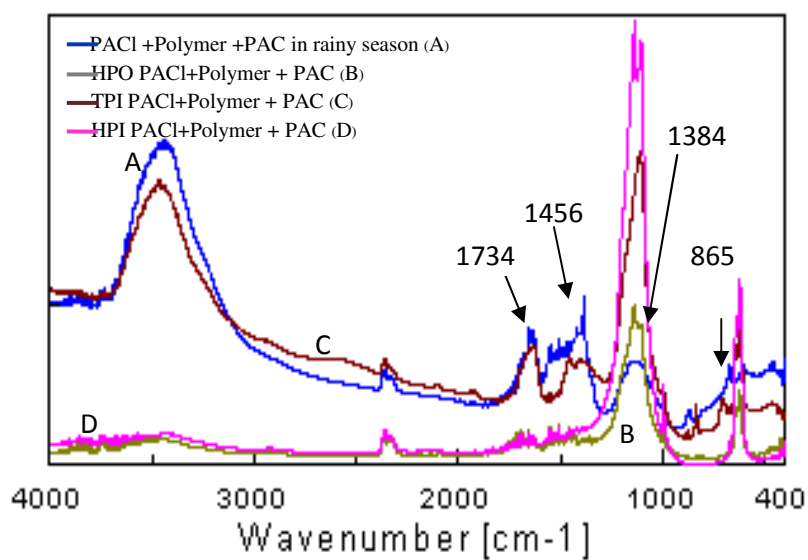
a)



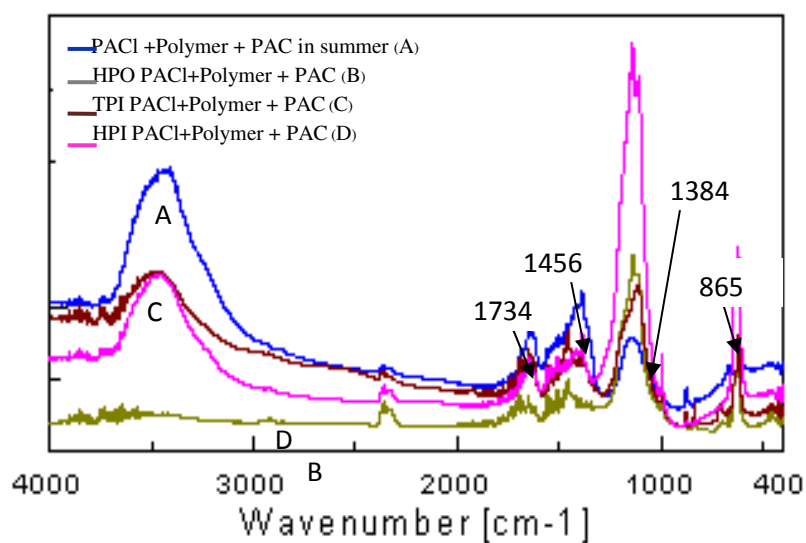
b)

Figure 5.17 FTIR spectra of DOM fraction in coagulated water with PACl combined with PAC

a) rainy season b) summer



a)



b)

Figure 5.18 FTIR spectra of DOM fraction in coagulated water with PACl combined with Polymer and PAC in a) rainy season b) summer

Table 5.7 Comparison FTIR spectra of raw water

Wavenumber (cm ⁻¹)		Assignment
Rainy season	Summer	
2950-2850	-	Aliphatic C-H,CH ₂ ,CH ₃ stretching
1700-1668	1725-1645	C=O stretching of carboxylic , Aldehydes and ketones and ester
1576-1589	1684-1594	C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinones
-	-	Aromatic C=C vibration
1520	1515	C=C stretching vibration of benzene, pyridines
1498-1423	1464-1436	Aliphatic C-H deformation
-	1400-1390	O-H bending vibration of carboxylic groups, C-O stretching of alcohol
1384	1384	C-H deformation of C-H ₃ groups
1195-1126	1280-1141	C-O stretching of ester, ethers, phenol and alcohol
1093	1086	C-O stretching of alcoholic compounds
919-744	880-750	C-H bending vibration of aromatic rings

The reviews of functional group were conducted for using as the reference in this study. Xue *et al.*, (2008) investigate the effect of bromide ions on the formation and speciation of THMs and structural characteristics of DOM fractions during chlorination of secondary effluent taken from the Wenchang Wastewater Treatment Plant (WWTP) (Harbin, China). The result shown that the four post-chlorination samples, which were without bromide addition, contained significant aliphatic C-H, C=O, C-O and C-Cl peaks. Shon *et al.*, (2006) reported that FTIR employed to analyze the functional groups of the different fractions on the fouled membrane surface. The main functional group of HP and TP was ketone groups (quinines) at a wavenumber of 1643cm⁻¹. A major peak found in all the fractions was at a wavenumber of 1651 cm⁻¹, which corresponded to carboxylic group (COOH, C=O, range 1670-1650 cm⁻¹).

Jarusutthirak *et al.*, (2002) studied the functional group of different fraction in biologically treated sewage effluent (BTSE). Their result showed that the functional group at peak 1540 and 1640 cm⁻¹, corresponded to primary and secondary amides. HP and TP fractions showed

a peak of 1720 cm^{-1} which were associated with carboxylic groups (humic and fulvic acids). Zularisam *et al.*, (2007) studied that the FTIR spectra of NOM in source water (Ulu Potian River) and hydrophobic NOM source water (Bekok Dam water) onto the hydrophobic ultrafiltration PSF membrane. The Ulu Pontion River showed significant peak at wavenumber of 1646 cm^{-1} , 1640 cm^{-1} , 1630 cm^{-1} and 1576 cm^{-1} , which are reflecting to the functional groups of primary and secondary amides. It also showed a peak wavenumber at 1040 cm^{-1} , which corresponded to C-O bonds of alcohols or ether, so clearly display to the existence of polysaccharide or *N*-acetyl amino sugar or hydrophilic character materials. For Bekok Dam water exhibited majors peak at wavenumber of 1720 cm^{-1} (C=O stretching band), which corresponded carboxylic groups associated to typical hydrophobic characteristic of humic substance.

Kerry *et al.*, (2002) used attenuated total reflection (ATR) and Fourier transform infrared (FTIR) spectrometry analyze surface waters from the Medina River, Texas and Beaver Lake, Arkansas water sample. The result showed the FTIR spectrum of components in Medina River water that fouled a polypropylene membrane (the polypropylene membrane spectrum has been digitally subtracted. The negative peaks near 2900 cm^{-1} are due to over subtraction of C-H stretching bands. The strongest absorption band is observed at 1034 cm^{-1} . Absorption in this region is due to C-O or Si-O bonds and is commonly associated with alcohols, ethers polysaccharides and silicates.

5.3.6 FEEM of DOM Fraction

Fluorescence EEMs are very useful for distinguishing between different types of organic matter (Her *et al.*, 2003; Baker, 2001; Marhaba, 2000; Coble *et al.*, 1990). EEM signatures of raw water and their hydrophilic, transphilic and hydrophobic fractions from raw water supply in rainy season and summer are presented in Figures 5.19

As can be seen from Figure 5.19, which presents EEM signatures of water samples and their hydrophilic, transphilic and hydrophobic fractions of raw water, it was found that raw water in rainy season exhibited the EEM peaks at $230\text{ nm}_{\text{Ex}}/350\text{ nm}_{\text{Em}}$ (peak A), $280\text{ nm}_{\text{Ex}}/350\text{ nm}_{\text{Em}}$

(peak B) and 265 nm_{Ex}/450 nm_{Em} (peak C) while raw water in summer exhibited peak A and peak B and peak C at the same positions.

In terms of DOM fractions, hydrophilic fractions of raw water from U-Tapao Basin, which were the major DOM fractions, exhibited the peak at the 330 nm_{Ex}/400 nm_{Em}, while FEEM peak at the 290 nm_{Ex}/400 nm_{Em} and 330 nm_{Ex}/400 nm_{Em} were observed from hydrophobic fraction whereas, EEM peak at the 290 nm_{Ex}/350 nm_{Em} was observed from transphilic fraction.

In case of coagulated water of all sample, hydrophobic fractions established broad peaks at 290-295 nm_{Ex}/400-410 nm_{Em} (peak A) with a peak at 330-350 nm_{Ex}/400-410 nm_{Em} (peak B); whereas the hydrophilic fraction exhibited a weak peak at around 330-350 nm_{Ex}/400-410 nm_{Em} (peak C). The transphilic fraction had a rather weak broad peak at 290-295 nm_{Ex}/350-355 nm_{Em} (peak D). The fluorescent peak positions of DOM fraction by enhanced coagulation are presented in Table 5.9.

Table 5.8: Summary of the FTIR spectra of DOM fractions of raw water and coagulated water

Fractionation	Water Samples	Rainy season	Summer
		Functional group	Functional group
HPO	Raw water	Carboxylic , aldehydes, ketones, aromatic C=C, Aliphatic C-H ester, ethers, phenol, alcohol carboxylic groups	Carboxylic , aldehydes and ketones aromatic C=C, carboxylic acids, ester, ethers, phenol, alcohol aromatic rings, carboxylic groups
	PACl 40 mg/L	Carboxylic , aldehydes, ketones aromatic C=C, ester, ethers, phenol and alcohol carboxylic groups	Carboxylic , aldehydes, ketones aromatic C=C, aliphatic C-H C-H ₃ groups, ester, ethers, phenol and alcohol carboxylic groups
	PACl 40 mg/L+ Polymer 1 mg/L	Carboxylic , aldehydes, ketones, aromatic C=C, alcoholic compounds, carboxylic groups	Carboxylic , aldehydes, ketones, aromatic C=C, ketones and quinones, aliphatic C-H ester, ethers, phenol and alcohol carboxylic groups
	PACl 40 mg/L+ PAC 80 mg/L	Carboxylic , aldehydes, ketones aromatic C=C, alcoholic compounds, carboxylic groups	Carboxylic , aldehydes, ketones aromatic C=C, aliphatic C-H, ester, ethers, phenol and alcohol carboxylic groups
	PACl 40 mg/L+Polymer 1 mg/L ++PAC 80 mg/L	Carboxylic , Aldehydes, ketones aromatic C=C, ester, ethers, phenol and alcohol carboxylic groups	Carboxylic , Aldehydes, ketones aromatic C=C , aliphatic C-H, ester, ethers, phenol and alcohol carboxylic groups

Table 5.8: Summary of the FTIR spectra of DOM fractions of raw water and coagulated water

Fractionation	Water Samples	Rainy season	Summer
		Functional group	Functional group
TPI	Raw water	Carboxylic , aldehydes, ketones, amide groups benzene, pyridines, ester, ethers, phenol, carboxylic groups	Carboxylic , aldehydes and ketones, carboxylic acids, ester, ethers, phenol, alcohol, Aliphatic C-H, carboxylic groups
	PACl 40 mg/L	Carboxylic , aldehydes, ketones , ester, ethers, aliphatic C-H, phenol and alcohol carboxylic groups	Carboxylic , aldehydes, ketones, amide groups benzenes, pyridines, aliphatic C-H, C-H ₃ groups, ester, ethers, phenol and alcohol carboxylic groups
	PACl 40 mg/L+ Polymer 1 mg/L	Carboxylic , aldehydes, ketones, , amide groups benzene, pyridines, alcoholic compounds, carboxylic groups	Carboxylic , aldehydes, ketones, , ketones and quinones, amide groups, ester, ethers, phenol and alcohol carboxylic groups
	PACl 40 mg/L+ PAC 80 mg/L	Carboxylic , aldehydes, ketones , amide groups, alcoholic compounds, carboxylic groups	Carboxylic , aldehydes, ketones , amide groups , ester, ethers, phenol and alcohol carboxylic groups
	PACl 40 mg/L+Polymer 1 mg/L +PAC 80 mg/L	Carboxylic , Aldehydes, ketones , amide groups, benzene, pyridines, ester, ethers, phenol and alcohol carboxylic groups	Carboxylic , Aldehydes, ketones , amide groups, benzene, pyridines, ester, ethers, phenol and alcohol carboxylic groups

Table 5.8: Summary of the FTIR spectra of DOM fractions of raw water and coagulated water

Fractionation	Water Samples	Rainy season	Summer
		Functional group	Functional group
HPI	Raw water	Carboxylic , aldehydes, ketones, ester, ethers, phenol, alcohol carboxylic groups	Carboxylic , aldehydes and ketones aromatic C=C, ester, ethers, phenol, alcohol, carboxylic groups
	PACl 40 mg/L	Carboxylic , aldehydes, ketones, ester, ethers, phenol and alcohol carboxylic groups	Carboxylic , aldehydes, ketones amide groups, aliphatic C-H, ester, ethers, phenol and alcohol carboxylic groups
	PACl 40 mg/L+ Polymer 1 mg/L	Carboxylic , aldehydes, ketones, amide groups, benzene, pyridines, alcoholic compounds, carboxylic groups	Carboxylic , aldehydes, ketones, ketones and quinones, amide groups, benzene, pyridines, aliphatic C-H, ester, ethers, phenol and alcohol carboxylic groups
	PACl 40 mg/L+ PAC 80 mg/L	Carboxylic , aldehydes, ketones amide groups, benzene, pyridines, alcoholic compound, carboxylic groups	Carboxylic , aldehydes, ketones amide groups , benzene, pyridines, ester, ethers, phenol and alcohol carboxylic groups
	PACl 40 mg/L+Polymer 1 mg/L++PAC 80 mg/L	Carboxylic , aldehydes, ketones , amide groups, benzene, pyridines, ester, ethers, phenol and alcohol carboxylic groups	Carboxylic , aldehydes, ketones, amide groups, benzene, pyridines, aliphatic C-H, ester, ethers, phenol and alcohol carboxylic groups

Table 5.9: Fluorescent peak positions of DOM fraction by enhanced coagulation

Water sample	Peak A	Peak B	Peak C	Peak D	fluorescent organic matter
PACl 40 mg/L	●	●	●		Tryptophan-like substances Humic and fulvic acids-like substances
HPO	●	●			Humic and fulvic acids-like substances
TPI			●		Tryptophan-like substances
HPI				●	Tryptophan-like substances
PACl 40mg/L+Polymer 1 mg/L	●	●	●		Tryptophan-like substances Humic and fulvic acids-like substances
HPO	●	●			Humic and fulvic acids-like substances
TPI			●		Tryptophan-like substances
HPI				●	Tryptophan-like substances
PACl 40mg/L+PAC 80 mg/L	●	●	●		Tryptophan-like substances Humic and fulvic acids-like substances
HPO	●	●			Humic and fulvic acids-like substances
TPI			●		Tryptophan-like substances
HPI				●	Tryptophan-like substances
PACl 40mg/L+Polymer 1 mg/L+PAC 80 mg/L	●	●	●		Tryptophan-like substances Humic and fulvic acids-like substances
HPO	●	●			Humic and fulvic acids-like substances
TPI			●		Tryptophan-like substances
HPI				●	Tryptophan-like substances

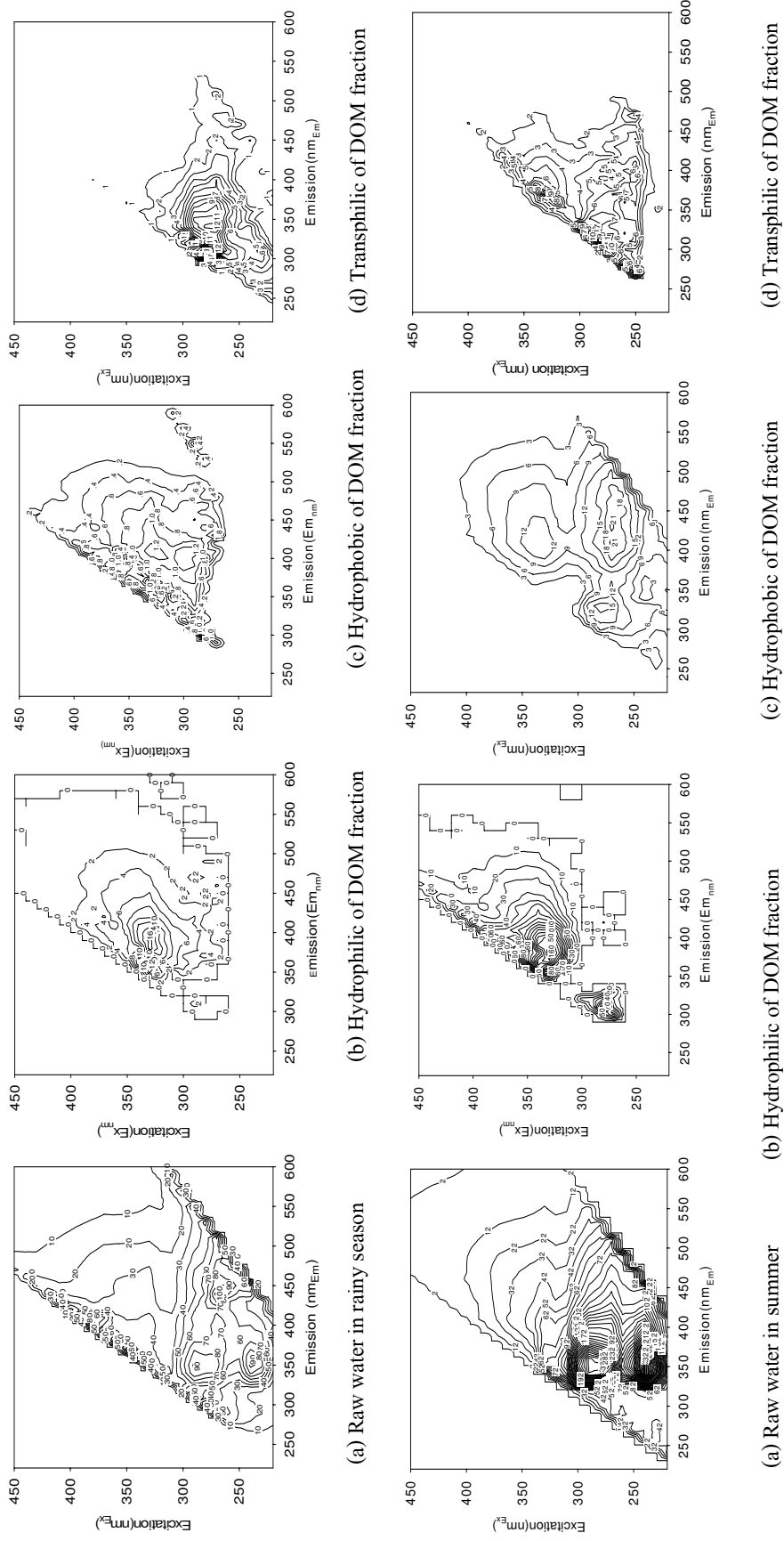


Figure 5.19: EEM signatures of raw water and their fractionated DOM from water treatment plant with contour interval of QSU in rainy season and summer

5.3.7 Specific THMFP and Nature of DOM

The specific THMFP values of the unfractionated waters and of each DOM fraction are defined as follows:

$$\text{Specific THMFP } (\mu\text{g THMFP/ mg DOC}) = \frac{\text{THMFP } (\mu\text{g THMFP/L})}{\text{DOC (mg DOC/L)}}$$

Specific THMFP represents the ability of the DOM in water to react with chlorine to form THMs. Figures 5.20 present the specific THMFP values of the raw water and coagulated water of DOM fraction in rainy season and summer. The specific THMFP sequences and specific THMFP values of the unfractionated water samples and of their three DOM fractions are tabulated in Table 5.10.

As can be seen from Figure 5.20 and Table 5.10, when considerably the specific THMFP of DOM fraction of the raw water, HPI was observed to give the highest specific THMFP at 171 and 118 of rainy season and summer, respectively, and followed by HPO fraction. While the specific THMFP values of TPI were moderately lower than those of the unfractionated raw water. In the case of overall of coagulated water, the value of specific THMFP of the hydrophilic and transphilic fraction were higher than that of coagulated water before fractionation. It can be stated that the hydrophilic fraction in raw water from U-Tapao Canal was slightly more reactive with chlorine to form THMs. It might due to the fact that the coagulation process could not remove the hydrophilic fraction. Therefore, the hydrophilic fractions still reacted with chlorine to form THMs. According to the studies by Xue *et al.*, (2008), the order of specific THMFP was observed to be HPO-A>TPI-A>TPI-N>HPI>HPO-N.

The FTIR of raw water and coagulated water of DOM fraction of rainy season and summer are illustrated in Figure 5.20. The results suggest that common functional groups of DOM in raw water and coagulated water of DOM fraction were carboxylic group, amide, amine, ketone, esters, ethers, phenol, alcohol, and aromatic aliphatic. These common functional groups particularly associated with the structural compositions comprising the common fluorescent

organic compounds in water, i.e. tryptophan-like substances and fulvic and humic-like substances. Based on the FEEM results, it was that tryptophan-like substances and humic and fulvic acids-like substances in the water samples. The functional groups found for each DOM fraction were also related since carboxylic group, amide, amine, ketone, esters, ethers, phenol, alcohol, and aromatic aliphatic, particularly for the DOM fractions, mainly composed of tryptophan-like and humic and fulvic acids-like substances.

According to studies by Samios *et al.*, (2005), fulvic and humic acids spectra indicated bands at about 1720 cm^{-1} , 1650 cm^{-1} , 1500 cm^{-1} , 1210 cm^{-1} , 1160 cm^{-1} , 1100 cm^{-1} . A fairly broad at 1700 cm^{-1} was due to a carbonyl stretch in carboxylic acids and a small band at 1650 cm^{-1} implies the presence of COO stretching of aromatic C=C. The band at 1435 cm^{-1} indicated aliphatic CH_2 and CCH_3 bending. The band at 1200 and 1100 cm^{-1} indicated C-O stretching and OH deformation of COOH and phenolic group, COH bending, CO stretching of alcohols and ether the presence of secondary alcohol, respectively. The band at 1388 and 1377 cm^{-1} indicated COO stretching and CH deformation, CO stretching of phenolic OH.

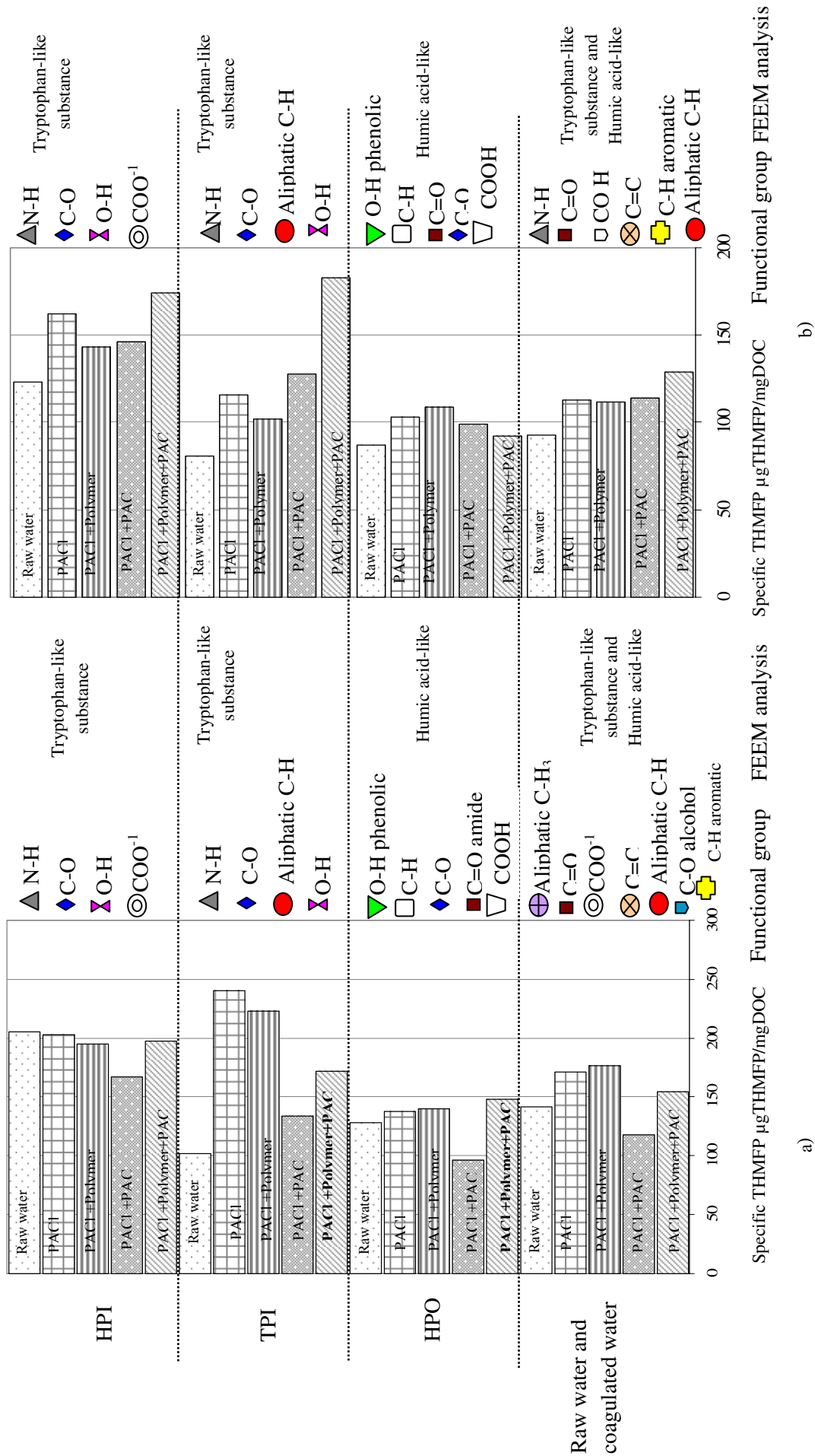


Figure 5.20 Specific THMFP of raw water and coagulated water of DOM fractions in rainy season and summer

Table 5.10 The mass distribution sequences and percent mass distribution of the three DOM fractions and of the hydrophobic, transphilic and hydrophilic DOM fractions of filtered water and coagulated water.

Water samples	Specific THMFP sequence from high to low Unfractionated water sample and three DOM fractions (Specific THMFP value, $\mu\text{g THMFP/mg DOC}$)
Raw water in rainy season	HPI (205) > RAW (142) > HPO (128) > TPI (102)
PACl	TPI (240) > HPI (203) > RAW (171) > HPO (138)
PACl+Polymer	TPI (223) > HPO (195) > RAW(177) > HPI (140)
PACl+PAC	HPI (167) > TPI (134) > RAW (118) > HPO (96)
PACl+Polymer+PAC	HPI (197) > TPI (172) > RAW (154) > HPO (148)
Raw water in summer	HPI (123) > RAW (93) > HPO (87) > TPI (81)
PACl	HPI (162) > TPI (116) > RAW (113) > HPO (103)
PACl+Polymer	HPI (143) > RAW (112) > HPO (109) > TPI (102)
PACl+PAC	HPI (146) > TPI (128) > RAW (114) > HPO (99)
PACl+Polymer+PAC	TPI (183) > HPI (174) > RAW (129) > HPO (92)

5.3.8 Concluding Remark

The hydrophilic, transphilic and hydrophobic fractions in raw water of rainy season were 31, 27, and 42 percent, respectively. Whereas that of summer the values of the hydrophilic, transphilic and hydrophobic fractions in raw water were 33, 23, and 44 percent, respectively. The enhanced coagulation by adding cationic polymer and PAC could be used to remove DOC from raw water by about 82 percent. Moreover, the enhanced coagulation could remove 88, 67, and 77 percent of THMFP by weight of hydrophobic, transphilic and hydrophilic fractions, respectively. The THMFP value of 729 and 508 $\mu\text{g/L}$ were observed in the raw water in rainy season and summer. This value came from the summation of the CHCl_3 -FP of 608 and 420 $\mu\text{g/L}$, CHCl_2Br -FP of 80 and 56 $\mu\text{g/L}$ and CHClBr_2 -FP of 39 and 32 $\mu\text{g/L}$, respectively. CHCl_3 , therefore, was the major THMs species in the raw water and made up about 83 percent of the total THMFP. The percentages of CHCl_2Br and CHClBr_2 were 11 percent and 6 percent, respectively. The enhanced coagulation by adding cationic polymer and PAC could be used to reduce THMFP 81 percent and 79 percent in rainy season and summer, respectively. HPO, TPI and HPI were characterized by aliphatic C-H ($2965\text{-}2927\text{ cm}^{-1}$, 1387 cm^{-1}), aromatic C=C ($1620\text{-}1594\text{ cm}^{-1}$) and aromatic C-H ($875\text{-}832\text{ cm}^{-1}$) peak. The aromatic C=C peak was more prominent in HPO than the other, which

exhibited the highest adsorption intensity in the FTIR spectrum of HPO. Moreover, all three fractions showed weak peaks for C-O ($1350-1000\text{ cm}^{-1}$) of particular interest. It was the significant peaks of amide-I ($1674-1652\text{ cm}^{-1}$) and amide-II ($1576-1556\text{ cm}^{-1}$) in the TPI spectrum (indicating amide such as amino sugar).

CHAPTER VI

RECOMMENDATION FOR FUTURE WORK

The recommendations for future studies are notified in the following statements.

1. The feasibility study moving the pumping station of Hat Yai placed to the new location should be considered. In addition, the operational costs of costs of process in this study must be concerned.
2. The other disinfectants such as ozone, ultraviolet (UV) radiation, potassium permanganate, and chlorine dioxide should be studied as an alternative application in water treatment systems. In addition, the economic cost benefit analysis should be considered.
3. The other chlorinated DBPs in terms of HAAs and HANs should be also considered.
4. Membrane process which is currently served as the advanced water purification techniques should be considered to be used for NOM removal.

REFERENCES

- Aiken, R., McKnight, D.M., Thorn, K.A., Thurman, E.M. (1992). Isolation of hydrophilic organic acids from water using nonionic macroporous resins." Organic Geochemistry 18(4): 567-573.
- Aiken R., Mck night D. M., Wershaw R. L. and McCarthy P. (1985). Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation and Characterization. Wiley, New York, NY
- Amy, L.; and Chadik, P. A. (1983). Cationic polyelectrolytes as primary coagulants for removing trihalomethane precursors. Journal of AWWA 75(10): 527-531.
- APHA, AWWA and WPCF. (1995). Standard methods for the examination of water and wastewater. 19th ed. Washington D. C., U.S.A.
- AWWA. (1990). Water Quality and Treatment. New York: American Water Works Association.
- AWWARF.(1991).Disinfection by products database and model project,American Water Works Association Research Foundation, Denver, Colorado.
- Barber, L.B., Leenheer, J.A., Noyes, T.I., and Stiles, E.A. (2001). Nature and transformation of dissolved organic matter in treatment wetlands. Water Sci Technol. 35: 4805-4816.
- Baker A. (2001). Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers. Water Sci Technol. 35: 948-953.
- Baker, A.,Curry,M.,(2004). Fluorescence of leachates from three contrasting landfills. Water Res.38:2605-2613.
- Benfield, L.D., Judkins, J.F. and Weand, B.L. (1982). Process Chemistry for Water and Wastewater Treatment. Englewood Cliffs, N.J.: Prentice-Hall
- Benoit,P-C.,Clouzot, L., Varrault, T.,Tusseau-v,M-H.,Verger,A.,and Mouchel,J-M.

- (2008). Dissolved organic matter from treated effluent of a major wastewater treatment plant: Characterization and influence on copper toxicity. Chemosphere. 73:593-599.
- Bolto, B.; Abbt-Braun, □; Dixon, D.; et al. (1999). Experimental evaluation of cationic polyelectrolytes for removing natural organic matter from water. Water Sci Technol. 40(9): 71-79.
- Bolto, B., Dixon, D., Eldridge, R., and King, S. (2002). Cationic Polymer and Clay or Metal Oxide Combinations for Natural Organic Matter Removal. Wat. Res. 35(11), 2669-2676.
- Carns, K.E. and Parker, J.D. (1985). Using Polymers with Direct Filtration. J. Am. Water Works Assoc. 77(5): 44-49.
- Carbaniss S.E., Zhou Q., Maurice P.A., Chin Y Aiken □R.(2000). A Log-normal Distribution Model for Molecular Weight of Aquatic Fulvic Acids. Water Sci Technol 34:1103-1109.
- Carlson, M.; and Hardy, D.(1998). Controlling DBPs with monochloramine. Journal of AWWA 90(2): 95-106.
- Chang, E. E., Chiang, P. C., Chao, S. H., and Liang, C. H. (1999). Effects of polydiallyldimethyl ammonium chloride coagulant on formation of chlorinated by products in drinking water. Chemosphere. 39(8), 1333-1346.
- Chang, C.Y., Hsieh, Y.H., Lin, Y.M., Hu, P.Y., Liu, C.C., and Wang, K.H. (2001). The Organic Precursors Affecting the Formation of Disinfection By-Products with Chlorine Dioxide. Chemosphere. 44, 1153-1158.
- Chang, E.E., Chiang, P.C., Tang, W.Y., Chao, S.H., and Hsing, H.J. (2005). Effect of Polyelectrolytes on Reduction of Model Compounds via Coagulation. Chemosphere. 58, 1141-1150.
- Chen, J., □u, B., LeBoeuf, E.J., Pan, H., Dai, S. (2002). Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. Chemosphere 48(1):59-68.

- Chen, W.; Westerhoff, P.; Leenheer, J. A.; et al.(2003). Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. Water Sci Technol. 37 (2003, November 24): 5701-5710.
- Cheng, R. C.; Krasner, S. W.; Green, J. F.; et al.(1995). Enhanced coagulation: a preliminary evaluation. Journal of AWWA 2: 91-103.
- Cheng,W.P.,Chi,F.H.,Yu,R.F.(2004).Evaluating the efficiency of coagulation in the removal of dissolved organic carbon from reservoir water using fluorescence and ultraviolet photometry.Environ.Monit.Assess.98:421-431.
- Chimongkol,P.,(2008). Removal of Dissolved Organic Matters and Bacteriophages in Natural Water by In-line Coagulation Combined with Ceramic Membrane. Master Thesis. Graduated School, Chulalongkorn University. Thailand
- Cho,J.,Amy,□,Yoon,Y.,Shon,J.(2002).Predictive Models and Factors Affecting Natural Organic Matter Rejection and Flux Decline in Ultrafiltration Membranes.Desalination.142:245-255.
- Cho,J., Amy,□and Pellegrino,J.(2000).Membrane filtration of natural organic matter:factors and mechanisms affecting rejection and flux decline with charged ultrafiltration UF membrane. Journal membrane Sci.164:89-110.
- Coble, P. □(1996). Characterization of marine and terrestrial DOM in sea water using excitation emission matrix spectroscopy. Mar Chem 51: 325-346.
- Coble, P. □; Green, S. A.; Blough, N. V.; et al. (1990). Characterization of dissolved organic matter in Black Sea by fluorescence spectroscopy. Nature 48: 432-435.
- Coble, P.□, Schultz, C.A., and Mopper, K. (1993). Fluorescence contouring analysis of DOC intercalibration experiment samples: a comparison of techniques. Marine Chemistry. 41: 173-178.
- Collins, M., Amy □, and Steelink C.(1986). Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: Implications for removal during water treatment. Environmental Science and Technology. 20(10): 1028-1032.

- Croue, J. P.; Martin, B.; Simon, P.; et al.(1993). Les matieres hydrophobes et hydrophiles des eaux de retenue-extraction, caracterisation et quantification. Water Supply 11: 79-90.
- Croue, J. P.; Martin, B.; Simon, P.; et al. (1999). Les matieres hydrophobes et hydrophiles des eaux de retenue-extraction, caracterisation et quantification. Water Supply 11: 79-90.
- Croue, J.P., Benedetti, M.F., Violleau, D., and Leenheer, J.A. (2003).
Characterization and Copper Binding of Humic and Nonhumic Organic Matter Isolation from the South Platte River: Evidence for the Present of Nitrogenous Binding Site. Environ. Sci. Technol. 37, 328-336.
- Davis, W.M., Erickson, C.L., Johnston, C.T., Delfino, J.J., Poster, J.E. (1999). Quantitative Fourier transform infrared spectroscopic investigation of humic substance functional group composition. Chemosphere 38(12):2913-2928.
- Day, McD. □; Beckett, R.; Hart, B. T.; et al.(1991). Characterization of natural organic matter from four Victorian freshwater systems. Australian Journal of Marine and Freshwater Research 42(6): 675-687.
- Edzwald, J. K. (1993). Coagulation in drinking water treatment: particles, organics and coagulants. Water Sci. Technol. 27(11): 21.
- Edzwald, J. K.; Becker, W. C.; and Wattier, K.(1985). Surrogate parameters for monitoring organic matter and THM precursors. Journal of AWWA 77(4): 122.
- Edzwald J.K. and Tobiason F.E.(1999). Enhanced Coagulation. USA Requirements and a Broader View. Water Sci. Technol 40(9):63-70.
- Fabrizio, M., Korshin, □ V. (2004). Probing the mechanisms of NOM chlorination using fluorescence: formation of disinfection by-products in Alento River water. Water Sci. Technol: Water Supply 4(4): 227-233.
- one, D-L., Seidel, J-L., Batiot, C., and Bamory, K.(2009). Using fluorescence spectroscopy EEM to evaluate the efficiency of organic matter removal during coagulation-flocculation of a tropical surface water (Agro reservoir). Journal Hazardous Materials 172:693-699.
- renier, A.D., Obolensky, A., and Singer, P.C. (1992). Technical Note: Comparing Predicted and Observed Concentrations of DBPs. J. Am. Water Works Assoc. 84(11), 99.

- Her, N., Amy, □, Mcknight, D., Shon, J., Yoon Y. (2003). Characterization of DOM as a function of MW by HPLC-SEC using UVA, DOC and fluorescence detection. Water Res. 37:4295-4303.
- Her, N., Amy, □, Chung, J., Yoon, J., Yoon, Y. (2008). Characterizing dissolved organic matter and evaluating associated nanofiltration membrane fouling. Chemosphere. 70:495-502.
- Hassan, K. Z. A., Bower, K., Miller, C. M. (2006). "Iron oxide enhanced chlorine decay and disinfection by-product formation. Journal of Environmental Engineering. 132(12):1609-1616.
- Ho, L., and Newcombe, □, (2005). Effect of NOM turbidity and floc size on the PAC adsorption of MIB during alum coagulation. Water Res. 39: 3668-3674.
- Hua, □, and Reckhow, D. A. (2007). Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size. Water Sci. Technol. 41(9): 3309-3315.
- Hua, □, and Reckhow, D. A. (2008). "DBP formation during chlorination and chloramination: effect of reaction time, pH, dosage, and temperature." American Water Works Association 100 (8): 82-95.
- Huang, W. and Yeh, H. (1999). Reaction of chlorine with NOM adsorbed on powdered activated carbon. Water Res. 33 (1): 65-72.
- Hudson, N., Baker, A., Ward, D., Reynolds, D. M., Bransdon, C., Carliell-Marquet, C., Browning, S., (2008). Can fluorescence spectrometry be used as a surrogate for the biochemical oxygen demand (BOD) (test in water quality assessment? An example from South West England. Sci of the Total Environment 391(1):149-158.
- IPCS. (2000). Environment Health Criteria 216: Disinfectants and Disinfectants-By Product. Available: <http://www.inchem.org/document/ehc/ehc216.htm>.
- Intanujit, K. (2009). Removal of Hydrophilic and Hydrophobic Organic Fraction in Raw Water Supply from U-Tapao Canal. Master Thesis. □raduated School, Prince of Songkla University. Thailand
- Janhom, T., Wattanchira, S., Pavasant, P. (2009). Characterization of brewery wastewater with spectrofluorometry analysis. Journal of Environment. 90:1184-1190.

- Jarusutthirak, C., Amy, J.L., Croue, J.P.(2002). Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes. Desalination.145.247-255.
- Ji, Q., Liu, H., Hu, C., Wang, D. and Li, J.(2008). Removal of disinfection by products precursors by polyaluminum chloride coagulation coupled with chlorination. Separation and Purification Technology 62: 464-469.
- Kanokkantapong, V., Marhaba, T.F., Panyapinyophol, B., and Pavasant, P.(2006). FTIR evaluation of functional groups involved in the formation of haloacetic acids during the chlorination of raw water. Journal of Hazardous Materials. 136 (2): 188-196.
- Kennedy, M.D., Chun, H.K., Yangali, V.A.Q., Heijman, B.J., and Schippers, J.C. (2005). Natural organic matter (NOM) fouling of ultrafiltration membranes: fractionation of NOM in surface water and characterization by LC-OCD. Desalination. 178: 73-83.
- Kerry, J. Howe., Kenneth, P.Ishida., Maark, M. Clark.(2002). Use of ATR/FTIR spectrometry to study fouling of microfiltration membranes by natural waters.Desalination.147:251-255.
- Kim, H-C. and Yu, M-J. (2005). Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control. Water Res. 39: 4779-4789.
- Kim, H., Hong, J. and Lee, S.(2006). Fouling of microfiltration membranes by natural organic matter after coagulation treatment: A comparison of different initial mixing conditions. Journal of Membrane Science 283: 266-272.
- Komatsu, K., Nakajima, F., Furumai, H., and Miki, O. (2005). Characterization of dissolved organic matter (DOM) removed by iron coagulation using spectrofluorometry and pyrolysis GC/MS analysis. Journal of Water Supply: Research and Technology-AQUA. 54 (3): 157-163.
- Kubicki J.D and Aplitz S.E. (1999). Model of Natural Organic Matter and Interactions with Organic Contaminants Part 2. Organic Geochemistry.30 (8):911-927.

- Krasner, S.W., McGuire, M.J., Jacangelo, J., Patania, N.L., Reagan, K.M., and Aieta, E.M. (1989). The Occurrence of Disinfection By-Products in US Drinking Water. *J. Am. Water Works Assoc.* 81(8), 41.
- Kasuga, I., Nakajima, F., and Furumai, H. (2003). Analysis of dissolved organic matter and bacterial community in degradation of algal bloom by EEMs and PCR-DNA. *Journal of Japan Society on Water Environment.* 26 (3): 171- 174.
- Khan M., Mostofa, Takahito Y., Eiichi K., Eiichiro T., Kazuhed H., and Mikio T. (2005). Three-dimensional fluorescence as a tool for investigating the dynamics of dissolved organic matter in the Lake Biwa watershed. *The Japanese Society of Limnology*, 6, 101-115.
- Lananowski, J., and Feuillade, (2009). Combination of biodegradable organic matter quantification and XAD-fractionation as effective working parameter for study of biodegradability in environment and anthropic samples. *Chemosphere.* 74: 605-611.
- Lee, J.F., Liao, P.M., Tseng, D.H., and Wen, P.T. (1998). Behavior of Organic polymers in Drinking Water Purification. *Chemosphere.* 37(6), 1045-1061.
- Lee, S., Park, , Amy, , Hong, S.K., Moon, S.H., Lee, D.H., and Cho, J. (2002). Determination of Membrane Pore Size Distribution Using the Fractional Rejection of Nonionic and Charged Macromolecules. *Journal of Membrane Sci.* 201, 191-201.
- Lee S. and Ahn K.-H. (2004). Monitoring of COD as an organic indicator in wastewater and treated effluent by fluorescence excitation-emission (FEEM) matrix characterization. *Water Science and Technology.* 50 (8): 57-63.
- Lee, N., Amy, , Croué, J-P., and Buisson, H. (2004). Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Research.* 38: 4511-4523.
- Lee, S., Kwon, B., Sun, M., Cho, J. (2005). Characterization of NOM included in NF and UF membrane permeates. *Desalination.* 173:131-142.
- Leenheer, J. A. (1981). Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environ. Sci. & Technol.* 15(5): 578-587.

- Letterman, R.D. and Pero, R.W. (1990). Contaminants in Polyelectrolytes Used in Water Treatment. *J. Am. Water Works Assoc.* 82(11): 87-97.
- Leu, R.J. and Hosh, M.M. (1988). Polyelectrolyte Characteristics and Flocculation. *J. Am. Water Works Assoc.* 80(4): 159-167.
- Liang, L., Singer, P. C. (2003). Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. *Envi Sci and Technol.* 37(13): 2920-2928.
- Lin, C.F., Liu, S.H., Hao, O.J. (2001). Effect of functional group of humic substances on UF performance. *Water Res.* 35 (10): 2395-2402.
- Malcom R.L and MacCarthy P. (1992). Quantitative evaluation of DAX-8 and XAD-4 resins used in tandem for removing organics solutes from water. *Environment International.* 18: 597-607.
- Marhuenda-Egea, F.C., Martinez-Sabater, E., Jorda, J., Moral, R., Bustamante, M.A., Paredes, C. and Perez-Murcia, M.D. (2007). Dissolved organic matter fractions formed during composting of winery and distillery residues: Evaluation of the process by fluorescence excitation-emission matrix. *Chemosphere* 68: 301-309.
- Martin-Mousset B, Croue J.-P, Lefebvre E and Legube B. (1997). Distribution and characterization of dissolved organic matter of surface water. *Wat Res.* 31 (3): 541-553.
- Marhaba, T.F., and Washington, M.B. (1998). Drinking Water Disinfection Byproducts: History and Current Practice. *Adv. Env. Res.* 2 (1), 103-115.
- Marhaba, T. F., Kochar, I.H. (2000). Rapid prediction of disinfection by-product formation potential by fluorescence. *Environmental Eng and Policy* 2: 29-36.
- Marhaba, T. F.; Bengraïne, K.; Pu, Y.; et al. (2003). Spectral fluorescence signatures and least squares regression: model to predict dissolved organic carbon in water. *Journal of Hazardous Materials* B73: 83-97.
- Marhaba, T. F.; and Pipada, N. S. (2000). Coagulation: effectiveness in removing dissolved organic matter fractions. *Environ. Eng. Sci.* 17(2): 107-115.

- Marhaba, T. F.; and Pu, Y. (2000). Rapid delineation of humic and non humic organic matter fraction in water. Journal of Hazardous Materials.73(3): 221-234.
- Marhaba, T. F.; Pu, Y.; and Bengraine, K. (2003). Modified dissolved organic matter fractionation technique for natural water. Water Res. 34(14): 3543-3550.
- Marhaba, T.F. and Pu, Y. (2000). Rapid delineation of humic and non-humic organic matter fractions in water. Journal of Hazardous Materials. A73: 221-234.
- Marhaba, T. F.; and Van, D. (2000). The variation of mass and disinfection by-product formation potential of dissolved organic matter fractions along a conventional surface water treatment plant. Journal of Hazardous Materials 73(3): 133-147.
- Mash, H., Westerhoff, P.K., Baker,L.A., Nieman, R.A., Nguyen, M.L.(2004).
.Dissolved organic matter in Arizona reservoir: assessment of carbonaceous sources.
Organic Geochemistry.35:831-843.
- Metcalf and Eddy. (2003). *Wastewater Engineering Treatment and Reuse*. 4th ed.
New York: Mc Graw-Hill.
- Morris, J. C.; and Baum B. (1978). Precursors and mechanisms of haloform formation in the chlorination of water supplies. Water Chlorination: Environmental Impact and Health Effects, eds. R. L. Jolley et al., Vol.2. Ann Arbor Science Publishers, Ann Arbor, MI.
- Musikavong C., Wattanachira S., Nakajima F. and Furumai H. (2007). Three-dimensional fluorescent spectroscopy analysis for evaluation of organic matter removal from industrial estate wastewater by stabilization ponds. Water Sci. and Technol. 55(11), 201-210.
- Musikavong C., and Wattanachira S. (2010). Pyrolysis ^{13}C /MS, FTIR, and Spectrofluorometry analysis for characterizing dissolved organic matter in raw water from U-Tapao Canal Basin, Songkhla, Thailand, *The proceeding of 8th Asian-Pacific Regional Conference on Practical Environmental Technologies*, Ubonratchathani, Thailand, March 24-27.

- Nagare, H., Aso, T., Ebie, Y. and Ebie, K. (2008). Removal of humic substances by repeated mixing with PACl. Conference proceedings international water association (IWA) specialist conference on: natural organic matter: from source to tap. 2-4 September 2008. Bath, UK.
- Nakajima, F.; Hanabusa, M.; and Furumai, H.(2002). Excitation-emission fluorescence spectra and trihalomethane formation potential in the Tama river, Japan. Water Sci. and Technol.: Water Supply 2(5-6): 481-486.
- National Environment Board Thailand, Environmental Quality Standard Division, Laboratory and Research Section. (1984). Seminar on Trihalomethane in Drinking Water in Bangkok Metropolitan Area. Bangkok.
- Oliver, B. □; and Shindler, D. B. (1980). Trihalomethanes from the Chlorination of Aquatic algae. Environ. Sci. & Technol. 14(12): 1502.
- Owen, D. M.; Amy, □ L.; Chowdhury, Z. K.; et al.(1995). NOM characterization and treatability. Journal of AWWA 87(1): 46-63.
- Park, N., Kim, J.H., and Cho, J. (2008). Organic matter, anion, and metal wastewater treatment in Damyang surface-flow constructed wetlands in Korea. Ecological Engineering.32:68-71.
- Peuravuori J., Monteiro A., Eglite L., and Pihlaja K.(2005). Comparative study for separation humic-type organic constituents by DAX-8, PVP and DEAE sorbing solids and tangential ultrafiltration: elemental composition size-exclusion chromatography, UV-vis and FTIR. Talanta. 65:408-422.
- Phumpaisanchai A. (2005). Removal of Hydrophobic and Hydrophilic Natural Organic Matters in Reservoirs by Alum Coagulation Master Thesis. □raduated School, Chiang Mai University. Thailand.
- Quanrud D.M., Lansey K.E., Ela W., Arnold R. □, (2003b). Fate of organics during soil aquifer treatment: biodegradability, chlorine reactivity, and genotoxicity. Journal of Water Health 01(1) 33-44.

- Rizzo, L., Belgiorno, V., Callo, M., and Meric, S. (2005). Removal of THM precursors from a high-alkaline surface water by enhanced coagulation and behavior of THMFP toxicity on *D. magna*. Desalination. 176:177-188.
- Ropru, R., and Martin, R.J. (2008). Natural organic matter (NOM) roof runoff and its impact on Fe^0 treatment system of dissolved metals. Chemosphere. 71:18-29.
- Rook, J. J. (1977). Formation of haloforms during chlorination of natural water. Water Treatment and Examinations 23: 234-243.
- Reynolds, T.D. and Richards, P.A (1996). Unit Operations and Processes in Environmental Engineering. 2nd. ed. Boston: PWS Publishing Company. 166 –218.
- Reckhow, D. A.; and Singer, P. C. 1990. Chlorination by-products in drinking water: from formation potentials to finish water concentration. Journal of AWWA 82: 173-180.
- Richardson, S.D., Thurton, A.D. Jr., and Collette, T.W. (1994). Multispectral Identification of Chlorine Dioxide Disinfection Byproducts in Drinking Water. Environ. Sci. Technol. 28(4), 592-599.
- Roccaro, P., Vagliasindi, F., A., Korshin, V. (2009). Changes in NOM fluorescence caused by chlorination and their associations with disinfection by-products formation. Environ Sci and Technol. 43(3): 724-729.
- Shon, H.K., Vigneswaran, S., Kim, In S., Cho, J., Ngo, H.H. (2006). Fouling of ultrafiltration membrane by effluent organic matter: A detailed characterization using different organic fractions in wastewater. Journal of Membrane Science. 278 :232-238.
- Shirra, R., Ilan, K., Carlos, D. (2008). Dissolved organic matter by granular-activated carbon adsorption as a pretreatment to reverse osmosis of membrane bioreactor effluents. Water Res. 42:1595-1605.
- Sierra, M.M.D., Govanela, M., Parlanti, E. and Soriano-Sierra E.J. (2005). Fluorescent fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and excitation/emission matrix techniques.

- Singer, P.C. (1999). Formation and Control of Disinfection By-product in Drinking Water, AWWA, Denver, USA.
- Stedmon, C. A., Markager, S., Bro, R. (2003). Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Marine Chemistry. 82(3-4): 239-254.
- Stevens, F. J.; Slocum, . (1982). Humic Chemistry. John Wiley & Sons, New York.
- Sposito (1989). The Chemistry of Soils. Oxford., New York.
- Swietlik J, and Sikorka E. (2004). Application of fluorescence spectroscopy in the studies of natural organic matter fractions reactivity with chlorine dioxide and ozone. Water Res. 38:3791-3799.
- Siddiqui, M. S.; and Amy, L. (1993). Factors Affecting DBP Formation During Ozone--Bromide Reactions. Journal of AWWA 85(1): 63.
- Samios, S., Lekkas, T.D., Nikolaou, A.D., lfinopoulos, S.K. Structural investigations of aquatic humic substances from different watersheds. Proceedings of the 9th International Conference on Environmental Science and Technology Rhodes island, reece, 1-3 September 2005
- Tan, Y., Kilduff, J.E., Kitis, M. and Karanfil, T. (2005). Dissolved organic matter removal and disinfection byproduct formation control using ion exchange. Desalination 176: 189-200.
- Teksoy, A., Alkan, U., Baskaya, H.S. (2008). Influence of the treatment process combinations on the formation of THM species in water. Separation and purification and technol 61:447-454.
- Thai meteorological department, the South East, (2008). U-Tapao Basin situation. [Online]. Available online from: <http://www.songkhla.tmd.go.th> [2011, March 2]
- Theiss J.C., et al. (1977). Test for Carcinogenicity of Organic Contaminants of United States Drinking Waters by Pulmonary Tumor Response in Strain A Mice, Cancer Res., 37:2717
- Thurman, E. M. (1985). Organic eochemistry of Natural Waters. Marinus Nijhiff/Dr. W. Junk, Dordrecht. The Netherlands.

- Thurman, E. M.; and Malcolm, R. L. (1981). Preparative isolation of aquatic humic substances. Environ. Sci. and Technol. 15(4): 463-466.
- Trussell, R. R.; and Umphres, M. D.(1978). The formation of trihalomethanes. Journal of AWWA 70(11): 604-612.
- Velasco, U., Uriarte, A., Velasco, J.(2007). Enhanced coagulation under changing alkalinity-hardness conditions and its implications on trihalomethane precursors removal and relationship with UV absorbance. Separation and Purification Technol 55:368–380.
- Verma, S., Prasad, B., Mishra, I-M., (2010). Pretreatment of petrochemical wastewater by coagulation and flocculation and the sludge characteristics. Journal of Hazardous Materials.178: 1055-1064.
- Vorchheimer, N. (1981). Synthetic Polyelectrolytes. In Schwoyer, W.L.K. (Ed.) Polyelectrolytes for Water and Wastewater Treatment (pp. 1-45). Boca Raton, Florida: CRC Press.
- Uriarte, Jon I. Ivarez., Unai Iriarte-Velascob, Noem Chimeno-Ala^onsa, Juan R. onzlez-Velasco (2010). The effect of mixed oxidants and powdered activated carbon on the removal of natural organic matter. Journal of Hazardous Materials.181:426-431.
- U. S. EPA. (1999). Enhanced coagulation and enhanced precipitative softening guidance manual: Office of water (4607)[Online]. Available online from: <http://www.epa.gov> [2010, October 10]
- U. S. EPA. (2003). National Primary Drinking Water Standard)[Online]. Available online from: <http://www.epa.gov> [2010, October 10]
- Uyak, V., Yavuz, S., Toroz, I., Ozaydin, S., and onceli, E.A., (2007). Disinfection by-product precursors removal by enhanced coagulation and PAC adsorption. Desalination 216:334-344.
- Wang, Z., Wu, Z., and Tang, S. (2009). Characterization of dissolved organic matter in a submerged membrane bioreactor by using three-dimensional excitation and emission matrix fluorescence spectroscopy. Water Res. 43: 1533-1540.

- World Health Organization, Guidelines for Drinking Water Quality, (1984).
Recommendations Vol.1, WHO, Geneva
- World Health Organization.(2004). WHO Guidelines for Drinking-Water Quality.
WHO, Geneva, Third Edition of the Switzerland
http://www.who.int/water_sanitation_health/dwq/guidelines3rd/en/
- Westerhoff, P., Chen, W., Esparza, M. (2001).Fluorescence analysis of a standard fulvic acid and tertiary treated wastewater. Journal of Environmental Quality 30(6): 2037- 2046.
- Xue S., Zhou Q,Wei L and Jia T.(2008).Trihalomethane formation potential of organic fractions in secondary effluent. Journal of Environmental Science.20:520-527.
- Yang, X., Shang, C., Lee, W., Westerhoff, P., Fan, C. (2008). Correlations between organic matter properties and DBP formation during chloramination. Water Res. 42(8-9): 2329-2339.
- Yan, M., Wang, D., Ni, J., Qu, J., Chow, C. and Liu, H. 2008 Mechanism of natural organic matter removal by polyaluminum chloride: Effect of coagulant particle size and hydrolysis kinetics. Water Research 42: 3361-3370.
- Zepp, R., Sheldon, W.M., and Moran, M.A. (2004). Dissolved organic fluorophores in southeastern US coastal waters: correction methods for eliminating Rayleigh and Raman scattering peaks in excitation-emission matrices. Marine Chemistry. 89: 15-36.
- Zhang,H.,Qu,,J.,Lin,H.,Zhao.(2008).Characterization of isolated fractions of dissolved organic matter from sewage treatment plant and the related disinfection by products formation potential.Journal of Hazardous Materials.
- Zhao, Z., Qu, J., Li, H., Li, X. and Leung, K. (2009). Disinfection characteristics of the dissolved organic fractions at several stages of a conventional drinking water treatment plant in Southern China. Journal of Hazardous Materials 172: 1093-1099.
- Zularisam A.W., Ismail A.Fand Salim R.(2006).Behaviors of natural organic matter in membrane filtration for Surface water treatment Desalination.194:211-231.

Zularisam A.W., Ismail, A.F., Salim,M.R., Sakinah,Mimi.,Hiroaki,O.(2006).Fabrication,fouling and foulant analyses of asymmetric polysulfone (PSF) ultrafiltration membrane fouled with natural organic matter (NOM) source waters.Journal of membrane Science.299:97-113.

Zularisam A.W., Ismail, A.F., Salim,M.R., Sakinah,Mimi.,Hiroaki,O.(2007).The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes.Desalination .212:191-208.

APPENDICES

APPENDIX A
CALIBRATION DATA AND CURVES

Table A-1: Calibration data of free chlorine residual

Concentration (mg/L)	Absorbance (cm ⁻¹)
0	0
0.1	0.0216
0.5	0.1122
1.0	0.1923
2.0	0.4270
3.0	0.5160
4.0	0.7410
5.0	0.8857

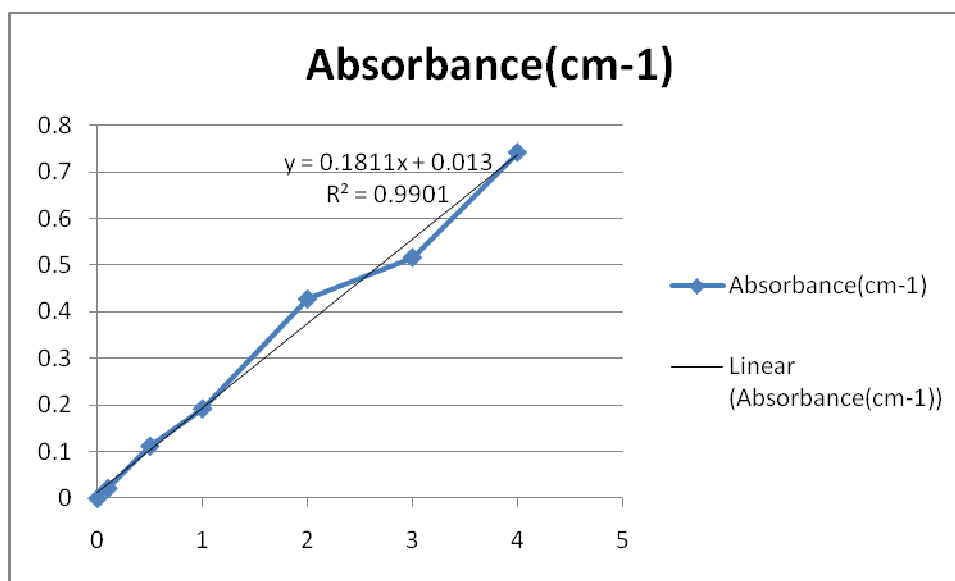
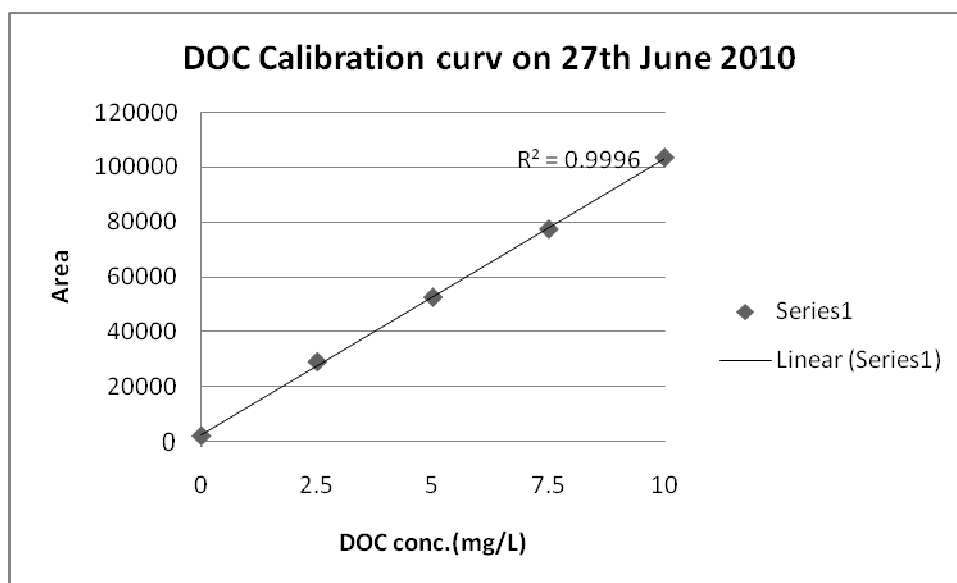


Table A-2: Calibration curve of DOC

concentration(mg/L)	Area (Counts)
0	2028
2.5	29006
5.0	52488
7.5	77264
10.0	103313



APPENDIX B
EXPERIMENTAL DATA

Table B-1: Residual turbidity and percentage of turbidity removal at different PACl dosages and pH at 7 in rainy season and summer.

PACl Dosage (mg/L)	pH at 7 in rainy season			pH at 7 in summer		
	Residual Turbidity (NTU)	Percentage of Turbidity Removal	Residual Alkalinity (mg/L as CaCO ₃)	Residual Turbidity (NTU)	Percentage of Turbidity Removal	Residual Alkalinity (mg/L as CaCO ₃)
Blank#	24	0	0	23	0	0
5	6.87	71	23	6.96	67	24
10	5.82	75	22	6.12	74	23
20	4.12	83	21	4.84	80	22
30	3.05	87	21	3.32	86	22
40	2.01	92	22	2.33	90	20

Table B-2: Residual turbidity and percentage of turbidity removal at different PACl+Polymer dosages and pH at 7 in rainy and summer

PACl+Polymer Dosage (mg/L)	pH at 7 in rainy season			pH at 7 in summer		
	Residual Turbidity (NTU)	Percentage of Turbidity Removal	Residual Alkalinity (mg/L as CaCO ₃)	Residual Turbidity (NTU)	Percentage of Turbidity Removal	Residual Alkalinity (mg/L as CaCO ₃)
Blank#	24	0	0	23	0	0
5	6.73	72	22	6.83	70	24
10	4.98	79	22	5.97	74	21
20	3.83	84	21	4.80	80	20
30	2.14	91	20	3.12	86	18
40	0.79	97	19	2.21	90	18

Table B-3: Residual turbidity and percentage of turbidity removal at different PACI+PAC dosages and pH at 7 in rainy season and summer

PACI+PAC Dosage (mg/L)	pH at 7 in rainy season			pH at 7 in summer		
	Residual Turbidity (NTU)	Percentage of Turbidity Removal	Residual Alkalinity (mg/L as CaCO ₃)	Residual Turbidity (NTU)	Percentage of Turbidity Removal	Residual Alkalinity (mg/L as CaCO ₃)
Blank#	24	0	NT	23	0	0
5	0.68	97	23	0.67	97	23
10	0.63	97	20	0.62	97	22
20	0.55	98	20	0.48	98	20
30	0.52	98	18	0.43	98	19
40	0.50	98	18	0.40	99	17

Table B-4: Residual turbidity and percentage of turbidity removal at different PACI+polymer+PAC dosages and pH at 7 in rainy season and summer.

PACI+polymer+PAC Dosage (mg/L)	pH at 7 in rainy season			pH at 7 in summer		
	Residual Turbidity (NTU)	Percentage of Turbidity Removal	Residual Alkalinity (mg/L as CaCO ₃)	Residual Turbidity (NTU)	Percentage of Turbidity Removal	Residual Alkalinity (mg/L as CaCO ₃)
Blank#	24	0	NT	23	0	0
5	0.78	96	21	0.61	97	22
10	0.74	97	20	0.68	97	18
20	0.72	97	18	0.55	98	17
30	0.66	97	15	0.39	98	15
40	0.49	98	15	0.36	98	14

Table B-5: UV-254 and percentage of UV- 254 reduction at different PACl dosages and pH at 7 in rainy season and summer

PACl Dosage (mg/L)	Rainy season				Summer			
	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction
Blank#	0.414	0	5.1	0	0.155	0	5.5	0
5	0.209	49	2.815	45	0.084	46	2.934	47
10	0.207	50	2.614	49	0.079	49	2.744	50
20	0.202	51	2.409	53	0.077	50	2.423	56
30	0.202	51	2.458	52	0.076	51	2.606	53
40	0.200	52	2.205	57	0.075	52	2.231	59

Table B-6: UV-254 and percentage of UV- 254 reduction at different PACl+polymer dosages and pH at 7 in rainy season and summer

PACl+Polymer Dosage (mg/L)	Rainy season				Summer			
	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction
Blank#	0.414	0	5.1	0	0.155	NT	5.5	0
5	0.210	49	2.734	45	0.114	26	3.2	41
10	0.117	51	2.544	50	0.093	40	2.7	51
20	0.114	52	2.043	60	0.071	54	2.3	58
30	0.114	52	2.197	57	0.069	55	2.1	62
40	0.113	53	1.887	63	0.059	62	1.9	65

Table B-7: UV-254 and percentage of UV- 254 reduction at different PACI +PAC dosages and pH at 7in rainy season and summer

PACI+PAC Dosage (mg/L)	Rainy season					Summer						
	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction
Blank#	0.414	0	5.1	0	0.155	0	5.5	0	0.155	0	5.5	0
5	0.206	50	4.92	4	0.068	56	5.23	56	0.068	56	5.23	5
10	0.193	53	4.66	9	0.068	56	4.71	56	0.068	56	4.71	14
20	0.181	56	4.23	17	0.067	57	2.71	57	0.067	57	2.71	51
30	0.178	57	2.21	57	0.065	58	2.21	58	0.065	58	2.21	60
40	0.159	62	2.04	60	0.053	66	1.74	66	0.053	66	1.74	68

Table B-8: UV-254 and percentage of UV- 254 reduction at different PACI +Polymer+PAC dosages and pH at 7in rainy season and summer

PACI+Polymer+PAC Dosage (mg/L)	Rainy season					Summer						
	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction	UV-254 (cm ⁻¹)	Percentage of UV-254 reduction	DOC mg/L	Percentage of DOC reduction
Blank#	0.414	0	5.1	0	0.155	0	5.5	0	0.155	0	5.5	0
5	0.184	56	2.193	57	0.083	46	2.393	46	0.083	46	2.393	56
10	0.172	58	2.146	58	0.075	52	2.346	52	0.075	52	2.346	57
20	0.158	62	2.274	55	0.068	56	2.574	56	0.068	56	2.574	53
30	0.154	63	1.992	61	0.061	61	2.192	61	0.061	61	2.192	60
40	0.128	69	0.842	83	0.046	70	0.834	70	0.046	70	0.834	85

Table B-9: Mass balance of DOM in raw water and coagulated water

Water sample	Fractionation					
	HPI ¹	TPI ²	HPO ³	HPI+TPI+HPO	Total ⁴	%Diff
Raw water in rainy	1.5	1.3	2.0	4.8	5.1	5.8
PACl	0.7	0.4	1.0	2.1	2.2	4.5
PACl +Polymer	0.6	0.4	0.8	1.8	1.9	5.2
PACl +PAC	0.55	0.5	0.85	1.9	2.0	5.0
PACl+Polymer+PAC	0.30	0.25	0.25	0.8	0.9	11
Raw water in summer	1.7	1.2	2.3	5.2	5.5	5.5
PACl	0.6	0.5	0.9	2.0	2.2	9.0
PACl +Polymer	0.6	0.5	0.7	1.8	1.9	5.3
PACl +PAC	0.5	0.4	0.7	1.6	1.7	5.8
PACl+Polymer+PAC	0.27	0.18	0.25	0.7	0.8	12.5

Remark: HPI¹ = Hydrophilic fraction

TPI² = Transphilic fraction

HPO³ =Hydrophobic fraction

Total⁴ = DOC before fraction %Diff = (Total - (HPI+TPI+HPO))*100/Total

Table B-10: Percent distribution of each organic fraction in raw water and coagulated water

Water sample	DOC (mg/L)	Percent distribution		
		HPI	TPI	HPO
Raw water in rainy	5.1	31	27	42
PACl	2.2	33	19	47
PACl + Polymer	2.2	30	25	45
PACl + PAC	1.9	33	22	44
PACl + Polymer + PAC	1.9	33	28	39
Raw water in summer	5.5	33	23	42
PACl	2.0	30	26	44
PACl + Polymer	1.7	32	25	43
PACl + PAC	0.9	38	31	31
PACl + Polymer + PAC	0.8	39	26	36

Table B-11: Percentage distribution of THMFP of each organic fraction in filtered water and coagulated water

Water sample	THMFP distribution of DOM	THMFP ($\mu\text{g/L}$)			
		HPI	TPI	HPO	HPI+TPI+HPO
Raw water in rainy	HPI (44%) TPI > (20%) HPO > (36%)	308	132	256	729
(1) PACl pH7	HPI (36%) TPI > (26%) HPO > (38%)	142	96	138	359
(2) PACl 40 mg/l +Polymer	HPI (35%) TPI > (27%) HPO > (38%)	117	89	112	318
(3) PACl 40 mg/l+PAC	HPI (38%) TPI > (27%) HPO > (35%)	92	67	82	241
(4) PACl 40 mg/l+polymer+PAC	HPI (44%) TPI > (30%) HPO > (26%)	59	43	37	139
Raw water in summer	HPI (41%) TPI > (21%) HPO > (38%)	210	97	201	508
(1) PACl pH7	HPI (40%) TPI > (23%) HPO > (37%)	97	58	93	248
(2) PACl 40 mg/l +Polymer	HPI (40%) TPI > (24%) HPO > (35%)	86	51	76	213
(3) PACl 40 mg/l+PAC	HPI (39%) TPI > (26%) HPO > (35%)	73	51	69	193
(4) PACl 40 mg/l+polymer+PAC	HPI (45%) TPI > (32%) HPO > (22%)	47	33	23	103

Table B-12: THMFP of Raw water, Coagulated water and their fractionated water in rainy season

Sample			THMFP ($\mu\text{g/L}$)				TTHMFP
			Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform	
Raw water supply	Raw water	Unfractionated	608	80	39	N.D.	729
		Hydrophobic	198	45	N.D.	N.D.	256
		Transphilic	132	N.D.	N.D.	N.D.	132
		Hydrophilic	254	35	19	N.D.	308
	PACl	Unfractionated	345	47	N.D.	N.D.	359
		Hydrophobic	116	22	N.D.	N.D.	138
		Transphilic	96	N.D.	N.D.	N.D.	96
		Hydrophilic	113	29	N.D.	N.D.	142
	PACl+Polymer	Unfractionated	263	55	N.D.	N.D.	318
		Hydrophobic	102	15	N.D.	N.D.	117
		Transphilic	89	N.D.	N.D.	N.D.	89
		Hydrophilic	76	36	N.D.	N.D.	112
	PACl+PAC	Unfractionated	182	59	N.D.	N.D.	241
		Hydrophobic	66	16	N.D.	N.D.	82
		Transphilic	67	N.D.	N.D.	N.D.	67
		Hydrophilic	65	27	N.D.	N.D.	92
PACl+Polymer+PAC	Unfractionated	107	32	N.D.	N.D.	139	
	Hydrophobic	26	11	N.D.	N.D.	37	
	Transphilic	43	N.D.	N.D.	N.D.	43	
	Hydrophilic	42	17	N.D.	N.D.	59	

Table B-13: THMFP of Raw water, Coagulated water and their fractionated water in summer

Sample		THMFP ($\mu\text{g/L}$)				TTHMFP	
		Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform		
Raw water supply	Raw water	Unfractionated	420	56	32	N.D.	508
		Hydrophobic	173	37	N.D.	N.D.	201
		Transphilic	97	N.D.	N.D.	N.D.	97
		Hydrophilic	168	33	N.D.	N.D.	210
	PACl	Unfractionated	198	50	N.D.	N.D.	248
		Hydrophobic	74	19	N.D.	N.D.	93
		Transphilic	58	N.D.	N.D.	N.D.	58
		Hydrophilic	72	25	N.D.	N.D.	97
	PACl+Polymer	Unfractionated	175	38	N.D.	N.D.	213
		Hydrophobic	56	20	N.D.	N.D.	76
		Transphilic	51	N.D.	N.D.	N.D.	51
		Hydrophilic	69	17	N.D.	N.D.	86
	PACl+PAC	Unfractionated	159	34	N.D.	N.D.	193
		Hydrophobic	59	10	N.D.	N.D.	69
		Transphilic	51	N.D.	N.D.	N.D.	51
		Hydrophilic	58	15	N.D.	N.D.	73
PACl+Polymer+PAC	Unfractionated	82	21	N.D.	N.D.	108	
	Hydrophobic	18	10	N.D.	N.D.	28	
	Transphilic	33	N.D.	N.D.	N.D.	33	
	Hydrophilic	35	12	N.D.	N.D.	47	

Table B-14: Characteristics of DOM fraction in raw water in rainy season

Parameter	Rainy season			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	2.0	1.3	1.5	4.8	5.1	5.8
UV-254 (cm ⁻¹)	0.078	0.042	0.068	-	0.414	-
SUVA (L/mg-m)	3.9	3.2	4.5	-	8.1	-
THMFP (µg/L)	256	132	308	696	729	4.5
%THMFP	36	20	44	100	-	-

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Table B-15: Characteristics of DOM fraction in raw water in summer

Parameter	Summer			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	2.3	1.2	1.7	5.2	5.5	5.5
UV-254 (cm ⁻¹)	0.052	0.028	0.031	-	0.155	-
SUVA (L/mg-m)	2.26	2.33	1.82	-	2.82	-
THMFP (µg/L)	183	97	210	508	510	2.0
%THMFP	38	20	41	100		-

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Table B-16 Characteristics of DOM fraction in coagulated water with PACl 40 mg/L in rainy season

Parameter	Rainy season			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	1.0	0.4	0.7	2.1	2.2	4.5
UV-254 (cm ⁻¹)	0.092	0.047	0.062	-	0.200	-
SUVA (L/mg-m)	9.2	11.7	8.9	-	9.52	-
THMFP (µg/L)	138	96	142	376	363	3.5
%THMFP	36	26	37	100	-	-

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Table B-17 Characteristics of DOM fraction in coagulated water with PACl 40 mg/L in summer

Parameter	Summer			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	0.9	0.5	0.6	2.0	2.2	9.0
UV-254 (cm ⁻¹)	0.031	0.012	0.015	-	0.059	-
SUVA (L/mg-m)	3.44	2.4	2.5	-	2.68	-
THMFP (µg/L)	93	58	97	248	251	2.0
%THMFP	37	23	40	100	-	-

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Table B-18 Characteristics of DOM fraction in coagulated water with PACl 40 mg/L combined with Polymer 1 mg/L in rainy season

Parameter	Rainy season			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	0.8	0.4	0.6	1.8	1.9	5.3
UV-254 (cm ⁻¹)	0.054	0.028	0.038	-	0.113	-
SUVA (L/mg-m)	6.8	7.0	6.3	-	6.28	-
THMFP (µg/L)	112	89	117	318	322	1.2
%THMFP	35	27	38	100	-	-

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Table B-19 Characteristics of DOM fraction in coagulated water with PACl 40 mg/L combined with Polymer 1 mg/L in summer

Parameter	Summer			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	0.7	0.5	0.6	1.8	1.9	5.3
UV-254 (cm ⁻¹)	0.031	0.018	0.018	-	0.059	-
SUVA (L/mg-m)	4.4	3.6	3.0	-	3.11	-
THMFP (µg/L)	76	51	86	213	229	6.9
%THMFP	35	24	40	100	-	-

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Table B-20 Characteristics of DOM fraction in coagulated water with PACl 40 mg/L combined with PAC 80 mg/L in rainy season

Parameter	Rainy season			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	0.85	0.5	0.55	1.9	2.04	6.9
UV-254 (cm ⁻¹)	0.083	0.036	0.062	-	0.159	-
SUVA (L/mg-m)	9.76	7.2	11.27	-	7.79	-
THMFP (µg/L)	82	67	92	241	256	5.9
%THMFP	35	27	38	100	-	-

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Table B-21 Characteristics of DOM fraction in coagulated water with PAC1 40 mg/L combined with PAC80 mg/L in summer

Parameter	Summer			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	0.7	0.4	0.5	1.6	1.7	5.9
UV-254 (cm ⁻¹)	0.029	0.021	0.034	-	0.053	-
SUVA (L/mg-m)	4.14	5.25	6.8	-	3.12	-
THMFP (µg/L)	69	51	73	193	206	6.3
%THMFP	35	26	39	100	-	-

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Table B-22 Characteristics of DOM fraction in coagulated water with PAC1 40 mg/L combined with Polymer 1 mg/L and PAC 80 mg/L in rainy season

Parameter	Rainy season			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	0.25	0.25	0.30	0.8	0.9	11.1
UV-254 (cm ⁻¹)	0.072	0.032	0.052	-	0.128	-
SUVA (L/mg-m)	28.2	12.8	17.3	-	14.22	-
THMFP (µg/L)	37	43	59	139	148	6.1
%THMFP	26	30	44	100	-	-

Note: %Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Table B-23 Characteristics of DOM fraction in coagulated water with PAC1 40 mg/L combined with polymer 1 mg/L and PAC 80 mg/L in summer

Parameter	Summer			HPO+TPI+HPI	Unfractionated water	% Diff
	DOM fractions					
	HPO	TPI	HPI			
DOC (mg/L)	0.25	0.18	0.27	0.7	0.8	12.5
UV-254 (cm ⁻¹)	0.028	0.013	0.021	-	0.046	-
SUVA (L/mg-m)	11.20	7.22	7.78	-	5.75	-
THMFP (µg/L)	23	33	47	103	115	10.4
%THMFP	22	32	45	100	-	-

Note: %Diff* = (Unfractionated water – fractionated water) / Unfractionated water × 100

APPENDIX C
CORRELATION BETWEEN THMFP AND DOM SURROGATE
PARAMETER

Correlation between THMFP and DOM surrogate parameters

In general, dissolved organic matter (DOM) was the term used to describe the complex metric of organic material in natural water. As mention earlier, it is not practical to analyze individual chemical compound of DOM. Consequently, DOM may be separated in term of surrogate parameters including DOC, UV-254, SUVA and THMFP.

In this study, surrogate parameters were considerably utilized to measure the quantity of DOM such as DOC, UV-254, SUVA and THMFP. From this point, the purpose of this section was to demonstrate the correlation among surrogate for DOM so as to allow one parameter such as DOC to be used as a surrogate for another parameter such as THMFP. Data of raw water and coagulated water were utilized to evaluate the correlation coefficients in this study.

According to AWWA (1993), it had been recognized that the correlation levels were divided in four categories as an $R^2 > 0.9$ was considered a good correlation, $0.7 < R^2 < 0.9$ a moderate correlation, $0.5 < R^2 < 0.7$ a fair correlation and $R^2 < 0.5$ a poor correlation. For the considerably poor correlation ($R^2 < 0.5$), regression analysis was not performed, hence, the slope and intercept for the equation were not accepted.

From the results obtained in the experiments, the correlation among surrogates for DOM were performed and the correlation coefficients determined were illustrated in Figures C-1 to C-2 and the overall correlation among surrogates for DOM were also conclusively demonstrated in Table C-1.

Looking at the conclusive results as shown in Table C-1, the THMFP was considered as dependent variable while DOC, UV-254 and SUVA were considered as independent variables. It was found that the correlation coefficient (R^2) of the regression analysis of THMFP and DOC of organic fractions from the result of raw water and coagulated water in rainy season and summer were classified as good correlation levels which R^2 values were 0.9027 and 0.9624, respectively, whereas, THMFP and UV-254 of organic fractions from the result of raw water and coagulated water in rainy season and summer were classified a moderate and as good correlation levels which R^2 values were 0.8851 and 0.9396, respectively, while the correlation coefficient (R^2) of the

regression analysis of THMFP and SUVA was lower than 0.5, which classified as a poor correlation.

Base on the results in this study it is possible to suggest that DOC was the suitable DOM surrogate parameters that could be used to describe the quantity of THMFP. Anyhow, the correlation coefficient of the regression analysis of THMFP and UV-254 was classified as a moderate correlation that could be used to describe the quantity of THMFP in raw water, coagulated water, and their fractionated water from water treatment plant. Edzwald *et al.*, (1985) reported that as a good correlation between THM formation potential (THMFP) and UV absorbance at 254 nm wavelength using raw and treat waters.

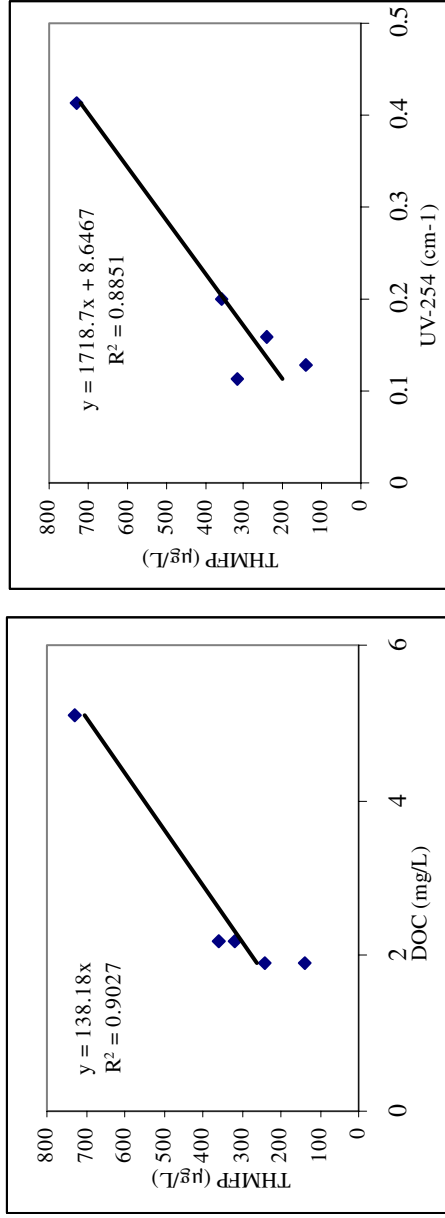


Figure C-1: Correlation between THMFP and DOM surrogate parameters of raw waters and coagulated waters before fractionation and their fractionated water in rainy season

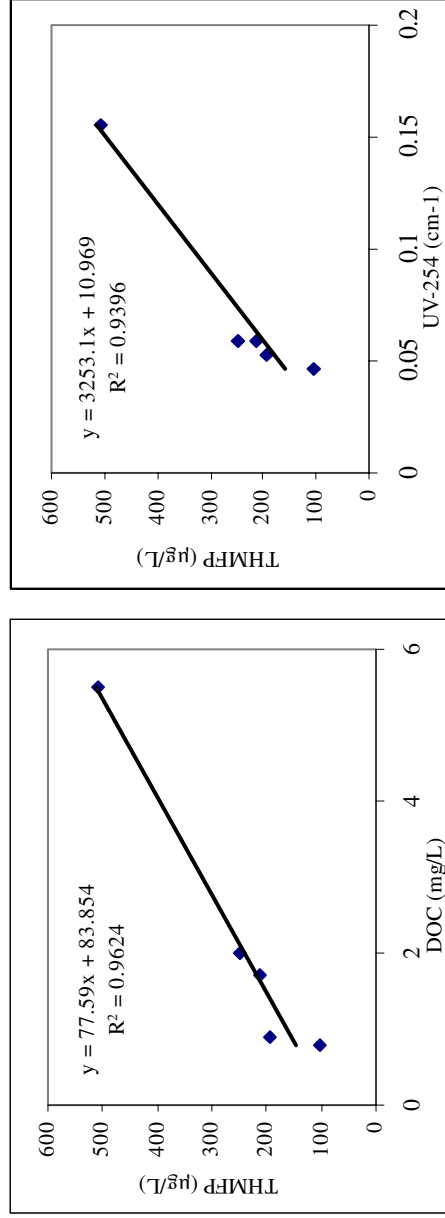


Figure C-2: Correlation between THMFP and DOM surrogate parameters of raw waters and coagulated waters before fractionation and their fractionated water in summer

TableC-1: Correlation between THMFP and DOM surrogate parameter

Dependent Variable	Independent Variable	Status	Season	N	R ²	Equation	Remark
THMFP	DOC	Raw waters, coagulated waters before fractionation and their fractionations	Rainy	5	0.9027	$Y=138.18X$	A good correlation
			Summer	5	0.9624	$Y=77.59X+83.854$	A good correlation
THMFP	UV-254	Raw waters, coagulated waters before fractionation and their fractionations	Rainy	5	0.8851	$Y=1718.7X+8.646$	A moderate correlation
			Summer	5	0.9396	$Y=3253.1X+10.969$	A good correlation
THMFP	SUVA	Raw waters, coagulated waters before fractionation and their fractionations	Rainy	5	<0.5	-	-
			Summer	5	<0.5	-	-

APPENDIX D
CALCULATE COST OF CHEMICALS

Calculate cost of chemicals

1. The use of 40 mg/L of PACl coagulation

Polyaluminium chloride 35% (W/W) Price = 4,480 baht /ton

PACl 35% = PACl 1 ton = 350 kg

PACl 350 kg price = 4,480 baht

PACl 1 kg price = $\frac{4,480}{350}$ baht

350

PACl 1,000 g price = $\frac{4,480}{350}$ baht

350

PACl 1×10^6 mg price = $\frac{4,480}{350}$ baht

350

Optimum Dose PACl 40 mg/L

PACl 1×10^6 mg price = $\frac{4,480}{350}$ baht

350

PACl 40 mg price = $\frac{4,480}{350} \times 40$ baht

$\frac{4,480}{350} \times 40$

= 0.000512 baht /L

= 0.512 baht /m³

2. The use of 40 mg/L of PACl and 1 mg/L of polymer coagulation

Polyaluminium chloride 35% Price = 4,480 baht /ton

PACl 35% = PACl 1 ton = 350 kg

PACl 350 kg price = 4,480 baht

PACl 1 kg price = $\frac{4,480}{350}$ baht

350

PACl 1,000 g price = $\frac{4,480}{350}$ baht

350

PACl 1×10^6 mg price = $\frac{4,480}{350}$ baht

350

Optimum Dose PACl 40 mg/L

PACl 1×10^6 mg price = 4,480 baht

350

PACl 40 mg price = 4,480 × 40 baht

350 1×10^6

= 0.000512 baht /L

= 0.512 baht /m³

Dry cationic polymer 100% price = 108,000 baht /ton

Polymer 1,000 kg price = 108,000 baht

Polymer 1×10^6 g price = 108,000 baht

Polymer 1×10^9 mg price = 108,000 baht

Optimum Dose of polymer = 1 mg/L

Polymer 1×10^9 mg price = 108,000 baht

Polymer 1 mg price = 108,000 × 1 baht

1×10^9

= 0.000108 baht /L

= 0.108 baht /m³

3. The use of 40 mg/L of PACl and 80 mg/L of PAC coagulation

Polyaluminium chloride 35% Price = 4,480 baht /ton

PACl 35% = PACl 1 ton = 350 kg

PACl 350 kg price = 4,480 baht

PACl 1 kg price = 4,480 baht

350

PACl 1,000 g price = 4,480 baht

350

PACl 1×10^6 mg price = 4,480 baht

350

Optimum Dose PACl 40 mg/L

PACl 1×10^6 mg price = 4,480 baht

350

$$\begin{aligned}
 \text{PACl 40 mg price} &= \frac{4,480 \times 40}{350 \times 1 \times 10^6} \text{ baht} \\
 &= 0.000512 \text{ baht /L} \\
 &= 0.512 \text{ baht /m}^3
 \end{aligned}$$

Powder activated carbon 100% price = 62,000 baht /ton

Activated carbon 1,000 kg price = 62,000 baht

Activated carbon 1×10^6 g price = 62,000 baht

Activated carbon 1×10^9 mg price = 62,000 baht

Optimum Dose of PAC = 80 mg/L

Activated carbon 1×10^9 mg price = 62,000 baht

$$\begin{aligned}
 \text{Activated carbon 80 mg price} &= \frac{62,000 \times 80}{1 \times 10^9} \text{ baht} \\
 &= 0.00496 \text{ baht /L} \\
 &= 4.96 \text{ baht /m}^3
 \end{aligned}$$

4. 4. The use of 40 mg/L of PACl and 1 mg/L of polymer and 80 mg/L of PAC coagulation.

PACl 35% = PACl 1 ton = 350 kg

PACl 350 kg price = 4,480 baht

PACl 1 kg price = $\frac{4,480}{350}$ baht

$$350$$

PACl 1,000 g price = $\frac{4,480}{350}$ baht

$$350$$

PACl 1×10^6 mg price = $\frac{4,480}{350}$ baht

$$350$$

Optimum Dose PACl 40 mg/L

PACl 1×10^6 mg price = $\frac{4,480}{350}$ baht

$$350$$

PACl 40 mg price = $\frac{4,480 \times 40}{350 \times 1 \times 10^6}$ baht

$$350 \times 1 \times 10^6$$

$$= 0.000512 \text{ baht /L}$$

$$= 0.512 \text{ baht /m}^3$$

Dry cationic polymer 100% price = 108,000 baht /ton

Polymer 1,000 kg price = 108,000 baht

Polymer 1×10^6 g price = 108,000 baht

Polymer 1×10^9 mg price = 108,000 baht

Optimum Dose of polymer = 1 mg/L

Polymer 1×10^9 mg price = 108,000 baht

Polymer 1 mg price = $\frac{108,000 \times 1}{1 \times 10^9}$ baht

$$\begin{aligned} &= 0.000108 \text{ baht /L} \\ &= 0.108 \text{ baht /m}^3 \end{aligned}$$

Powder activated carbon 100% price = 62,000 baht /ton

Activated carbon 1,000 kg price = 62,000 baht

Activated carbon 1×10^6 g price = 62,000 baht

Activated carbon 1×10^9 mg price = 62,000 baht

Optimum Dose of PAC = 80 mg/L

Activated carbon 1×10^9 mg price = 62,000 baht

Activated carbon 80 mg price = $\frac{62,000 \times 80}{1 \times 10^9}$ baht

$$\begin{aligned} &= 0.00496 \text{ baht /L} \\ &= 4.96 \text{ baht /m}^3 \end{aligned}$$

Table D-1: Comparing the costs of chemicals as follow

Coagulant	Optimum Dose (mg/L)	Price(bath/ton)	Costs / water production 1 m ³ (bath)
1.PACl	40 mg/L	4,480	0.512
2.PACl+polymer	PACl 40 mg/L and polymer 1mg/L	4,480 108,000	0.512 } 0.62 0.108 }
3.PACl+PAC	PACl 40 mg/L and PAC 80 mg/L	4,480 350,000	0.512 } 5.47 4.96 }
4.PACl+polymer+PAC	PACl 40 mg/L combined with polymer 1mg/L and PAC 80 mg/L	4,480 108,000 350,000	0.512 } 5.58 0.108 } 4.96 }

VITAE

Name Kanjane Srimuang

Student ID 5110120002

Educational Attainment

Degree	Name of Institution	Year of Graduation
Bachelor of Science(B.Sc) Environmental Science	Thaksin University, Songkla, Thailand	2008

List of Proceeding

Srimuang, K., Suksaroj, C., Tachapattaworakul Suksaroj, T., and Musikavong, C. (2009). Removal of Dissolved Organic Matter by Enhanced Coagulation: A FTIR Analysis. Proceeding of the 9th National Environmental Conference. March 24-27, Ubonratchathani, Thailand.