Reduction of Fractionated Dissolved Organic Matter in Raw Water Supply by Membrane Process

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Thesis Title Reduction of Fractionated Dissolved Organic Matter in Raw Water Supply by Membrane Process
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ABSTRACT

The conventional water treatment system consisting of coagulation, sedimentation, sand filtration and chlorination is widely used for producing water supply because this system has a high potential to produce a huge quantity of clear water and no need the complicated technologies in operation. But this system requires a large area for water treatment plant and not efficiency enough for removing organic matters especially dissolved organic matters (DOM) contained in water. For further study of DOM removal, hybrid ultrafiltration process (UF) combining traditional raw water treatment was studied in this research. This research aims to study the reduction of DOM surrogate parameters (DOC and UV-254) and DOM characterization (by resin adsorption, FEEM and FT-IR), including the change of THMFP in the raw water supply from Sri-Trang Reservoir and U-Tapao Canal water (which has the differences of water quality and characteristics) in rainy season and dry season by hybrid immerseble polysulfone hollow fiber UF membrane combined with coagulation process. The different pre-treatment processes, the coagulation operated with polyaluminum chloride (PACl) (20 mg/L for Sri-Trang Reservoir water and 40 mg/L for U-Tapao Canal water) controled pH at 7 and microfiltration process (MF) with pore size of 0.1 μm were investigated for treating the raw water samples prior to UF membrane process. The resin adsorption technique using DAX-8 was employed to fractionate DOM into hydrophobic (HPO) and hydrophillic (HPI) fractions. Results show that the raw water from Sri-Trang Reservoir in both seasons had HPO > HPI, whilst, HPI > HPO for raw water from U-Tapao Canal in both seasons. Concerning the application of FEEM technique, tryptophan, humic and fulvic like substances were detected in both water sources. After the UF membrane process, the hybrid coagulation-UF membrane process could effectively reduce DOC and UV-254 from Sri-Trang Reservoir water approximately 65 percent and 66 percent while 75 percent and 73 percent of U-Tapao Canal water, respectively. For the hybrid MF-UF process, it could reduce DOC and UV-254 from Sri-Trang Reservoir water approximately 59 percent and 55 percent while 70 percent and 53 percent for that of U-Tapao Canal water, respectively. In regard to Trihalomethane Formation Potential (THMFP) analysis, chloroform was found as the major THM specie follow by bromodichloroform. The hybrid coagulation-ultrafiltration membrane process could reduce the THMFP sligthly more effective than the hybrid MF-UF membrane process that were 88 percent and 86 percent for both water sources, respectively. Significantly, HPI was the major fraction of DOM in raw water and was the main precursor of THMFP. To better understand the characteristics of DOM in water samples, FT-IR analysis also used to explain the characteristics of DOM. It indicated that the both hybrid UF processes had an efficiency to reduce DOM especially the C-O stretching of alcohols, ethers and carbohydrates. However, the treated water quality after hybrid UF processes in this study meet water quality standard of water supply in Thailand.

ชื่อวิทยานิพนธ์ การลดกลุ่มสารอินทรีย์ละลายน้ำในน้ำดิบประปาโดยใช้กระบวนการเมมเบรน
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บทคัดย่อ

ระบบผลิตน้ำแบบดั้งเดิมที่ประกอบด้วยกระบวนการโคแอกกูเลชัน การตกตะกอน การกรองทราย และการฆ่าเชื้อโรคด้วยคลอรีน ถูกนำมาใช้อย่างแพร่หลายในการผลิตน้ำประปา เนื่องจากเป็นระบบที่สามารถผลิตน้ำประปาในปริมาณมากและใช้เทคโนโลยีไม่ซับซ้อนในการดำเนินการ แต่ข้อเสียของระบบนี้คือต้องการพื้นที่และมีประสิทธิภาพไม่เพียงพอในการกำจัดสารอินทรีย์โดยเฉพาะสารอินทรีย์ละลายน้ำ ดังนั้นจึงมีการศึกษาการกำจัดสารอินทรีย์ละลายน้ำในน้ำดิบประปาโดยใช้กระบวนการอัลตราฟิลเตรชันร่วมกับระบบผลิตน้ำประปาแบบดั้งเดิม งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาประสิทธิภาพการลดสารอินทรีย์ละลายน้ำในน้ำดิบประปา โดยใช้กระบวนการอัลตราฟิลเตรชันเมมเบรนชนิดเส้นใยกลวง ติดตั้งจมตัวภายในถังปฏิกรณ์ ร่วมกับการใช้กระบวนการโคแอกกูเลชัน ด้วยสารสร้างตะกอนชนิด Polyaluminum Chloride (PACl) ที่ความเข้มข้น 20 mg/L สำหรับ น้ำดิบอ่างศรีตรัง และ 40 mg/L สำหรับน้ำดิบคลองอู่ตะเภา ควบคุมค่า pH 7 และไมโครฟิลเตรชันเมมเบรน ขนาดรูกรอง 0.1 ไมครอน เป็นกระบวนการบำบัดน้ำขั้นต้นก่อนเข้าสู่กระบวนการอัลตราฟิลเตรชัน สำหรับบำบัดน้ำดิบประปาจากอ่างเก็บน้ำศรีตรังและคลองอู่ตะเภา อำเภอหาดใหญ่ จังหวัดสงขลา (ซึ่งมีคุณภาพน้ำและลักษณะสมบัติที่แตกต่างกัน) ทั้งในฤดูฝนและฤดูแล้ง สารอินทรีย์ชนิดชอบน้ำและไม่ชอบน้ำถูกแยกโดยใช้เรซิ่นชนิด DAX-8 จากการทดลองพบว่า น้ำดิบจากอ่างเก็บน้ำศรีตรังทั้งสองฤดูกาลมีการกระจายตัวของ สารอินทรีย์แบบไม่ชอบน้ำมากกว่าสารอินทรีย์แบบชอบน้ำ ส่วนน้ำดิบจากคลองอู่ตะเภามีการกระจายตัวของสารอินทรีย์แบบชอบน้ำมากกว่าสารอินทรีย์แบบไม่ชอบน้ำ การตรวจวัด fluorescent excitation-emission matrix (FEEM) พบว่าในน้ำดิบประปาและน้ำที่ผ่านกระบวนการร่วมอัลตราฟิลเตรชันเมมเบรนสามารถตรวจพบสารอินทรีย์กลุ่มเทปโตฟาน กลุ่มฮิวมิคและฟูลวิคแอซิด และเมื่อผ่านกระบวนการอัลตราฟิลเตรชัน พบว่ากระบวนการร่วมโคแอกกูเลชันและอัลตราฟิลเตรชันเมมเบรนสามารถลด Fluorescent Intensity ได้ดีที่สุดคือร้อยละ 65 และร้อยละ 66 สำหรับน้ำจากคลองอู่ตะเภาสามารถลดได้ร้อยละ 75 และร้อยละ 73 ตามลำดับ ส่วนกระบวนการร่วมไมโครฟิลเตรชัน

และอัลตราฟิลเตรชันเมมเบรนสามารถลดสารอินทรีย์ละลายน้ำของอ่างเก็บน้ำศรีตรังในรูปของ DOC และ UV-254 ได้เพียงร้อยละ 59 และร้อยละ 55 ส่วนน้ำจากคลองอู่ตะเภาสามารถลดได้ร้อยละ 70 และร้อยละ 53 ตามลำดับ ในการศึกษาศักยภาพการก่อตัวของสารไตรฮาโลมีเทน (THMFP) พบว่า คลอโรฟอร์มเป็นสารประกอบหลักของ THMs รองลงมาคือ โบรโมไดคลอโรฟอร์ม สำหรับประสิทธิภาพการลด THMFP นั้นพบว่า กระบวนการร่วมโคแอกกูเลชันและอัลตราฟิลเตรชันเมมเบรนสามารถลด THMFP ได้มากกว่ากระบวนการร่วมไมโครฟิลเตรชันและอัลตราฟิลเตรชันเมมเบรน โดยสามารถลดได้ร้อยละ 88 และร้อยละ 86 ตามลำดับ นอกจากนี้ยังพบว่าสารอินทรีย์กลุ่มชอบน้ำในน้ำตัวอย่างจากคลองอู่ตะเภาเป็นสารตั้งต้นหลักในการเกิด THMFP แต่สารอินทรีย์กลุ่มไม่ชอบน้ำในน้ำตัวอย่างจากอ่างเก็บน้ำศรีตรังเป็นสารตั้งต้นหลักในการเกิด THMFP และเพื่อเข้าใจลักษณะสมบัติของสารอินทรีย์ในน้ำมากขึ้น การวิเคราะห์โดยใช้เทคนิด FT-IR เพื่อหาหมู่ฟังก์ชันของสารอินทรีย์ถูกนำมาใช้ในการศึกษาครั้งนี้ โดยจากการทดลองพบว่า กระบวนการร่วมอัลตราฟิลเตรชันเมมเบรนสามารถลดสารอินทรีย์ในน้ำได้โดยเฉพาะ C-O stretching of alcohols, ethers และ carbohydrates นอกจากนี้พบว่าคุณภาพน้ำที่ผ่านการบำบัดจากกระบวนการร่วมอัลตราฟิลเตรชันเมมเบรนผ่านเกณฑ์มาตรฐานคุณภาพของน้ำประปาในประเทศไทย

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abs.	Absorbance
Al	Aluminium
$Al(OH)_3$	Aluminium hydroxide
Al_2O_3	Aluminium Oxide
Al_2SO_4	Aluminium Sulfate
$AlCl_3$	Aluminium Chloride
Amu	Apparent molecular unit
AMW	Apparent Moleccular Weight
AWWA	American Water Work Association
^{0}C	Degree Celsius
$CaCO_3$	Calcium Carbonate
$CHBr_3$	Bromoform
$CHCl_2Br$	Bromodichloroform
$CHCl_3$	Chloroform
$CHClBr_2$	Dibromochloroform
Cl	Chlorine
cm	Centimeter
DI	Deionized Water
DBPFP	Disinfection by Product Formation Potential
DBPs	Disinfection by-Product
DOC	Dissolved Organic Carbon
EDTA	Disodiumethylenediamune tetraacetate dehydrate
DOM	Dissolved Organic Matter
DPD	*N, N-diethyl-p*-phenylenediamine
ECD	Electron Capture Detector
$FeCl_3$	Ferric Chloride
FEEM	Fluorescent Excitation-Emission Matrix

LIST OF ABBREVIATIONS

FTIR	Fourier-Transform Infrared
g/cm^3	Gram/Cubic/ Centimeter
g/L	Gram/Liter
g/mol	Gram/Molar
GC	Gas Chromatograph
hr	Hour
HAAs	Haloacetic acid
HANs	Haloacetonitrile
HPI	Hydrophilic
HPO	Hydrophobic
I	Iodine
KHP	Potassium Hydrogen Phthalate
KI	Potassium Iodine
L/mg-m	Liter/milligram-meter
m	Meter
M	Molar
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
CH_4	Methane
µg/L	Microgram/Liter
MF	Microfiltration
µm	Micrometer
mg/L	Milligram/Liter
min	Minute
MW	Molecular Weight
MWCO	Molecular Weight Cut Off
MWD	Molecular Weight Distribution

LIST OF ABBREVIATIONS

NF	Nanofiltration
nm	Nanometer
NOM	Natural Organic Meter
NTU	Nepheo Turbidity Unit
ppm.	Part per Million
PACl	Polyaluminum Chloride
QSU	Quinine Sulfate Unit
RO	Reverse Osmosis
SS	Suspended Solid
STHMFP	Specific Trihalomethane Formation Potential
SUVA	Specific Ultraviolet Absorption
S.D.	Standard Deviation
THMFP	Trihalomethane Formation Potential
THMs	Trihalomethanes
TMP	Trans Membrane Pressure
TOC	Total Organic Carbon
TTHM	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UF	Ultrafiltration
UV	Ultraviolet
UV254	Ultraviolet absorbtion at wave length 254 nanometer
UVA	Ultraviolet Absorption

CHAPTER 1

INTRODUCTION

1.1Motivation

According to the conventional water treatment process, the chemicals added during a process, especially in coagulation process, are effective in removing and/or reducing only to a certain group of Natural Organic Matter (NOM) in raw water supply. Consequently, the remaining of NOM serve as precursors can react with chlorine (Cl_2) which is widely used as a disinfectant in a disinfection process and, hence, cause the carcinogenic substances in water supply. These substances are well known as disinfection by products (DBPs) such as Trihalomethanes (THMs), Haloacetic acids (HAAs) and other halogenated organics that can be responsible for health problems. (Rook, 1974 and Marhaba and Washington, 1998).

The water treatment plant in Hatyai, where utilizing raw water supply from U-Tapao Canal and the Prince of Songkla University (PSU) water treatment plant where utilizing raw water supply from Sri-Trang reservoir have might be faced this same problem. Especially, dissolved organic matters (DOM) in terms of humic acids and fulvic acid-like substances including tryptophan-like substances which were detected in raw water supply from U-Tapao Canal (Inthanuchit *et al.,*2009) and Sri-Trang reservoir (Kueseng *et al.,*2009). But the tryptophan-like substance usually presented by domestic wastewater (Musikavong *et al.,* 2007). Because U-Tapao canal and Sri-Trang reservoir, other than being the raw water sources for the water supply production, they also be the collected place for wastewater discharge from many places such as households, industrial factories, agricultural activities, etc. Thereby, these raw water sources are contaminated by those dissolved organic matters.

Normally, DOM can be fractionated into 2 fractions in terms of hydrophobic and hydrophilic groups by using the resin adsorption method. Differing quantities and nature of DOM fractions have differing potential to form THMs.

The coagulation process successfully remove DOM in raw water supply from U-Tapao canal and Sri-Trang reservoir in a certain level. Inthanuchit *et al.,*(2009) reported that the coagulation with 40 mg/L Polyaluminum Chloride (PACl) at pH 7 could reduce the organic substance in terms of ultraviolet absorption at wavelength 254 nm (UV-254) and dissolved organic carbon (DOC) from U-Tapao canal for 50% and 54%, respectively. For Sri-Trang reservoir, Kueseng *et al.,* (2009) reported that the coagulation with 20 mg/L Polyaluminum Chloride (PACl) at pH 7 could reduce UV-254 and DOC for 62% and 48%, respectively. In order to reduce DBPs, is should be more effective to remove DOM prior to react with Cl_2 to form THMs.

For further study of DOM removal, the use of hybrid processes combining traditional raw water treatment with membrane process such as microfiltration (MF) and ultrafiltration process (UF) were studied. The MF and UF process is more widely used nowadays in water treatment to remove NOM in raw water supply (Zularisam *et al.,* 2006), hence, more cost-effective than previously was in terms of higher permeate flux compared to nanofiltration and reverse osmosis and high efficiency of NOM removal (Shon *et al.,*2004). Ates *et al*., (2009) reported that UF process could remove NOM in terms of UV-254 and DOC for 74% and 61%, respectively. Beside, Choksuchart *et al.,* (2002) carried out experiments to determine the optimum conditions for the UF of surface water. The raw water was a clay suspension prepared by adding clay powder in demineralized water or tap water. The results showed that without coagulation small clay suspended particles stay dispersed and sedimentation occurs more slowly. On the other hand, the pretreatment by coagulation was an excellent method for particle removal. The optimal dose of FeCl3 coagulant was 0.1 g/g clay. In these investigations aeration reduced the floc size, but no apparent consequences on the filtration rate were observed.

Moreover, it is strictly related with the protection of membranes against the fouling phenomenon that occurs inside the membrane pores and cake formation on the membrane surface causing permeate flux decline (Jacob *et al.,* 1998 and Belford *et al.,* 1994). Furthermore, the use of traditional techniques improves the quality of permeate which is important, especially for potable water production (Alpatova *et al.,* 2004)

As these results, this research discussed the results obtained from the lab-scale studies designed to investigate the efficiency of hybrid ultrafiltration process with coagulation and microfiltration process as a pre-treatment technique for natural water treatment from U-Tapao canal and Sri-Trang reservoir, in order to remove as much as DOM and also THMs formation potential (THMFP) created from two DOM fraction in raw water supply.

1.2 Objectives:

- To evaluate the removal of DOM in raw water supply by hybrid ultrafiltration process combined with PACl coagulation and microfiltration process.
- To investigate THMFP reduction by hybrid ultrafiltration process combined with PACl coagulation and microfiltration process.
- To fractionate DOM into 2 fractions in terms of hydrophobic and hydrophilic groups and to investigate THMFP created from each DOM fraction.

1.3 Hypotheses:

- Hybrid ultrafiltration process combined with PACl coagulation and combined with microfiltration process may enhance DOM removal efficiency.
- Different DOM fractions may produce different THMFP.
- It is possible to use this hybrid UF process instead of conventional system

1.4 Scopes of the study:

- Water from U-Tapao canal and Sri-Trang Reservoir were collected as water samples.
- Water samples were taken in Rainy season and Dry season.
- Two differences pretreatment method including PACl coagulation and MF process were used prior to UF process.
- DOM surrogates (DOC, UV-254, FEEM and THMFP) were analyzed to determine water quality.
- DOM in raw water and treated water were fractionated into two fractions which consist of hydrophilic (HPI) and hydrophobic (HPO) by utilizing the resin fractionation (DAX-8).
- THMFP in raw water and treated water including THMFP were determined.

CHAPTER 2

LITERATURE REVIEW

2.1 Background on Membrane Treatment

2.1.1 History and Evolution of Membrane Treatment Processes

Micro-porous membranes were first used and patented in the 1920's (Belfort *et al.,* 1994), although they were limited primarily to laboratory use until the 1950's. Initially, they were used for enumerating bacteria, removing microorganisms and particles from liquid and gas streams, and fractioning and sizing macro-molecules such as proteins (MWH, 2005). In the 1950's industries began incorporating membrane filtration, primarily for the sterilization of liquid pharmaceuticals and intravenous solutions. Membrane filtration also slowly began to be used for industrial waste treatment, in order to separate oils, fats, acids and brine.

There are four main categories of membranes used in drinking water applications today: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). These membranes are generally classified by pore size, molecular weight cut-off (MWCO) and the applied pressure that they require. Pore size is sometimes expressed as MWCO, which is a measure of the removal characteristics of a membrane in terms of atomic weight or mass, as opposed to pore size; typically measured in daltons (AWWA, 2005). Table 2-1 provides a concise summary of the four membrane types, as well their applications, pore size and operating pressure:

The membrane modules are a part of a larger system which includes all of the operational concepts and conditions that make up a treatment system (Schäfer *et al.,* 2005). Membrane processes now are used in environmental, chemical, food, beverage, pharmaceutical, and various other industries for separation applications. In water and wastewater treatment, their application as an advanced physical process for clarification and disinfection is established and rapidly gaining popularity (Sethi *et al.,* 2000). Since the early 1990's, there has been rapid growth in the use of low-pressure micro-filtration (MF) and ultra-filtration (UF) membrane processes for the production of potable water. Generally, UF membranes are very successful in removing turbidity. Turbidity in water is caused by suspended matter such as clay, silt, organic matter, plankton and other microscopic organisms that interfere with the passage of light through the water (American Public Health Association, 1998). Turbidity is an indicator of major sources of water impurities in waters, and therefore is an ongoing parameter of interest for all water treatment processes. The UF membranes can yield permeate streams consistently with turbidity values of less than 0.1 NTU (Nephlometric Turbidity Unit). The widespread growth of the use of low pressure membrane systems on large scale applications has occurred for several reasons. A major reason is the changes in the regulatory requirements for drinking water, requiring lower filtered water turbidity and removal of chemical disinfectant-tolerant micro-organisms (AWWA, 2005).

Table 2.1 Major membrane filtration processes used in drinking water treatment

Type	Operating pressure (bar)	Pore size (μm)	Primary applications	Microbes removed
MF	0.3-0.5	≥ 0.1	Removal of particles and turbidity	Algae, protozoa and most bacteria
UF	0.3-0.5	≥ 0.01	Removal of dissolved nonionic solutes	Algae, protozoa, most bacteria and viruses
NF	5-10	≥ 0.001	Removal of divalent ions (softening) and dissolved organic matter	Algae, protozoa, most bacteria and viruses
RO	10-50	≥ 0.0001	Removal of monovalent ions (desalination)	Algae, protozoa, most bacteria and viruses

MF and UF systems are particulate filters and unlike nano-filtration (NF) and reverse osmosis (RO) do not remove dissolved constituents. This treatment aspect makes them more suitable for use as a replacement to conventional filters. The cost of low pressure membranes systems is also a major driver for increased membrane application compared with conventional treatment technologies. Every year, the capital cost of MF and UF systems has decreased as economies of scale and a competitive market force innovative developments. Generally, low pressure membrane facilities are one half to one third the cost of an NF or RO facility (Farahbakhsh *et al.,* 2004). In addition, the implementation of innovative backwash or cleaning strategies has reduced operational cost, by reducing the degree of fouling that occurs on the surface and inside the pores of the membranes.

One other key factor that has increased the usage of membrane systems is their operational flexibility. These systems can be used in conjunction with other treatment processes to achieve additional removal. There are several pre-treatment techniques available to use in combination with a MF or UF membrane: pre-filtration, pH adjustment, coagulation, bio-filtration adsorption and pre-oxidation (Kimura *et al.,* 2005).

2.1.2 Description of Membrane Treatment Processes

Process Description

Low pressure membrane processes are generally used for the removal of turbidity in water, and reasonably large pathogens and most bacteria (Klijn *et al.,* 2000). The MF process is not very effective at removing NOM (Jacangelo *et al.,* 1997), as these compounds are more efficiently targeted by UF processes and much more efficiently by NF. The two major issues that utilities have to deal with on a regular basis with UF membrane processes are the quality of the water product, which is related to the rejection of targeted solutes and particulates, and the impact of membrane fouling leading to permeate flux decline and consequent reduction in the efficiency of the membrane filtration process (Linhua *et al.,* 2001).

Membrane processes are modern physicochemical separation techniques that use differences in permeability and size of contaminant as a separation mechanism (MWH, 2005). Effective membrane treatment will remove all or most of the contaminants to produce a water which, with effective disinfection, is of minimum risk to human health, aesthetically acceptable, and economically affordable (Westerhoff *et al.,* 1996).

During the treatment process, the contaminated raw water is fed into the membrane module via a pump, which ensures that water is drawn through by vacuum. This pressurized water is fed into the membrane module, and onto the membrane surface. Generally, the feed stream flows perpendicularly to the membrane surface, although in some cases, the water is top-loaded onto the surface, called dead-end filtration. This set-up is no longer a common practice, as it induces membrane fouling much more than the modern approach of the cross-flow filtration. The volume of water that accumulates in the permeate stream is quantified in terms of membrane flux, which is defined as the amount permeate flow produced per membrane surface area and time. This relationship is shown below:

$$J = \frac{Q}{A} \tag{1}$$

By Q represents the volumetric flow rate being fed into the membrane (m^3/day), and A represents the nominal surface area of the given membrane module (m^2).

Both low pressure membrane systems (MF and UF) remove particulate matter and turbidity as well as larger micro-organisms and viruses. Effluent turbidity values have been consistently reported to be lower than 0.1 NTU (Karimi *et al.,* 1999). Another key feature of UF membranes is their ability to remove particulate metals such as iron and manganese, as MF membranes do not have this consistent capability (Gangloff, 2000). The removal of organic matter and more specifically humic substances by UF membranes is considered to be a challenge due to the associated organic fouling that occurs. Further discussion regarding this topic will be discussed in subsequent sections of this chapter.

Membrane structure and configuration

The structure of a membrane refers to the way it is constructed to optimize surface area, and reduce the degree of fouling by incoming feed water. The most common types of structures are Flat sheet, Tubular/capillary, Spiral wound and Hollow fiber membrane as shown in Figure 2.1.

Hollow fiber membranes have gained popularity in the last decade to become the most commonly used configuration in low pressure membrane filtration (MF or UF) for water treatment (MWH, 2005). These membranes usually consist of several hundred fibers encased in a module, whether it is full, pilot or bench scale. They are generally open tubes that are plug resistant and do not accumulate particles between the fibers. The internal fiber diameters are quite small to avoid fiber collapse when exposed to high pressure, range anywhere between 0.4 to 1.5 mm (AWWA, 2005). These membranes can be exposed to frequent backwash cycles, which make them an attractive module type given that fouling is the primary limitation to the technology.

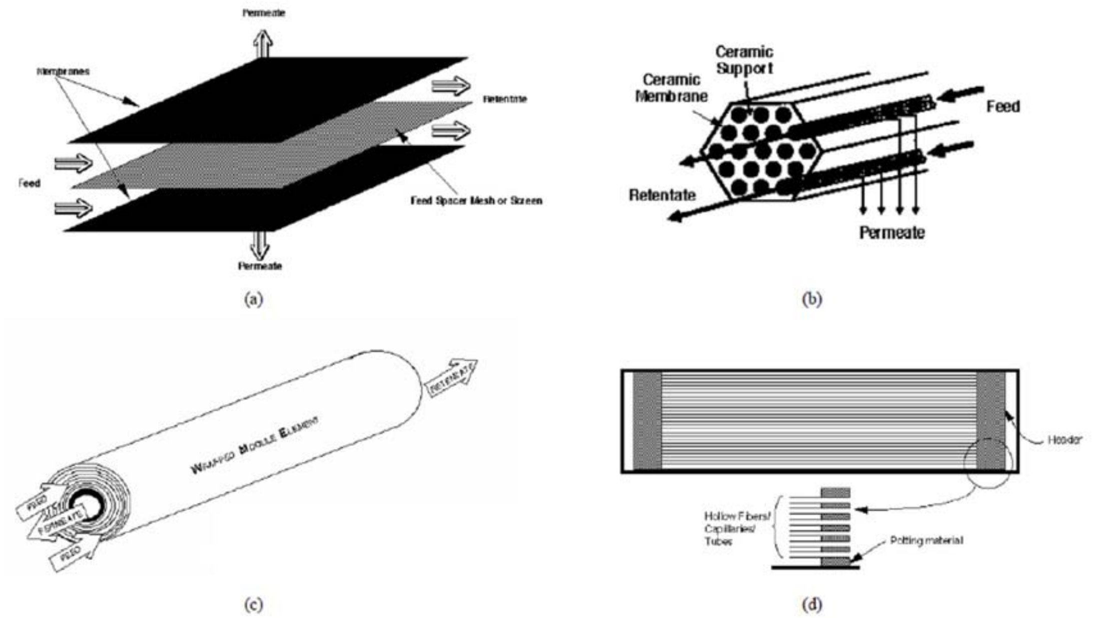


Figure 2.1 Membrane types a) Flat sheet membrane b) Tubular/Capillary membrane c) Spiral wound membrane and d) Hollow fiber membrane

Two types of flow regimes are used in practice, the first being the outside – in configuration, where the membrane is submerged in the feed water, and the untreated water is sucked in through the many porous fibers via a vacuum, and combined to become the permeate stream. The second configuration is the inside-out, where water is pumped into the membrane, and filtered through the fibers exiting into the surrounding water. The advantage of the second flow regime is that the water flows through a narrow channel, and therefore allows for good control over module hydrodynamics. Hollow fiber membranes offer a very high specific surface area to volume ratio, because of the small inner lumens of the fibers, and therefore have the ability to treat a larger volume of water.

Membrane material

Membrane performance is influenced strongly by the physical and chemical properties of the material (MWH, 2005). As technology is evolving, membranes are being built with more sophisticated materials and with unique applications for the given source water. The most frequently used membrane materials in both municipal and industrial water treatment are polymer based: Cellulose acetate, acrylic, nylon, polypropylene (PP), polyamide (PA), polyamide-hydrazide (PAH), polyimide (PI), polysulfone (PS) and polyethersulfone (PES). Ceramics and zirconia based materials have also gained popularity, but have not grown to be as popular as the polymer based modules.

Polymers are almost ideal membrane materials, since they can be easily produced with pores of almost any size and are flexible enough to be configured into a wide range of constructions, including flat sheets and hollow fiber cartridge materials (Klijn *et al.,* 2000). However, there are several drawbacks to polymer membranes; the one that stands out most is the tendency toward fouling and clogging. This particularly can be the result of contamination from biological growth. Nevertheless, the advantages of polymers, coupled with the growing use of cross-flow designs, which minimize clogging by directing fluids toward the membrane at an angle, will ensure that for the vast majority of applications, polymers will remain the material of choice for years to come.

Membrane cleaning

Membrane modules experience a great deal of wear and tear during the treatment of contaminated water. It is crucial to the life of a membrane that is well maintained and cleaned; otherwise it will have to be replaced, representing a substantial cost to the overall process. There are several ways that a membrane can be maintained in its best working order, mainly by pretreatment, air-sparging, backwashing and chemical cleaning.

2.2 Membrane Fouling

2.2.1 Introduction

The main limitation to the use of membranes in drinking water treatment is its high energy consumption that can mainly be attributed to membrane fouling, which causes the applied pumping action to work harder to maintain a constant flux (Kimura *et al.,* 2005). Membrane fouling is the process by which the permeate flux through the membrane is reduced as a result of particles accumulating on the surface, forming a cake layer, or the adsorption of particles (both suspended particles and dissolved material) inside the membrane pores (AWWA, 2005). Membrane fouling can be divided into two types: reversible and irreversible fouling. As previously mentioned, reversible fouling can be restored by backwash cycles, while irreversible fouling requires chemical cleaning to be mitigated. There are four major types of fouling mechanisms that affect drinking water membranes: Organic fouling, bio-fouling, scaling and colloidal/particulate fouling

Organic fouling is caused by both dissolved and suspended particles that adsorb inside the pores and on the surface of the membrane. There are several factors already discussed that have the potential to influence organic fouling caused by NOM, although there are three primary ones: MW distribution, the membrane surface and chemical composition of the feed water. Bio-fouling is the growth of living micro-organisms on the surface or inside the pores of a membrane. The living organisms use the membrane as a support, and in doing so reduce the permeate flux and cause fouling. It has been shown that chlorine dioxide removes bio-film from water systems and prevents biological growth from forming when dosed at a continuous low level. Hypochlorite on the other hand has been proven to have little effect on bio-films (Soffer *et al.,* 2005).

Fouling has received a great deal of attention from water treatment research experts, as many situations show that there is no clear distinction as to whether it is the dissolved or suspended particles that contribute to fouling most. Howe and Clark (2002) concluded that the most significant membrane fouling occurs in the presence of small colloidal matter, ranging from about 3-20 nm in diameter. Their findings demonstrate that the majority of dissolved organic matter (DOM) by itself does not cause membrane fouling, but rather the actual foulant is a relatively small fraction of bulk DOM. Combe *et al.,* (1999) found that NOM adsorbs both inside pores and on the membrane surface, forming a gel layer, which thickens over time reducing the overall flux across the membrane surface.

2.3 Background on Coagulation

Coagulation and flocculation is defined as the process by which small particles in aqueous solution destabilize because by chemical addition, and aggregate together, forming larger particles known as flocs. With a neutral suspension, the flocculation rate can be enhanced, and the concentration of the given particle distribution in the solution can be reduced (AWWA, 1999). The coagulation process is a complicated one, with many mass transfers and active species that take part in the reaction steps. The process can be broken down into three key steps: Coagulant formation, particle destabilization (coagulation) and inter-particle collisions (flocculation). Enhanced coagulation, often referred as low pH coagulation is often used to increase the removal of TOC and other particles. This is accomplished by reducing the raw water pH to an optimal level: a pH in the range of 4.5-5.5 for iron based coagulants and 5.5-6.5 for aluminum based coagulants (Sharp *et al.,* 2006). In order to understand the mechanism by which coagulants function, one needs to be familiar with the exact type and their form.

The two main ways in which hydrolyzing coagulants act to remove particles are charge neutralization and sweep flocculation. Charge neutralization is a reasonably simple mechanism, which involves the specific adsorption of the cationic hydrolysis products from solution onto the negatively charged particles. NOM and other particles can be destabilized by small amounts of hydrolyzing coagulant. Desirable destabilization corresponds with the neutralization of particle charge, which then leads to aggregation of the neutral particles (Gregory and Duan, 2001). It is important to note that larger amounts of the positively charged coagulants (over dosing) can cause charge reversal, leaving the particles positively charged and thus re-stabilized. When charge neutralization is the dominant mechanism, the coagulant dose is generally considered to be proportional to the concentration of particles in solution, although in some cases; required doses can still be dominated by the type of NOM found in the water, and not simply the concentration.

In some cases it is found that a higher coagulant dose is more effective, due to extensive hydroxide precipitation and the process known as sweep flocculation (Jiang, 2001). Sweep flocculation can overcome two of the primary disadvantages of destabilization by charge neutralization: The first being the fact that very accurate control of the coagulant dose is required to give optimum destabilization, and the second is the fact that the coagulation rate depends on the particle concentration, and can therefore be extremely low for dilute solutions. Sweep flocculation avoids both of these problems by using much higher doses, forming larger quantities of amorphous hydroxide precipitates. The target particles are enmeshed in this growing precipitate, and then can be removed by sedimentation, giving the term “sweep floc”. Sweep floc is the mechanism that takes place when the water pH is above the zero point of charge for the dissolved species formed from the coagulants such as alum.

2.3.1 Polyaluminum Chloride (PACl) Coagulation

The term polyaluminum chloride or PACl refers to a class of soluble aluminum products in which aluminum chloride has been partly reacted with base. The relative amount of OH-, compared to the amount of Al, determines the basicity of a particular PACl product. The chemistry of PACl is often expressed in the form $Al_n(OH)_mCl_{(3n-m)}$. Basicity can be defined by the term m/(3n) in that equation. Solutions of PACl are not as acidic as alum; consequently they do not tend to decrease the pH as much as an equivalent amount of alum. Another difference is that PACl is formulated so that it already contains some of the highly cationic oligomers of aluminum-materials that are especially effective for the modification of colloidal charges. A particularly stable and important ionic species in PACl and related soluble aluminum chemicals has the formula $Al_{12}(OH)_{24}AlO_4(H2O)_{127}$.

Polyaluminum chloride (PACl) is increasingly used for water treatment. Against the conventional use of aluminium sulphate (alum), it is showing distinct advantages. PACl are synthetic polymers dissolved in water. They react to form insoluble aluminium poly-hydroxides which precipitate in big volumetric flocs. The flocs absorb suspended pollutants in the water which are precipitated with the PACl and can together be easily removed. PACl can be used as a flocculant for all types of water treatment, drinking water, industrial waste water, urban waste water and in the paper industry. The advantages of PACl over Alum is consist of lower dosage requirement, no requirement for any neutralising agent (soda, lime), shorter flocculation time, smaller amount of sludge, reduced number of back washing steps, higher quality of the treated water and alum can contains any type of hazardous metals in some conditions.

2.3.2 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).

2.3.2.1 Double Layer Compression

Double layer compression involves electrostatic repulsion. It occurs when counterions is added as coagulant. Surrounding the negatively charged colloidal particle is an inner fixed layer and outer diffused layer of counterions. The concentration of counterions 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 counterions 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.

2.3.2.2 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.

2.3.2.3 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.

2.3.2.4 Interparticle 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).

2.4 The Origin of Natural Organic Matter

One of the important groups of substances that exist in surface and ground waters today is NOM. Natural organic matter (NOM) is primarily made up of humic substances, which are polyphenolic molecules that give rise to yellow-brown water that is aesthetically undesirable. The NOM also has the potential to combine with disinfection compounds such as chlorine, to form such disinfection by-products (DBP) as organo-chlorines (Rook, 1974; Marhaba and Washington, 1998 and Maartens *et al.,* 1999). These byproducts have been proven to act as carcinogens in bench-scale animal studies (Singer, 1999). The potential for NOM to complex with metals also exists, and as a result, can potentially increase metal solubility, having direct adverse effects on human health (Jones and Bryan, 1998). Humic substances are a major component of suspended and dissolved NOM in aquatic environments. They are mainly derived from soil and are also produced within natural water and sediments by chemical and biological processes such as the decomposition of vegetation (AWWA, 1999). A major component of NOM found in natural waters is humic substances. Humics are anionic poly-electrolytes of low to moderate molecular weight, ranging between 2000-5000 Dalton (Da), dominated by phenol groups. The negative charge is caused by the carboxyl and phenolic groups that make up the structure of the compound. They have both aromatic and aliphatic components, allowing them to be surface active, which is the ability of a compound to lower the surface tension of a given medium in which it is dissolved (Kokkola *et al.,* 2006). In addition to humic substances, proteins, polysaccharides, and other classes of biopolymers also contribute to NOM in natural waters. Monomeric species such as simple sugars and amino acids are also present in natural water sources, but they are much less abundant, as they are subject to relatively rapid biodegradation (AWWA, 2000).

2.5 Dissolved Organic Matter (DOM) and Their Surrogates

DOM is a complex mixture of various compounds with widely different chemical properties from simple structure to very complex polymers in natural water (Henze, 1992). DOM consists of humic substances, amino acids, sugar aliphatic acids, and a large number of organic molecules (Pirnie Inc., 1993). Leenheer and Croue (2003) defined DOM as a complex mixture of aromatic and aliphatic hydrocarbon structures with attached amide, carboxyl, hydroxyl, ketone, and various minor functional groups. Specifically, natural water source such as river, reservoir and groundwater, are utilized as the source of raw water to produce water supply. DOM has been commonly quantified by using surrogate, nonspecific parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV- 254), specific ultraviolet absorbance (SUVA) and trihalomethane formation potential (THMFP) (USEPA,1999).

DOMs can be distinguished by fluorescent spectrometry wavelengths scanning of both excitation and emission, and obtained three-dimensional fluorescent spectroscopy results (fluorescent excitation-emission matrix, FEEM). FEEM provides information on the putative origin of fluorescent organic matter in water. It may identify the matter as a tyrosine-like substances, tryptophan-like substances, humic acid and fulvic acid-like substances, and so on (Nakajima et al. 2002; Chen et al. 2003; and Sierra et al. 2005). And Fourier transform infrared (FTIR) to identify the functional groups of DOM.

2.5.1 Dissolved Organic Carbon (DOC)

TOC is the measure of all organic substances contained in water samples including suspended fractions that could be removed by coagulation and sedimentation. DOC is defined as the fraction of TOC that passes through a 0.45 μm filter paper. Since some types of 0.45 μm filter paper are produced using cellulose nitrite or cellulose acetate membrane, organic substances could leach from these filter papers after the filtration process. Thus, GF/F filter paper with a pore size of 0.7 μm is used in DOC analysis.

2.5.2 Ultraviolet Absorbance at Wavelength 254 nm (UV-254)

UV-254 is used to provide an indication of the aggregate concentration of UV absorbing organic constituents, such as humic substances and various aromatic compounds (APHA, AWWA, WEF, 1995). As noted by Edzwald et al. (1985), humic aromatic compounds and molecules with conjugated double bonds absorb UV light, whereas simple aliphatic acids, alcohol, and sugars do not. Most research has utilized the measurement at the UV-visible at the wavelength of 254nm as the representative for the relative quantity of aromatic-humic organic substances (Leenheer and Croue, 2003). UV absorbance is a well-known technique for measuring the presence of naturally occurring organic matter such as humic substances. UV analysis is also affected by pH and turbidity (Edzwald *et al.,* 1985). UV absorption is a useful surrogate measure for DOM or precursor of THMs because humic substrates strongly absorb ultraviolet radiation (Eaton, 1995).

2.5.3 Specific Ultraviolet Absorption (SUVA)

The ratio between UV absorbance to DOC, referred to as specific ultraviolet absorbance (SUVA) (L/mg-m) demonstrates a relative index of humic content (Edzwald, 1993 and Owen *et al.,* 1993). SUVA could suggest the nature of DOM and its consequent THM formation (Krasner *et al.,* 1996). Higher SUVA values tend to indicate higher humic content. The SUVA of a humic sample depends upon the molecular weight of the substance (Petterson *et al.,* 1995). SUVA can be used as an indicator of its coagulation (or softening) ability to remove THM precursors. Water having a high SUVA value (SUVA > 3 L/mg-m) has been found to contain organic matter that is more humic-like in character, higher in AMW, and more readily removed by coagulation (Edzwald, 1993) whereas lower SUVA values (< 3 L/mg-m) indicate the presence of organic matter of lower AMW that is more fulvic-like in character and more difficult to remove. With regard to wastewater treatment plants, Fukushima et al. (1996) reported that the SUVA of total DOM increased as the lake water, influenced by pedogenic DOC, was allowed to further stabilize through biodegradation over a long period of time. Imai et al. (2002) reported that since a biological treatment was employed in sewage treatment plants, it should produce effluent water with higher SUVA values than that of influent wastewater.

2.5.4 Trihalomethanes Formation Potential (THMFP)

Trihalomethanes (THMs)

Trihalomethanes (THMs) were formed when chlorine reacted with naturally occurring humic substances in water treatment plants and water distribution systems. The first identification of chloro- and bromo-trihalomethanes (THMs) was done by Johannes Rook in 1974. The first class of halogenated disinfection by- products (DBPs) discovered in chlorinated drinking water. Since that time, the reduction of THMs has been the subject of intensive investigation in the water treatment field. Symon et al. (1975) described a survey of halogented organic compounds from 80 water supply plants. THMs have been found to be the most widespread organic contaminants in drinking water, and occur at higher concentrations than other disinfection by-products. The four THMs (chloroform, bromodichloroform, dibromochloroform and bromoform) are formed when chlorine-based disinfectants are added to source water with fairly high organic content, such as surface water. THMs are included among the 25 volatile organic compounds regulated under the Safe Drinking Water Act (SDWA) of 1987. These compounds are persistent and mobile, and pose a cancer risk to humans (Pereira, 1983; Munro *et al.,* 1986). Chloroform ($CHCl_3$), the most common THM, is a proven animal carcinogen and a suspected human carcinogen.

THMs can be taken in by drinking the water and breathing its vapors (for example when showering). They are then metabolized and eliminated rapidly. Most THMs are metabolized into a less-toxic form, but some are transformed into more reactive substances, especially at high concentrations. The THMs are absorbed, metabolized and eliminated rapidly by mammals after oral or inhalation exposure. Following absorption, the highest tissue concentrations are attained in the fat, liver and kidneys. THMs induce cytotoxicity in the liver and kidneys of rodents exposed to doses of about 0.5 mmol/kg of body weight. A maximum contaminant level (MCL) of 100 μg/L for total trihalomethanes (TTHMs) in finished drinking water was established by the US.Environmental Protection Agency (USEPA) in the National Interim Primary Drinking Water Regulations in 1979. The USEPA has set a new MCL of 80 μg/L for stage 1 of the disinfection by product rule (D/DBP Rule; USEPA 1998). In stage 2, the D/DBP Rule may lower the MCL for THMs to 40 μg/L.

Trihalomethanes Formation Potential (THMFP)

Total trihalomethanes (TTHMT) is the sum of all four compound concentrations, chloroform, bromodichloroform, dibromochloroform and bromoform, produced at any time T (usually measured in days). $TTHM_0$ is the total THMs concentration at the time of sampling. It can range between non-detectable to several hundred micrograms per liter if the samples have been chlorinated. $TTHM_7$ is the total concentration of all four THMs compounds produced during the reactions of the sample precursors with excess free chlorine over a 7-day reaction time at the standard reaction conditions, which were as follows: free chlorine residual at least 3 mg/L and not more than 5 mg/L at the end of a 7-day reaction (incubation) period with sample incubation temperature of 25±2°C, and pH controlled at 7±0.2°C with phosphate buffer. THMFP or ΔTHMFP is the difference between the final TTHMT concentration and the initial $TTHM_0$ concentration. For samples that do not contain chlorine at the time of sampling, $TTHM_0$ will be close to zero. Therefore the term THMFP may be used. For samples that contain chlorine at the time of sampling, a $TTHM_0$ value will be detected. Therefore the term ΔTHMFP may be used when reporting the difference between the TTHM concentrations (Standard method, 1995).

THMFP has also only been commonly employed to measure the DOM in water at drinking water supply facilities. The THMFP of treated wastewater has not been widely evaluated due to treated wastewater being perceived as less aromatic (Aieta, 1998). Nevertheless, treated wastewater seems to have much higher DOC concentrations than most surface water used as drinking water supplies. A survey of five wastewater treatment plants in southern California, USA demonstrated that DBPs in treated wastewater was found to be higher than that of influent wastewater (National Research Council, 1998). Musikavong *et al.,* (2005) reported that the level of THMFP in the treated wastewater of the industrial estate in northern Thailand was moderately high when compared with other surface waters in Thailand (Wattanachira *et al.,* 2003, Homklin 2004, Janhom 2004, Panyapinyopol et al. 2005; and Phumpaisanchai 2005).

2.5.5 Fluorescent Excitation-Emission Matrix, FEEM

Chen *et al,.* (2003) defined excitation and emission boundaries into five regions based largely upon supporting literature. FEEM peaks have been associated with humic-like, tyrosine-like, tryptophan-like, or phenol-like organic compounds. In general, 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). Peaks at intermediate excitation wavelengths (250 nm - 280 nm) and shorter emission wavelengths (<380 nm) are related to soluble microbial by product-like material (Region IV). 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, FEEM with minimum excitation wavelengths of 250 nm indicated shoulders of FEEM peaks located at shorter excitation wavelengths. Therefore, peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Region III).

Coble *et al.,* (1993) proposed that the fluorescent peak of humic-like and protein-like substances were at $230nm_{Ex}/420\text{-}450nm_{Em}$ and $340nm_{Ex}/420\text{-}450nm_{Em}$, and $220nm_{Ex}/300\text{-}340nm_{Em}$ and $275nm_{Ex}/300\text{-}340nm_{Em}$, 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 ($275nm_{Ex}/310nm_{Em}$), tryptophan-like and protein-like ($275nm_{Ex}/340nm_{Em}$), humic-like ($260nm_{Ex}/380\text{-}460nm_{Em}$), marine humic-like ($312nm_{Ex}/380\text{-}420nm_{Em}$) and humic-like ($250nm_{Ex}/420\text{-}480nm_{Em}$).

Leenheer and Croue (2003) presented the major fluorescent components in a FEEM. Humic-like substances exhibited fluorescent peaks at 330-350nm$_{Ex}$/420-480nm$_{Em}$ and 250-260nm$_{Ex}$/380-480nm$_{Em}$, whereas the fluorescent peak of marine humic-like substances was found at 310-320nm$_{Ex}$/380-420nm$_{Em}$. Protein-like and tyrosine-like substances exhibited a fluorescent peak at 270-280nm$_{Ex}$/300-320nm$_{Em}$, while tyrptophan-like substances exhibited a fluorescent peak at 270-280nm$_{Ex}$/320-350nm$_{Em}$.

Janhom (2004) characterized the fluorescent organic matter in reservoir water of the Northern-Region Industrial Estate, Lumphun province, Thailand. A fluorescent peak at 275nmEx/410nmEm representing humic-like substances was detected.

Sierra *et al.,* (2005) used single-scan and FEEM techniques to identify the fluorescent fingerprints of fulvic and humic acids from various origins. They noted that the in the case of fulvic acids, the Ex/Em pairs were approximately 260nmEx/460nmEm and 310nmEx/440nmEm, whereas in the case of humic acids, their excitation and emission maxima were red-shifted. The corresponding Ex/Em pairs were located at approximately 265nmEx/525nmEm and 360nmEx/520nmEm.

Phumpaisanchai (2005) used the FEEM to characterize the fluorescent organic matter in water from the Mae-Hia reservoir, Chiang Mai province and Bhumibol Dam reservoir in Tak province, Thailand. Fluorescent peaks at 260nmEx/420nmEm and 330nmEx/400nmEm were detected in the water from the Mae-Hia reservoir, whereas fluorescent peaks at 260nmEx/420nmEm and 330nmEx/410nmEm were found in the water from the Bhumibol Dam reservoir. These observation lead to the conclusion that, humic acid-like and fulvic acid-like substances were the major fluorescent organic matter in both the Mae-Hia reservoir and Bhumibol Dam reservoir.

Musikavong *et al.,* (2005) demonstrated correlations of THMFP and fluorescent intensity of the influent wastewater and water samples from each pond at the wastewater treatment plant of the Northern Region Industrial Estate, Lamphun, Thailand. Their reported results showed that FEEM could be used to quantify the THMFP in the water source.

2.5.6 Fourier Transform Infrared (FTIR)

A large number of research works have been allocated to the identification of functional groups that could potentially lead to the formation of disinfection by-products as this helped in the future development of the abatement technology to prevent the formation of such compounds, e.g. amino acid, aromatic characteristic organics, etc. In the interpretation of the functional groups, Fourier transform infrared (FTIR) is a crucial instrument. FTIR has been widely used for the structural investigation of humic substances. Samples exposed to infrared light absorb energy corresponding to the vibrational energy of atomic bonds. The resulting absorption spectrum is a unique fingerprint of compound. FTIR analysis allowed the identification of inorganic and organic functional groups as well as elemental composition.

2.6 Membrane Filtration for DOM Removal

Lee *et al.,* (2004) reported that the ceramic tight-UF membranes exhibited the potential to more effectively remove DBP precursors than natural organic matter in terms of DOC, versus the tested polymeric membranes proved to be very effective at removing DBP precursors, compared with DOM with respect to DOC and UVA. Filtration using ceramic membranes is rarely used in drinking water compared to polymeric membranes, though a titanium dioxide nanofiltration (NF) membrane was tested to effectively reject mono- and di-valent anions by charge interaction between the negative-charged membrane surface and the anions (Puhlfur *et al.,* 2000).

Ates *et al.,* (2009) reported that hollow fiber UF process could remove DOM in terms of UV-254 and DOC for 74% and 61%, respectively.

2.7 DOM Removal by Coagulation

The removal of organic contaminants by the coagulation process has been studied for decades. Most of the work shows that coagulation substantially reduces the concentration of organic particles; a primary type being components of DOM (Randtke, 1988). It is difficult to predict the percentage removal of DOM from surface waters with coagulation, as it depends on a variety of conditions such as organic matter characteristics and operating conditions. Removal of particulate DOM is achieved primarily through colloidal destabilization, followed by sedimentation and filtration (Randtke, 1988). DOM is traditionally removed by coagulation with the trivalent Al and/or Fe metal ions. The coagulation mechanisms that are thought to dominate with regards to DOM removal are charge neutralization for colloidal material and charge complexation for soluble compounds (Sharp *et al.,* 2006).

In general, the process is maximized under similar conditions that also provide maximum turbidity removal, although maximum turbidity removal can also be achieved over a broader range of conditions. This occurs under acidic conditions with a pH in the range of 4.5-5.5 for iron based coagulants and 5.5-6.5 for aluminum based coagulants (Sharp *et al.,* 2006). Dissolved NOM removals by coagulation ranged between 10 and 90 %, with an average removal of about 30 %. Greater removals were seen when more highly colored waters containing organic matter of higher molecular weight were being treated with a metal coagulant.

In summary, it was concluded that there was not a substantial difference between aluminum and iron based salts. The coagulant dose plays a very important role in the removal of DOM, generally following one of two patterns. In the one case, the removal increases very quickly within a given range of coagulant dose, and then the concentration stabilizes after that. The second pattern showed that the concentration decreases very gradually, eventually reaching an optimum removal at a much higher concentration than that for the first behavior type (Randtke, 1988).

Several other experimentally based research projects have been undertaken, yielding several conclusions that helped to further the understanding of what effect coagulation has on the removal of DOM in any given source water. The use of specific ultraviolet absorbance (SUVA) as an indicator of the nature of the DOM and the effectiveness of the coagulation process has been explored very thoroughly (Edzwald *et al.,* 1999). SUVA is defined as the normalized UV absorbance of a water sample with respect to the DOC concentration. It is expressed in units of m-1 of absorbance per mg/L of DOC (Weishaar *et al.,* 2003).

The humics based portion of the NOM was characterized based on the corresponding SUVA values. Waters with high concentrations of aquatic humics generally have high SUVA values, rising as high as 6-7 L/mg.m). Removal of 50 % or greater is expected for such waters using aluminum based coagulants such as alum or PACl. As the SUVA value of a given water source decreases, so should the removal capacity of the coagulant. Waters that display a SUVA value less than 3.0 generally correspond to removals of less than 30 % (Weishaar *et al.,* 2003).

2.8 Background on the Use of Pre-Coagulation of DOM to Low Pressure Membrane System

When the drinking water industry began to utilize membrane filtration, the water sources being treated with membranes were generally high quality, low turbidity lakes that required minimal treatment (Howe and Clark, 2006). Membranes were able to stand alone, and provide high quality effluent, without the need to integrate other treatment processes. With the high level of success, membrane treatment processes are being implemented for lower quality water sources that required more extensive treatment, and as a result coagulation pre-treatment for membrane filtration is now becoming more common.

The results obtained from research evaluating coagulation as a pre-treatment to low pressure membrane filtration has been inconsistent in quantifying its effects on fouling and flux decline. Several studies have shown improved membrane performance, while others have shown decreased membrane performance. Several studies have shown that the use of coagulation has the potential to either stabilize or improve permeate flux across the membrane surface, while others have shown that the coagulant addition contributes further to the undesirable fouling phenomenon.

Howe and Clark (2006) conducted a study to further understand the effect of pre-coagulation. Their primary objective was to evaluate the effect of coagulant type, its dose, and application conditions on membrane performance. Five different natural surface waters were used, coupled with three different membrane materials. After all of the results were combined, it was concluded that coagulant dose was the most significant factor in determining the severity of fouling, and in turn whether the membrane performance was better or worse. At low doses, the membrane fouling was worse when compared with no coagulant. These doses were generally coupled with minimal floc formation.

Enhanced coagulation has been implemented in pre-treatment research by several authors. As previously mentioned, it is the removal of DOM under conditions of high coagulant dosages, combined with a low pH in the range of 4-6 (AWWA, 2005). It is important to note that elevated coagulant doses will contribute to a reduced pH level. Alum consumes 0.5 mg/L of alkalinity as $CaCO_3$ for each mg/L of alum; each mg/L of ferric chloride consumes 0.93 mg/L of alkalinity as $CaCO_3$. If the dose of alum and/or ferric chloride is increased beyond the available alkalinity it could result in a small concentration of coagulant passing through the treatment process. This occurs because the alkalinity helps to limit the reduction in pH and once it is consumed the lower pH may lead to an increased concentration of dissolved metal than can move downstream to the next treatment stage. When a dose that induces enhanced coagulation was used, the membrane performance was also improved for all coagulants. The third major conclusion that came out of this research was the fact that there exists a linear relationship between the quantity of DOC removed and the increased membrane performance. This conclusion was independent of coagulant type, as whichever one was most effective at removing DOC in given water source was also most efficient at improving membrane fouling.

Maartens *et al.,* (1999) studied the reduction in fouling of polysulfone UF membranes used for the purification of natural brown water, collected from Suurbraak, in the Southern Cape of South Africa. The raw water was pre-treated by coagulation and by changing the pH of the feed solution. The research showed that the pH of the feed water has a significant influence on the adsorption of NOM onto the membrane surface. The lowest adsorption occurred at a feed water pH of 7. At this pH level, NOM molecules contained equal amounts of COO- and COOH groups (quantified using a non-aqueous titration method) resulting in a very stable conformation of NOM which lowered the interactive forces between the membrane surface and the foulant molecules. The UF membrane yielded the best performance at this pH value in terms of permeate flux, colour rejection and foulant adsorption. Direct filtration eliminates the use of a flocculation tank, coupled with a reduced coagulant dose. The raw water develops pinpoint flocs while traveling towards the membrane surface, much smaller than the conventional floc formation that occurs in a flocculation tank. Direct filtration treatment of the raw water with the metal ion coagulants decreased overall system performance, by increasing the rate at which the membrane fouled, and increasing the frequency of backwash and chemical cleaning. Therefore it was concluded that no obvious advantages were obtained by this pre-treatment method.

Kabsch-Korbutowicz (2006) studied the pre-coagulation of natural water flowing from the Great Batorow Peatbag River in Poland, followed by membrane filtration using polyethersulphone and regenerated cellulose UF membranes. Pre-coagulation of the feed water with aluminum based coagulants improved the elimination of NOM substances by approximately 15-20 %. The highest removals were observed when PACl products were used, with values ranging between 20-25 % improvements over experiments completed without the pre-coagulation. The highest membrane permeability was observed when alum was used. More importantly, the NOM removal and fouling results were proportional, and therefore the system could be optimized to meet the requirements of both system components. The coagulant dose had a significant impact on the permeate flux of the membranes as well. At low Al doses that would normally not be used if coagulation was the sole treatment process, membrane fouling was higher in comparison to water that was not exposed to any pre-treatment step. Laine *et al.,* (1999) performed similar experiments with regenerated cellulose membranes, discovering elevated concentrations of PACl products yielded a more consistent flux across the membrane surface, and in turn reduced the degree of fouling that occurred.

Kimura *et al.,* (2005) studied the use of pre-coagulation with sedimentation as a pre-treatment to pilot scale polysulfone UF plant at an existing drinking water treatment facility in Ebetsu, Japan. The effect of metal based pre-coagulation on irreversible membrane fouling was studied and compared to a previous study performed (Kimura *et al.,* 2004) where a similar type of membrane effluent was used as a drinking water source. The study performed in 2004 investigated the water permeability consistency using a chemical cleaning process, and analyzed the composition of the membrane fouling components that desorbed from the membrane after the cleaning cycle. The study concluded that polysaccharide-like organic compounds were primarily responsible for the inducement of irreversible fouling. The results observed using this raw water source, supported the fact that pre-coagulation in some cases would not be effective in mitigating irreversible fouling, as coagulation does not target polysaccharides efficiently. The second study incorporated coagulation, showing very positive results. The pre-treatment significantly mitigated the organic membrane fouling, mainly by reducing the concentration of components that had the potential to cause reversible fouling, which was largely composed of DOM. The study did re-emphasize that irreversible fouling cannot be mitigated with the use of coagulation as pre-treatment to UF membranes (Kimura *et al.,* 2005).

Several other authors have suggested that coagulation, whether it is with sedimentation or direct filtration (i.e. without sedimentation), induced membrane fouling. Shrive *et al.,* (1999) performed a pilot scale membrane trial using water taken from the Ohio River with polypropylene microfiltration membranes. The purpose of these experiments was to assess the degree of fouling of the membrane when exposed to a water source that was purposely under dosed (1-5mg/L) with alum or PACl. The experiments were performed with sedimentation and in-line coagulation to observe the difference it made on the membrane fouling as well. A large decrease in flux was observed for all coagulants during the in-line coagulation as a pre-treatment, while much less of a decline was observed when coagulation was coupled with sedimentation.

Karimi et al., (1999) observed very similar results when pre-treating feed water to a polypropylene ultra-filtration membrane with 3-5 mg/L of ferric chloride. The treated surface water taken from the Californian interior accelerated the rate of fouling, as observed by increasing trans-membrane pressure. In some cases, the use of a coagulation pre-treatment process not only accelerates the rate of fouling, but also substantially increases the cost of the overall system, in some cases making it prohibitive to implement. Schäfer *et al.,* (2001) concluded in a polypropylene membrane study that pre-treating water containing Suwannee River humic and fulvic acid solutions with ferric chloride significantly increased fouling of micro and ultra-filtration pilot scale membranes. The coagulant dose would also increase the operating cost of the system, emphasizing that the correct dose is crucial to both the efficiency of the system and the overall cost.

Guigui et al. (2002) reported that good conventional coagulation conditions in terms of coagulant type, dose and pH should also provide good performance and final water quality for in-line coagulation with UF. UF membranes also shown to remove DBP precursors up to 30% and addition of organic polymers and chemical coagulants upstream of UF enhances DOM removal (Siddiqui *et al.,* 2000). A hybrid process of ultrafiltration with in-line coagulation improved the removal of natural humic acids greatly compared to direct UF, such as pre-coagulation at pH 7, DOC and UV removals were increased from 28% to 53% and 40% to 78% respectively and In-line coagulation also reduced the rate of membrane fouling and resulted in more constant permeate flux and very slight increase of transmembrane pressure during a filtration circle. (Wang *et al.,* 2006).

In some cases, the results achieved through the study of coagulation pre-treatment were not so much inconclusive, but more so the fact that similar results could have been achieved with a simpler process. Carroll et al. (2000) found that pre-treating water prior to micro-filtration using a polypropylene membrane with 35 mg/L of alum reduced the quantity of reversible fouling by a substantial amount. Moreover, it was discovered that similar results could be achieved by filtering the feed water through a 0.2 μm filter, in doing so removing the particulates that were contained in the water. This comparative worked highlighted the fact that the coagulation in this case was successful at removing particulate foulants, but had no noticeable effect on the dissolved material. Comparing these findings to those of Howe and Clark (2006), several contrasts were observed. The latter work concluded that coagulant dose was the most important factor in quantifying fouling, rather than the state of composition of the TOC in the feed water. Maartens *et al.,* (1999) stated that certain types of fouling cannot be mitigated at all with coagulation pre-treatment, and therefore attention should be focused on other aspects of the experimental design, in hopes of reducing membrane fouling. However, it is worth noting that Howe and Clark (2006) emphasized that an enhanced coagulation process (reduced pH) will yield improved permeate flux, and should be used as a base-lime for future coagulation pretreatment experiments.

2.9 The Future of Low Pressure Membrane Systems

Membrane technology for drinking water applications has the potential to be the most promising development in water treatment, as it could provide permeate quality that exceeds the present regulatory requirements for drinking water consumption (Farahbakhsh *et al.,* 2004). The technology itself will gain more popularity and research-driven membrane trials will yield more efficient full-scale systems that require less energy input, coupled with membrane modules that have extended life expectancies. (Zularisam *et al.,* 2006).

There are still a variety of problems that limit the expansion of membrane technology: the primary one being the fouling phenomenon. In the 21st century, further understanding is required into what fractions of NOM contribute to fouling most, and one can improve process design and operating conditions to minimize this effect. Just as important are issues such as membrane surface area and robustness, the cost of the operation and maintenance associated with the required high trans-membrane pressure, and the cost of chemicals required cleaning the membranes. However, these problems should not be considered a downfall to the further advancement of the technology, but rather as reasons to come up with methods of improvement and optimization. Zularisam *et al*., (2006) stresses that there is need for further research and development of new membrane materials that are more resistant to both chemical cleaning and mechanical wear and tear. The improvement of cleaning strategies and reduced energy costs will help to increase implementation and improve sustainability of membrane systems. Experts most familiar with membrane filtration processes predict that future low pressure membrane systems will be larger in capacity with smaller footprints, therefore increasing the available surface area, while reducing the overall space requirement. One way in which membrane treatment technologies will be improved in the future, is by integrating them with other processes such as coagulation pre-treatment. Government guidelines and regulations governing the use of membrane filtration are expected to expand, and become more standardized, so that researchers, manufacturers and plant operators alike can be on the same page with respect to the implementation of techniques for reducing membrane fouling. The applicability of these systems is also expected to expand, as studies have proved in many cases that membrane systems are the preferred option for pathogen and DOM removal.

CHAPTER 3

METHODOLOGY

3.1 Studied Site

3.1.1 U-Tapao Canal

U-Tapao Canal is the main canal of Songkhla lake basin in southern Thailand. It originates from the Sankarakiri Mountain Range and the Khao Ban Thad Mountain Range in Songkhla province which has 90 kilometers long and it has a capacity of about $2,160\times10^3$ cubic meter. U-Tapao Canal collects natural and discharged water from rural areas and from Hat Yai City and drain into Songkhla Lake. Besides, it is also a main raw water source for water supplied production in urban and local area. As shown in Figure 3.1 and Figure 3.2, the selected sampling point situated at the pumping station of a water treatment plant in Hat Yai Provincial Waterworks Authority, Songkhla province (UTM 661975 772906).

Figure 3.1 Sampling site at a pumping station, Hat Yai Provincial Waterworks Authority

Figure 3.2 Sampling site at a pumping station, Hat Yai Provincial Waterworks Authority

3.1.2 Sri-Trang Reservoir

Sri-Trang reservoir is located in the Prince of Songkla University (PSU), Songkhla Province, Thailand which has the low turbidity in range of 3-14 NTU throughout a year (Kueseng *et al.,* 2009). It was constructed to purpose of collecting runoff from the mountain and rain water with a maximum capacity of 500,000 m^3 for using as a raw water source in PSU water treatment plant where produce a water supply approximately 1,500-3,000 m^3/day to the communities, faculties, offices and dormitories that are located in the area of the campus. Water samples from Sri-Trang reservoir were taken at the pumping station of the PSU water treatment plant (UTM 666327 774845) as shown in Figure 3.3.

Figure 3.3 Sampling point at Sri-Trang Reservoir, Prince of Songkhla University

3.2 Sample Collection and Preservation

The raw water samples were collected at pumping stations from U-Tapao Canal in Hat Yai water treatment plant and from Sri-Trang Reservoir in PSU, Hat Yai campus for 2 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 season. The collected water samples were preserved at a temperature of 4 °C until the experiments.

3.3 Procedure

3.3.1 Experiment Procedure

The experimental procedures are shown in the following steps and conclusively described in the diagram in Figure 3.4.

1. All of raw 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 (FEEM), and fourier transform infrared (FTIR) .The filtered waters were kept at 4°C until they were analyzed.

2. Subsequently, resin adsorption procedures were used to fractionate five liters of the filtered water into three dissolved organic matter (DOM) fractions; namely hydrophobic (HPO)and hydrophilic (HPI) fraction. The two DOM fractions were analyzed for their UV-254, DOC, SUVA, FEEM, FTIR and THMFP.
3. Raw water samples were divided into 2 portions:
   - Portion 1: For hybrid ultrafiltration (UF) with pore size of 0.008 μm combined with microfiltration (MF) with pore size of 0.2 μm as a pre - treatment experiment and its fractionated water analysis.
   - Portion 2: For hybrid ultrafiltration (UF) combined with coagulation as a pre-treatment experiment and its fractionated water analysis.
4. Two different techniques of raw water pre-treatment were conducted prior to UF process including coagulation and MF process for comparing the efficiency of turbidity and DOM reduction.
5. Analytical parameters of water samples from two portions were turbidity, alkalinity UV-254, DOC, SUVA, FEEM, FTIR and THMFP.
6. The water samples from two portions were then fractionated into two fractions. The two DOM fractions were analyzed for their UV-254, DOC, SUVA, FEEM, FTIR and THMFP.

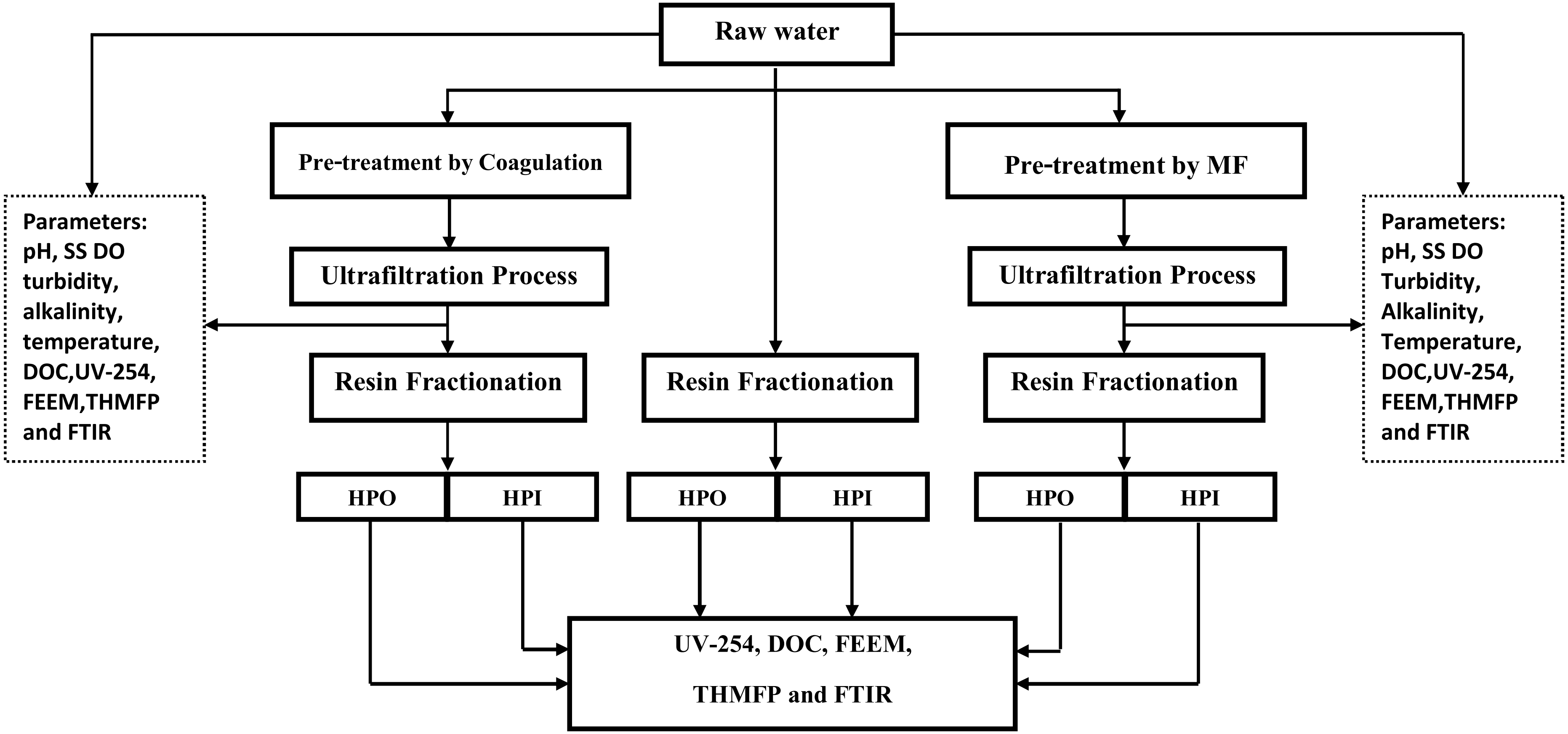


Figure 3.4 Diagram of experimental procedure of water samples

3.3.2 Membrane Modules

The immerseble polysulfone hollow fiber microfiltration membrane (MF) model MF2505Mi with pores size of 0.1 μm and ultrafiltration membrane (UF) Model UF2505Mi with a nominal pores size of 0.008 μm operating in an outside/in and dead end filtration mode provided by Polymem, France, were used in this study. The characteristics of the membrane module have been presented in Table 3.1 and Figure 3.5.

Each new membrane as received from the manufacturer was vacuum sealed in a plastic wrapping that contained a thin coating of glycerin on the interior, so as to ensure the membrane fibers remained moist during transportation and storage. Prior to use, membranes were cleaning by running deionized water (DI) through them for at least 1 hour and soak in 0.1 N NaOH solutions for 30 minutes following by rinsing with deionized water, to ensure all residual glycerin was removed. After being used, the membranes were cleaned by submerging them in a 200 mg/L sodium hypochlorite (NaOCl) solution for 5-7 h, and then rinsed with DI water. Membranes were cleaned after each trial, and stored in ultra-pure water in the refrigerator for future use. The TMP of each membrane was checked before the experiment.

Table 3.1 Characteristic of membrane modules

Items	**Membrane Module**	
	UF2505M1i	**MF2505Mi**
Membrane Area (m^2)	0.38	
MWCO (Da)	10,000	-
Pore size (μm)	0.008	0.1
Permeability pure water @20°C (l/h.m^2.b)	100	1,000
Maximum transmembrane Pressure (bars @20°C)	-0.7	
Membrane Material	Polysulfone	
Vessel Material	U-PVC	

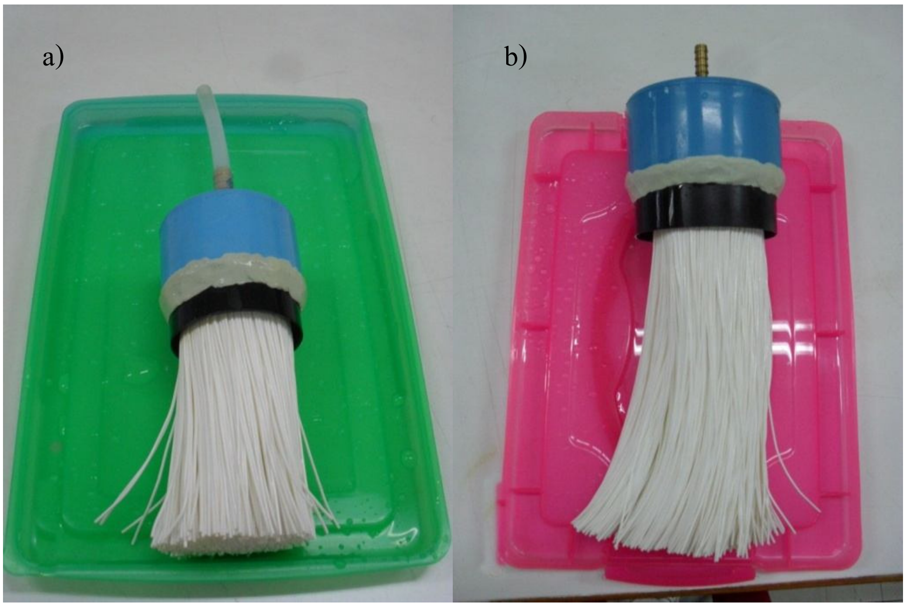


Figure 3.5 Hollow fiber membrane modules a) ultrafiltration membrane (UF) and b) microfiltration membrane (MF)

3.3.3 Pre-treatment Methods

Two different techniques of raw water pre-treatment were conducted prior to UF process including coagulation and MF process for comparing the efficiency of turbidity and DOM reduction.

3.3.3.1 Coagulation Experiment

Most coagulation processes in water treatment generally use alum as coagulant in order to mainly remove turbidity in water. Therefore, PACl may be suitable for DOM removal and its THMFP reduction in water.

The experiment utilized a multistage stirrer apparatus and simultaneous tests were conducted. The water samples entered in each jar were pH adjusted to each desired pH level. They were then placed on Phipps and Bird Jar-Tester as shown in Figure 3.6, coagulating with a rapid mix at 100 rpm for one minute, flocculating at 30 rpm for 30 minutes and settling for 1 hour. The desired PACl doses were added during rapid mixing at high speeds. Concurrently, lime or caustic soda was added if necessary, to maintain pH in low alkalinity water when pH control was desired. After a given time of Jar-Test cessation and floc formation, the supernatant samples were split into 2 portions. The coagulated water samples from portion 1 were filtered through 0.7 μm GF/F filter paper prior to determine their turbidity, alkalinity, DOC, UV-254, SUVA and FEEM. And coagulated water samples from portion 2 were use for ultrafiltration experiment.

Polyaluminum Chloride (PACl) typically in powder form was used in this study as a chemical coagulant. The coagulation process used 40 mg/L PACl for raw water from U-Tapao Canal and 20 mg/L PACl for raw water from Sri-Trang Reservoir as coagulants and controlled pH at 7 operating by Jar Test.

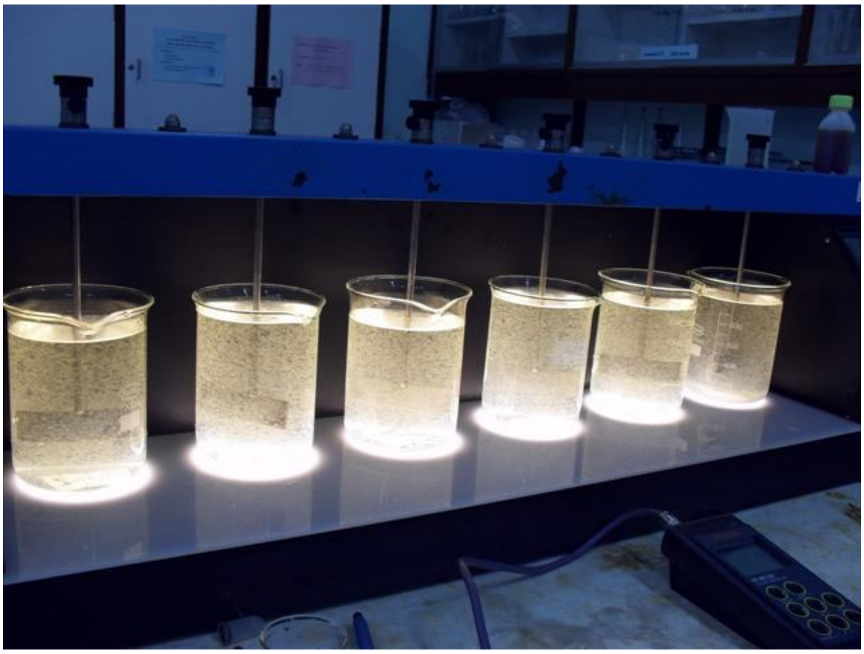


Figure 3.6 The experimental jar-test apparatus

3.3.3.2 Microfiltration Experiment

For microfiltration process (MF), raw water was sucked from the outside to inside of membrane with transmembrane pressure of - 0.18 bars. Then, the pre-treated water was analyzed for water quality and DOM reduction prior to UF process.

3.3.4 The Operation of Ultrafiltration

The lab-scale UF dead-end filtration experiment was conducted as shown in Figure 3.7. The UF membrane module was immersed in a reactor vertically. The reactor which has effective volume of 1 liter was fed with pre-treated water through a constant level tank and the effluent was drawn directly from the membrane module in outside-in operation by using a suction pump. A vacuum gauge was set between membrane module and the suction pump to monitor the transmembrane pressure (TMP).

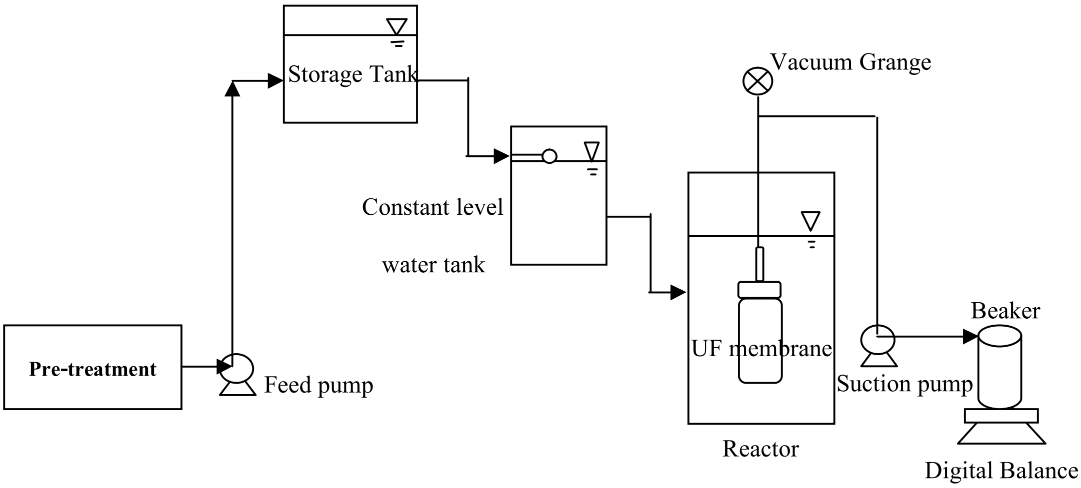


Figure 3.7 Schematic of ultrafiltration process

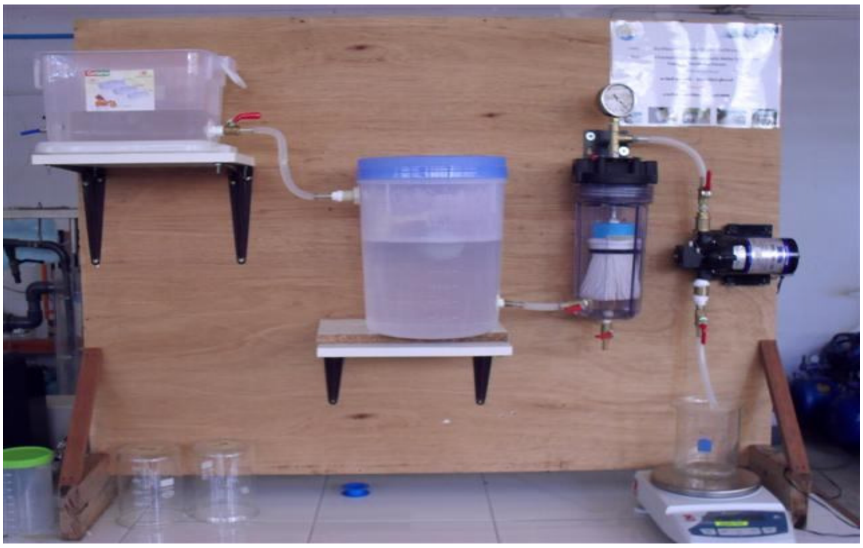


Figure 3.8 The pictorial of experimental set-up of ultrafiltration process

3.3.5 Flux Measurement

The permeate flux was measured as a function of time at a constant pressure of -0.2 bars for 120 minutes and the permeate volume was determined using a digital balance.

Initial flux was measured by measuring the filtration time of 1 liter of DI water (average value from 2-3 times) by the controlled pressure at -0.2 bars. The initial flux measurement was performed before sample filtration of every experiment in order to check membrane fouling after the chemical cleaning process (not less than 90% recovery). Similarly, water sample flux was measured as the same procedure as the initial flux measurement.

3.3.6 Resin Fractionation Procedure

The resin fraction procedures were used to fractionate five liters of filtered water into two dissolved organic matter (DOM) fractions; namely the hydrophobic (HPO) and hydrophilic (HPI) fractions by using a DAX-8 resin (Leenheer, 1981). The two DOM fractions were analyzed for their UV-254, DOC, THMFP, FEEM and FTIR. The diagram of the resin fractionation procedure (Marhaba, Pu, and Bengraine, 2003) is presented in Figure 3.9 and the specification of resin is described as follows:

DAX-8:

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

The water samples were acidified to pH 2 and passed through DAX-8 column by the flow rate slower than 12 bed volumes/hr. The effluent from DAX-8 resin is defined as HPI fraction. After all samples were run through the columns, each column was separately back eluted with 0.1 N NaOH for 0.25 bed volumes followed by 0.01 N NaOH for 1.25 bed volumes/hr. The eluted from DAX-8 is defined as HPO.

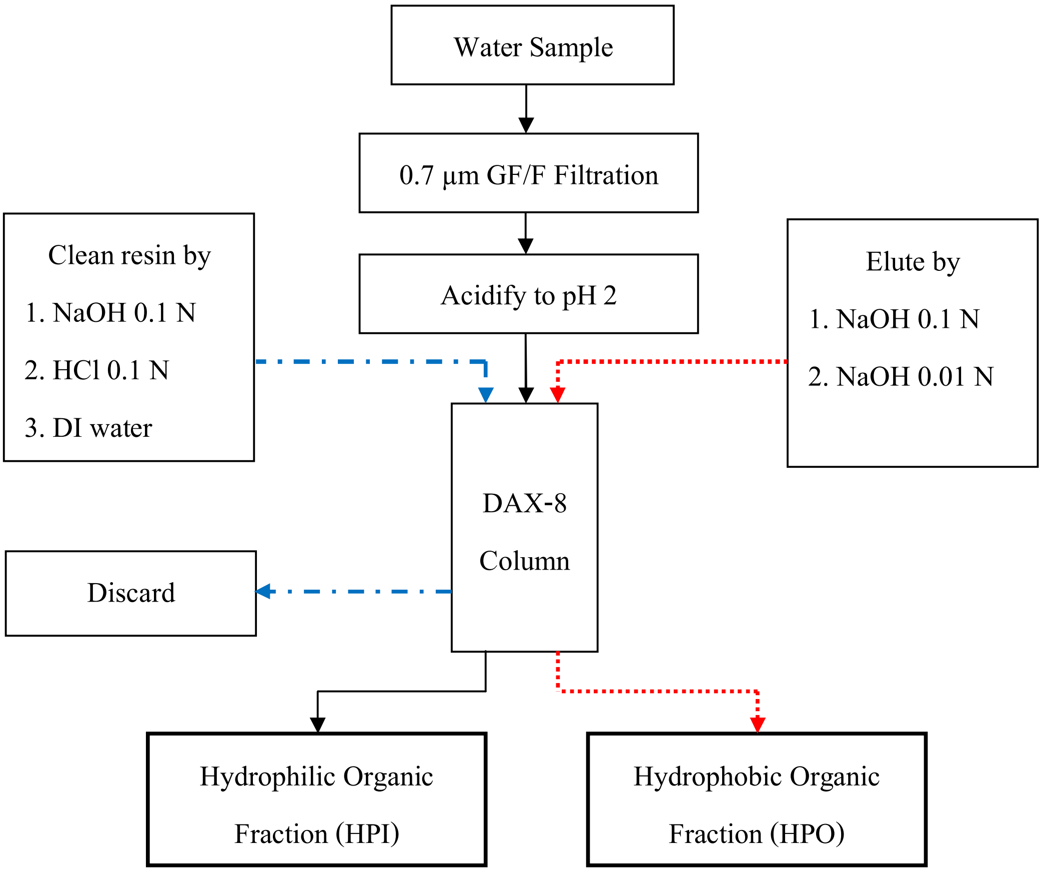


Figure 3.9 Resin fractionation procedures

3.3.5.2 Resin Preparation

DAX-8

- Refine the resin with 0.1 N NaOH for 24 h.
- Rinse the resin with DI water to remove NaOH
- Purify the resin by acetone for 24 h in a set of Soxhlet extraction apparatus
- Purify the resin by 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 DI water respectively, until the DOC and conductivity of the effluent water is less than 0.1 mg/L and 10 µs/cm, respectively.

3.4 Analytical Methods

3.4.1 Physico-chemical Parameters

The water samples were analyzed for pH, turbidity, alkalinity, UV-254, DOC, SUVA, FEEM, FTIR and THMFP. The summary of analytical methods and standards used for analyzing the mentioned parameters demonstrated in Table 3.3. These parameters are described below.

The analyzed parameters were done by duplicate samples. The results of these analyses should be within ±5%, or corrective action is necessary.

3.4.1.1 pH

pH was directly measured by a Model F-21 Horibra pH-meter with an accuracy of ± 0.01 pH unit. The unit was daily calibrated with buffer solutions at pH 4.00, 7.00 and 9.00.

3.4.1.2 Temperature

Temperature was directly measured by Horiba Thermometer, Model D-13E.

3.4.1.3 Turbidity

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

3.4.1.4 Alkalinity

Alkalinity was measured in accordance with Standard Method 2320 B.

3.4.1.5 Suspended Solids

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

3.4.1.6 Dissolved Oxygen

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

3.4.2 DOM Parameters

3.4.2.1 DOC

The samples were filtered through a combusted 0.7 μm GF/F filter paper prior to measurement by O.I. analytical 1010 TOC Analyzer. DOC of water samples were measured in accordance with standard method 5310 Total Organic Carbon (TOC); section 5310 C Persulfate-Ultraviolet Oxidation Method.

3.4.2.2 UV-254 nm

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 H_2SO4 prior to the measurement.

3.4.2.3 Specific Ultraviolet Absorption (SUVA)

Specific UV absorbance (SUVA) (Lm^{-1} mgC^{-1}) was calculated as the ratio of UV absorbance at 254 nm to DOC value in $mgCL^{-1}$

3.4.2.4 Fluorescence Excitation-Emission Matrix (FEEM)

FEEM is the total sum of emission spectra of a sample at different excitation wavelengths, recorded as a matrix of fluorescent intensity in coordinates of Excitation (Ex) and Emission (Em) wavelengths, in a definite spectral window. FEEM represent in physical signatures by JASCO FP-6200 Spectrofluorometer.

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 and HPI fractions from the resin fractionation process were diluted with DI water to their original DOCs, which was calculated by using the mass balance from the resin fractionation results. The two DOM fractions were then adjusted to a pH of about 7±0.2.

Quinine Sulfate Standard

The quinine sulfate $[(C_{20}H_{24}N_2O_2)_2H_2SO_42H_2O]$ 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 μg/L of quinine sulfate solution at 450 nm with an excitation wavelength of 345 nm (Kasuga *et al*., 2003).

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: Fast
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

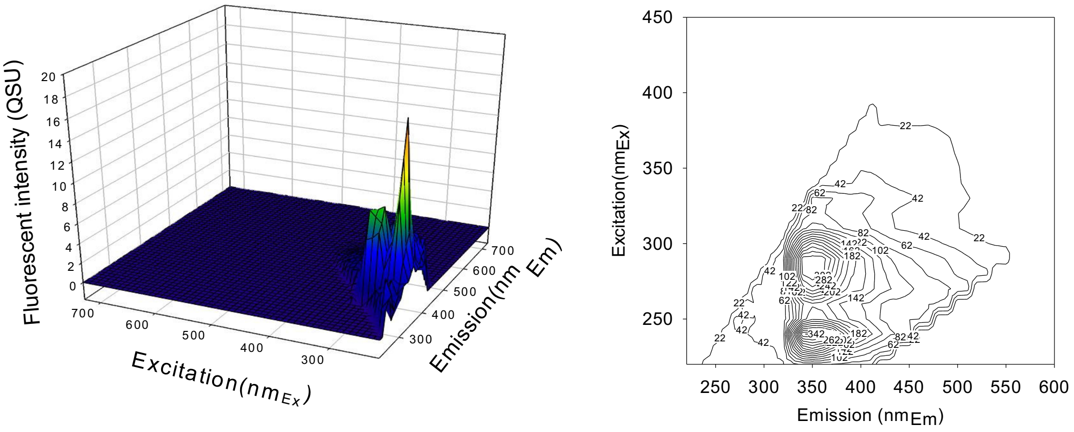
FEEM measurement procedure

- Check the Raman Test Photometric Stability. The value should be less than ±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 DI water.
- Measure the FEEM of the water samples
- Subtract the FEEM of the water samples with the FEEM of the DI 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 X 2 $\leq$ Em (Komatsu *et al.,* 2005)
- Remove the Rayleight and Raman scattering peaks at Em ± 10-15nm of each Ex (Zepp *et al.,* 2004)

FEEM interpretation

FEEM can provide information on the putative origin of fluorescent organic matter of DOM in water.

Moreover, fluorescent excitation-emission wavelengths that exhibited fluorescent emission intensities were classified as fluorescent peaks as illustrated in Figure 3.10. In this study, the use of FEEM fluorescent emission intensities at peak position was utilized to evaluate the reduction of fluorescent organic matter of DOM after treatment process.



a)

b)

Figure 3.10 Sample of the Fluorescent Excitation-Emission Matrix (FEEM) a) the three-dimensional view and b) contour view (contour interval of 2 QSU) with fluorescent peaks and its sections of a FEEM

3.4.2.5 FT-IR

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

3.4.2.6 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*-dechthyl-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)

At least two replications of each measurement for the THMFP analysis were performed and DI 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 3.2 HP 6890 GC method condition analyze THMs

Manufacture name/model	**HP 6890 GC**
Inlet conditions	Mode: Split Initial temp: 225 ºC Pressure: 31.14 psi Split ration: 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 um Film thickness: 0.25 um Mode: constant flow Initial flow: 9.6 mL/min Init pressure: 31.15 psi
Detector	ECD Temperature: 300 ºC Mode: Constant make up flow Make up flow: 60.0 mL/min Make up Gas type: Nitrogen
Injection temperature	225 ºC
Initial temperature	60 ºC initial time 1.00 min
Temperature program	10 ºC/minute to 100 ºC 1 minute 10 ºC/minute to 130 ºC 1 minute 10 ºC/minute to 180 ºC 1 minute
Final time duration	16 minute

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 oC	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

CHAPTER 4

CHARACTERISTICS OF RAW WATER AND DOM REDUCTION BY DIFFERENCE PRE-TREATMENT TECHNIQUES

4.1 Characteristics of Sri-Trang Reservoir Water and U-Tapao Canal Water

The summary of the characteristics of raw water from Sri-Trang Reservoir and U-Tapao Canal during the period in rainy season (2009) and dry season (2010) is presented in Table 4.1.

Table 4.1 Characteristics of raw water from Sri-Trang Reservoir and U-Tapao Canal

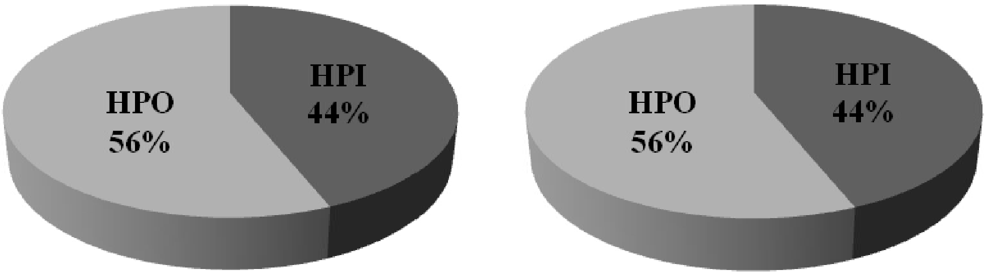
Parameters	Sri-Trang Reservoir		U-Tapao Canal	
	Rainy Season	**Dry Season**	**Rainy Season**	**Dry Season**
pH	7.01±0.03	7.05±0.03	6.85±0.11	7.19±0.02
Alkalinity (mg/Las $CaCO_3$)	8.33±0.58	9.00±1.00	9.70±0.58	11.0±1.00
Conductivity (s/cm)	49.9±1.16	51.5±1.12	57.9±0.96	51.5±1.12
Turbidity (NTU)	8.03±0.18	8.42±0.04	40.0±2.00	23.0±2.00
UV-254 (cm^{-1})	0.05±0.01	0.07±0.01	0.19±0.01	0.15±0.01
DOC (mg/L)	4.08±0.18	4.55±0.17	9.77±0.15	6.13±0.06
SUVA (L/mg-m)	1.24±0.14	1.51±0.10	1.90±0.01	2.46±5.41

As shown in Table 4.1, the average pH of Sri-Trang Reservoir and U-Tapao Canal water in rainy season and dry season were 7.01, 7.05 and 6.85, 7.19, respectively. And alkalinity values were 8.33, 9.0 and 9.7, 11.0 mg $CaCO_3$/L, respectively. It can be noticed that pH of the two raw water sources was nearly neutral which is suitable for coagulation whereas alkalinity was slightly low in both seasons (< 20 mg $CaCO_3$/L). In order to prevent pH drop by alkalinity consuming during coagulation/flocculation process, this experiment requires the additional alkalinity in case of low alkalinity raw water. Turbidity and DOC values of Sri-Trang

Reservoir water in dry season were higher than those in rainy season but were on the opposite for U-Tapao Canal water. However, turbidity and SUVA also were low contained in raw water sources. The case of low turbidity water may have affected to the flocs formation in the coagulation/flocculation process and low SUVA was reported to imply low aromatic character (Korshin *et al.*, 1997) and therefore this result implied that coagulation process is not efficient enough to remove DOM from raw water sources.

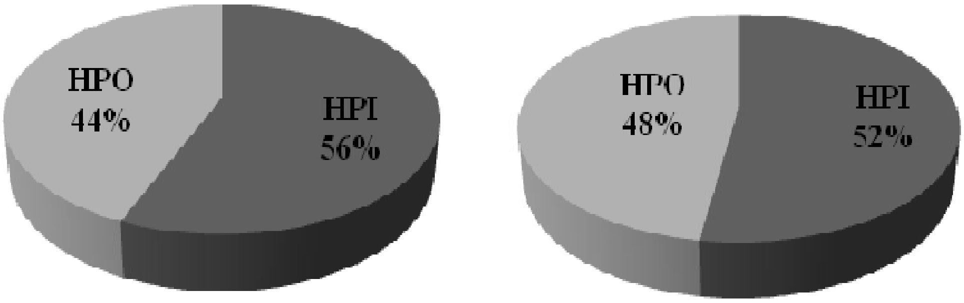
For the percent distribution of DOM fractions of Sri-Trang Reservoir raw water in both seasons is depicted in Figure 4.1. It was observed that HPO and HPI fractions accounted for 56 percent and 44 percent of total DOC, respectively. As reported by Mash *et al.*, (2004), the major DOM fraction in raw water from reservoirs was HPO fractions with its percent distribution of 50-65 percent. On the other hand, the percent distribution of DOM fractions in both seasons of U-Tapao Canal raw water is depicted in Figure 4.2. It was observed that HPO and HPI fractions in rainy season accounted for 44 percent and 56 percent of total DOC and 48 percent and 52 percent for dry season, respectively. As reported by Musikavong *et al.,* (2007), the major DOM fraction in raw water from river water with DOC values in range of 3.8-8.4 mg/L were HPI fractions with its percent distribution more than 50 percent. HPO is primarily made up of humic substances; they are mainly derived from soil and are also produced within natural water and sediments by chemical and biological processes such as the decomposition of vegetation and HPI is primarily made up of non-humic substances, they are might be derived from households or industrials wastewater discharge which has HPI fraction as a major fraction contained. (AWWA, 1993).

From the results, it can be stated that the quality of water obtained from Sri-Trang Reservoir in both two seasons is insignificantly different, but for U-Tapao Canal raw water, it can be stated that raw water in rainy season had DOM contained larger than raw water in dry season. The reason is in rainy season the natural organic substances and discharged water from rural areas and from Hat Yai City drain into U-Tapao Canal that might cause the higher DOM contained in rainy season as shown in Figure 4.2. Moreover, in rainy season the sediments which settled on the bottom of U-Tapao Canal were flush up, it might be cause of the increasing of DOC value.



a) b)

Figure 4.1 Percent distribution of organic fraction of Sri-Trang Reservoir raw water in a) rainy season and b) dry season



a) b)

Figure 4.2 Percent distribution of organic fraction of U-Tapao Canal raw water in a) rainy season and b) dry season

Fluorescent excitation-emission matrix (FEEM) is very useful for distinguishing between different types of organic matter (Her *et al*., 2003; Baker, 2001; Marhaba, 2000; Coble *et al*., 1993). The observation of DOM characteristic in raw water from Sri-Trang Reservoir by FEEM technique was found that this technique could detect three strong fluorescent peaks from raw water and each peak contained in the same position in both seasons including; peak A at 280 nm_{Ex}/410-430 nm_{Em}, peak B at 330 nm_{Ex}/390-410 nm_{Em} and peak C at 280 nm_{Ex}/ 360-370 nm_{Em} as shown in Figure 4.4. And the DOM observation by FEEM technique from U-Tapao Canal water found that this technique could detect four strong fluorescent peaks from raw water and each peak also contained in the same position in both seasons including; peak A at 275 nm_{Ex}/ 430-470 $nm_{Em,}$

peak B at 330 nm_{Ex}/390-410 nm_{Em}, peak C at 280 nm_{Ex}/360-370 nm_{Em} and peak D at 230 nm_{Ex}/360-370 nm_{Em} as shown in Figure 4.5. From these results, it could be observed that the fluorescent peaks detected from two raw water sources had the same position as each other.

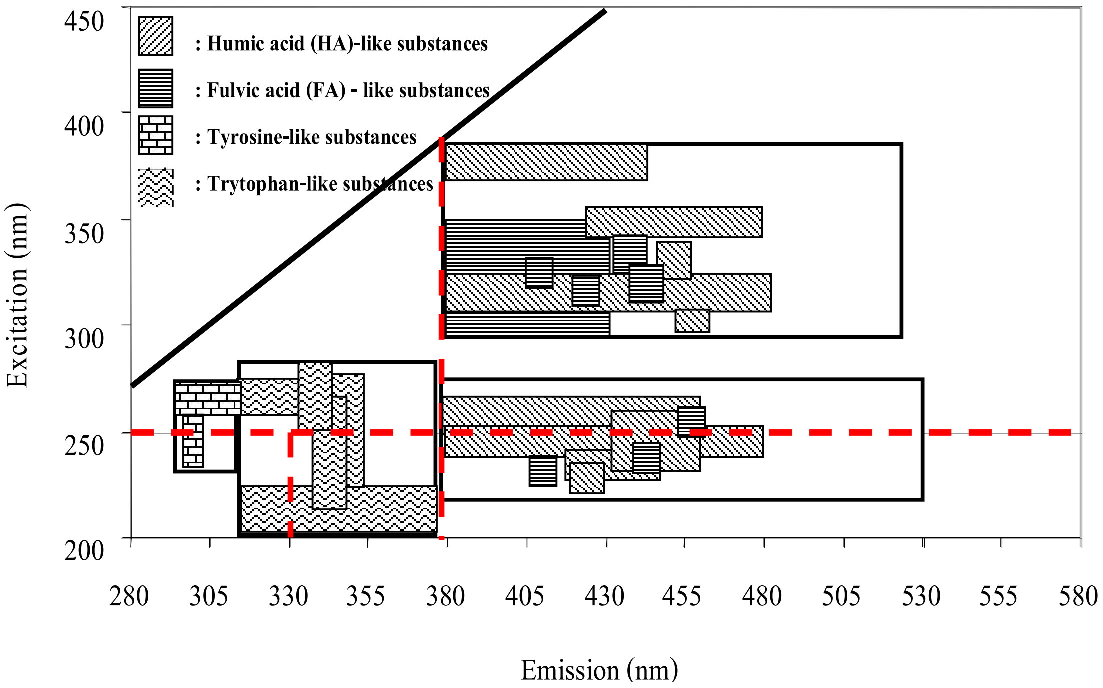


Figure 4.3 Location of FEEM peaks and excitation and emission wavelength boundaries for FEEM regions developed by Musikavong *et al.*, 2007

Using consistent excitation and emission wavelength boundaries for each FEEM as shown in Figure 4.3, peak A, peak B, peak C and peak D might represent the humic-like substance, fulvic-like substance and tryptophan-like substance for peck C and D, respectively. Moreover, raw water from U-Tapao Canal could be detected two strong fluorescent peaks of tryptophan-like substance. Consequently, humic-like, fulvic-like and tryptophan-like substances should be the major fluorescent DOM in raw water from Sri-Trang Reservoir and U-Tapao Canal. It must be noted that in general, tryptophan-like substances cannot be detected in natural water sources but found in household wastewater. If tryptophan-like substances are present, it is most-likely that the raw water is contaminated with municipality discharge (Musikavong *et al.*, 2007).

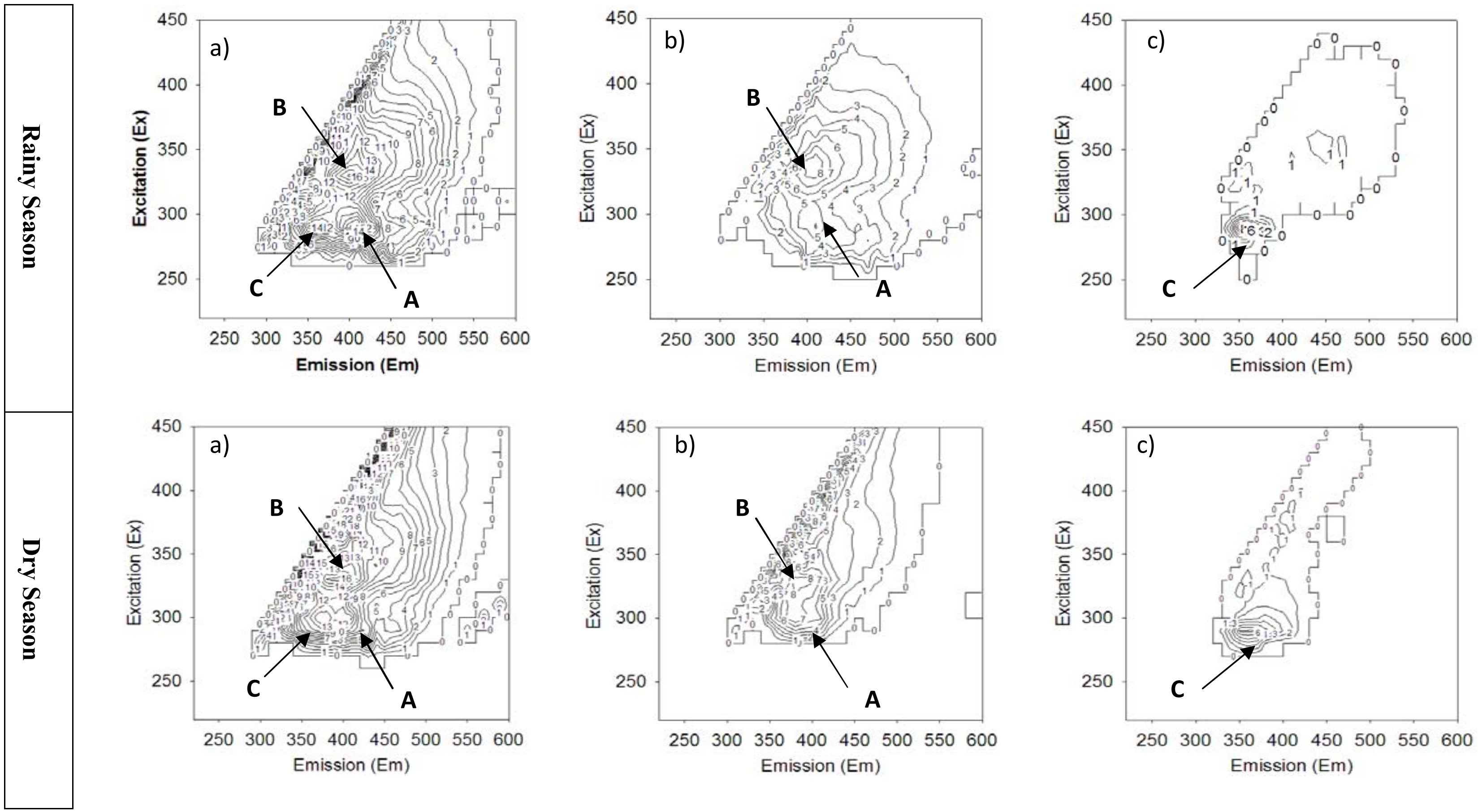


Figure 4.4 FEEM and fluorescent peaks of a) unfractionated Sri-Trang Reservoir raw water, b) HPO fraction and c) HPI fraction in the contour graph with 4 QSU contour interval for Rainy Season and Dry Season

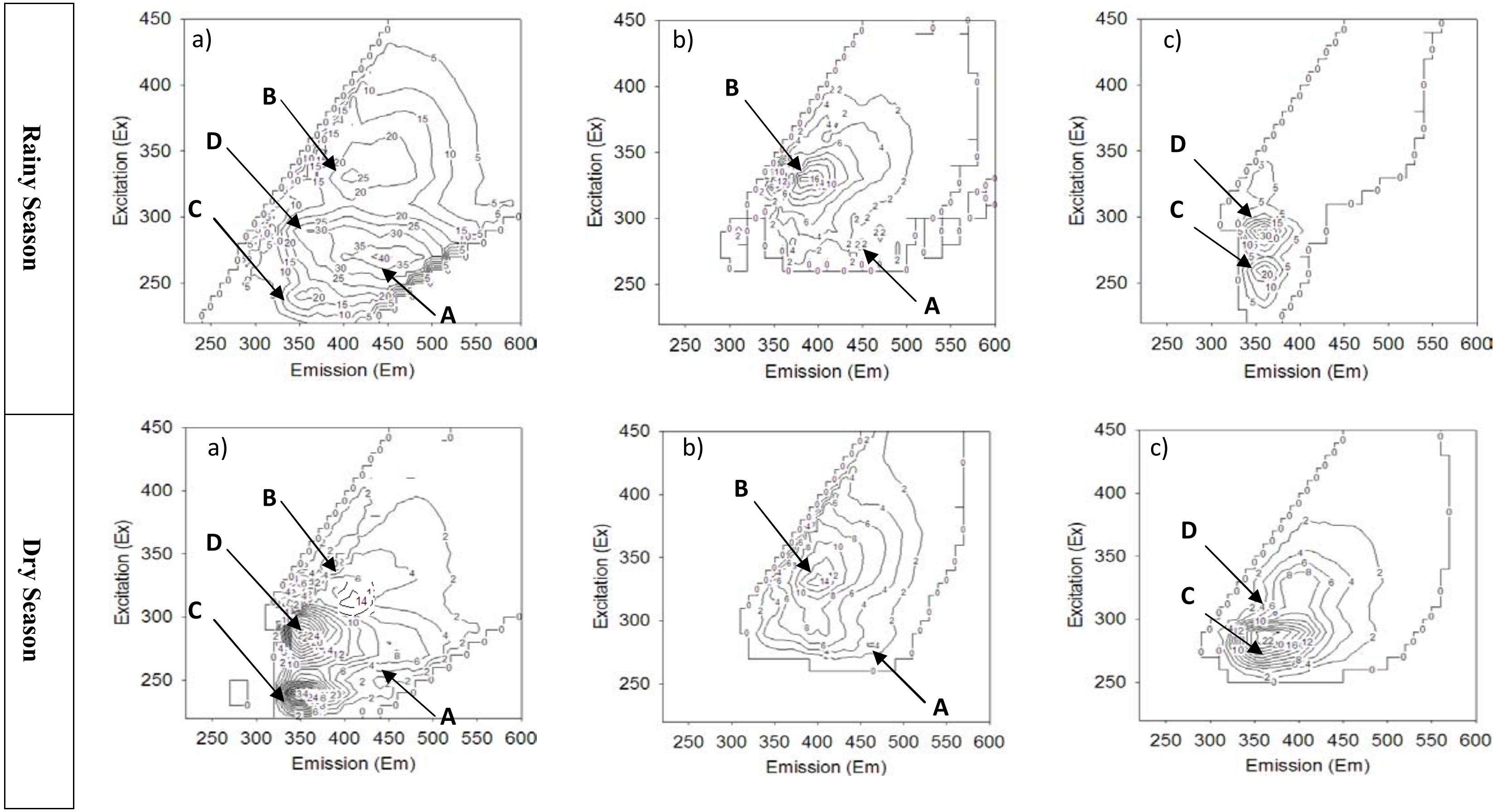


Figure 4.5 FEEM and fluorescent peaks of a) unfractionated U-Tapao Canal raw water, b) HPO fraction and c) HPI fraction in the contour graph with 4 QSU contour interval for Rainy Season and Dry Season

These demonstrate the relationships between FEEM peak position and organic compound and might be utilized to explain the characteristics of organic compound in the studied waters. In this study was to characterize DOM fractions in waters by utilizing FEEM technique, thus FEEM peaks of the major DOM fractions were compared with the location of FEEM peaks based on literature reports and operationally define excitation and emission wavelength boundaries for FEEM regions reported by Musikavong *et al*., 2007. This might explain the contained organic compounds of DOM in water. According to observed FEEM signature results of two fractionated raw water in both seasons, HPO from both water sources illustrated two strong fluorescent peaks which located on the same position as peak A and peak B in unfractionated raw water. HPI in raw water from Sri-Trang Reservoir illustrated only one fluorescent peak which located on the same position as peak C and HPI in raw water from U-Tapao Canal illustrated two fluorescent peaks which are located on the same position as peak C and peak D as depicted in Figure 4.4 and 4.5. Briefly, it can be stated that FEEM signatures could be used to monitor the major DOM fraction in water sources by determining the peak position and fluorescent intensity. In addition, the FEEM spectra were divided in to five regions, characteristic of specific components of DOM (Chen *et al*., 2003).

THMFP has been commonly used to determine the THMs at the completion of the reaction condition between DOM and the excess amount of chlorine. The THMFP was determined from the summation of the Chloroform ($CHCl_3$), Bromodichloroform ($CHCl_2Br$), Dibromochloroform ($CHClBr_2$), and Bromoform ($CHBr_3$). The results from the evaluation of THMFP of raw water from Sri-Trang Reservoir in both seasons (Figure 4.6) revealed that the total THMFP of raw water in rainy season and dry season were 437 μg/L and 512 μg/L, respectively. For the evaluation of THMFP of raw water from U-Tapao Canal in both seasons (Figure 4.7) revealed that the total THMFP of raw water in rainy season and dry season were 542 μg/L and 393 μg/L, respectively.

The U.S.EPA revised has issued the Disinfectants/Disinfection By-Products (D/DBP) rule reduced the MCL for THMs to 80 ppb for Stage 1 D/DBP and 40 ppb for Stage 2 (USEPA, 2003). In water samples of Sri-Trang Reservoir in rainy season and dry season, the dominant species of THMs were $CHCl_3$ and $CHCl_2Br$. For rainy season, the maximum concentrations of THMs detected in chlorinated water sample during study were 422 µg/L for $CHCl_3$ and 16 µg/L for $CHCl_2Br$. Whereas that of summer, the maximum concentrations of THMs were 441 µg/L for $CHCl_3$ and 71 µg/L for $CHCl_2Br$. For U-Tapao Canal raw water, the dominant species of THMs also were $CHCl_3$ and $CHCl_2Br$. For rainy season, the maximum concentrations of THMs detected in chlorinated water sample during study were 487 µg/L for $CHCl_3$ and 55 µg/L for $CHCl_2Br$. In summer, the maximum concentrations of THMs were 300 µg/L for $CHCl_3$ and 93 µg/L for $CHCl_2Br$. When considering the presence of THMs species, it was found that chloroform was the major THM specie in the raw water from both water sources in this study and in other raw water supply sources in Thailand. As illustrated in Figure 4.6 and 4.7, chloroform species of all DOM fractions in both raw water presented in the greatest level that were more than 90 percent of total THMFP. The reason of this phenomenon might be from chlorine adding in water samples which effect to chloroform formation. This observation also corresponded well with the results of previous research (Rodriguez *et al*., 2003).

The THMFP of raw water obtained in this study were compared with other raw water sources in Thailand (as shown in Table 4.2). 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 hybrid UF processes. It was commonly employed to reduce the level of the DBPs was to reduce the level of DOM prior to it being chlorination.

As can be seen from Figure 4.6, THMFP value of Sri-Trang Reservoir raw water of each organic fraction in rainy season and dry season found that HPO were the major fraction that contributed THM formation. THMFP values of HPO and HPI fractions of raw water in rainy season were 256 µg/L and 177 µg/L whereas about 272 µg/L and 237 µg/L for dry season. The most chloroform approximately 56 percent was found that came from the chlorination of HPO fraction and 44 percent of HPI fraction for raw water from Sri-Trang Reservoir. From these results, it can be stated that the THMFP values created from HPO fractions was higher than the THMFP values created from HPI fractions. These results are similar to reported results from Kueseng *et al*. (2010) that HPO fraction in raw water from Sri-Trang Reservoir could create

THMs at around 58 percent. In addition, THMFP value of U-Tapao Canal raw water of each organic fraction in rainy season and dry season found that HPI were the major fraction that contributed THM formation. The THMFP values of HPO and HPI fractions of raw water in rainy season were 233 µg/L and 307 µg/L whereas about 167 µg/L and 222 µg/L for dry season. The most chloroform approximately 57 percent was found that came from the chlorination of HPI fraction and 43 percent of HPI fraction. It can be implied that THMFP reduction was relative result of chloroform reduction. These results are similar to reported results from Inthanuchit *et al.* (2009) that HPI fraction in raw water from U-Tapao Canal could create THMs at around 57 percent and HPI fraction at around 43 percent.

The comparison of THMFP from Sri-Trang Reservoir water in both seasons as can be seen in Figure 4.6 found that water samples in dry season had a larger amount of THMs than those in rainy season. Whereas, the comparison of THMFP from U-Tapao Canal in both seasons found that water samples in dry season had a larger amount of THMs than those in dry season which corresponded with the studies of Kueseng *et al.*, (2010) and Inthanuchit *et al.*, (2009). Trusell and Umphres, (1978) and Wei *et al.*, (2008) reported that temperature and seasonal variations had a relationship for forming of THMs, and, water samples in dry season had a higher potential for THMs forming (especially chloroform) than that of rainy season. This might be due to the amount of DOM contained in dry season Sri-Trang Reservoir raw water was higher than those of rainy season which is consistent with DOC value as mentioned early. Therefore, THMs should be strictly controlled especially in dry season. In contrast to the amount of THMFP from U-Tapao Canal, water samples in rainy season had a higher potential for forming of THMs (especially chloroform) than that of dry season. This might be due to the amount of DOM contained in rainy season raw water was higher than those of rainy season which is consistent with DOC, UV-254 and FEEM value in rainy season were higher than those of dry season as mentioned early. Panyapinyopol *et al.*, 2005 reported that the organic fractions with larger quantity could potentially lead to more THMs formed during the chlorination. Therefore, THMs should be strictly under controlled especially in rainy season.

Table 4.2 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 (µg/L)	$CHCl_3$-FP (µg/L)	$CHCl_2Br$-FP (µg/L)	$CHClBr_2$-FP (µg/L)	$CHBr_3$-FP (µg/L)
The Chao Phraya River Bangkok, Thailand (Panyapinyopol *et al.,* 2005)	August 2003	313	262 (84%)^1	43.8 (14%)	6.9 (2%)	ND^2
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 *et al.,* 2005)	April 2005	318	292 (92%)	25.6 (8%)	ND	ND
Raw water from Sri-Trang Reservoir of this study in rainy season	September 2009	437	422 (96%)	16 (4%)	ND	ND
Raw water from Sri-Trang Reservoir of this study in dry season	April 2010	512	441 (86%)	71 (14%)	ND	ND
Raw water from U-Tapao of this study in rainy season.	September 2009	542	487 (90%)	55 (10%)	ND	ND
Raw water from U-Tapao of this study in dry season.	April 2010	393	300 (76%)	93 (24%)	ND	ND

Remark: ^{1}( ) = percent distribution and ^{2}ND = Not detected

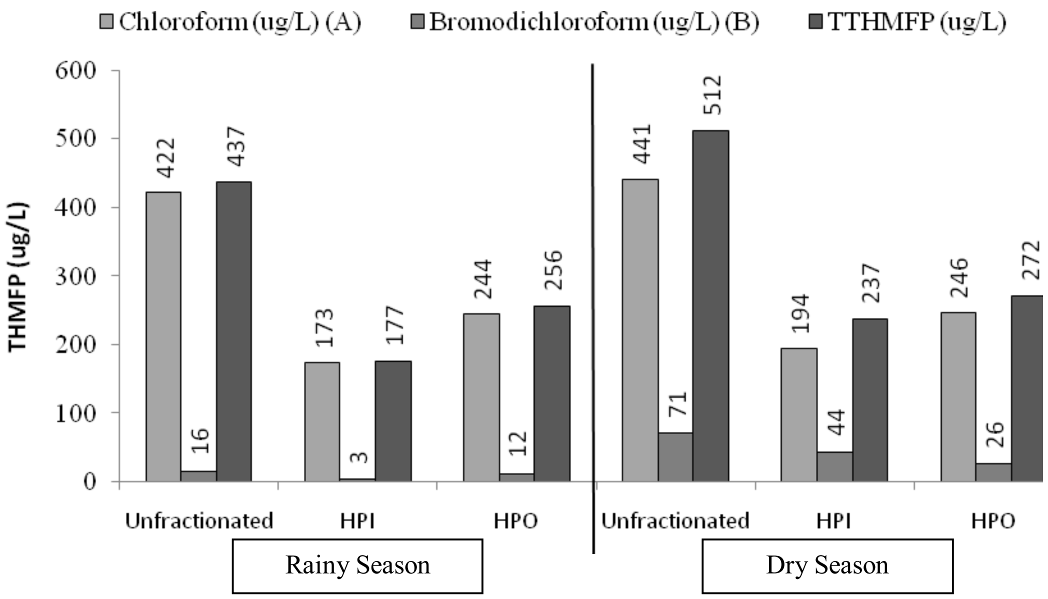


Figure 4.6 THMFP and THMs species of Sri-Trang reservoir raw water in rainy season and dry season

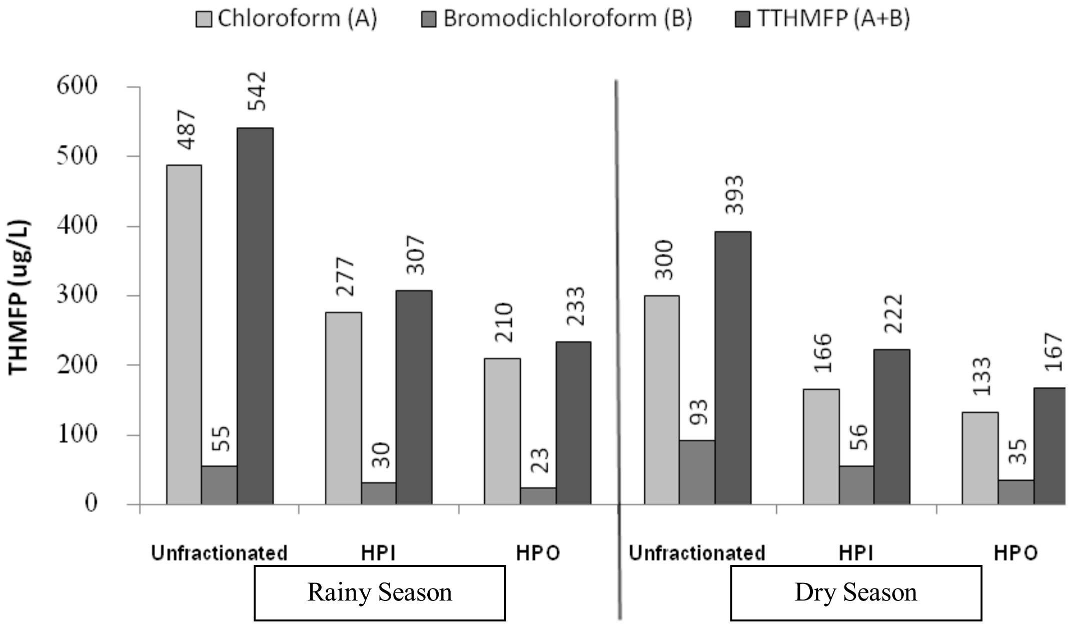


Figure 4.7 THMFP and THMs species of U-Tapao Canal raw water in rainy season and dry season

To better understand the characteristic of raw water in Sri-Trang Reservoir and U-Tapao Canal water, the result of FT-IR analysis was also observed. FT-IR spectroscopy has been widely used for gross characterization of DOM and can provide valuable information on the structural and functional properties of DOM molecules (Chen *et al.,* 2002). Many researchers utilized FT-IR to determine functional group of DOM in ground water (Her *et al*., 2008), reservoir water (Zularisam et al., 2007), river water (Kanokkantapong *et al*., 20006; Zularisam *et al*., 2007 and Kim and Yu, 2005) and wastewater (Xue *et al*., 2008 and Benoit *et al*., 2008). The FT-IR spectra of DOM from raw water are shown in Figure 4.8 and Table 4.3. Interpretation of the absorption bands of DOM was performed as described by Aiken *et al*., (1985) and Kanokkantapong *et al*., (2006). The band at around 3400 cm^{-1} is generally attributed to O-H or H-bonded N-H groups. The peak at 1660 cm^{-1} was attributed to the C=O stretching of amide groups (amide I band). The bands in range of 1420-1400 cm^{-1} were attributed to O-H bending vibration of carboxylic groups, respectively. The C-O stretching of alcohols, ethers and carbohydrates were illustrated by the strong peaks at 1150-1090 cm^{-1}. The alcoholic C-O bonds may have originated from polysaccharide-like substance (Her *et al*., 1994). In addition, the existence of the C-H bending vibration of aromatic ring was indicated by the peak at 860 cm^{-1}. Moreover, bands in the 590-667 cm^{-1} were attributed to deformation of COOH.

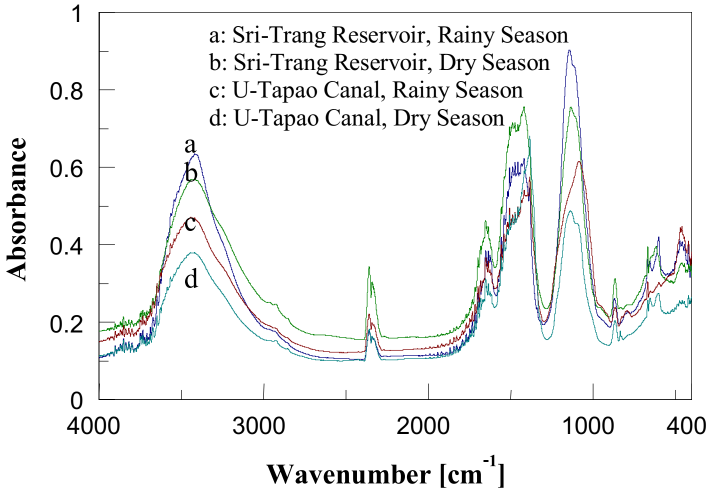


Figure 4.8 FT-IR spectra of raw water from Sri-Trang Reservoir and U-Tapao Canal in a) rainy season and b) dry season

Table 4.3 FTIR spectra of raw water from Sri-Trang Reservoir and U-Tapao Canal

Wavenumber (cm^{-1})		Assignment
Sri-Trang Reservoir	U-Tapao Canal	
3400	3404	O-H groups or H-bonded N-H groups
1660	1660	C=O stretching of amide groups (amide-1)
1520	1515	C=C stretching vibration of benzene, pyridines
1420-1400	1420-1400	O-H bending vibration of carboxylic groups, C-O stretching of alcohol
1150-1190	1150-1190	C-O stretching of ester, ethers, phenol and alcohol
860	860	C-H bending vibration of aromatic rings
590-667	590-667	Hydrogen-bonded OH stretching vibration carboxylic groups

4.2 Reduction of DOM by coagulation and MF process as a pre-treatment

The obtained optimal condition of PACl coagulation for raw water supply from the Sri-Trang Reservoir and U-Tapao Canal was at pH 7 and alum dosage at 20 mg/L for Sri-Trang Reservoir water and 40 mg/L for U-Tapao Canal water using turbidity, DOC, and UV-254 as criteria that are depicted in Appendix B. The pre-treatment efficiency of raw water by PACl coagulation and MF process for Sri-Trang Reservoir and U-Tapao Canal are hastily demonstrated through parameters listed in Table 4.4 and Table 4.5.

Table 4.4 Water quality of Sri-Trang Reservoir after pre-treatment processes

Parameters	**Rainy Season**			**Dry Season**		
	Raw water	**MF**	**Coagulation**	**Raw water**	**MF**	**Coagulation**
Turbidity (NTU)	8.03	2.26	2.44	8.42	2.27	2.48
UV-254 (cm^{-1})	0.05	0.029	0.024	0.07	0.027	0.021
DOC (mg/L)	4.08	1.93	1.91	4.55	1.94	1.87

Table 4.5 Water quality of U-Tapao Canal after pre-treatment processes

Parameters	**Rainy Season**			**Dry Season**		
	Raw water	**MF**	**Coagulation**	**Raw water**	**MF**	**Coagulation**
Turbidity (NTU)	40.0	4.31	4.43	23.0	3.47	3.83
UV-254 (cm^{-1})	0.19	0.096	0.079	0.15	0.086	0.071
DOC (mg/L)	9.77	4.8	4.7	6.13	3.60	3.42

As can be seen from Table 4.4 and Table 4.5, the MF process and coagulation process as pre-treatment techniques could effectively reduce the turbidity from both raw water sources which less than 5 NTU. Typically, the coagulation process has traditionally been used to remove turbidity from drinking water supplies. Considering the DOC and UV-254, DOC is commonly used as the primary surrogates. Humic-like include aromatic hydrocarbon, while non-humic like include aliphatic hydrocarbons. UV-254 includes aromatic compounds. The obtained results, UV-254 and DOC reduction by MF and coagulation process, Sri-Trang Reservoir water samples in rainy season, the use of MF process reduced UV-254 and DOC approximately 42 percent and 53 percent, while, the use of 40 mg/L of PACl reduced UV-254 and DOC approximately 52 percent and 53 percent, respectively, whereas that of dry season at the same condition reduced UV-254 and DOC about 61 and 57 percent for MF process, whilst, 70 percent and 60 percent for PACl coagulation process, respectively. For U-Tapao Canal water samples in rainy season, the use of MF process reduced UV-254 and DOC approximately 50 percent and 51 percent, while, the use of 40 mg/L of PACl reduced UV-254 and DOC approximately 58 percent and 52 percent, respectively, whereas that of summer at the same condition reduced UV-254 and DOC about 43 and 41 percent for MF process, whilst, 53 percent and 59 percent for PACl coagulation process, respectively.

Moreover, DOM removal efficiency by FEEM also studied. The level of fluorescent intensities depends upon the level of organic substances in the water. In case of high organic content in water the high value of fluorescent intensities are observed, whereas in case of low organic content, low values of fluorescent intensities are obtained (Homklin, 2004). Musikavong *et al.,* (2007) suggested that the fluorescent intensity in the QSU units of each fluorescent peak could be further utilized to determine the quantity of all fluorescent organic matters in water by adding the fluorescent intensities of all FEEM peaks. The reduction in the fluorescent organic matters could therefore be reflected by the difference in the total fluorescent intensities of the total fluorescent organic matter by hybrid UF process. Table 4.6 illustrated the average values of fluorescent intensity summation of all FEEM peaks from all water samples in both seasons of Sri-Trang Reservoir water samples to evaluate the reduction of fluorescent organic compounds in Sri-Trang Reservoir water through MF process and coagulation process.

Table 4.6 Reduction of FEEM peaks in water samples from Sri-Trang Reservoir by MF and coagulation processes

Process	Fluorescent Intensity (QSU)			Total (QSU)	Total Removal Efficiency (%)
	Humic (280 nmEx/ 410-430 nmEm)	**Fulvic** (330 nmEx/ 390-410 nmEm)	**Tryptophan** (280 nmEx/ 360-370 nmEm)		
Rainy Season					
Raw water	14	16	14	44	-
MF	10	11	9	30	32
PACl	9	10	8	27	39
Dry Season					
Raw water	13	16	13	42	-
MF	9	10	8	27	36
PACl	7	8	5	20	52

For total fluorescent organic matter reduction as shown in Table 4.6, it was found that in rainy season MF process could reduce total fluorescent organic matter by 32 percent which was higher than that of coagulation process by 39 percent, while, MF process could reduce total fluorescent organic matter by 36 percent and by 52 percent for PACl coagulation process in dry season. The results implied that humic and fulvic acid-like substances and tryptophan-like substance could moderately reduce by pre-treatment techniques especially for PACl coagulation.

In case of the total fluorescent organic matter reduction of U-Tapao Canal water as can be seen from Table 4.7 found that the results had a same trend of fluorescent reduction as Sri-Trang Reservoir's results. In rainy season, the MF process could reduce total fluorescent organic matter by 31 percent which was higher than that of coagulation process by 40 percent, while, MF process could reduce total fluorescent organic matter by 45 percent and by 53 percent for PACl coagulation process in dry season. These could support the results of DOC and UV-254 reduction.

Table 4.7 Reduction of FEEM peaks in water samples from U-Tapao Canal by MF and coagulation processes

Process	Fluorescent Intensity (QSU)			Total (QSU)	Total Removal Efficiency (%)
	Humic (275 nmEx/ 430-470 nmEm)	**Fulvic** (330 nmEx/ 390-410 nmEm)	**Tryptophan** (280 nmEx/ 360-370 nmEm)		
Rainy Season					
Raw water	40	25	50	115	-
MF	28	19	32	79	31
PACl	24	16	30	70	40
Dry Season					
Raw water	8	14	58	80	-
MF	5	8	31	44	45
PACl	4	6	27	37	53

From these results it can be stated that the pre-treatment by PACl coagulation had an efficiency to remove turbidity and DOM surrogate parameter in terms of DOC and UV-254 better than that of MF process. The reason of this phenomenon is the mechanism of PACl coagulation for removing DOM in raw water was the charge neutralization and DOM has been adsorbed onto the aluminum flocs and settle down under gravity while MF process reduces DOM by size exclusion mechanism. Due to the 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). These pre-treatment techniques should be strictly connected prior to ultrafiltration process with the protection of membranes against the fouling phenomenon that occurs inside the membrane pores and on the membrane surface as a cake formation process causing permeate flux decline.

CHAPTER 5

CHARACTERIZATION AND REDUCTION OF DOM BY HYBRID ULTRAFILTATION PROCESS

5.1 DOM Reduction by Hybrid UF Processes

This section was aimed at considering the effectiveness of DOM removal from Sri-Trang Reservoir and U-Tapao Canal water in rainy season and dry season by comparison between the coagulation with the optimum PACl dose combined with UF and MF combined with UF in order to compare the effectiveness of DOM removal.

Based on the results in Figure 5.1, Sri-Trang Reservoir water samples in rainy season, about 4.0 mg/L of DOC in raw water was promptly reduced to 1.7 mg/L by hybrid UF process combined with MF and reduced to 1.5 mg/L by hybrid UF process combined with coagulation. At these processes, the removal of 58 percent and 64 percent of DOC from the UF treated water samples were observed. For Sri-Trang Reservoir water samples in dry season, DOC reduced from 4.4 mg/L to 1.8 mg/L, approximately 60 percent by hybrid UF process combined with MF and reduced to 1.5 mg/L by hybrid UF process combined with coagulation, approximately 66 percent. In case of UV-254 reduction, UV-254 values of Sri-Trang Reservoir water samples in rainy season decreased from 0.05 cm^{-1} to 0.03 cm^{-1}, approximately 50 percent, by hybrid MF+UF process and reduced to 0.02 cm^{-1}, approximately 64 percent by hybrid PACl+UF process. For dry season, UV-254 decreased from 0.07 cm^{-1} to 0.03 cm^{-1}, approximately 61 percent by MF+UF process and reduced to 0.02 cm^{-1} by PACl+UF process, approximately 68 percent. In addition, the results also show that both of the hybrid UF processes were effective in reducing HPO fraction but lesser for HPI fraction. And HPI fraction still remains the major fraction in water after hybrid UF processes.

As illustrated in Figure 5.2, U-Tapao Canal water samples in rainy season, DOC decreased from 9.8 mg/L to 2.9 mg/L, respectively by hybrid MF+UF process and reduced to 2.7 mg/L by hybrid PACl+UF process. These conditions could remove about 70 percent and

75 percent of DOC, respectively. For U-Tapao Canal water samples in dry season, about 7.1 mg/L of DOC in raw water was reduced to 2.2 mg/L by hybrid MF+UF process, approximately 68 percent DOC reduction and reduced to 2.0 mg/L by hybrid PACl+UF process, approximately 71 percent. In case of UV-254 reduction, UV-254 values of U-Tapao Canal water samples in rainy season decreased from 0.19 cm^{-1} to 0.09 cm^{-1}, approximately 53 percent, by hybrid MF+UF process and reduced to 0.05 cm^{-1}, approximately 73 percent by hybrid PACl+UF process. For dry season, UV-254 decreased from 0.16 cm^{-1} to 0.08 cm^{-1}, approximately 50 percent by hybrid MF+UF process and reduced to 0.05 cm^{-1} by PACl+UF process, approximately 70 percent. In addition, the results also show that both of the hybrid UF processes were effective in reducing HPO fraction and HPI fraction. And HPI fraction still remains the major fraction in water after hybrid UF processes which same as the result of Sri-Trang Reservoir water samples.

Interestingly, the hybrid UF process combined with coagulation had the efficiency to remove DOM in terms of DOC and UV-254 better than UF process combined with MF. The reason for this phenomenon is UV-254 could detect DOM in form of most aromatic organic, which could be reduced effectively by coagulation (AWWA, 1993). Some tiny organic substances have been adsorbed onto the aluminum flocs and settle down under gravity prior to UF process. Aromatic organic such as humic substances (HPO) which has particle size in range of 0.0025-0.01 whereas UF membrane has a nominal pore size of 0.008 µm, hence, UF process has an effectiveness to remove humic substances but not 100 percent due to particles of humic substance which if smaller than 0.008 µm can flow through UF membrane pore size. On the other hand, the DOC removal by UF process combined with MF relies on the sieving mechanism. MF which has pore size of 0.1 µm could not sufficient to reduce DOC and UV-254, according to the size distribution of organics substances is smaller than MF pore size. Therefore, to enhance the efficiency of UF process combined with MF, a smaller pore size such as 0.05 µm of MF membrane should be observed in the future.

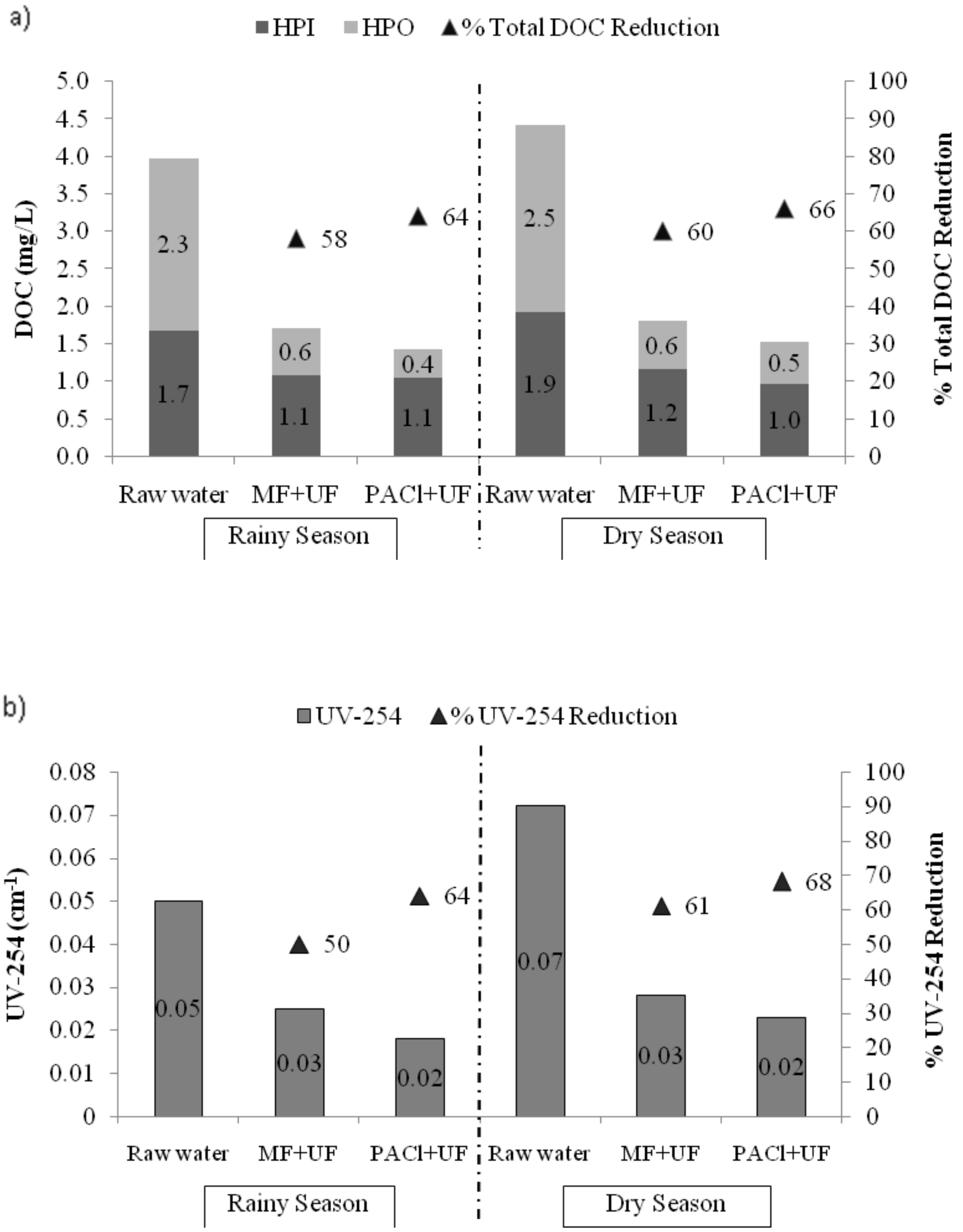
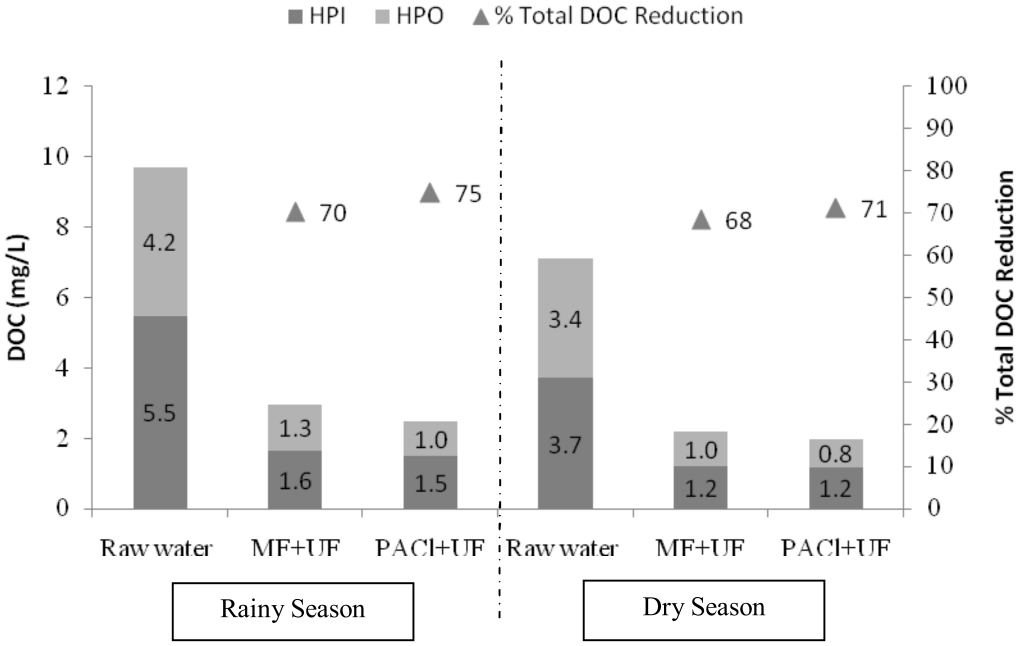


Figure 5.1 Changes in a) DOC and b) UV-254 of raw water and treated water from Sri-Trang Reservoir by UF process



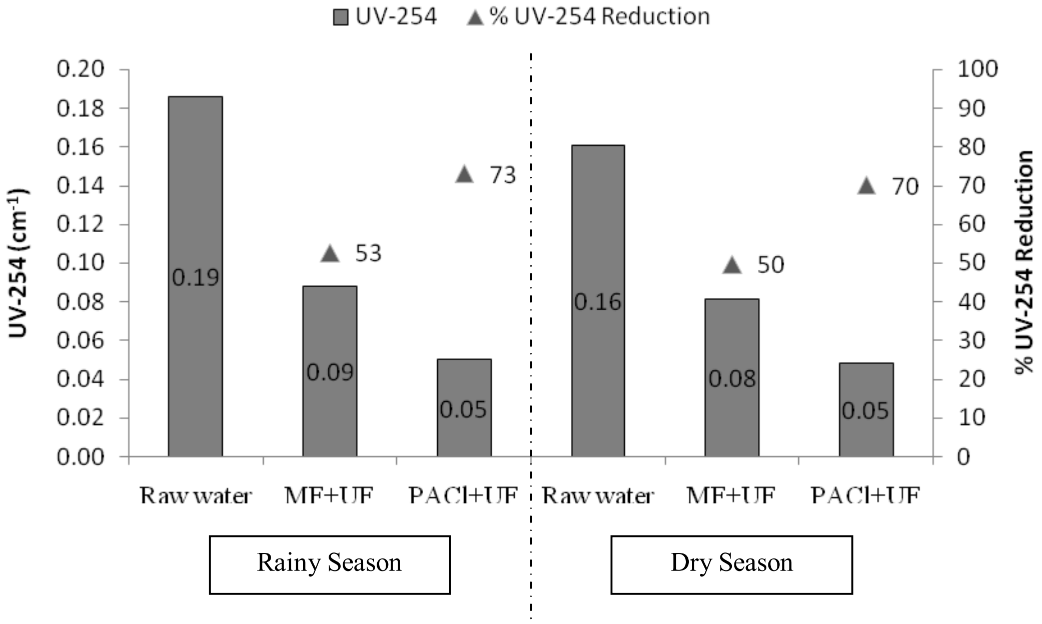


Figure 5.2 Changes in a) DOC and b) UV-254 of raw water and treated water from U-Tapao Canal by UF process

This section can be concluded that an appropriate condition to remove DOM considering in DOC and UV-254 removal in Sri-Trang Reservoir water would be the coagulation (with PACl dose of 20 mg/l) combined with UF membrane. The reduction of organic matter significantly indicating rejection of DOM not only by the pore size exclusion but also other separation mechanisms such as adsorption onto the membrane surface, adsorption onto particles in the cake layer or sieving as a result of physical constriction of the membrane pores due to irreversible fouling.

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 hybrid UF process was evaluated by the reduction of the summation of the fluorescent intensities of overall outstanding peaks. The results of these analyses were compared with the DOC results in order to assess the usefulness of the FEEM technique for determining fluorescent organic matter and the reduction of fluorescent organic matter by hybrid UF process.

FEEM result obtained is demonstrated in Figure 5.3 (Sri-Trang Reservoir) and Figure 5.4 (U-Tapao Canal) by hybrid UF process in rainy season and dry season, a total of three fluorescent peaks were detected strong broad peaks from Sri-Trang Reservoir hybrid UF treated water samples of humic-like substance at 280 nm_{Ex}/410-430 nm_{Em} (Peak A), fulvic-like substance at 330 nm_{Ex}/390-410 nm_{Em} (Peak B) and tryptophan-like substance at 280 nm_{Ex}/ 360-370 nm_{Em} (Peak C). And four fluorescent peaks were detected strong broad peaks from U-Tapao Canal hybrid UF treated water samples including peak A at 275 nm_{Ex}/ 430-470 nm_{Em} (humic-like), peak B at 330 nm_{Ex}/390-410 nm_{Em} (fulvic-like), peak C at 280 nm_{Ex}/360-370 nm_{Em} (tryptophan-like) and peak D at 230 nm_{Ex}/360-370 nm_{Em} (tryptophan-like).

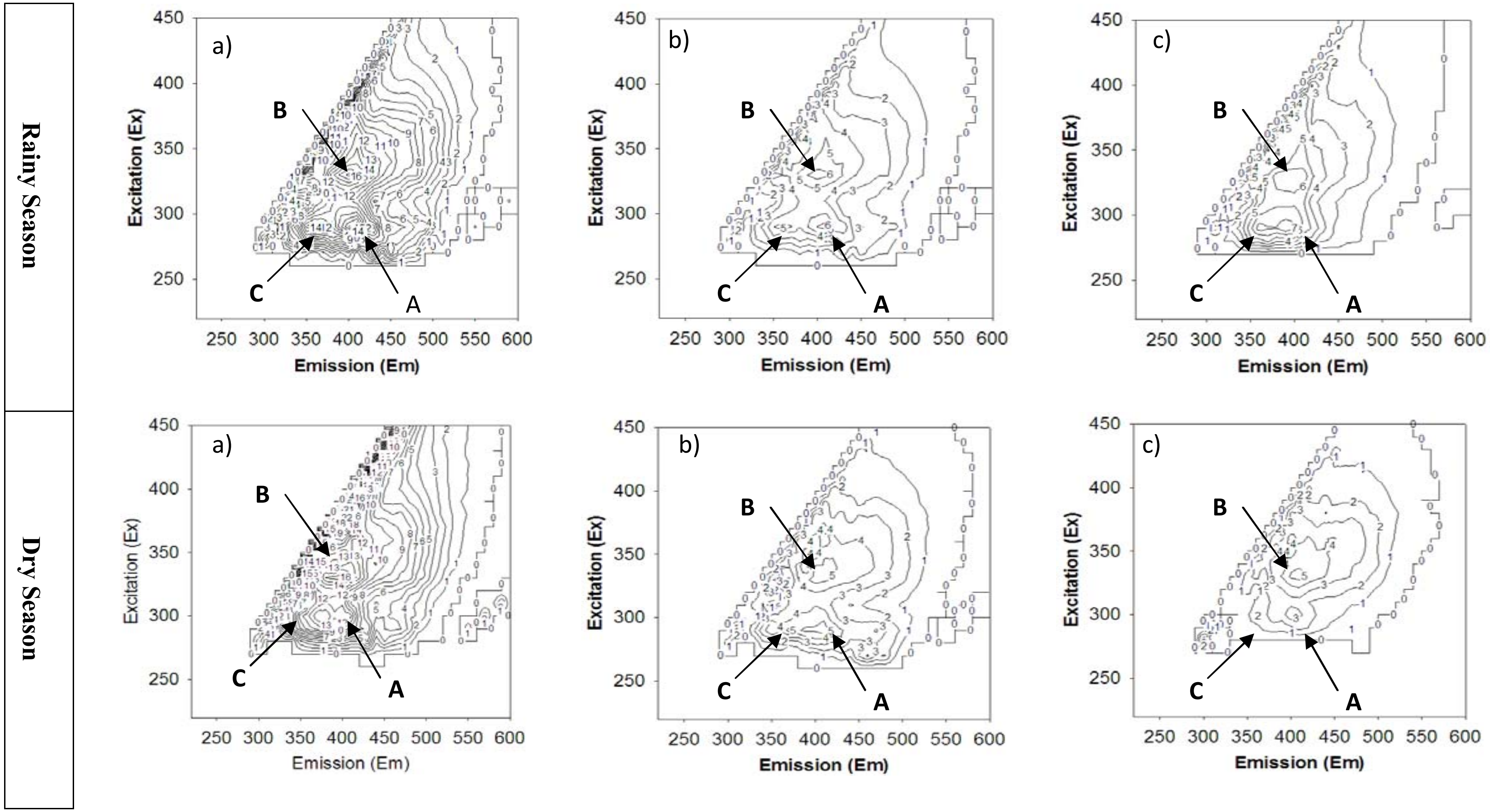


Figure 5.3 FEEM and fluorescent peaks of a) unfractionated Sri-Trang Reservoir raw water, b) MF+UF and c) PACl+UF in the contour graph with 4 QSU contour interval for Rainy Season and Dry Season

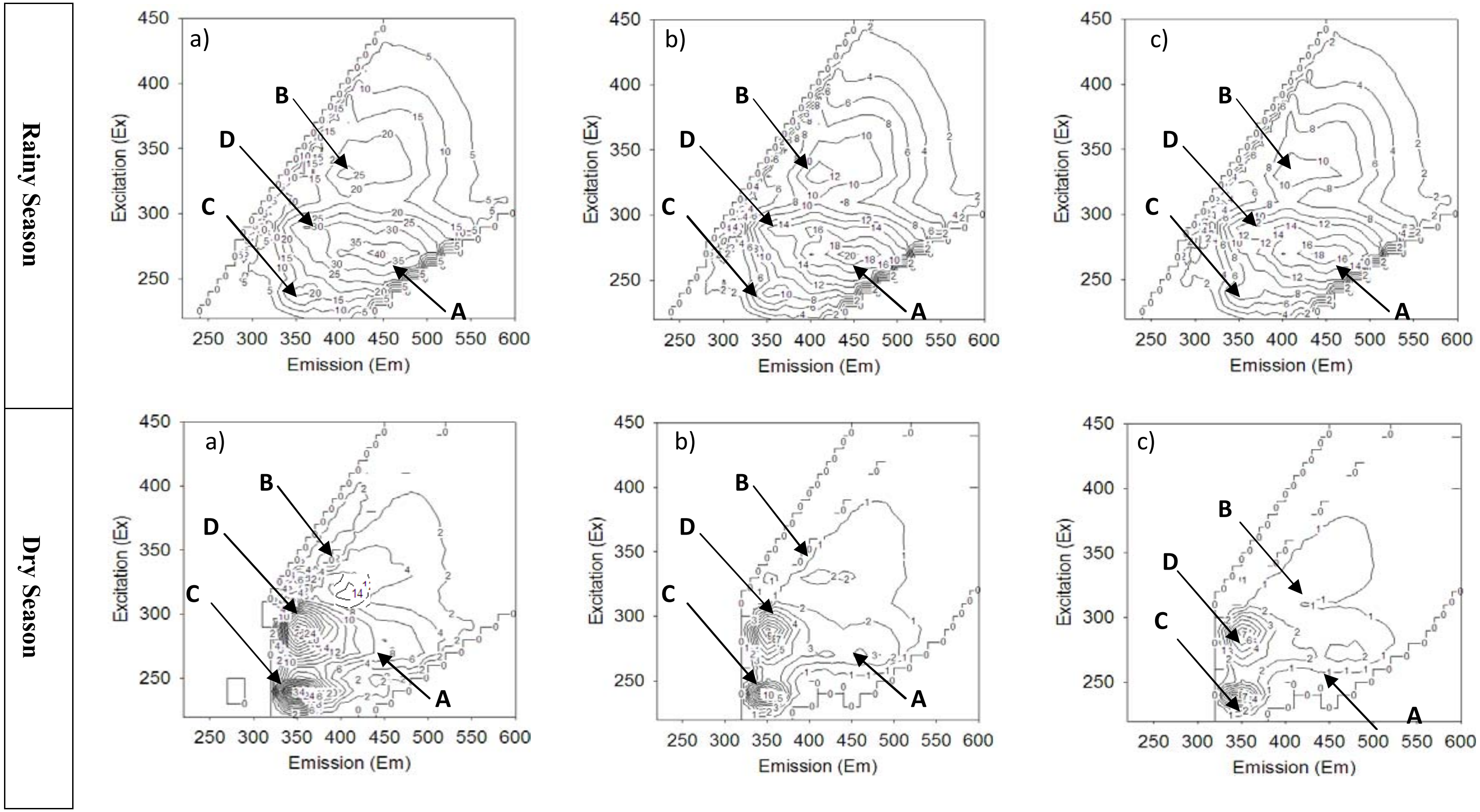


Figure 5.4 FEEM and fluorescent peaks of a) unfractionated U-Tapao Canal raw water, b) MF+UF and c) PACl+UF in the contour graph with 4 QSU contour interval for Rainy Season and Dry Season

Fluorescent organic matter of each FEEM peak could be defined as follows: peak A is humic acid-like substances, peak B is fulvic acid-like substances, peck C and peak D are tryptophan-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 outstanding peaks in the FEEM of raw water and hybrid UF treated water are illustrated in Table 5.1.

As illustrated in Table 5.1, the reduction efficiency of Sri-Trang Reservoir water samples in rainy seasons and dry season by the hybrid UF process on the fluorescent intensity of each peak found that the treated water by hybrid MF+UF process could reduce humic-like substances at peak A by 57 percent and 64 percent, fulvic-like substances at peak B by 63 percent and 69 percent, the tryptophan-like substances at peak C was reduced by 64 percent and 71percent, respectively. For the hybrid PACl+UF process, the humic-like substances at peak A was reduced by 50 percent and 77 percent, fulvic-like substances at peak B was reduced by 63 percent and 69 percent and the tryptophan-like substances at peak C was reduced by 71 percent and 77 percent, respectively.

The reduction of fluorescent intensity at each peak of U-Tapao Canal water samples in rainy seasons and dry season by the hybrid MF+UF process, the humic-like substances at peak A was reduced by 50 percent and 63 percent, fulvic-like substances at peak B by 52 percent and 85 percent, the tryptophan-like substances at peak C was reduced by 52 percent and 70 percent, respectively. For the hybrid PACl+UF process, the humic-like substances at peak A was reduced by 55 percent and 75 percent, fulvic-like substances at peak B was reduced by 60 percent and 93 percent and the tryptophan-like substances at peak C and peak D was reduced by 60 percent and 79 percent, respectively.

The summation of fluorescent intensities of peaks A, B, and C was utilized to represent the total fluorescent organic matter of the Sri-Trang Reservoir water samples in rainy season and dry season which was mainly included of humic and fulvic acid-like substances and tryptophan-like substances. The hybrid MF+UF process, total fluorescent organic matter was reduced by 61 percent and 67 percent, respectively. While, the hybrid PACl+UF process could reduce total fluorescent organic matter by 61 percent and 76 percent, respectively. And The summation of fluorescent intensities of peaks A, B, C and D was utilized to represent the total fluorescent organic matter of the U-Tapao Canal water samples in rainy season and dry season which was mainly included of humic and fulvic acid-like substances and tryptophan-like substances. The hybrid MF+UF process, total fluorescent organic matter was reduced by 51 percent and 73 percent, respectively. While, the hybrid PACl+UF process could reduce total fluorescent organic matter by 58 percent and 79 percent, respectively.

Based on the FEEM results, it can be stated that the both hybrid UF processes could remove tryptophan-like substances more slightly than humic and fulvic acid-like substances. And the hybrid PACl+UF process could reduce the summation of fluorescent intensities higher than that of hybrid MF+UF process.

Table 5.1 Fluorescent intensity at peak positions and reduction efficiency of Sri-Trang Reservoir raw water and treated water by hybrid UF process

Water samples	**Fluorescent intensity (QSU)**			**Total**	**Reduction efficiency (%)**			**%Total Reduction**
	Peak A[1]	**Peak B [2]**	**Peak C[3]**	**(QSU)**	**Peak A[1]**	**Peak B [2]**	**Peak C[3]**	**(QSU)**
Raw water in rainy season	14	16	14	44	-	-	-	-
(1) MF+UF	6	6	5	17	57	63	64	61
(2) PACl+UF	7	6	4	17	50	63	71	61
Raw water in dry season	13	16	13	42	-	-	-	-
(1) MF+UF	5	5	4	14	64	69	71	67
(2) PACl+UF	3	5	2	10	77	69	77	76

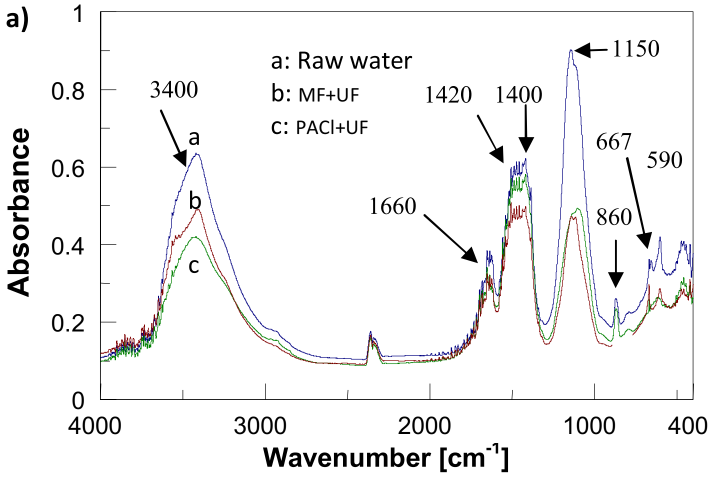
Remark: 1= Humic acid like substances (280nmEx/410-430nmEm)
2= Fulvic acid like substances (330nmEx/390-410nmEm)
3= Tryptophan like substances (280nmEx/360-370nmEm)

Table 5.2 Fluorescent intensity at peak positions and reduction efficiency of U-Tapao Canal raw water and treated water by hybrid UF process

Water samples	Fluorescent intensity (QSU)			Total (QSU)	Reduction efficiency			%Total Reduction (QSU)
	Peak A[1]	Peak B[2]	Peak C^3+D^4		Peak A[1]	Peak B[2]	Peak C^3+D^4	
Raw water in rainy season	40	25	50	115	-	-	-	-
(1) MF+UF	20	12	24	56	50	52	52	51
(2) PACl+UF	18	10	20	48	55	60	60	58
Raw water in dry season	8	14	58	80	-	-	-	-
(1) MF+UF	3	2	17	22	63	85	70	73
(2) PACl+UF	2	1	14	17	75	93	79	79

Remark: 1= Humic acid like substances (275nmEx/430-470nmEm)
2= Fulvic acid like substances (330nmEx/390-410nmEm)
3= Tryptophan like substances (280nmEx/360-370nmEm)
4= Tryptophan like substances (230nmEx/360-370nmEm)

According to the FT-IR Analysis of Sri-Trang Reservoir and U-Tapao Canal water samples as shown in Figure 5.5, 5.6 and Table 5.3, there was a change in the FT-IR character of UF treated water samples comparing to raw water in both seasons. The absorbance of the peak at 1660, 1420 and 1400 cm^{-1} were a slightly decreased by both hybrid UF processes and the absorbance of the peak in 1150-1090 cm^{-1} region were greater decreased than those peak. It indicated that the both hybrid UF processes had an efficiency to reduce DOM especially the C-O stretching of alcohols, ethers and carbohydrates.



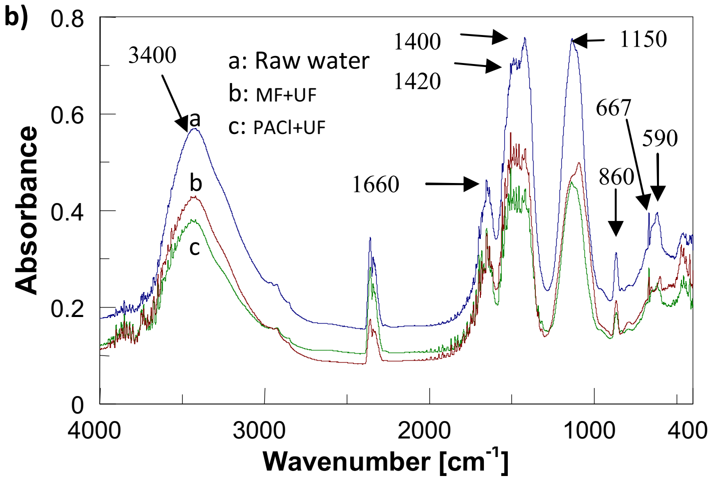


Figure 5.5 FT-IR spectra of Sri-Trang raw water and treated water by hybrid UF processes in a) rainy season and b) dry season

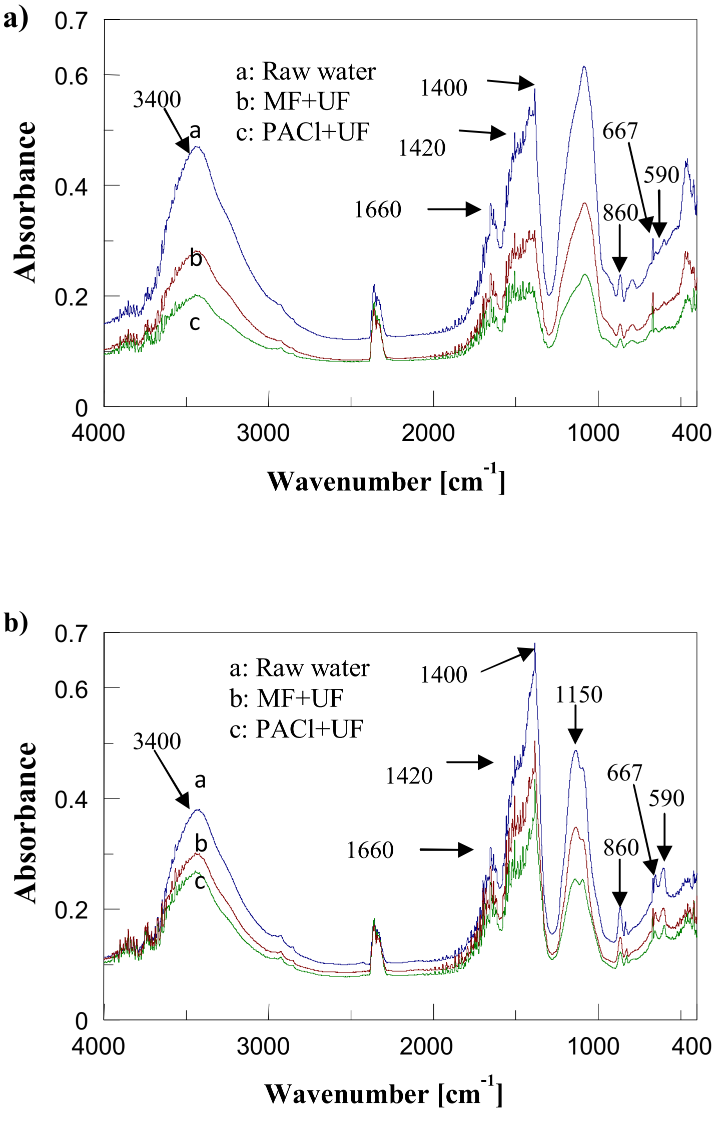


Figure 5.6 FT-IR spectra of U-Tapao raw water and treated water from U-Tapao Canal by hybrid UF processes in a) rainy season and b) dry season

Table 5.3 FTIR spectra of raw water from Sri-Trang Reservoir and U-Tapao Canal

Wavenumber (cm^{-1})		Assignment
Sri-Trang Reservoir	U-Tapao Canal	
3400	3404	O-H groups or H-bonded N-H groups
1660	1660	C=O stretching of amide groups (amide-1)
1520	1515	C=C stretching vibration of benzene, pyridines
1420-1400	1420-1400	O-H bending vibration of carboxylic groups, C-O stretching of alcohol
1150-1190	1150-1190	C-O stretching of ester, ethers, phenol and alcohol
860	860	C-H bending vibration of aromatic rings
590-667	590-667	Hydrogen-bonded OH stretching vibration carboxylic groups

5.2 Reduction of Trihalomethanes Formation Potential by Hybrid UF Processes

As can be seen from Figure 5.7, THMFP values of Sri-Trang Reservoir raw water in rainy season and dry season were 433 µg/L and 509 µg/L, respectively. While THMFP of 56 µg/L and 58 µg/L were observed from treated water by the hybrid MF+UF process which could reduce THMFP in raw water in rainy season and dry season by 87 and 85 percent, respectively. And THMFP of 52 µg/L and 70 µg/L were observed from treated water by the hybrid PACl+UF process which could reduce THMFP in raw water in rainy season and summer by 88 and 86 percent, respectively. For the THMFP values of U-Tapao Canal water sample as illustrated in Figure 5.8 found that THMFP of raw water in rainy season and dry season were 541 µg/L and 389 µg/L, respectively. After the hybrid MF+UF process, THMFP of 75 µg/L and 70 µg/L were observed which could reduce THMFP in raw water in rainy season and dry season by 86 and 82 percent, respectively. And THMFP of 67µg/L and 50 µg/L were observed from treated water by the hybrid PACl+UF process which could reduce THMFP in raw water in rainy season and dry season by 88 and 87 percent, respectively.

From the results, it can be observed that the hybrid UF process could reduce the THMFP values from both water sources more than 80 percent which higher than the DOC and UV-254 reduction. It might be due to the great removal of the C-O stretching of alcohols, ethers and carbohydrates in FT-IR analysis and this DOM functional group might be has a high reactivity with chlorine to form THMs. Therefore, the remaining of DOM functional group after hybrid UF process which has a low reactivity with chlorine also create a low level of THMFP.

In addition, chloroform ($CHCl_3$) and dichlorobromomethane ($CHCl_2Br$) were the THMFP species observed in this study. When considering the presence of THMs species, it was found that chloroform was the major THMFP species in all of water samples from both water sources while dichlorobromomethane was found in minority. Based on the obtained results, the use of hybrid UF processes could reduce THMFP and THM species. The hybrid UF process could reduce $CHCl_3$ from Sri-Trang Reservoir and U-Tapao Canal water samples in rainy season and dry season for 87 percent and 86 percent which was the major THM species reduced. According to the report of the WHO (2004) which the Metropolitan Waterworks Authority (Thailand) 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 µg/L and 60 µg/L, respectively. From these results, it can be stated that the THMFP values of treated water from both water sources by hybrid UF process in this study met the WHO standard and also the standard of Thailand Metropolitan Waterworks Authority.

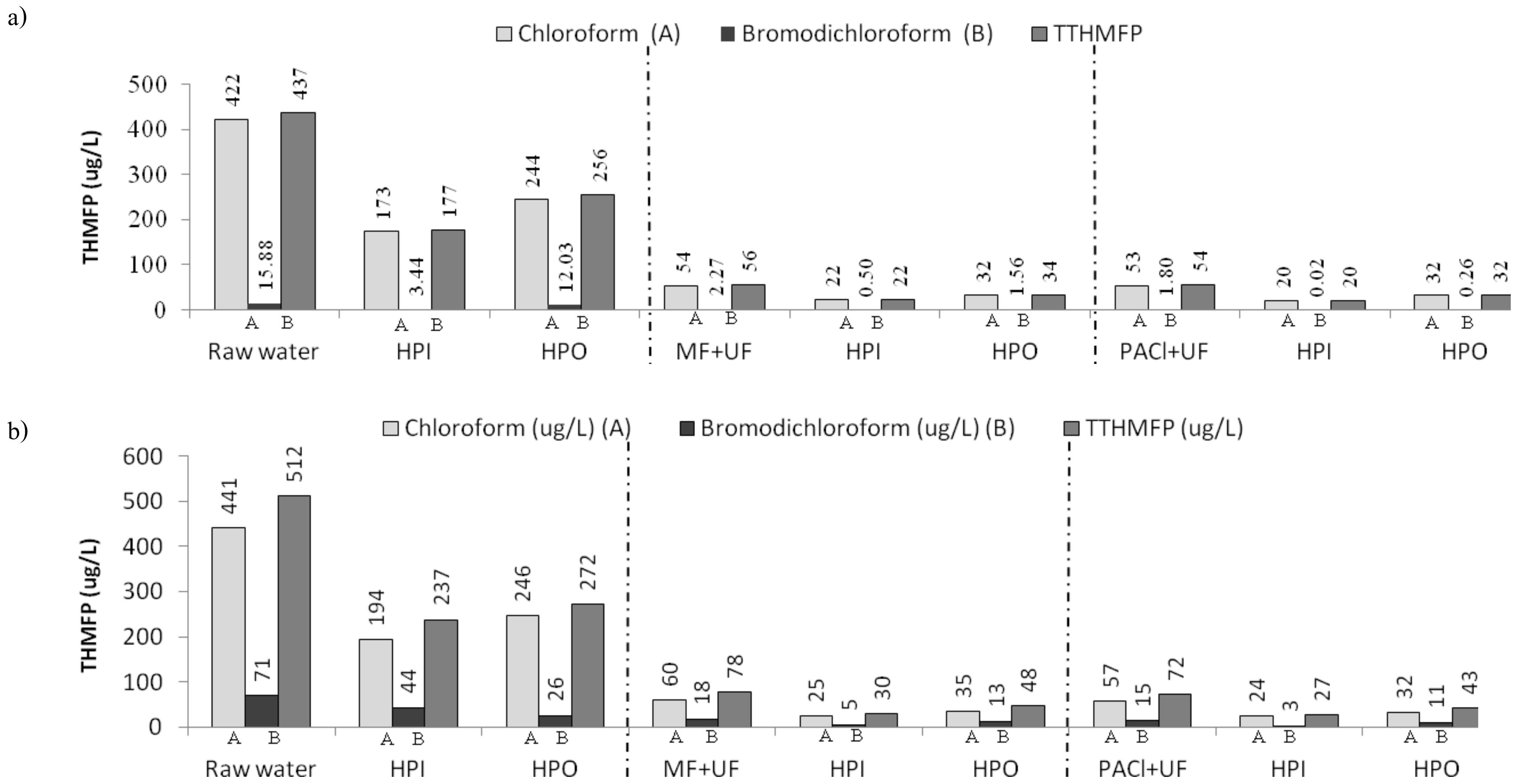


Figure 5.7 Reduction of THMFP and THM species of Sri-Trang Reservoir water by hybrid UF processes in

a) rainy season and b) dry season

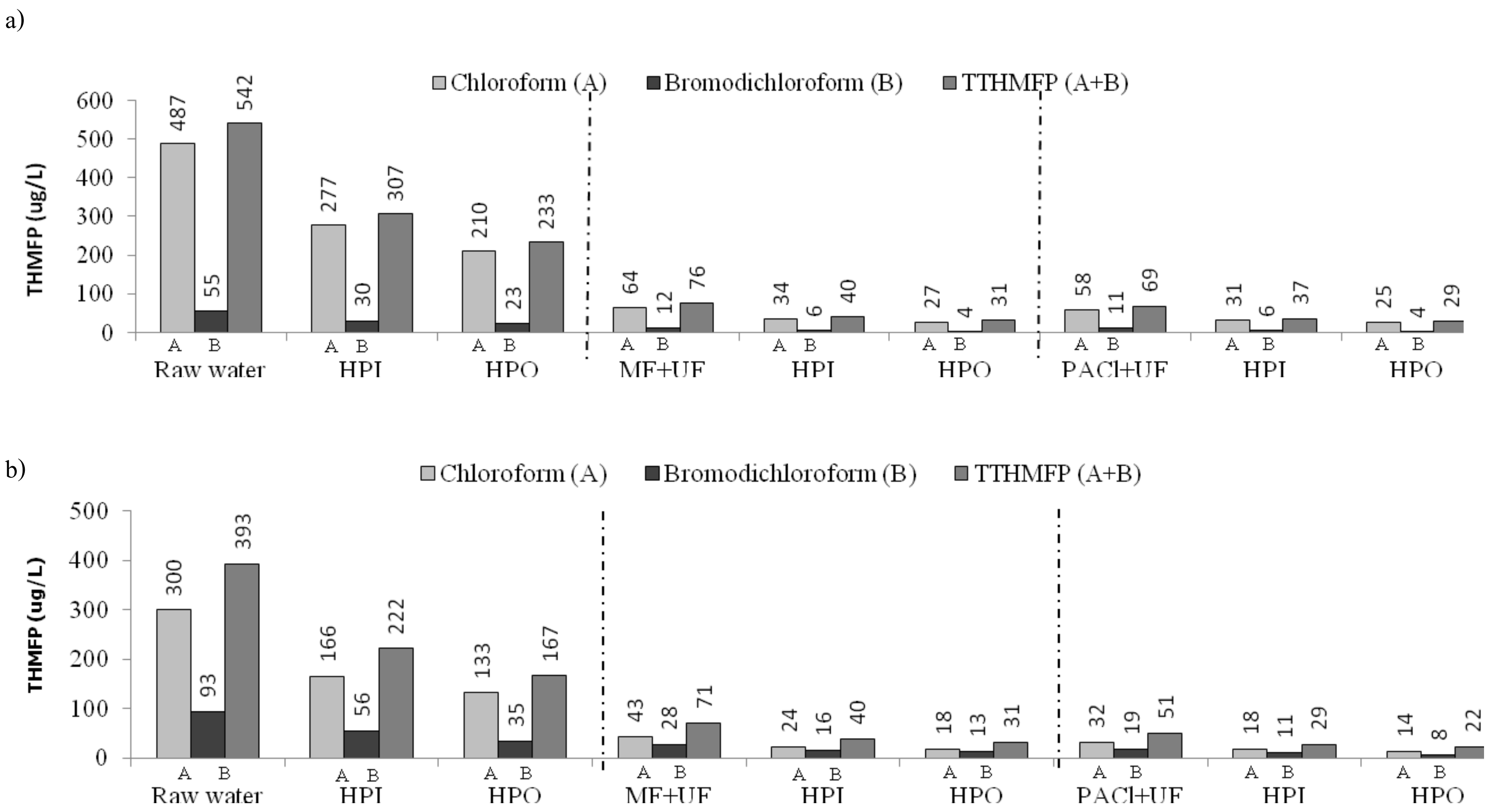


Figure 5.8 Reduction of THMFP and THM species of U-Tapao Canal water by hybrid UF processes in

a) rainy season and b) dry season

Moreover, the percent THMFP distribution of DOM fraction from Sri-Trang Reservoir water as shown in Table 5.4 indicates that the main precursor of THMFP was HPO fraction (~ 60%) in both seasons which is similar to the study of Kueseng *et al.*, (2010). For the percent THMFP distribution of DOM fraction from U-Tapao Canal water as shown in Table 5.5 indicate that the main precursor of THMFP was HPI fraction (~ 60%) in both seasons which is similar to the study of Inthanuchit *et al.*, (2009) but totally difference from the results of Sri-Trang Reservoir. To better understand the reactivity of each organic fraction on the formation of THMs, the specific THMFP (STHMFP) was observed in this analysis. The total THMFP was defined as the ratio between THMFP from each organic fraction and DOC of the water samples. This was to give an overall picture of how THMs were formed in the water samples. The specific THMFP, on the other hand, was the ratio between THMFP and DOC of each organic fraction to illustrate the ability of the DOM in water to react with chlorine to form THMs. The specific THMFP values of Sri-Trang Reservoir raw water and hybrid UF processes treated water are presented in Figure 5.9 and Figure 5.10 for STHMFP of U-Tapao Canal water samples.

Table 5.4 THMFP distribution and reduction of HPI and HPO from Sri-Trang Reservoir water

Sample	%THMFP distribution of HPI and HPO	THMFP (µg/L)			% THMFP Reduction		
		HPI	**HPO**	**HPI+HPO**	**HPI**	**HPO**	**HPI+HPO**
Rainy Season							
1) Raw water	HPI (41%) < HPO (59%)	177	256	433	-	-	-
2) MF+UF	HPI (39%) < HPO (61%)	22	34	56	88	87	87
3) PACl+UF	HPI (38%) < HPO (62%)	20	32	52	89	88	88
Dry Season							
1) Raw water	HPI (47%) < HPO (53%)	237	272	509	-	-	-
2) MF+UF	HPI (39%) < HPO (61%)	30	48	78	87	82	85
3) PACl+UF	HPI (39%) < HPO (61%)	27	43	70	89	84	86

Table 5.5 THMFP distribution and reduction of HPI and HPO from U-Tapao Canal water

Sample	%THMFP distribution of HPI and HPO	THMFP (μg/L)			% THMFP Reduction		
		HPI	HPO	HPI+HPO	HPI	HPO	HPI+HPO
Rainy Season							
1) Raw water	HPI (57%) >HPO (43%)	307	233	541	-	-	-
2) MF+UF	HPI (56%) > HPO (44%)	42	33	75	86	86	86
3) PACl+UF	HPI (55%) > HPO (45%)	37	30	67	88	87	88
Dry Season							
1) Raw water	HPI (57%) > HPO (43%)	222	167	389	-	-	-
2) MF+UF	HPI (56%) > HPO (44%)	39	31	70	82	81	82
3) PACl+UF	HPI (56%) >HPO (44%)	28	22	50	87	87	87

As can be seen from Figure 5.9 and Figure 5.10, when comparing the specific THMFP of each DOM fraction of raw water from Sri-Trang Reservoir and U-Tapao Canal and hybrid UF processes treated water in both rainy season and dry season, HPO fraction demonstrated itself as the highest active source for the formation of THMs for all of samples despite the quantity of HPI fraction was larger than HPO fraction after UF experiment (Figure 5.6a). This indicated that HPO was strongly reactive with chlorine in THMs formation. In addition, when comparing the specific THMFP of each DOM fraction with that of the unfractionated water, the specific THMFP values of HPI was moderately lower than those of the unfractionated water, while the specific THMFP of HPO was moderately lower than that of the unfractionated water. This could be used to support the observation that the summation of the THMFP of the two DOM fractions was much lower than the THMFP of the unfractionated water.

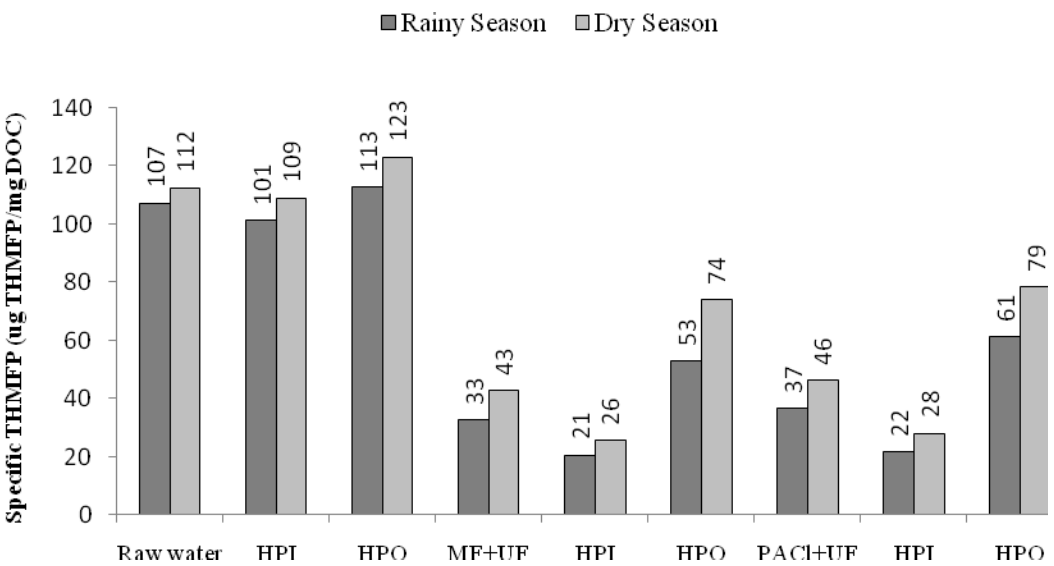


Figure 5.9 Specific THMFP of Sri-Trang Reservoir raw water, MF+UF and PACl+UF in rainy season and dry season and specific THMFP of the two fractions in the water samples

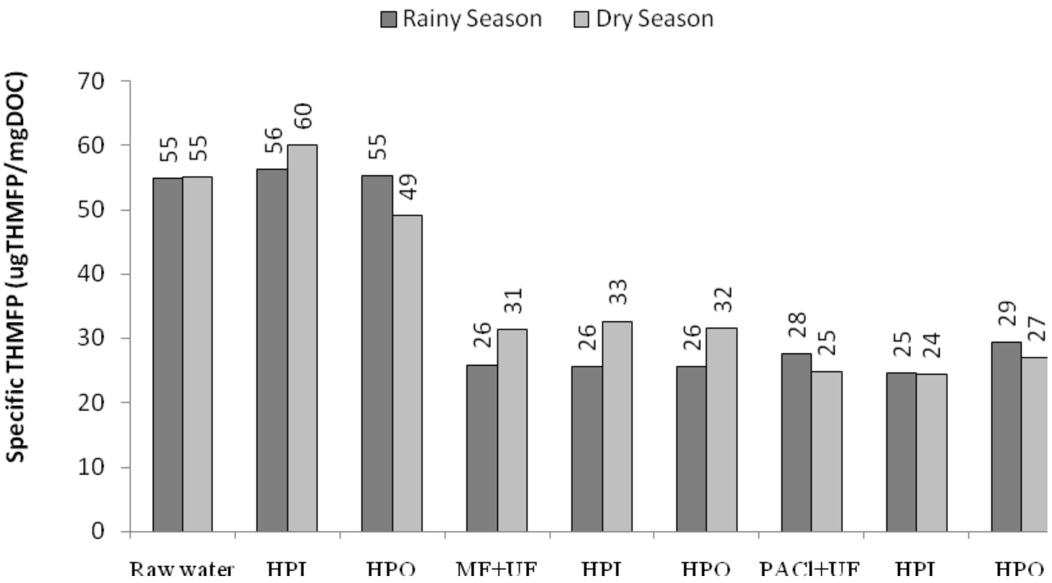


Figure 5.10 Specific THMFP of U-Tapao Canal raw water, MF+UF and PACl+UF in rainy season and dry season and specific THMFP of the two fractions in the water samples

5.3 Effect of coagulation and MF on UF membrane flux decline

The effect of coagulation and MF process on UF behavior from Sri-Trang Reservoir water also observed as shown in Figure 5.11 where the measured flux is plotted against time. Figure 5.11 shows that the rates of permeate flux decline were different according to the pre-treatment process. With the coagulation process, the UF flux decreased gradually to about 9 percent for rainy season of the initial flux after 120 min and 14 percent for dry season, in contrast to MF process, the membrane flux decreased to 24 percent and 27 percent of the initial flux for the same time, respectively. This suggests that the UF membrane flux declines slowly with 20 mg/L of PACl coagulant and declines more with MF process. These results corresponded with the effect of coagulation and MF process on UF behavior from U-Tapao Canal water (Figure 5.12) that the UF membranes flux declines gradually with 40 mg/L of PACl to about 14 percent for rainy season of the initial flux after 120 min and 13 percent for dry season, whilst, declines rapidly with MF process which decreased to 28 percent and 26 percent of the initial flux for the same time, respectively.

It is interesting to note that the flux decline showed a slower rate for filtration of coagulated water than for filtration of MF pre-treated water. These changes in flux decline represent the configuration of the cake formed on the surface of the membrane. The cake is mainly of porous and loose structure, this cake represents lower resistance to filtration. Chen *et al*., (2007) reported that HPO fraction was responsible for rapid decline in ultrafiltration flux. Coagulation pretreatment selectively removes the HPO fraction of NOM, leaving the HPI fraction in supernatant water. Therefore, residual DOM plays an important role in determining the rate of fouling in UF with coagulation pre-treatment. In ultrafiltration of coagulated water, the flux experienced slow decline. On the basic of the previous results and discussions, a role of coagulation is postulated to interpret the effect of coagulation on fouling. As the coagulated water was filtered by UF process, the flocs deposited on the surface of the membrane and formed the cake that absorbed the residual DOM substances. The cake might be easily removed by backwashing and flushing, because it was not closely adhered to the surface. In contrast to the MF process as a pre-treatment, MF uses a size sieving mechanism which has pore size of 0.1 µm that could effectively reduce particles which larger than 0.1 μm in water but lesser for particles smaller than 0.1 μm such as humic substances which have particle sizes in range of 0.0025-0.01 μm and the particle size analysis results could support that the pre-treated water by MF process had the particle size smaller than 0.1 μm. As the MF pre-treated water was filtered, the DOM substances that remained in the water after MF process were rejected by the UF membrane, the substances smaller than 0.008 μm were plugged or adsorbed into the pores of UF membrane, causing irreversible fouling, while for large size colloids and particulates, they would deposit or accumulate onto the membrane surface. During the filtration, more and more fine colloids and DOMs adsorbed and plugged into the membrane pore walls, resulting in the decrease of the membrane flux as shown in Figure 5.11 and Figure 5.12.

However, the applications of coagulation dose have drawbacks. First, it forms a large portion of the operating costs, due to chemicals consumption and the increased disposal costs of the concentrate stream. Second, coagulant residuals in the permeate, caused by overdosing, reduce the product quality and can lead to issues in downstream processes. In some cases it is even observed that dosing of coagulant adversely acts the performance of membrane filtration (Maartens *et al*., 1999). Therefore, the MF process had a possibility to be used as a pre-treatment in the future.

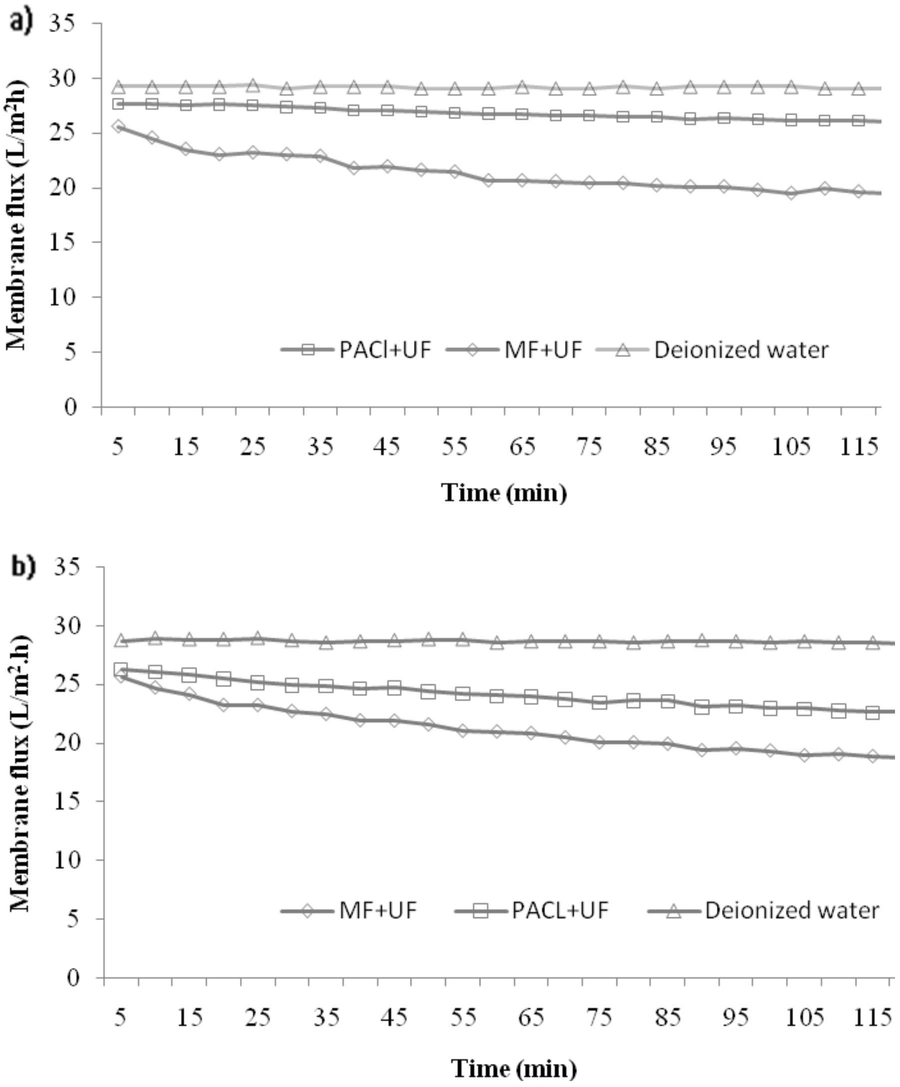


Figure 5.11 Effect of coagulation and MF on membrane flux decline in a) rainy season and b) dry season of Sri-Trang Reservoir

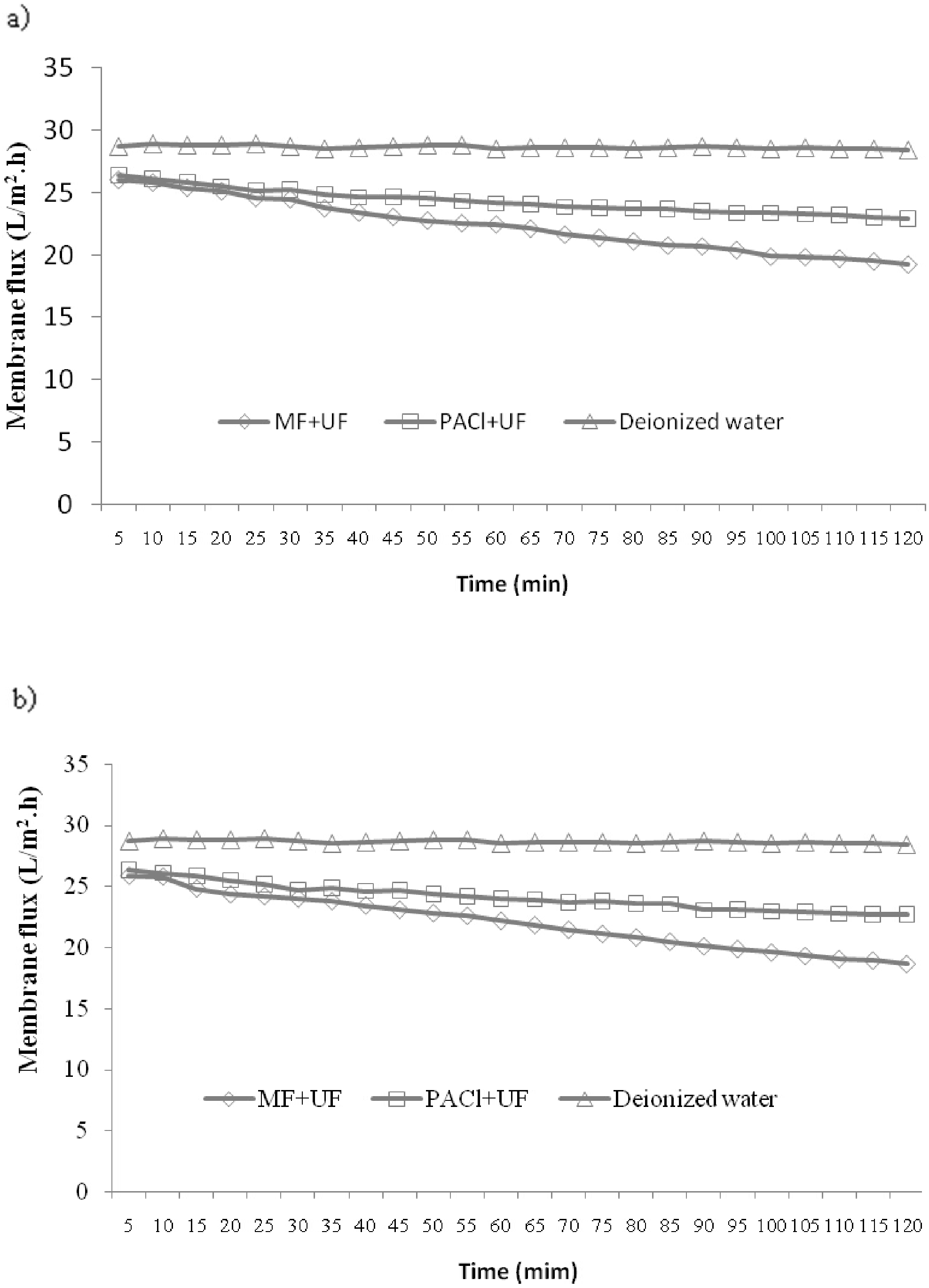


Figure 5.12 Effect of coagulation and MF on membrane flux decline in rainy season and b) dry season of U-Tapao Canal

CHAPTER 6

SUMMARY AND PROSPECT

6.1 Summary

Based on the obtained results from the study of DOM surrogate parameters (DOC and UV-254) removal, DOM characterization (FEEM and FT-IR) and change of THMFP from raw water and treated water by hybrid immerseble polysulfone hollow fiber UF membrane combined with coagulation process and MF process with pore size of 0.1 μm as a pre-treatment and the effect of coagulation and MF on UF membrane flux decline of Sri-Trang Reservoir which are reported and discussed in chapter 4 and chapter 5 and U-Tapao Canal water which are reported and discussed in chapter 6 and chapter 7, the following conclusions could be drawn.

1. The characteristics of raw water depend on month and season. The raw water from U-Tapao Canal had a higher variation than raw water from Sri-Trang Reservoir. Season also play a major part in the DOC distribution of raw water. DOC distribution in raw water from Sri-Trang Reservoir in dry season was higher than that of rainy season whereas DOC distribution in raw water from U-Tapao Canal in rainy season was higher than that of dry season.
2. The resin adsorption technique using DAX-8 showed that HPO fraction was the major fraction of DOM (56 percent) in raw water from Sri-Trang Reservoir whereas the major fraction of DOM in raw water from U-Tapao Canal was HPI fraction (52-56 percent).
3. The hybrid coagulation-ultrafiltration membrane process could reduce DOM in terms of UV-254 and DOC from Sri-Trang Reservoir water and U-Tapao Canal water more effectively than the hybrid microfiltration-ultrafiltration membrane process.
4. A coagulation process as a pre-treatment could produce permeates flux higher than MF pre-treatment comparing in the same time in both Sri-Trang Reservoir water and U-Tapao Canal water.

5. The reduction of THMFP consideration of Sri-Trang Reservoir water and

U-Tapao Canal water, the hybrid ultrafiltration combined with microfiltration had almost the same removal efficiency as hybrid ultrafiltration combined with coagulation process in this study.

6. HPO fraction was the main precursor of THMFP in Sri-Trang Reservoir water samples and THMFP of water samples in dry season had a higher potential for forming of THMs (especially chloroform) than that of rainy season. Therefore, THMs should be strictly controlled especially in dry season, whilst, HPI fraction was the main precursor of THMFP in U-Tapao Canal water samples and THMFP of water samples in rainy season had a higher potential for forming of THMs (especially chloroform) than that of dry season. Therefore, THMs should be strictly controlled especially in rainy season.

7. FEEM technique could detect three strong fluorescent peaks; peak A at

280 nm_{Ex}/410-430 nm_{Em} (humic-like substances), peak B at 330 nm_{Ex}/390-410 nm_{Em} (fulvic-like substances) and peak C at 280 nm_{Ex}/ 360-370 nm_{Em} (tryptophan-like substances) in raw water and treated water by hybrid UF processes of Sri-Trang Reservoir and each peak contained in the same position in both seasons whereas this technique could detect four strong fluorescent peaks from raw water and treated water by hybrid UF processes and each peak contained in the same position in both seasons including; peak A at 280 nm_{Ex}/360-370 nm_{Em}, peak B at 280 nm_{Ex}/360-370 nm_{Em} (tryptophan-like substances), peak C at 275 nm_{Ex}/ 430-470 nm_{Em} (humic-like substances) and peak D: 330 nm_{Ex}/390-410 nm_{Em} (fulvic-like substances)

8. FTIR analysis found functional groups including H-bonded N-H groups at around 3400 cm^{-1}, C=O stretching of amide groups at 1660 cm^{-1}, O-H bending vibration of carboxylic groups at the bands in range of 1420-1400 cm^{-1}, C-O stretching of alcohols, ethers and carbohydrates were

illustrated by the strong peaks at 1150-1090 cm^{-1}, the C-H bending vibration of aromatic ring was indicated by the peak at 860 cm^{-1} and the bands in the 590-667 cm^{-1} were COOH. And the both of hybrid UF processes had an efficiency to reduce DOM especially the C-O stretching of alcohols, ethers and carbohydrates

9. From the results, it can be stated that the hybrid ultrafiltration with pore size of 0.008 μm has a potential to be used in the PSU water treatment plant and Hat Yai water treatment plant that use raw water from Sri-Trang Reservoir and U-Tapao Canal water instead of the conventional water treatment system in the case of DOM reduction. Especially the hybrid ultrafiltration combined with microfiltration with pore size of 0.1 μm, because of no coagulant and low chemicals need for microfiltration as a pre-treatment. In addition, the hybrid MF-UF process might reduce the sludge which has a high level of Aluminium contained disposal to natural water sources.

6.2 Prospects

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

1. To enhance the efficiency of UF process combined with MF, the pore size variation of MF membrane should be observed to investigate the optimum condition of hybrid MF-UF process in the future and coagulation using other coagulants such as ferric chloride is recommended.

2. The foulant accumulated onto the UF membrane surface should be observed to better understand DOM rejection by UF process.

3. In addition to study the enhancing of hybrid UF processes, the economic cost benefit analysis must be considered.

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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

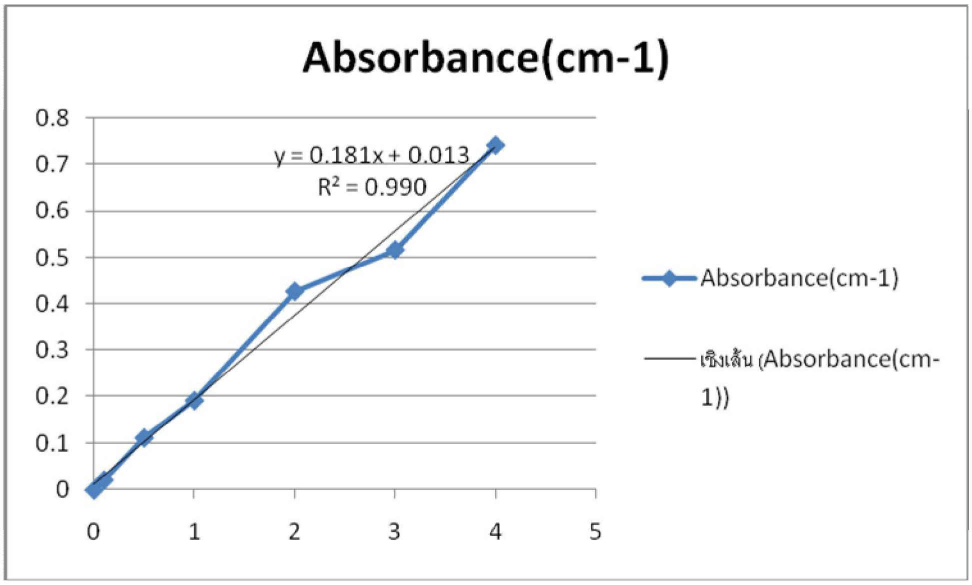
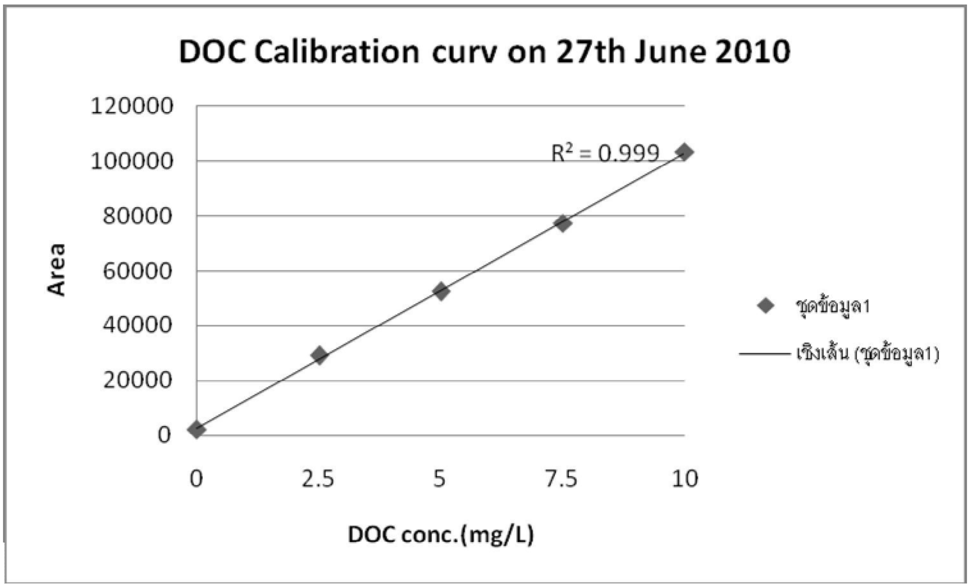


Table A-2: Calibration curve of DOC

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 FTIR spectra of tryptophan-like and humic acid-like substances.

Wavenumber (cm^{-1})			Assignment
DOM	Tryptophan substances	Humic acid substances	
3670-3300	3404	3670 – 3300	OH group
3100-3000	-	3077-3030	Aromatic C-H stretching
2950-2850	-	2950-2850	Aliphatic C-H,CH_2,CH_3 stretching
1730-1710	1700-1668	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	-	-	Aromatic C=C vibration
1570-1550	-	-	N-H bending vibration of amide groups (amide-2)
1465-1440	1456-1414	1440	Aliphatic C-H deformation
1420-1400	-	1400-1390	O-H bending vibration of carboxylic groups, C-O stretching of alcohol
1380-1370	-	-	C-H deformation of C-H_3 groups
-	1357-1315	1390-1322	Salts of carboxylic acids
1300-1000	1231-1157	1280-1137	C-O stretching of ester, ethers, phenol and alcohol
-	1099-1007	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

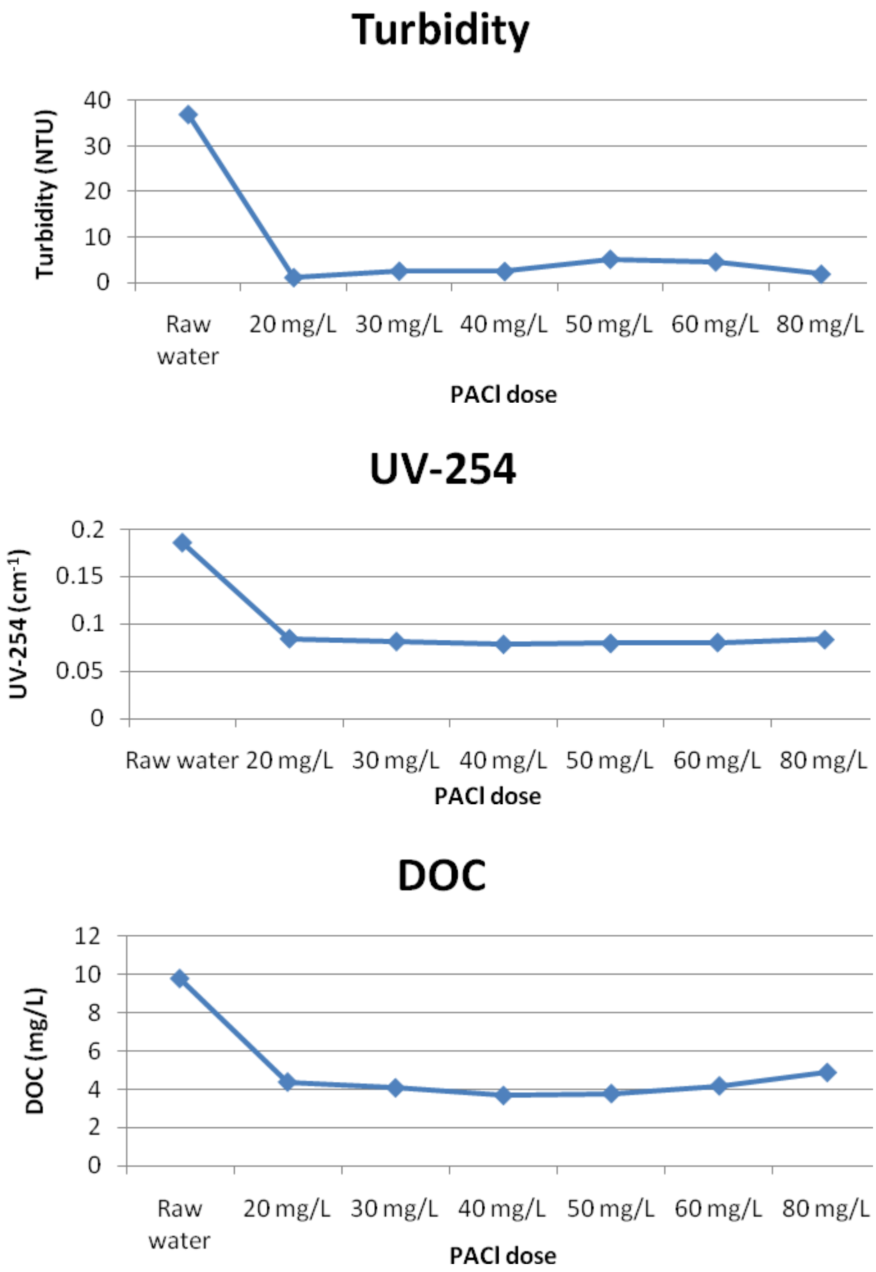


Figure B-1 Changes in Turbidity, UV-254 and DOC of U-Tapao Canal water by Jar Test Experiment

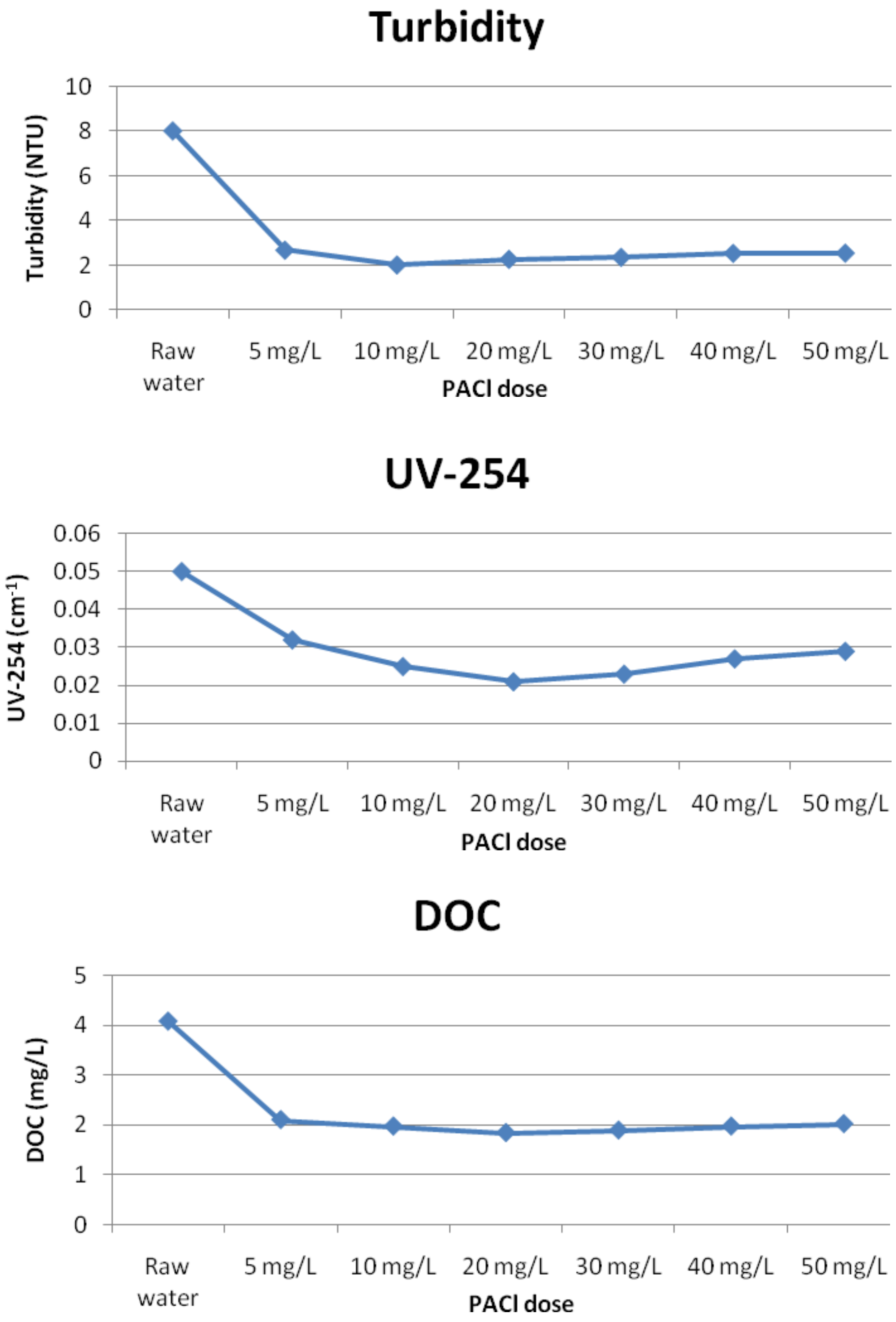


Figure B-2 Changes in Turbidity, UV-254 and DOC of Sri-Trang Reservoir raw water by Jar Test Experiment

VITAE

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List of Publications and Proceedings

[1] Warintorn Banchapattanasakda, Charongpun Musikavong, Thunwadee Suksaroj and Chaisri Suksaroj. "The Determination of Dissolved Organic Matter Reduction in Raw Water Supply by Hybrid Ultrafiltration Process". *The 9th National Environmental Conference. 24-27 March 2010.* Ubonratchatani University, Thailand.

[2] Warintorn Banchapattanasakda, Charongpun Musikavong, Thunwadee Suksaroj, Suraphong Wattanachira and Chaisri Suksaroj. "Reduction of Dissolved Organic Matter in Raw Water Supply Reservoir by Hybrid Ultrafiltration Process". *The 8th International Symposium on Southeast Asian Water Environment 24-26 October 2010.* Graceland Hotel, Phuket, Thailand.