

TRIHALOMETHANE FORMATION IN CHEMICAL CLEANING WATER OF CERAMIC  
MEMBRANE BY SODIUM HYPOCHLORITE

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จุฬาลงกรณ์มหาวิทยาลัย

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By	Mr. Prattakorn Sittisom
Field of Study	Environmental Management
Thesis Advisor	Associate Professor Suraphong Wattanachira, D.Eng.

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ปรีดถกร สิทธิสม : การเกิดสารไตรฮาโลมีเทนในน้ำล้างทำความสะอาดของเซรามิกเมมเบรนโดยใช้โซเดียมไฮโปคลอไรท์. (TRIHALOMETHANE FORMATION IN CHEMICAL CLEANING WATER OF CERAMIC MEMBRANE BY SODIUM HYPOCHLORITE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. สุรพงษ์ วัฒนะจิระ, 84 หน้า.

ในปัจจุบัน เพื่อการส่งเสริมคุณภาพชีวิตที่ดีขึ้น จำเป็นต้องมีการควบคุมมาตรฐานคุณภาพน้ำในการอุปโภค บริโภคที่สูงขึ้น ดังนั้น จึงได้มีการพัฒนาเทคโนโลยีขั้นสูงในการผลิตน้ำประปาขึ้น โดยหนึ่งในเทคโนโลยีได้รับการยอมรับและได้รับความสนใจเป็นอย่างมากคือ กระบวนการกรองด้วยเซรามิกเมมเบรน แต่อย่างไรก็ตาม การอุดตันของเซรามิกเมมเบรนเป็นปัญหาสำคัญที่เกิดขึ้นในกระบวนการกรองด้วยเซรามิกเมมเบรน ซึ่งนำไปสู่การลดลงของประสิทธิภาพในกระบวนการกรอง งานวิจัยนี้มีวัตถุประสงค์หลักเพื่อศึกษาการก่อตัวของสารไตรฮาโลมีเทนในน้ำล้างทำความสะอาดของเซรามิกเมมเบรน ที่ได้จากการล้างย้อนด้วยวิธีการกายภาพและเคมีเพื่อกำจัดสิ่งอุดตันที่เคลือบอยู่บนผิวหน้าของเซรามิกเมมเบรนที่ใช้ในการกรองน้ำดิบที่เก็บจากแม่น้ำปิง

จากผลการทดลองพบว่า สารอินทรีย์คือสาเหตุหลักที่ก่อให้เกิดการอุดตันของเซรามิกเมมเบรน ในการกำจัดสารอินทรีย์ที่เคลือบผิวเซรามิกเมมเบรนได้เลือกใช้โซเดียมไฮโปคลอไรท์ ในการล้างทำความสะอาดเซรามิกเมมเบรน เนื่องจากสารกำจัดสารอินทรีย์ออกจากเซรามิกเมมเบรนได้ดี แต่โซเดียมไฮโปคลอไรท์สามารถทำปฏิกิริยากับสารอินทรีย์ และก่อให้เกิดสารไตรฮาโลมีเทน ซึ่งเป็นสารก่อมะเร็ง การทดลองเพื่อศึกษาโอกาสในการก่อตัวของสารไตรฮาโลมีเทน ได้ดำเนินการภายใต้สภาวะในการทำปฏิกิริยาที่ต่างกัน 16 แบบ คือมีความเข้มข้นของโซเดียมไฮโปคลอไรท์ที่ใช้ แบ่งเป็น 2,000 3,000 4,000 และ 5,000 mg/L และแต่ละความเข้มข้นแบ่งเวลาสัมผัส ออกเป็น 4 ช่วงเวลา คือ 6, 8, 10 และ 12 ชั่วโมง ตามลำดับ โดยผลการทดลองแสดงให้เห็นว่าสารไตรฮาโลมีเทนก่อตัวที่ทุกสภาวะ โดยความเข้มข้นสูงสุดของสารไตรฮาโลมีเทนที่พบคือ 887.59  $\mu\text{g/L}$  ที่ความเข้มข้นโซเดียมไฮโปคลอไรท์ 5,000 mg/L และเวลาสัมผัส 12 ชั่วโมง

นอกจากนี้ยังได้ศึกษาประสิทธิภาพในการฟื้นฟูฟูลักซ์ จากการใช้โซเดียมไฮโปคลอไรท์ และเวลาสัมผัสที่แตกต่างกัน ผลการทดลองพบว่าสภาวะที่ทำให้ประสิทธิภาพการฟื้นฟูฟูลักซ์เกิดขึ้นได้สูงสุดเท่ากับ 69.68% ที่ความเข้มข้นโซเดียมไฮโปคลอไรท์ 5,000 mg/L และเวลาสัมผัส 12 ชั่วโมง

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PRATTAKORN SITTISOM: TRIHALOMETHANE FORMATION IN CHEMICAL CLEANING WATER OF CERAMIC MEMBRANE BY SODIUM HYPOCHLORITE. ADVISOR: ASSOC. PROF. SURAPHONG WATTANACHIRA, D.Eng., 84 pp.

At present, ceramic membrane filtration is one of the best promising technologies having been received intensive attention. However, the major problem in membrane filtration is membrane fouling which lead to degradation of filtrated water quality. In this study, Trihalomethanes formation in chemical soaking investigation was the main objective. Ping River water was used as feed raw water in the ceramic membrane filtration. Physical backwashing and chemical soaking were conducted to remove foulants which coated in ceramic membrane surface.

The results showed the organic matter was the main cause of ceramic membrane fouling. Sodium hypochlorite (NaOCl) was used for organic matter removal during chemical soaking experiment. However, the chlorine can react with organic matter to form Trihalomethanes (THMs), which is a carcinogen. THMs formation by using sodium hypochlorite (NaOCl) in chemical soaking water was investigated. In the experiment, sixteen fouled membranes were soaking in the various conditions. The concentration of NaOCl was varied at 2,000, 3,000, 4,000 and 5,000 mg/L and each concentration was varied with different soaking times at 6, 8, 10 and 12 hours, respectively. THMs were found in every condition and increased with the increasing of NaOCl concentration. The highest THMs concentration is 887.59 $\mu$ g/L which obtained at 5,000 mg/l of NaOCl concentration with 12 hours of soaking time. From this study, THMs formed in every condition, so chemical soaking water could be treated or should be studied for appropriate treatment technology.

The effects of sodium hypochlorite (NaOCl) concentration and soaking time on the flux recovery of fouled ceramic membrane were also investigated. The results showed that the highest efficiency of flux recovery is 69.68% which obtained at 5,000 mg/l of NaOCl concentration with 12 hours of soaking time.

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## LIST OF ABBREVIATIONS



CHBr <sub>3</sub>	Bromoform
CHCl <sub>2</sub> Br	Bromodichloromethane
CHCl <sub>3</sub>	Chloroform
CHClBr <sub>2</sub>	Dibromochloromethane
Cl	Chlorine
cm	Centimeter
°C	Degree Celsius
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EPA	Environmental Protection Agency
g/cm <sup>3</sup>	Gram per Cubic Centimeter
g/L	Gram per Liter
g/mol	Gram per Molar
GC	Gas Chromatograph
hr	Hour
L/mg-m	Liter per milligram-meter
m <sup>3</sup> /m <sup>2</sup> -d	Cubic Meter per Square Meter - Day
MF	Microfiltration
mg/l	Milligram per Liter
NOM	Natural Organic Matter
NTU	Nepheo Turbidity Unit

s	Second
SUVA	Specific Ultraviolet Absorption
THMs	Trihalomethanes
TOC	Total Organic Carbon
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
UV-254	Ultraviolet absorbtion at wave length 254 nanometer
UV	Ultraviolet Absorbtion

## CHAPTER I

### INTRODUCTION

#### 1.1 Motivations

Clean water is needed for human wellbeing and essential for good health. So, a good water quality is very important to healthy life. But, about a billion people in many countries have not had a safe and sustainable water supply in the last decade because water demand already exceeds supply in many parts of the world.

A worldwide nowadays problem in the availability of potable water is due to the continuous growth in water demand not balanced by an adequate recharge. Moreover, water sources are suffering from a worsening of their quality due to the indiscriminate discharge of both domestic and industrial effluents without adequate treatments.

The technologies that improve water treatment capabilities are poised for significant growth due to the continuous increased demand for water. Specific water improvement technologies that allow water to be reused or poor quality water to be used for human consumption such as Ceramic Membrane Filtration (Macedonio, 2011).

Nowadays, membrane technology, an alternative water treatment, has emerged to comply with existing water quality regulations. In addition, because of its less

treatment space uses, less chemical requirement, and it also works with low energy use. The application of membrane filtration is used to produce drinking water due to its ability to remove the contaminants including particulates, colloids and pathogens. From material classification of membrane, ceramic membrane has widely been used for industry because of its advantages such as chemical resistant and thermal stability. It is well known that ceramic membranes are very resistant to severe chemical environments and they can be used for longer periods.

However, fouling is the major limitation of membrane filtration. Membrane fouling is one of the main disadvantages. Fouling is defined as the loss of membrane permeability due to the accumulation of solutes onto the surface of the membrane or into its pores. Organic matter was a major cause of permeate flux decline during drinking water treatment with membranes.

DOM is the major component of organic matter which can specify in the form of dissolved organic carbon (DOC). DOM is a complex mixture of organic materials which varies in size, functional groups and reactivity (Yee et al, 2009). In tropical countries such as Thailand, the surface water contains high amounts of DOC. So, membrane fouling caused by DOM is a major concern in ceramic membrane filtration because DOM causes irreversible fouling when the water is treated by membrane filtration. And DOC accumulated on membrane surface which can form THMs from chemical cleaning process by using chlorine compound agent (Monthakanti, 2011).

Chemical cleaning also controls membrane fouling, particularly inorganic scaling and organic and biofouling that is not removed with backwash. Chemical cleaning is



conducted for each membrane unit separately and is typically staggered to minimize the number of units undergoing cleaning at any time.

The goal of chemical cleaning is to restore the transmembrane pressure of the system to its clean level. Any foulant that is removed by either the backwash process is known as reversible fouling. Over time, membrane processes also experience some degree of irreversible fouling which cannot be removed through backwashing. Irreversible fouling occurs in all membrane systems, and eventually requires chemical cleaning or membrane replacement.

This study investigated the filtrated water and backwash water characteristics and THMs formation in chemical soaking water. Moreover, this study has also focused on the comparison of fouled ceramic membrane recovery between different chemical soaking conditions.

## 1.2 Objectives

- To investigate THMs formation by using sodium hypochlorite in chemical soaking water.
- To study the characteristics of ceramic membrane soaking water for irreversible fouling.
- To study the characteristics of ceramic membrane backwash water for reversible fouling.
- Investigate the effects of water backwashing for reversible fouling and chemical cleaning for irreversible fouling on performances of ceramic membrane filtration.

## 1.3 Hypothesis

- Sodium hypochlorite used for cleaning ceramic membrane can be reacted with natural organic matter coated on the ceramic membrane surface to form hazardous substance, trihalomethanes.

## 1.4 Scopes of study

- Water from Ping River was selected as water samples.
- DOM surrogates (DOC, UV-254 and SUVA) were analyzed to determine water quality.

- Fe, Mn and DOC were analyzed to determine ceramic membrane fouling characteristic.
- Sodium hypochlorite (NaOCl) was used in chemical soaking with 4 different concentrations and each concentration varied 4 soaking times.
- THMs in chemical soaking water were determined.



## CHAPTER II

### BACKGROUND AND LITERATURE REVIEWS

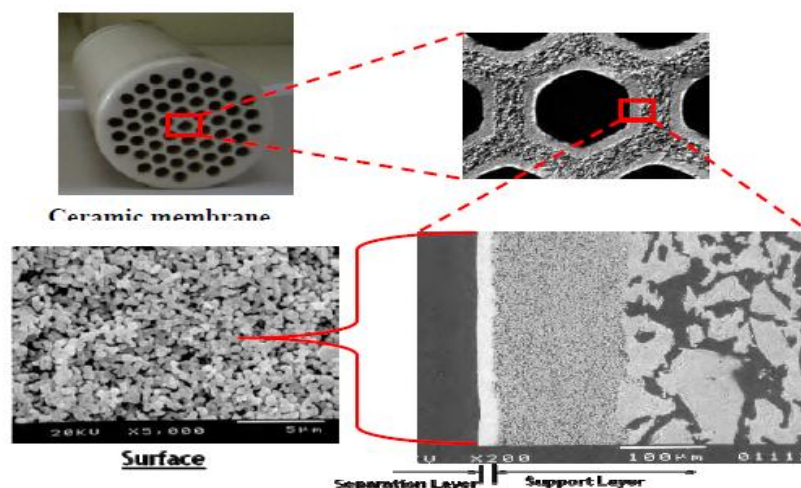
#### 2.1 Ceramic membrane filtration

Nowadays, water sources all over the world have been and are being polluted seriously by both common and new emerging pollutants. At the same time, a high quality drinking water is required to obtain a better life. Therefore, advanced technologies are developed and applied gradually in water treatment plants to effectively remove pollutants in water sources and to meet the strict potable water regulations. Among these technologies, membrane filtration is one of the best promising technologies having been received intensive attention. Through membrane filtration, (i) water quality regulations not only from chemical and physical aspects (such as organic matters and turbidity), but also from biological aspect such as pathogens, could be better achieved; (ii) the performance of the membrane system is less affected by fluctuate influent or other environmental factors in achieving good quality drinking water; and (iii) some conventional processes, such as the sedimentation and sand filtration processes, can be replaced by the membrane process in water treatment plants. As a result, construction area could be reduced and cost could be saved (Li et al., 2011).

Membrane filtration technology, particularly pressure-driven techniques such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) plays a very important role in water purification nowadays. UF and MF processes are

an alternative to the conventional clarification and filtration methods (Tomaszewska et al., 2002).

Ceramic membranes are usually composite ones consisting of several layers of one or more different ceramic materials. They generally have a macroporous support, one or two mesoporous intermediate layers and a microporous (or a dense) top layer. As shown in Figure 2.1.



**Figure 2. 1** The magnification of ceramic membrane structure (Source: Meta Water Co., Ltd. Confidential Report, 2008)

Ceramic materials are generally very stable chemically, thermally and mechanically, and in addition are frequently bio inert. They are therefore ideal materials for many applications in the chemical and pharmaceutical industry or in water and wastewater processing. However, the major problem in membrane filtration is membrane fouling. Membrane fouling is also cause of the quality of permeate declined and membrane degradation. According to the type of fouling, membrane fouling can be categorized into 4 types: inorganic fouling/scaling, particles/colloids

fouling, microbial/biological fouling, and organic fouling (Liu et al., 1998). Maartens et al (1999) reported treatment of the natural brown water with pre-coagulation increased DOM adsorption and decreased hollow-fiber UF (made from polysulfone) performance. Fouling control is very important procedure in membrane separation systems. A number of techniques were carried out including pretreatment processes of feed water (coagulation), improvement of operating conditions (i.e. transmembrane pressure, crossflow velocity, and backwashing), and membrane regeneration (i.e. chemical cleaning of membrane) (S. S. Madaeni et al., 2001).

The cleaning process which normally used to regenerate ceramic membrane is chemical cleaning and backwashing process. The pre-chlorination process was used to control fouling of ceramic membrane. The chlorine reacts with organic matter which accumulated in the pore size of ceramic membrane and cleaning organic matter from the ceramic membrane. The pre-chlorination process not only for fouling control but also use for microbial or virus disinfection during disinfection process in water supply system. However, the addition of chlorine or chlorinated compounds can cause the formation of disinfection by-product (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) which its potential adverse health effects.

## 2.2 Membrane backwashing

When organic is accompanied by fouling formation on the feed side of the membrane surface, yielding a permeate flux reduction, increasing power consumption, and requiring more frequent periodical membrane cleaning (C. Hyeok et al., 2005, J.J. Qin et al., 2009). Fouling type and accumulation rate depend strongly on feed water quality. Raw water fouling components and concentration decrease significantly when using various pretreatment methods, such as sand filtration, microfiltration (M. Marek et al., 2004), activated carbon and ultrafiltration (M. Sylwia et al., 2004). Despite pretreatment, a fouling layer may develop on the membrane surface during the filtration process. To resume the original product permeation rate, a backwash (BW) cleaning method must be used for the membrane followed by chemical cleaning of the membrane surface occasionally. The need for chemical cleaning is related to the need to remove fouling residues on the membrane surface that are not removed by backwashing.

### 2.2.1 Physical Backwash

Backwash is generated when water is forced through the filter, counter to the flow direction used during treatment operations. This action cleans the media by dislodging accumulated particles, including microorganisms, captured by the filter media. Backwash water typically averages 3% to 6% of total plant production.

### 2.2.2 Chemical Cleaning

The irreversible part of the fouling can only be removed by chemical cleaning. In regular intervals the backwash is combined with application of chemical cleaners (enhanced chemical backwash). A chemical cleaning can be applied when the enhanced chemical backwash alone is not able to restore the membrane performance to a sufficient degree. The stability of the dead-end filtration process is governed by the efficiency of the backwash process and the degree of irreversible fouling. Membrane chemical cleaning was performed either as a backwash cleaning without removing the membrane from the mixed liquor or as an extensive cleaning after the experiment completion.

### 2.3 Natural Organic Matter

Natural organic matter (NOM) is defined as a complex matrix of organic materials present in all natural waters. As a result of the interactions between the hydrological cycle and the biosphere and geosphere, the water sources used for drinking water purposes generally contain NOM. Thus the amount, character and properties of NOM differ considerably in waters of different origins and depend on the biogeochemical cycles of the surrounding environments. Moreover, the range of organic components of NOM may vary also on the same location seasonally, due to for example rainfall event, snowmelt runoff, floods or droughts. Floods and droughts are the main impacts of climate change on water availability and quality. It has been suggested that these changes may be the reason for an increase in the total amount of NOM, which has



been noted to occur on several areas around the world during the past 20 years. Besides the quantity of NOM, the quality of NOM has been noted to alter as well, since other important characteristics of NOM, e.g. specific UV absorbance (SUVA), have also increased. The changes in NOM quantity and quality have a significant influence on selection, design and operation of water treatment processes.

NOM found in natural waters consists of both hydrophobic and hydrophilic components, where the largest fraction is generally hydrophobic acids, which makes up approximately 50% of the TOC in water. These hydrophobic acids can be described as humic substances comprising of humic acids (HA), fulvic acids (FA) and humin. Hydrophobic NOM is rich in aromatic carbon, phenolic structures and conjugated double bonds, while hydrophilic NOM contains more aliphatic carbon and nitrogenous compounds, such as carbohydrates, sugars and amino acids. Physical and chemical fractionation of aquatic NOM at specific pH can be used to classify organic solutes into these broadly defined hydrophobic and hydrophilic fractions (Chow et al., 2004; Leenher, 2004; Sharp et al., 2006a,b). Whilst these fractions are more operationally than structurally defined, organic compounds can be judiciously assigned to a particular fraction according to their chain length and functional groups (Swietlik et al., 2004; Buchanan et al., 2005)

Another approach to define hydrophobicity is determination of SUVA value (which is UV-254 absorbance divided by the TOC concentration). High SUVA value indicates that the organic matter is composed largely of hydrophobic, high molar mass (HMM) organic material, in comparison of low SUVA value which means that water includes mainly organic compounds which are hydrophilic, low molar mass (LMM) and low in charge density (Sharp et al., 2006a,b). The different NOM fractions exhibit different properties in terms of treatability by coagulation, coagulant demand, chlorine and ozone reactivity and disinfection by-product formation potential (DBPFP) (Sharp et al., 2006a,b; Fabris et al., 2008).

### **2.3.1 Dissolved Organic Matter (DOM)**

Natural organic matter (NOM) is broken down organic matter that comes from plants and animals in the environment. Basic structures are created from cellulose, tannin, cutin, and lignin, together with other various proteins, lipids, and sugars. NOM is very important in the movement of nutrients in the environment and plays a role in water retention on the surface of the earth. Dissolved organic matter (DOM) is mainly consisting of NOM.

### 2.3.2 DOM characteristic

DOM has been classified according to a wide variety of scheme, one of which involves the origin of the plants that serve as a starting material for the DOM (Saether and Caritat, 1997). DOM is a complex mixture of hydrophilic and hydrophobic organic materials which vary in size, functional groups and reactivity. DOM fractions have been characterized according to molecular weight distributions, the presence of certain functional groups, acid-base and redox characteristics, aromatic/aliphatic character, chelating/complexation abilities, and trace element composition. The humus fraction of DOM has been further fractionated into fulvic acid and humic acid prior to analysis. Processes which occur in nature, one is interested in the behavior of DOM as it exists in situ, not in the behavior of the humic or fulvic acid fraction of that DOM.

According to Kennedy et al (2005), characterizing the DOM using a range of techniques, in addition to the quantitative measure of dissolved organic carbon (DOC), allows understanding and prediction of a water's susceptibility to coagulation, disinfection and formation of disinfection by-products. For example, monitoring DOM character by measuring the very hydrophobic fraction will allow operators to better control coagulant dose to optimize DOC removal.

### 2.3.3 Total Organic Carbon (TOC)

TOC measures the amount of organically bound carbon in water samples. The organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. TOC is independent of the oxidation state of organic matter and does not measure other organically bound elements such as hydrogen and nitrogen (APHA, AWWA, and WEF, 1995).

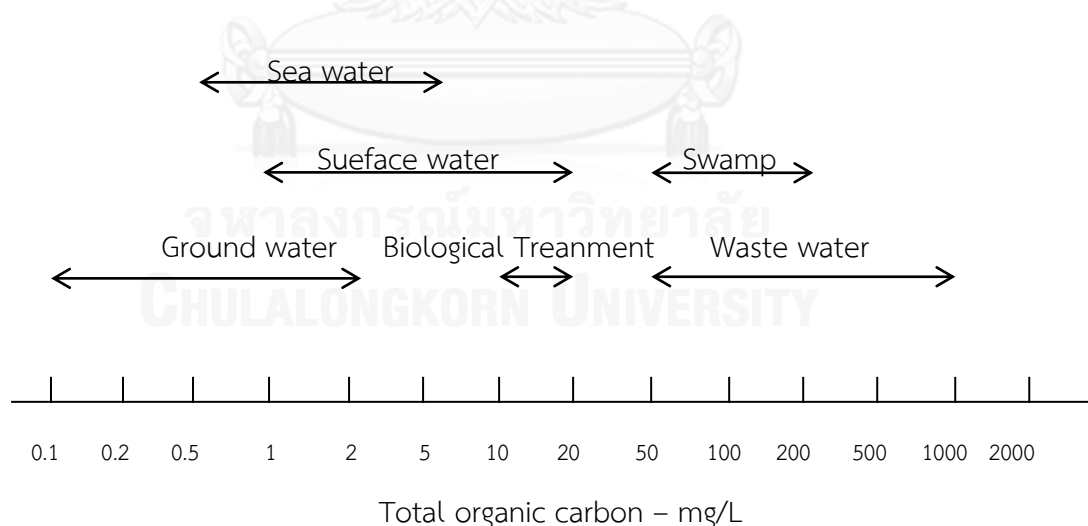
The removal of TOC is a conservation indicator of the removal of the precursors of trihalomethane and haloacetic acids, the most common DBPs (Miltner, Nolan, and Summers, 1994). Therefore, the percent removal of TOC is correlated to the percent removal of DBPs. The USEPA proposed the percentage TOC required for enhanced coagulation and softening. It will depend upon the TOC and alkaline concentration in raw water. The details are shown in Table 2.1 (USEPA, 1999).

**Table 2. 1** Percent removal of TOC requirements for enhanced coagulation and softening

Source Water TOC (mg/L)	Source Alkalinity (mg/L as CaCO <sub>3</sub> )		
	0 - 60	>60 - 120	>120
2.0 – 4.0	35%	25%	15%
4.0 – 8.0	45%	35%	25%
>8.0	50%	40%	30%

(Source: USEPA 1999)

Kavanaugh (1978) demonstrated range of TOC for a variety of natural water, shown in Figure 2.2



**Figure 2. 2** Range of TOC reported for a variety of natural water

### 2.3.4 Dissolve Organic Carbon (DOC)

Dissolved organic carbons are defined as the fraction of TOC that passes through a 0.45- $\mu\text{m}$ -pore-diam filter (Standard method, 1995). DOC is independent of the oxidation state of the organic matter. Organic carbon in natural water can be composed in two fractions, particulate organic carbon (POC) and dissolved organic carbon (DOC). In surface water, between 50 and 60 % of humic substances is DOC (Thurman, 1985).

### 2.3.5 UV Absorbance at Wavelength 254 nm (UV- 254)

Ultra-violet (UV) absorption at a wavelength of 253.7 nm 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 absorb UV light.

Organic compounds that are aromatic or that have conjugated double bonds absorb light in the ultraviolet (UV) wavelength region. Therefore, 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, Becker and Wattier, 1985). UV absorption is a useful surrogate measure for

NOM or precursor of THMs because humic substrates strongly absorb ultraviolet (UV) radiation (Eaton, 1995)

### 2.3.6 Specific Ultraviolet Absorbance

The ratio between UVA absorbance to DOC, referred to as specific absorbance (SUVA) ( $\text{cm}^{-1}\text{mg}^{-1}\text{L}$ ) demonstrates a relative index of humic content (Edzwald, 1993 and Owen et al., 1993). Specific absorbance could suggest the nature of NOM and its consequent THM formation (Krasner et al., 1996). Higher specific absorbance values tend to indicate higher humic content. Specific absorbance of a humic sample depends upon the molecular weight of the substances. (Pettersen 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 ( $\text{SUVA} > 3 \text{ L/mg-m}$ ) have been found to contain organic matter that is more humic-like in character, higher in apparent molecular weight (AMW), and more readily removed by coagulation (Edzwald, 1993) whereas lower SUVA values ( $< 3\text{L/mg-m}$ ) indicate the presence of organic matter of lower AMW that is more fulvic-like in character and more difficult to remove.

## 2.4 Trihalomethane

Chlorine has been used as an oxidant in drinking water treatment over the last 100 years. Although many benefits have been gained using chlorine as an oxidant, there are also disadvantages. One of the most important disadvantages is the formation of organic halogen compounds, such as trihalomethanes (THMs), as a consequence of the reaction of chlorine with the natural organic matter present in both surface and groundwater. The natural organic matter present in water bodies is a complex mixture of organic substances such as humic and fulvic acids, proteins, lipids, hydrocarbons and aminoacids. Furthermore, humic acid substances constitute the major fraction of natural organic matter in water supplies. These substances and more precisely the most soluble fraction of humicmatter, which are aromatic compounds with nucleophilic character, react with chlorine generating THMs. They have been known to cause cancer and other toxic effects in human beings. Concerns regarding the potential health effects of these by products have prompted several industrialized countries to develop a number of regulations.

The oxidant by-product regulation in the United States has set maximum concentration levels for total THM species (chloroform, bromodichloromethane, dibromochloromethane and bromoform) and five haloacetic acids species (monochloro-, dichloro-, trichloro-, monobromo- and dibromoacetic acid) of 80 and 60  $\mu\text{g/l}$ , respectively. European Union regulations limit THMs to 100  $\mu\text{g/l}$ . The World Health Organization guidelines are 200  $\mu\text{g/l}$  for chloroform, 60  $\mu\text{g/l}$  for bromodichloromethane, 100  $\mu\text{g/l}$  for dibromochloromethane, 90  $\mu\text{g/l}$  for



dichloroacetonitrile and 100 µg/l for dibromoacetonitrile. Moreover, in accordance with Royal Decree 140/2003 the maximum concentration of THMs in water in Spain is set at 100 µg/l as the sum of chloroform, bromoform, bromodichloromethane and dibromochloromethane.

#### 2.4.1 Chemistry of Trihalomethanes (THMs)

Trihalomethanes (THMs) are halogen-substituted single-carbon compounds with a general formula of  $\text{CHX}_3$ , where X may be fluorine, chlorine, bromine or iodine, or combinations thereof. THMs are a group of organic chemicals formed in water when chlorine reacts with natural organic matters (such as humic acids from decaying vegetation). The primary biochemical ancestors of THM identified by many researchers are humic substances including humic acid and fulvic acid (Rook, 1976; Trussell and Umphes, 1978; Oliver and Lawrence, 1979). These materials also contribute to the natural color of the water (Amy et al., 1983). Bromine was also identified as a precursor in the natural water, since its presence in chlorinated water may be oxidized by chlorine to form hypobromous acid (HOBr), which led to the formation of brominated THM species. Gould et al. (1983) also observed iodine, to a lesser extent.

Four THM species that actually occur in water supplies: Chloroform ( $\text{CHCl}_3$ ), Bromodichloromethane ( $\text{CHBrCl}_2$ ), Dibromochloroform ( $\text{CHBr}_2\text{Cl}$ ) and Bromoform ( $\text{CHBr}_3$ ).

Table 2.1 shows the chemical and physical properties of THMs that include Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform.

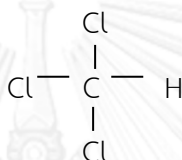
**Table 2. 2** Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform basic chemical and physical characteristics.

Empirical Formula	Molecular Weight (g/mol)	Specific Gravity (g/cm <sup>3</sup> )	Boiling Point (°C)	Melting Point (°C)	Solubility in water (g/L)
CHCl <sub>3</sub>	119.37	1.472	61.0	- 63	8.1
CHCl <sub>2</sub> Br	163.82	1.472	90.1	- 57.1	Insoluble
CHClBr <sub>2</sub>	208.29	2.380	120.0	- 63	4.75
CHBr <sub>3</sub>	257.73	2.894	150.0	8.3	Insoluble

(Source: Ghazali, 1989)

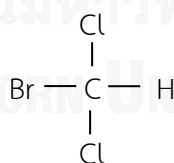
### 2.4.1.1 Chloroform

Chloroform is not only causes the depression on the central nervous system, but also hepatotoxicity, nephrotoxicity, teratogenicity and carcinogenicity (USEPA, 1998). The basic chemical and physical characteristics of Chloroform or trichloromethane (CHCl<sub>3</sub>) are shown in Table 2.1 and its chemical structure is as follows:



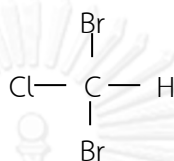
### 2.4.1.2 Bromodichloromethane

The basic chemical and physical characteristics of dichlorobromomethane or Bromodichloromethane (CHCl<sub>2</sub>Br) are shown in Table 2.2 and its chemical structure is as follows:



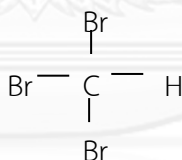
### 2.4.1.3 Dibromochloromethane

The basic chemical and physical characteristics of Dibromochloromethane or chlorodibromomethane ( $\text{CHClBr}_2$ ) are shown in Table 2.3 and its chemical structure is as follows:



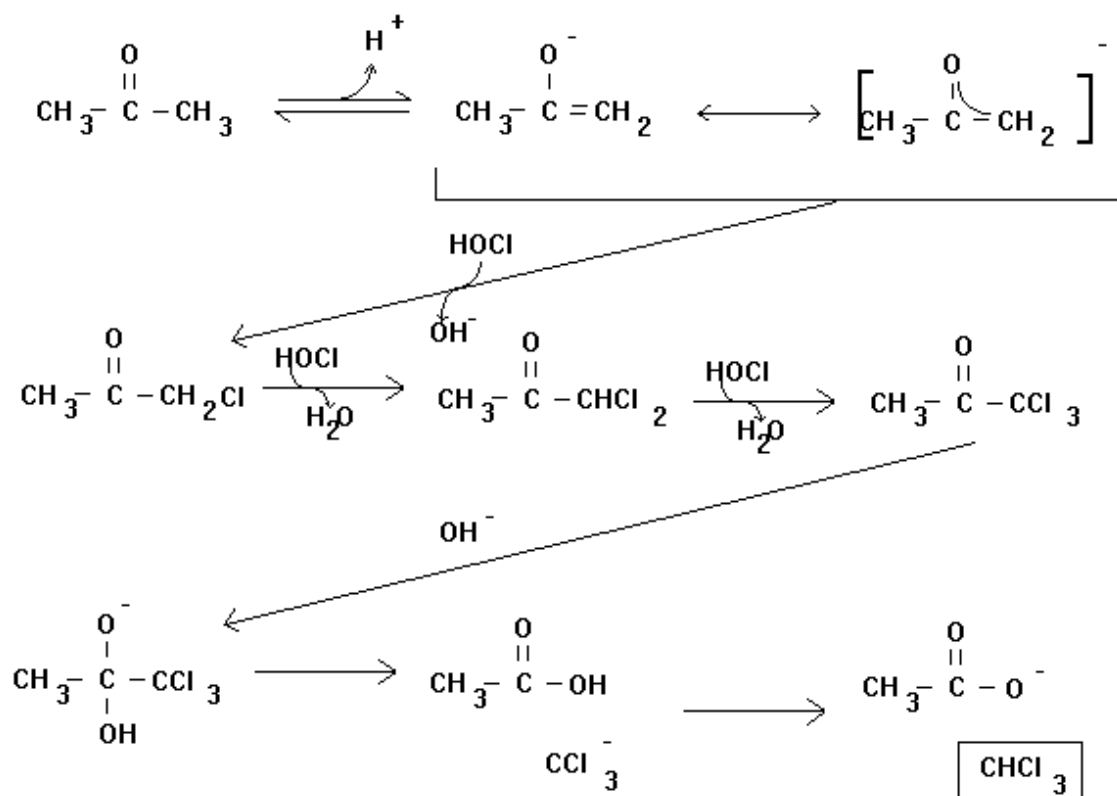
### 2.4.1.4 Bromoform

The basic chemical and physical characteristics of Bromoform or tribromomethane or methyl tribromide ( $\text{CHBr}_3$ ) are shown in Table 2.3 and its chemical structure is as follows:



### 2.4.2 Possible Reaction Pathway of THMs in Water Treatment

Reckhow and Singer (1990) summarized a series of possible reactions that the basic steps by which chloroform can be produced during water treatment, as follows:



### 2.5 Sodium Hypochlorite (NaOCl)

Sodium hypochlorite is a green/yellow liquid with the characteristic smell of chlorine. It was first used as a bleaching agent and was then discovered to be effective in controlling wound infections. Subsequently, it is most commonly known as household bleach and as a disinfectant, a bleaching agent, in medical treatments and used in the disinfection of drinking water.

Today, approximately 70% of the total amount of sodium hypochlorite produced is used to make bleach used for household cleaners and laundry additives, used for their bleaching, disinfecting and stain-removing properties.

It is also used for a number of industrial processes such as for commercial laundering, in the manufacture of paper and pulp, for industrial chemical synthesis and disinfection of swimming pools.

Perhaps one of the most important applications of sodium hypochlorite is in the disinfection of public water supplies to prevent the transmission of waterborne diseases such as cholera and typhoid.

#### **Literature reviews:**

At present, the both common and new emerging pollutants have polluted into water sources all over the world seriously. At the same time, a high quality drinking water is required to obtain a better life. Therefore, advanced technologies are developed and applied gradually in water treatment plants to effectively remove pollutants in water sources and to meet the strict potable water regulations. Among these technologies, membrane filtration is one of the best promising technologies having been received intensive attention (Li et al., 2011). Especially, microfiltration (MF) and ultrafiltration (UF) membrane applications are receiving increased consideration associated with water quality and cost reduction by improvement in membrane technology (Sangyoup et al., 2004).

The membrane is used to remove particulate matter such as inorganic particles as well as microorganisms including bacteria and virus. European waterworks microfiltration membranes are now made from organic material. Recent developments showed that membranes made from inorganic materials could be promising in membranes technology in the future, because of their unique characteristics including a hydrophilic surface and a high resistance against mechanical, chemical or thermal stress (Lerch et al. 2005, Heijman and Bakker 2007, NGK 2008, METAWATER 2009).

To operate the system, the pore size of membranes used ranged from 0.01 to 0.4  $\mu\text{m}$ . The fluxes obtained ranged from 0.05 to 10 m/d, strongly depending on the configuration and membrane material. Typical values for inner skin membranes are reported as 0.5-2.0 m/d and for outer skin membranes as 0.2-0.6 m/d at 20°C. The applied trans-membrane pressure ranges from 20 to 500 kPa for inner skin membranes and from -10 to -80 kPa for outer skin membranes (Cicek, N., 2003).

When the ceramic membrane starts fouling, membrane chemical cleaning was performed either as a backwash cleaning without removing the membrane. For backwash cleaning, the membrane was filled with hypochlorite solution (750 mg/L of active chlorine) throughout the backwash and left for 2 h, followed by cleaning solution discharge, and then filled with hydrochloric acid diluted to pH 2. For extensive cleaning, the membrane was soaked in several cleaning solutions with aeration applied under the membrane. The cleaning solutions and the duration of their application for soaking were respectively: tap water for 2 h; hypochlorite solution

(750 mg/L) for 24 h; hydrochloric acid (pH = 2) for 1 h; sodium hydroxide (pH = 12) for 8 h; hypochlorite solution (750 mg/L) for 24 h. Some of the permeability loss due to fouling was regained but short term cleaning could not restore the initial permeability. So, chemical backwash cleaning with hypochlorite solution was performed, followed by acid cleaning with hydrochloric acid. It should be noted that acidic cleaning was responsible for about 80% of the permeability recovery, while the hypochlorite recovered the rest (M. Matošić et al., 2009).

The presence of natural organic matter (NOM) in both surface and groundwater supplies produces toxic by-products, mainly trihalomethanes (THMs), during oxidation steps in drinking water production. An oxidant that has used in drinking water treatment over the last century was chlorine.

A direct chlorination of synthetic samples, prepared by diluting humic stock solution in distilled water, with a dissolved organic carbon close to 3mg/l produces a THM concentration of around 1600  $\mu\text{gCCl}_3/\text{l}$  (measured as THMFP). The use of chlorination in the preoxidation operation has an effect similar to that of the  $\text{O}_3/\text{TiO}_2$  process in relation to the final concentration of THMs (R. Mosteo et al., 2009).



## CHAPTER III

### METHODOLOGY

#### 3.1 Studied site

Water samples in this study are collected from Ping River. Ping River water is utilized daily as raw water source for water supply production to Chiang Mai consumers. The details of raw water are shown in following.

Ping River is located in Chiang Mai, Thailand. The sampling point is situated 10 km upstream far from Chiang Mai municipal area as shown in figure 3.1 and 3.2. Ping River water is currently the main water source utilized to producing water supply for Chiang Mai city. In general, turbidity of Ping River varies due to season changes. However, it typically contains high concentration of suspended solid measured in term of “Turbidity value” between 50 - 220 NTU and high as 300 NTU in rainy season. Water samples from Ping River used in this study will be pumped from the depth of about 30 centimeters below water surface at the sampling point.



Figure 3. 1 Sampling point in Ping River,  
Chiang Mai Province.



Figure 3. 2 Sampling point in Ping River, Chiang Mai  
Province

### 3.2 Experimental procedure

- Raw water from Ping River was collected in June 2013, summer for the experiment. Physical and chemical characteristics of raw water: Turbidity, DOC, UV-254, SUVA, Fe, Mn, pH and temperature was analyzed.
- Raw water was fed into a batch-type ceramic membrane filtration unit and filtrated water was analyzed for Turbidity, DOC, UV-254, SUVA, Fe, Mn, pH and temperature in each lap of filtration.
- Physical backwash by clean water was conducted for reversible fouling removal after the filtration reached the lowest acceptable flux at  $10 \text{ m}^3/\text{m}^2\text{-d}$ .
- Backwash water was 5% of total unit production.
- Backwash water characteristics were Turbidity, DOC, UV-254, SUVA, Fe, Mn, pH and temperature.
- Chemical soaking was conducted for a completely fouled ceramic membrane which physical backwash cannot recovery. Characteristic parameters of chemical soaking water were THMs, Turbidity, DOC, UV-254, SUVA, Fe, Mn, pH and temperature.

### 3.3 Unit operation

The experiments were operated by using batch-type ceramic membrane filtration unit as shown in Figure 3.3. Advanced ceramic membrane modules with 0.1  $\mu\text{m}$  pore size, total surface area of 0.042  $\text{m}^2$ , 3 centimeters in diameter, 10 centimeters height and 55 tubular channels as illustrated in Figure 3.4 was utilized under upflow mode of operation and controlled pressure of 200 kPa.

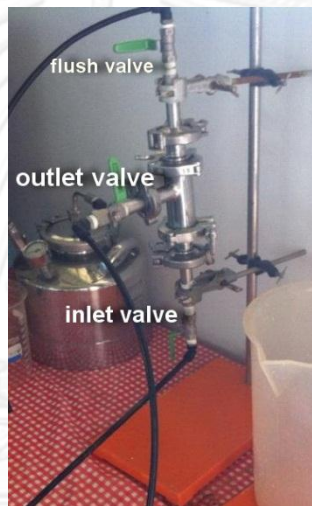


Figure 3. 3 Batch-type ceramic membrane filtration unit



Figure 3. 4 Ceramic membrane modules pore size 0.1  $\mu\text{m}$

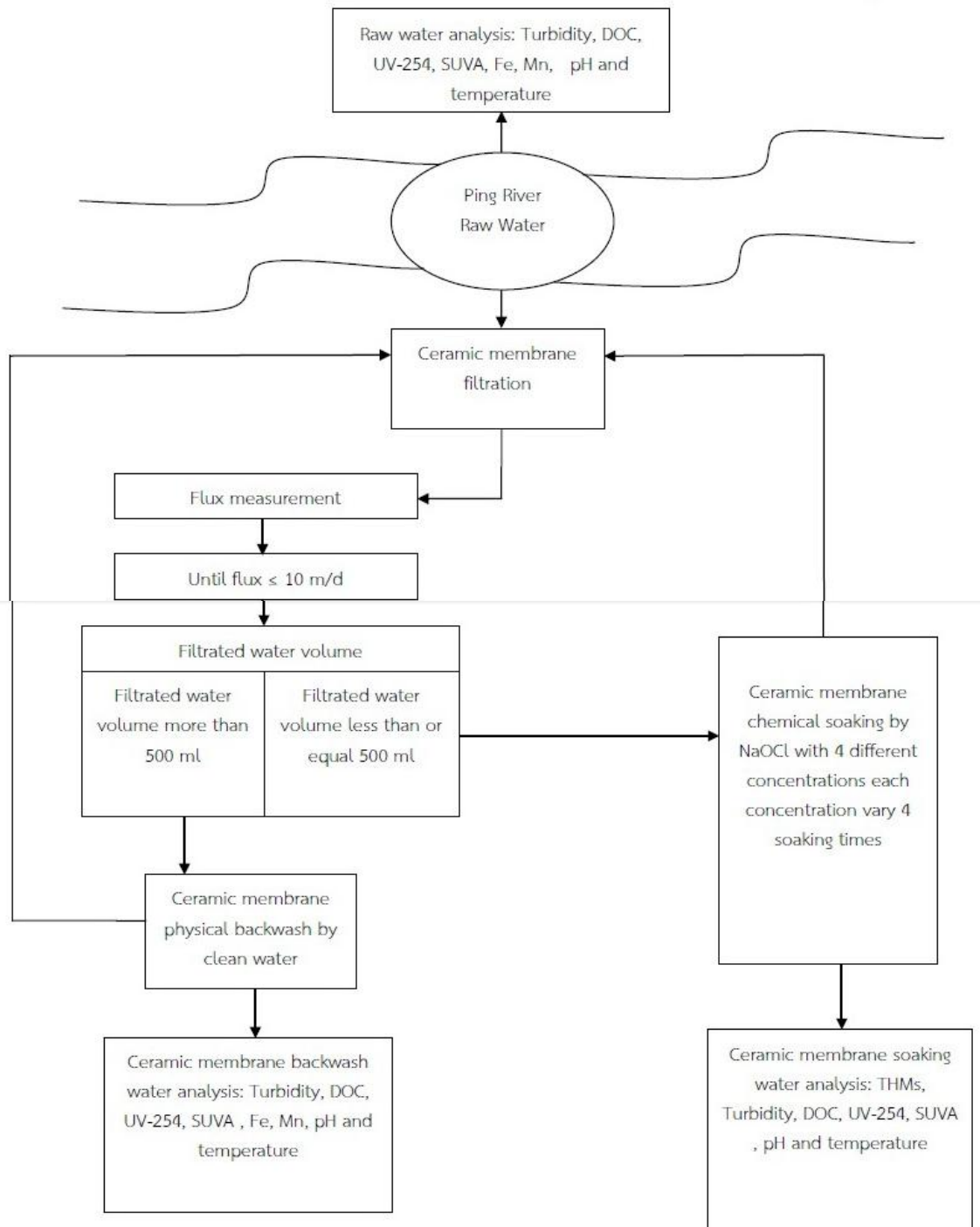


Figure 3. 5 Schematic diagram of the experiments

### 3.4 Flux measurement

Flux of ceramic membrane was determined from the following equation,

Flux calculation:

$$J = \frac{dV}{dt.A}$$

where  $J$  is the filtration flux,  $A$  is effective filtration area,  $dV$  is filtration volume and  $dt$  is filtration time.

### 3.5 Ceramic membrane fouling experiment

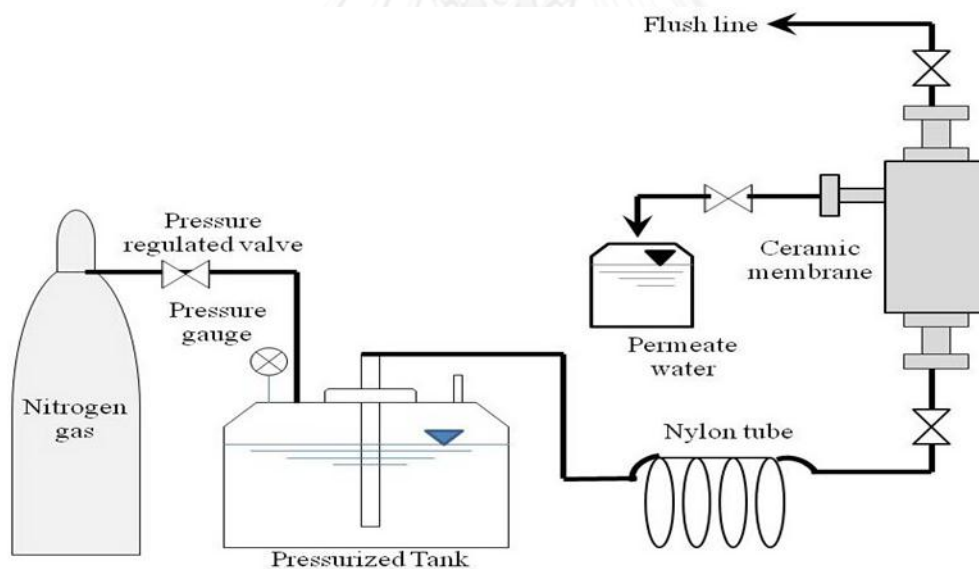


Figure 3. 6 Schematic diagram of filtration system

The experiment was a simulation, which created the fouled ceramic membranes under the same condition, and it was set the lowest flux as 10 m/d by raw water measurement every 500 ml.

The experiment did in the batch-type experiment. The fouled ceramic membrane was defined by measuring the flux of ceramic membrane with clean water. If filtration flux for filtrated water volume more than 500 ml was less than 10 m/d, the fouling was defined as a reversible fouling and ceramic membrane can be regenerated by using physically backwashed with clean water. If filtration flux was less than 10 m/d for filtrated water volume less than or equal 500 ml, the fouling was defined as an irreversible fouling and ceramic membrane can be regenerated by soaking with chemical. Fouled ceramic membranes were prepared by filtrated the ceramic membrane with Ping River water until the membrane was fouled with irreversible fouling (flux less than 10 m/d for filtrated water volume less than 500 ml).

### **3.6 Membrane Cleaning**

#### **3.6.1 Physical Cleaning**

Backwash is generated when water is forced through the filter, counter to the flow direction used during treatment operations. This action cleans the media, when reversible fouling occurred, by dislodging accumulated particles, including microorganisms, captured by the filter media.

Backwash water typically averages 3% to 6% of total unit production and 5% of total unit production was selected for this experiment. This test was conducted at a steady pressure 200 kPa.

### 3.6.2 Chemical Cleaning

The irreversible part of the fouling can only be removed by chemical soaking. In regular intervals the soaking is combined with application of chemical cleaners (NaOCl). A chemical soaking can be applied when the enhanced chemical backwash alone is not able to restore the membrane performance to a sufficient degree. The stability of the dead-end filtration process is governed by the efficiency of the backwash process and the degree of irreversible fouling.

In this experiment, all other conditions except NaOCl concentrations and soaking times were the same for chemical soaking experiment. Effect of NaOCl on fouled ceramic membrane regeneration and flux recovery was tested at chemical doses of 2,000, 3,000, 4,000, and 5,000 mg/l at room temperature and each concentration was varied with different soaking times at 6, 8, 10 and 12 hours, respectively.



### 3.7 Analytical methods

#### 3.7.1 Turbidity

The HACH Turbidity meter Model 2100 used to measure turbidity.

#### 3.7.2 DOM surrogate parameter

##### 3.7.2.1 DOC

The samples were filtered through a combusted 0.7  $\mu\text{m}$  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

##### 3.7.2.2 UV-254 nm

UV-254 of water samples were measured in accordance with standard method 5910 B Ultraviolet Absorption Method. The samples were filtered through a 0.7  $\mu\text{m}$  GF/F filter paper prior to measurement by Perkin-Elmer Model Lambda 25, UV/VIS spectrophotometer.

### 3.7.2.3 THM

THMs were measured in accordance with standard method 5710, formation of Trihalomethanes and Other Disinfection By-Products. Gas Chromatography was used (Agilent 6890 Series Gas Chromatographic with ECD detector) under the following conditions:

#### *Inlet Condition*

Mode: Split, Initial temp: 225°C, Pressure: 31.33 psi, Split ratio: 10:1  
Split flow 15.9 mL/min, Gas Type: Helium and Total flow: 20.5 mL/min

#### *Oven Condition*

The temperature programs of oven adjusted for analyzing THMs are shown in Table 3.2.

#### *Detector Condition*

Temperature: 300 °C, Mode: Constant make up flow, Makeup flow: 60 mL/min, Makeup Gas Type: Nitrogen

**Table 3. 1** Temperature programs for analyzing THMs

Ramp	Rate (°C/min)	Final temperature (°C)	Holding time of final temperature (min)
1	15	180	1.00*
2	15	130	1.00
3	15	180	1.00

Initial temperature: 75°C, Initial temperature holding time: 1.00 min

### 3.7.3 pH

pH directly measured by a Model F-21 Horibra pH-meter with an accuracy of  $\pm 0.01$  pH unit which in calibrated with buffer solutions at pH 4.00, 7.00 and 9.00.

### 3.7.4 Temperature

Thermometer used for temperature measurement.

### 3.7.5 Fe and Mn

The Hach DR/890 Colorimeter used to measure Fe and Mn.

## CHAPTER IV

### RESULTS AND DISCUSSIONS

This research was conducted in order to achieve the objectives mentioned in chapter 1. The raw water source of feed water is Ping River water. Water samples were used to operate in batch-type ceramic membrane filtration unit to investigate membrane fouling on ceramic membrane, filtrated water and backwash water characteristics. The operation of batch-type ceramic membrane filtration unit was run at The Ceramic Membrane Research Center for Portable Water, Chiang Mai. EHWL Laboratory at Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University where was chemical soaking experiments were conducted to find the THMs formation and soaking water characteristics.

#### 4.1 Raw water characteristics

Surface water from Ping River, Chiang Mai, Thailand is selected as raw surface water. The sampling point is situated 10 km upstream far from Chiang Mai municipal area. Ping River water is currently the main water source utilized to producing water supply for Chiang Mai city. In general, turbidity of Ping River varies due to season changes. However, it typically contains high concentration of suspended solid measured in term of Turbidity value between 50 - 220 NTU and high as 300 NTU in rainy season. Water samples from Ping River used in this study were pumped from the depth of about 30 centimeters below water surface at the sampling point.

Table 4.1 summarizes the typical characteristics of raw water. The physical and chemical properties in raw water as Dissolved Organic Carbon (DOC), UV-254, SUVA, Turbidity, pH, Temperature, Fe and Mn were 3.861 mg/l, 0.1092 1/cm, 0.1092 1/cm, 2.83 L/mg-m, 70.0 – 80.0 NTU, 7.67, 26.5°C, 0.100 mg/l and 0.754 mg/l , respectively.

**Table 4. 1** Characteristics of raw water

Parameter	Value	Unit
DOC	mg/l	3.861
UV-254	1/cm	0.1092
SUVA	L/mg-m	2.83
Turbidity	NTU	70.0 – 80.0
pH	s.u.	7.67
Temperature	Degree Celsius	26.5
Fe	mg/l	0.100
Mn	mg/l	0.754

The pH value for Ping River is nearly neutral. Water samples were collected from Ping River in hot season. So, the river flew steadily and the turbidity values were

between 70.0 – 80.0 NTU. Ping River water is the natural source which is the plants and animals habitat. So, the turbidity of water sample caused by various sediment, particle, colloid, organic and inorganic matter.

Additionally, SUVA value in Ping River water was 2.83 L/mg-m, it contains mostly non-humic matters. Because SUVA values of less than 3 L/mg-m signify water contain primarily non-humic material. SUVA values of 4 -5 L/mg-m are typical of water containing primarily humic material (Edzwald and Van Benschoten, 1990)

#### **4.2 Filtrated water characteristics**

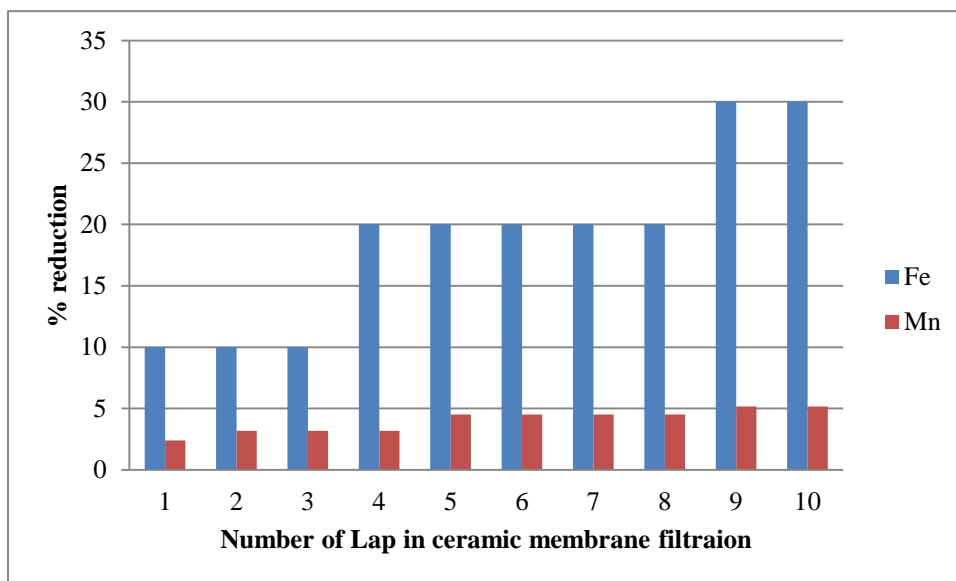
Fouled ceramic membranes were created under the same condition of batch-type ceramic membrane filtration unit which mentioned in chapter 3. When filtration reached the acceptable lowest flux, clean water backwash was operated to remove the reversible fouling. In this study, 10 laps of filtration were operated in each ceramic membrane module to make a completely fouled ceramic membrane. So, filtrated water sample in every lap was collected to be analyzed.

Table 4.2 shows the filtrated water characteristics as DOC, UV-254, SUVA, Turbidity, pH, Temperature, Fe and Mn. The results showed that all parameters except SUVA, pH and temperature were slightly decrease after each lap of ceramic membrane filtration.

**Table 4. 2** Filtrated water characteristics

Parameters	Unit	Lap									
		1	2	3	4	5	6	7	8	9	10
DOC	mg/l	3.628	3.542	3.533	3.326	3.318	3.281	3.264	3.184	3.122	2.901
UV-254	1/cm	0.1080	0.1020	0.1000	0.0951	0.0942	0.0937	0.0933	0.0927	0.0912	0.0865
SUVA	L/mg-m	2.98	2.88	2.83	2.86	2.84	2.86	2.86	2.91	2.92	2.98
Turbidity	NTU	0	0	0	0	0	0	0	0	0	0
pH	s.u.	7.67	7.67	7.67	7.67	7.67	7.67	7.67	7.67	7.67	7.67
Temperature	Degree Celsius	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5	26.5
Fe	mg/l	0.09	0.09	0.09	0.08	0.08	0.08	0.08	0.08	0.07	0.07
Mn	mg/l	0.736	0.730	0.730	0.730	0.720	0.720	0.720	0.720	0.715	0.715

Filtrated water was really clear, the turbidity less than 0.01 NTU. The experiment performed that ceramic membrane pore size 0.1  $\mu\text{m}$  can remove turbidity effectively. But for the inorganic matter such as Fe and Mn, they were slightly reduced as show in Figure 4.1



**Figure 4. 1** The percent of inorganic matters reduction in each lap of operation

Ping River water contains 0.1 mg/L and 0.754 mg/L of Fe and Mn, respectively. As shown in Figure 4.1 the maximum reduction of Fe was from the value 0.1 mg/L to approximately 0.07 mg/L, it was 30% reduction of Fe and the maximum reduction of Mn was from the value 0.754 mg/L to approximately 0.715 mg/L, it was 5.12% reduction of Mn. But the reduction values of the inorganic matters were very low.

SUVA values in filtrated water show that it contains mostly non-humic matters. Because SUVA values of less than 3 L/mg-m signify water contain primarily non-humic material.

The DOC concentration was reduced significantly as well as Fe reduction. But Fe concentration was lower than DOC concentration 40 times. So, this result indicated that DOC was the main cause for ceramic membrane fouling. The ceramic membrane filtration reduced DOC up to 25% in filtrated water as shown in Figure 4.2.



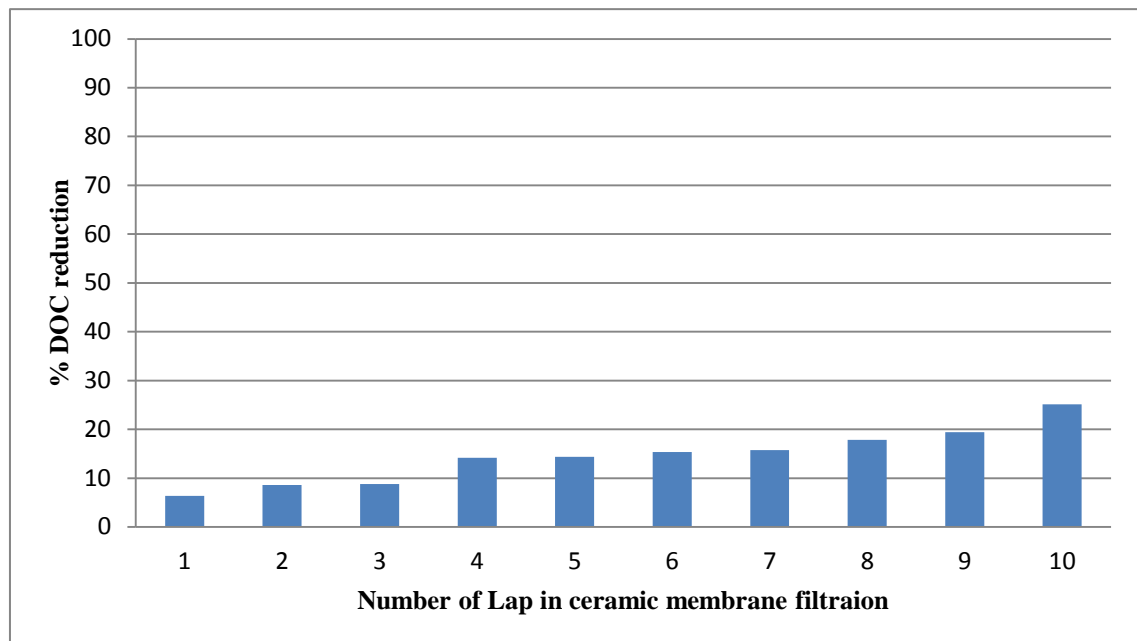
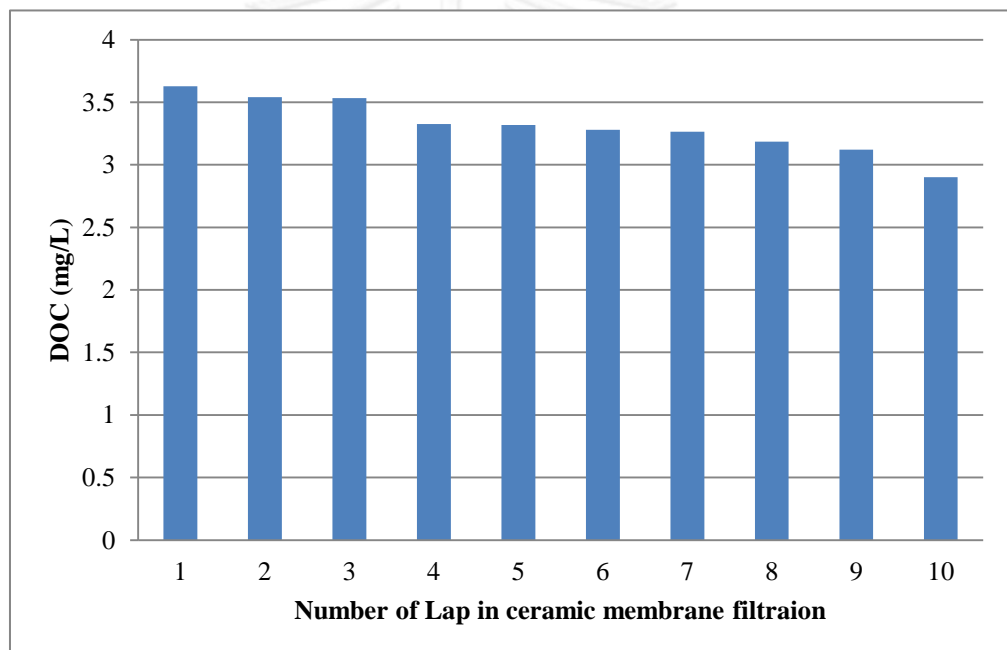


Figure 4. 2 The percent of DOC reduction in each lap of filtration

A study was conducted to compare the changes of flux after recovery, which initial flux is  $68.57 \text{ m}^3/\text{m}^2\text{-d}$ , and the quality of filtrated water. From the Figure 4.2 that shows the percent of DOC reduction and Figure 4.3 shows the DOC concentration in filtrated water in each lap of operation. The DOC concentration was significantly removed through the ceramic membrane filtration; DOC concentration in filtrated water at the 10<sup>th</sup> lap was less than those at the 1<sup>st</sup> lap. The ceramic membrane was physically backwashed by using clean water for the reversible fouling in the 10 laps of operation and soaked by chemical solution for the irreversible fouling after the 10<sup>th</sup> lap of operation.

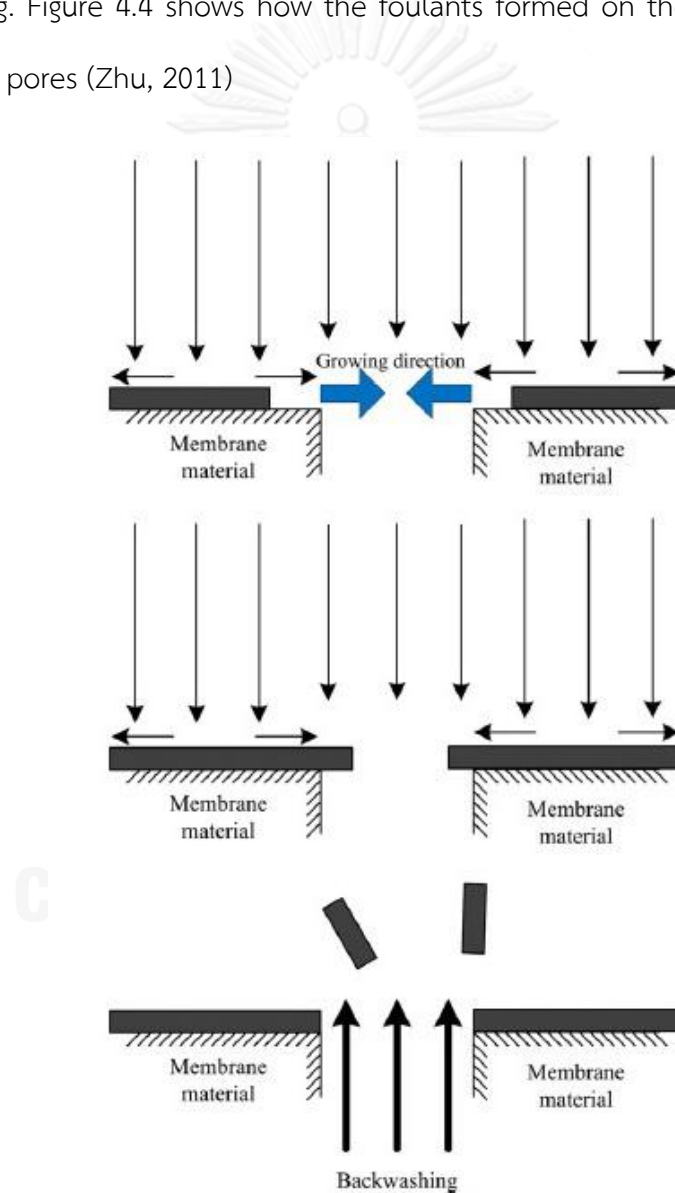
The results showed that DOC reduction in every lap of ceramic membrane filtration because ceramic membrane pores were getting smaller from foulants in raw water, it led DOC cannot pass through the ceramic membrane as much as early filtration lap. So, it indicated that organic matter accumulated on the ceramic membrane surface which could not remove by using physical backwash and caused irreversible fouling that required chemical soaking.



**Figure 4. 3** The changing of DOC concentration in filtrated water at each lap of operation

### 4.3 Backwash water characteristics

Dissolved organic and colloidal matter most likely adsorbs into membrane surface, pores and blocks them, the occurrence of which is also called fouling. These types of matter are difficult to blow away from a membrane under pressure-fixed backwashing. Figure 4.4 shows how the foulants formed on the ceramic membrane surface and pores (Zhu, 2011)



**Figure 4. 4** Foulant increases on ceramic membrane surface from filtration and decrease by backwashing

Foulants began to form on the membrane surface where there is no pore. This layer then extended to cover the surface with pores, and began to contribute the fouling. If the foulants continued to grow, the backwashing would be operated to remove the foulants but only partially removed them off.

Clean water was used in the physical backwash to remove the reversible fouling in ceramic membrane filtration. 5% of total water production was selected for this experiment. This test was conducted at a steady pressure 200 kPa.

Table 4.3 shows the backwash water characteristics as DOC, UV-254, SUVA, Turbidity, pH, Temperature, Fe and Mn. All parameters except SUVA, pH and temperature were slightly increase after each lap of backwashing.

**Table 4. 3** Backwash water characteristics

Parameter	Unit	Lap									
		1	2	3	4	5	6	7	8	9	10
DOC	mg/l	2.641	2.768	2.886	3.185	3.21	3.287	3.411	3.528	3.642	3.881
UV-254	1/cm	0.071	0.073	0.078	0.083	0.085	0.091	0.093	0.094	0.098	0.112
SUVA	L/mg-m	2.70	2.65	2.72	2.62	2.66	2.79	2.74	2.67	2.70	2.89
Turbidity	NTU	35	52	74	110	120	144	171	195	214	230
pH	s.u.	7.56	7.56	7.56	7.56	7.5	7.5	7.5	7.5	7.5	7.5
Temperature	Degree Celsius	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5
Fe	mg/l	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.04	0.04
Mn	mg/l	0.211	0.230	0.241	0.250	0.250	0.253	0.270	0.277	0.284	0.302

DOC removal after each time of backwashing was increasing related to Turbidity in backwash water as shown in Figure 4.5

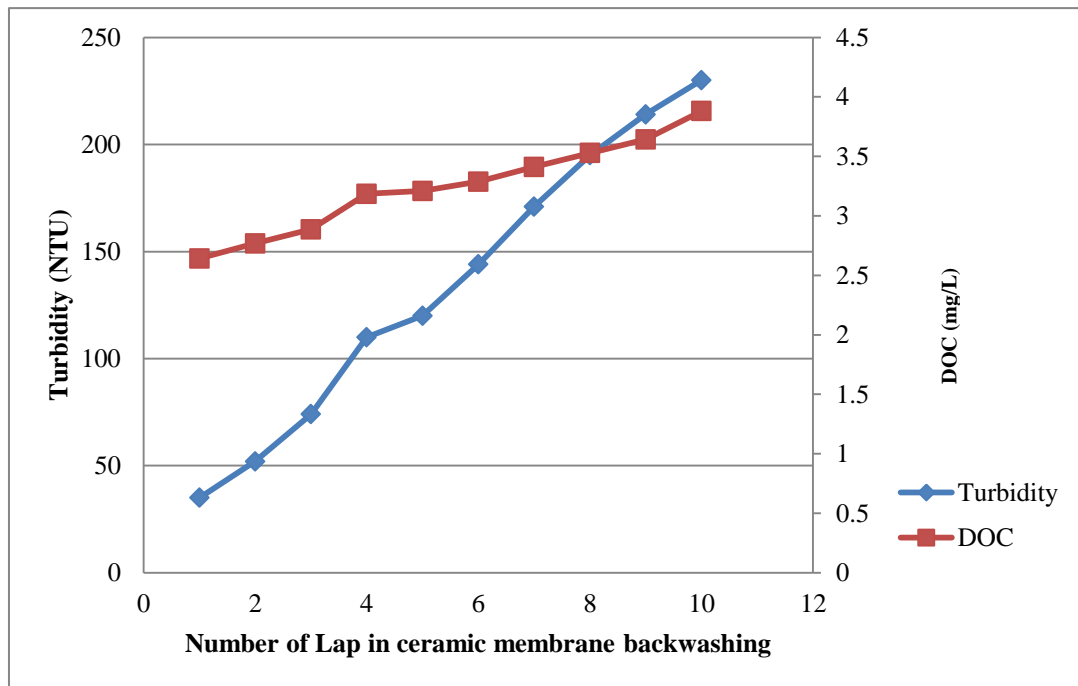


Figure 4. 5 DOC and Turbidity increase in each lap of backwashing

DOC concentration and Turbidity increased in each lap because backwash water volume was decreasing as the total filtration volume was also decreasing from the fouling occurrence which related to the result that mentioned in 4.2.1, DOC reduction and the organic matter accumulated on ceramic membrane surface.

SUVA values in backwash water show that it contains mostly non-humic matters. Because SUVA values of less than 3 L/mg-m signify water contain primarily non-humic material.

The inorganic matters were also partially removed by backwashing as the organic and turbidity did as shown in the Figure 4.6

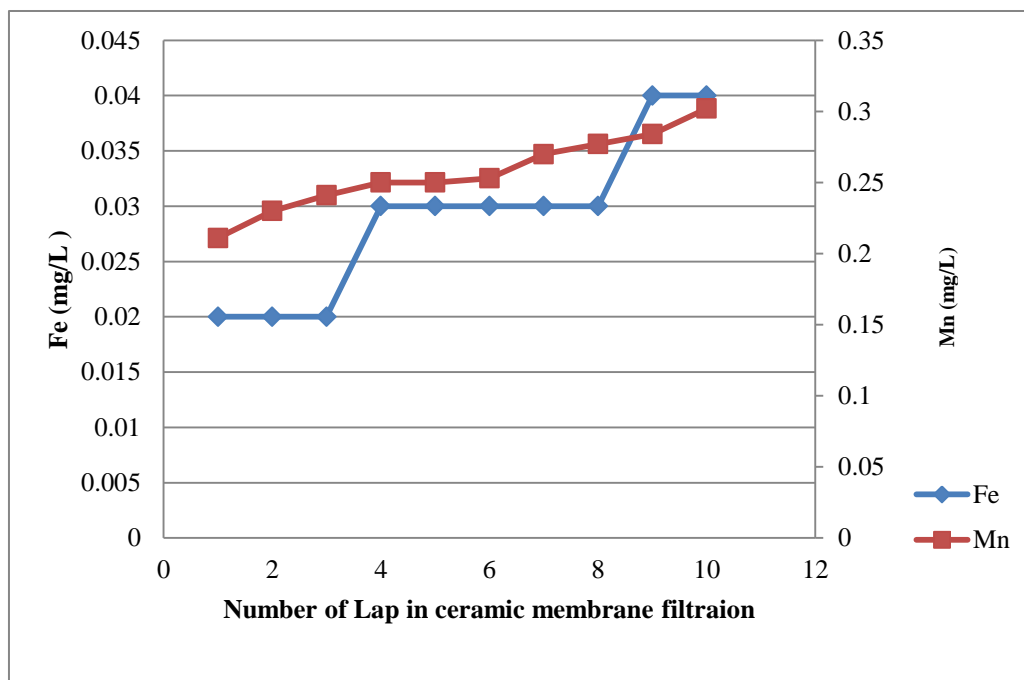


Figure 4. 6 Fe and Mn concentration in backwash water

#### 4.4 Soaking water characteristics

The main objective in this study is THMs formation investigation in chemical soaking water. The early results showed the organic matter which accumulated on ceramic membrane surface was the main cause for ceramic membrane fouling. According to Homklin (2004) reported in the water which contained DOM could occur the reaction between DOM and chlorine compound would create the carcinogens, THMs and other substances.

After ceramic membrane was completely fouling that was not removed with backwashing. Chemical soaking was conducted for each ceramic membrane

separately in different condition for the module recovery and THMs formation observation.

In this experiment, all other conditions except NaOCl concentrations and soaking times were the same for chemical soaking experiment. Effect of NaOCl on fouled ceramic membrane regeneration and flux recovery was tested at chemical doses of 2,000, 3,000, 4,000, and 5,000 mg/l at room temperature and each concentration was varied with different soaking times at 6, 8, 10 and 12 hours, respectively.

The inorganic matters, Fe and Mn, were partially removed in chemical soaking as shown in Figure 4.7 and Figure 4.8 Along to Strugholtz's study (2005) in organic matter and mineral can be removed by citric and oxalic which are more effective for foulants removal from the membrane.



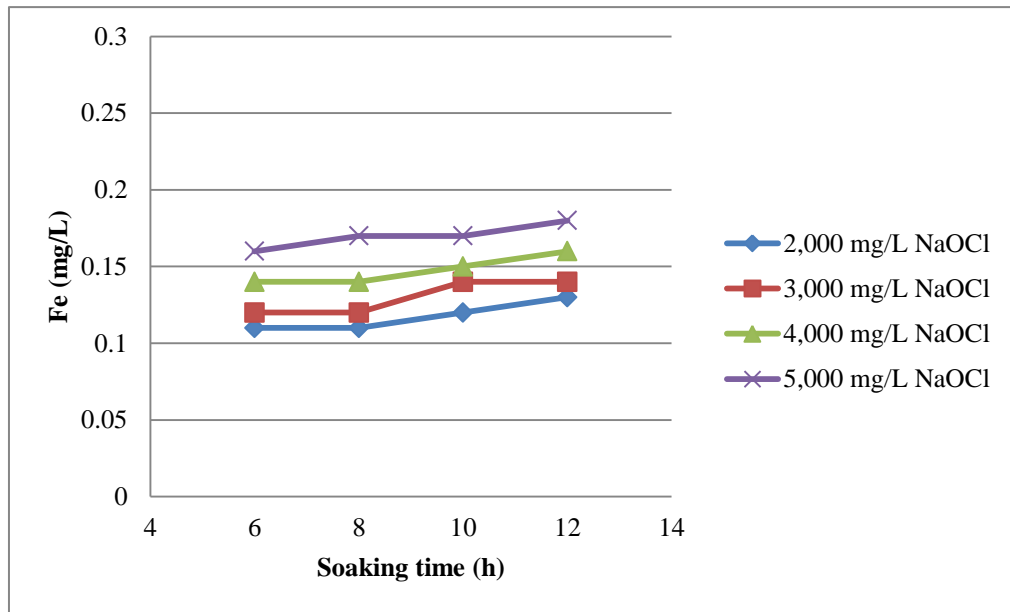


Figure 4. 7 Fe removals in different chemical soaking condition

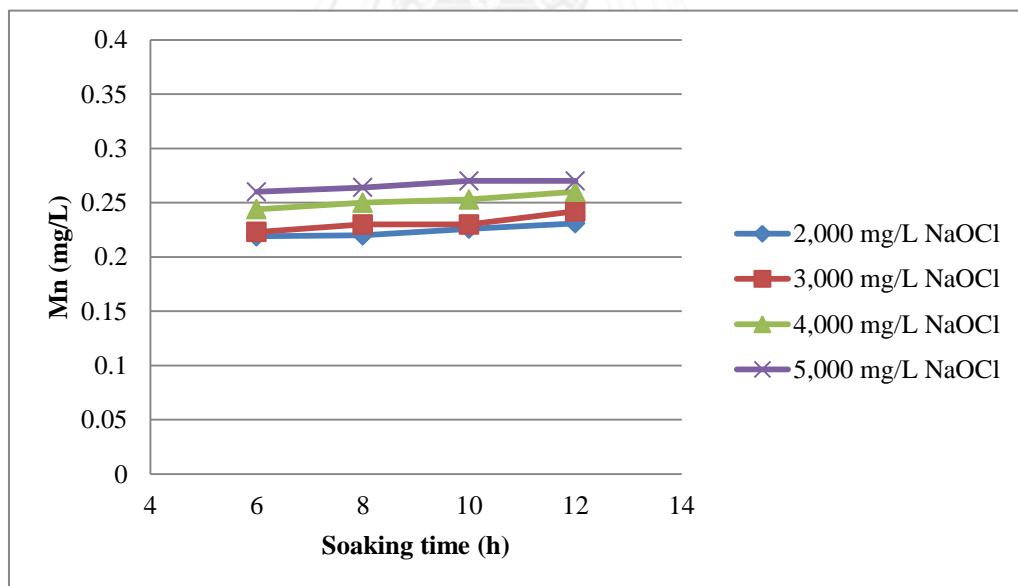


Figure 4. 8 Mn removals in different chemical soaking condition

DOC removal from chemical soaking by sodium hypochlorite was very effective. The results indicate the cleaning efficiency increase with the increase of

NaClO concentration and contact time as shown in Figure 4.9. The higher concentration of NaClO can enhance the ability to oxidize and remove foulants from the membrane (Xu, 2012). Actually, NaClO has been reported as a functional reagent for removal of foulant such as organic substances through oxidation.

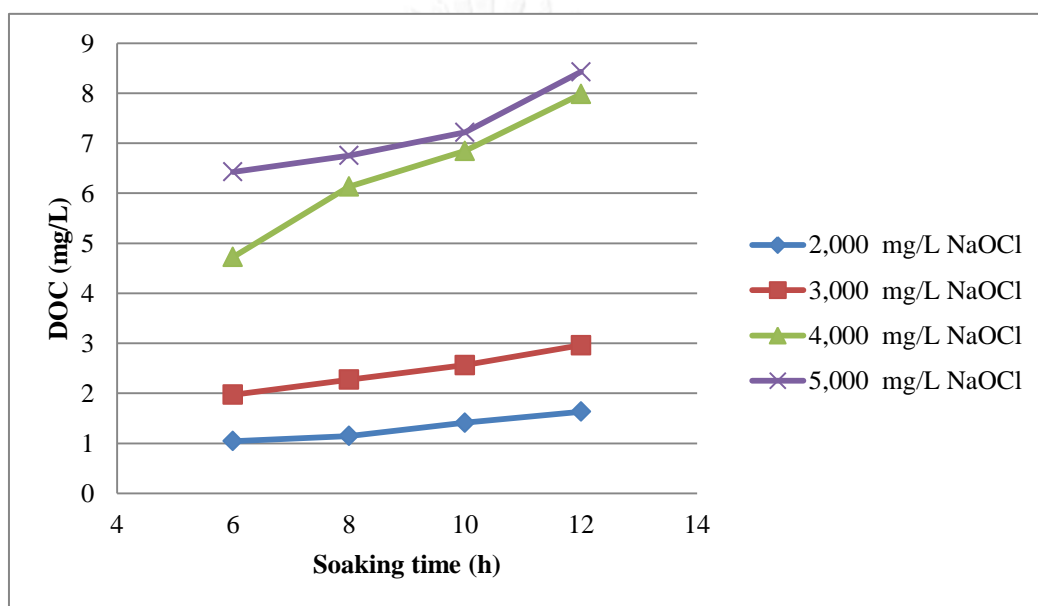


Figure 4. 9 DOC in chemical soaking water from different condition

SUVA values in soaking water show that it contains more humic matters. Because SUVA values of more than 3 L/mg-m signify water contain primarily humic material in chemical dose 2,000 mg/L NaOCl. And SUVA values in soaking water show that it contains mostly non-humic matters. Because SUVA values of less than 3 L/mg-m signify water contain primarily non-humic material in chemical dose 3,000, 4,000 and 5,000 mg/L NaOCl. The SUVA values are shown in Table 4.4.

**Table 4. 4** SUVA values in soaking water

Soaking time (h)	NaOCl concentration (mg/l)			
	2,000	3,000	4,000	5,000
6	4.82	2.84	2.38	1.88
8	4.45	2.50	1.90	1.85
10	3.70	2.24	1.76	1.75
12	3.32	2.06	1.54	1.53

Trihalomethanes (THMs) formation was measured in soaking water for fouled ceramic membrane recovery. THMs are the carcinogen when DOM in the water reacts with chlorine after adding chlorine dosing solution. THMs concentration depends on DOM concentration in water sample. If in the water has high DOM, it can form high THMs (Montakanti, 2011).

THMs values of soaking water are presented in Figure 4.10. Gang (2002) reported that the possible reason is that the THMs formed from the DOC decompose easily, which could favor formation of more THMs.

THMs were formed in 2,000 mg/L NaOCl soaking water as 206.19, 232.51, 283.32 and 334.30  $\mu\text{g/L}$  in 6, 8, 10 and 12 h soaking times, in 3,000 mg/L NaOCl soaking water as 291.34, 358.57, 383.32 and 432.29  $\mu\text{g/L}$  in 6, 8, 10 and 12 h soaking

times, in 4,000 mg/L NaOCl soaking water as 471.82, 542.33, 559.30 and 571.35  $\mu\text{g/L}$  in 6, 8, 10 and 12 h soaking times, in 5,000 mg/L NaOCl soaking water as 665.30, 714.90, 825.34 and 887.59  $\mu\text{g/L}$  in 6, 8, 10 and 12 h soaking times.

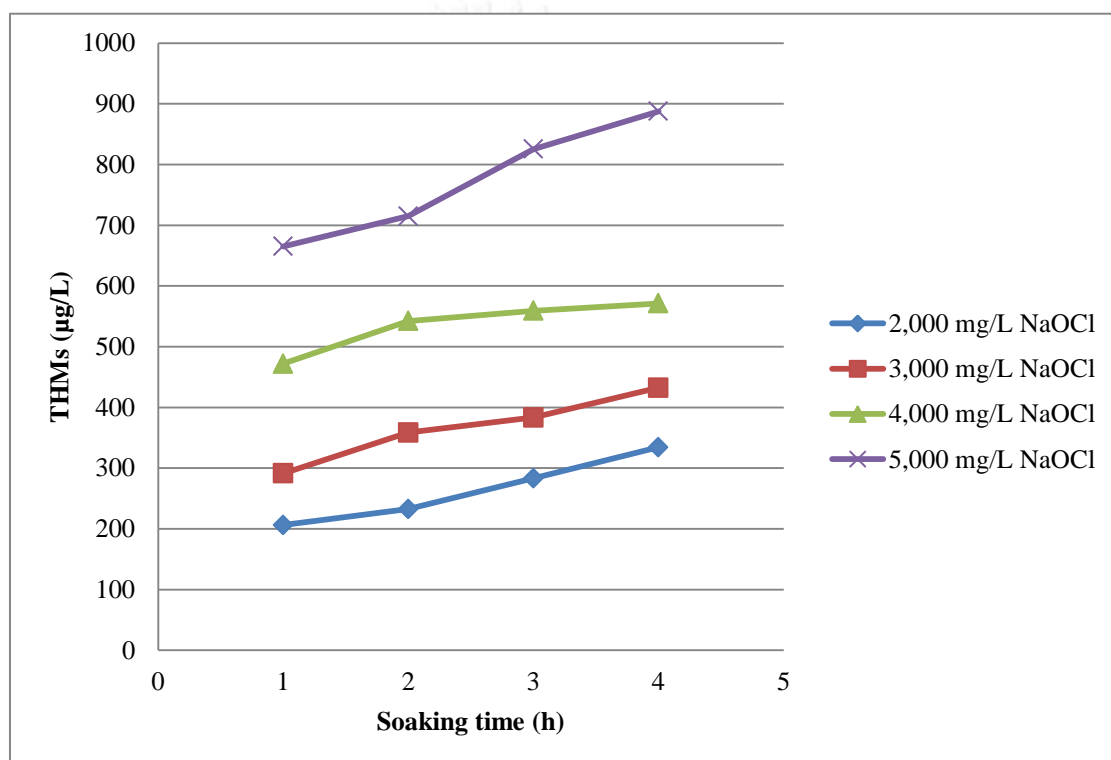


Figure 4. 10 THMs in chemical soaking water in different condition

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In the United States has set maximum concentration levels for total THM species (chloroform, bromodichloromethane, dibromochloromethane and bromoform) 80  $\mu\text{g/L}$ . European Union regulations limit THMs to 100  $\mu\text{g/L}$ . And The World Health Organization guidelines are 200  $\mu\text{g/L}$  for chloroform, 60  $\mu\text{g/L}$  for bromodichloromethane, 100  $\mu\text{g/L}$  for dibromochloromethane, 90  $\mu\text{g/L}$  for dichloroacetonitrile and 100  $\mu\text{g/L}$  for dibromoacetonitrile. However, the THMs

concentration levels are set only in drinking water. In this study, THMs were formed in chemical soaking water which not provided for consumption. But if chemical soaking water was released in to the environment, it exceeds the concentration levels for total THMs in drinking water.

#### 4.5 Effect of physical cleaning on flux recovery

The average initial flux is  $68.57 \text{ m}^3/\text{m}^2\text{-d}$ , Figure 4.11 shows the flux reduction after physical clean by clean water. As mentioned in the early result, DOM accumulated on the ceramic membrane surface which cannot remove completely by the physical cleaning. So flux reduction was measured for fouled ceramic membrane preparation.

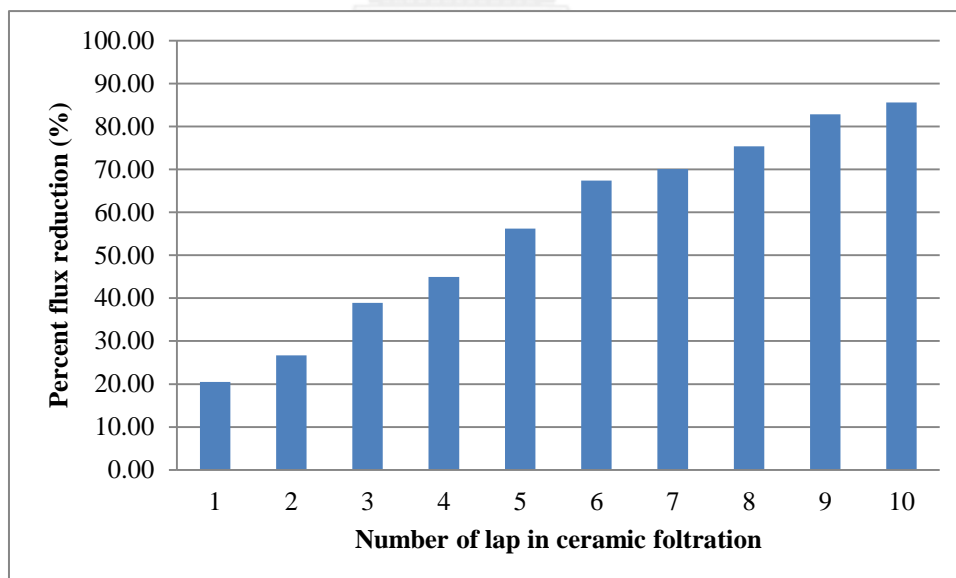


Figure 4. 11 Percent flux reduction after physical cleaning in each filtration lap

## 4.6 Effect of chemical soaking on flux recovery

### 4.6.1 Effect of chemical dose on flux recovery

Following the evaluation of ceramic membrane fouling, the effect of chemical dose on flux recovery of fouled ceramic membrane was essentially investigated. Within the chemical dose (2,000, 3,000, 4,000 and 5,000 mg/l NaOCl) tested, flux was very different after recovery in various chemical addition. Flux recovery, presented in Table 4.5, was calculated by using following equation,

$$J = \frac{dV}{dt.A}$$

where  $J$  is the recovery flux,  $A$  is effective filtration area,  $dV$  is filtration volume and  $dt$  is filtration time.

**Table 4. 5** Flux ( $\text{m}^3/\text{m}^2\text{-d}$ ) measurement after chemical soaking

Soaking time (h)	NaOCl concentration (mg/l)			
	2,000	3,000	4,000	5,000
6	32.02	37.91	40.88	45.63
8	33.57	38.68	42.07	47.18
10	34.55	39.31	42.26	47.53
12	34.61	39.79	42.54	47.78

From the results, it was found that flux recovery increased with the increasing of chemical concentration from 2,000 to 3,000, 4,000 and 5,000 mg/l of NaOCl, respectively. The highest flux after chemical soaking was found at 5,000 mg/L of NaOCl added which the highest NaOCl concentration in this studied. Due to NaOCl can reacted with organic matter which accumulated on the fouled ceramic membrane surface layer and caused an irreversible fouling, the higher concentration of NaOCl can cause the higher reaction and also enhanced the flux recovery of fouled ceramic membrane.

Percent of flux recovery of each chemical soaking condition were determined by comparing with the initial flux of ceramic membrane and the results are shown in Table 4.6.

**Table 4. 6** Percent (%) flux recovery

Soaking time (h)	NaOCl concentration (mg/l)			
	2,000	3,000	4,000	5,000
6	46.70	55.29	59.61	66.54
8	48.96	56.67	61.35	68.80
10	50.36	57.31	61.63	69.31
12	50.80	58.03	62.03	69.68

The results from Table 4.6 showed that the highest percent flux recovery was found in the range of 66.54 - 69.68% at 5,000 mg/L of NaOCl. The increasing of NaOCl concentration was highly increased percent flux recovery. From the obtained results, it can be indicated that the different of concentration in chemical soaking was affected the flux recovery of fouled ceramic membrane.



#### 4.6.2 Effect of soaking time on flux recovery

In addition to the flux recovery enhancement, chemical soaking time also investigated. Each concentration performed under following soaking time: 6, 8, 10 and 12 h. Soaking time effected insignificantly to flux recovery in each chemical dose. Figure 4.12 shows trend of flux after recovery and the percent flux recovery is presented in Figure 4.13 From the obtained results, it was found that percent flux recovery was increased when the soaking time increase from 6 h to 8 h. However, percent flux recovery was slightly increased at the soaking time higher than 8 h in each chemical dose. This indicates that the increasing of soaking time was not significantly affected the flux recovery of fouled membrane.

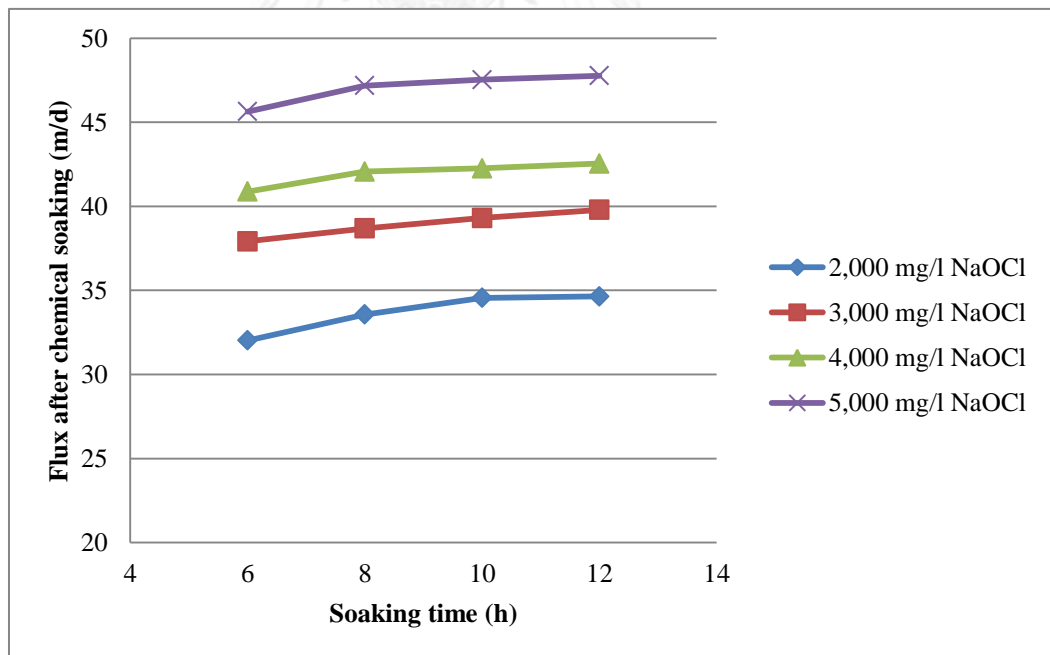


Figure 4. 12 Flux on various NaOCl concentrations and soaking times

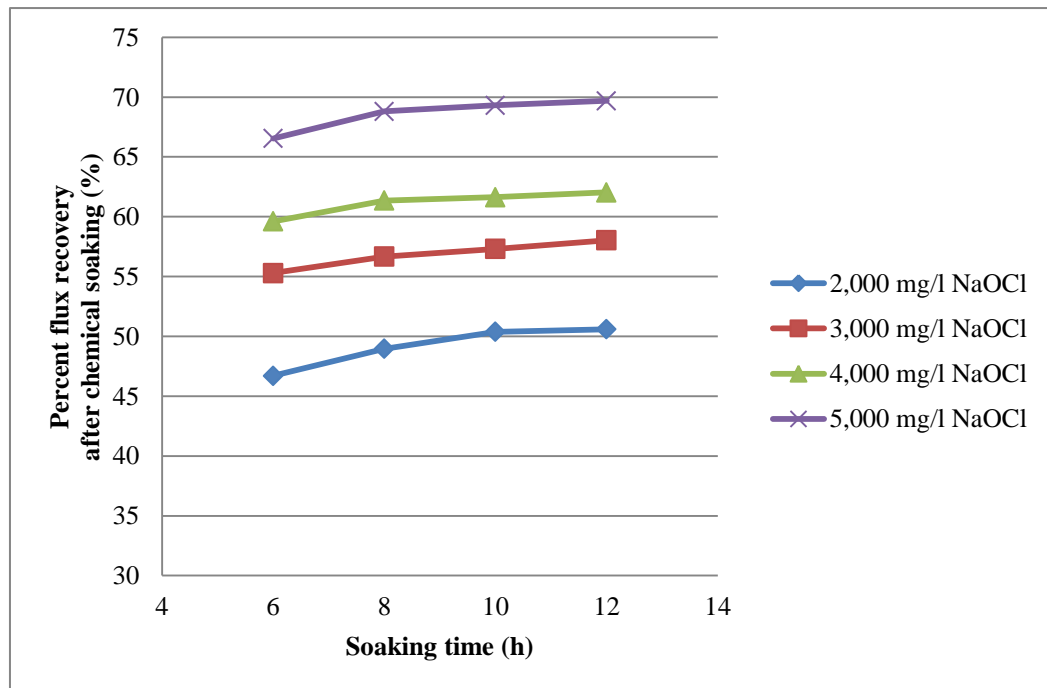


Figure 4. 13 Percent flux recovery on various NaOCl concentrations and soaking times

## CHAPTER V

### CONCLUSIONS

This study focused on Trihalomethanes (THMs), which is carcinogen, formation in chemical soaking water of ceramic membrane. THMs are a group of compounds which can form when chlorine is used and reacts with natural organic matter.

Fouling is the most disadvantage of ceramic membrane filtration system in water treatment. From the experimental results, organic matter was the major cause of ceramic membrane fouling.

Based on the obtained results, the irreversible fouling is a main problem for ceramic membrane fouling, according to organic matter which covered on the membrane surface and reduced membrane flux. In term of fouled ceramic membrane reclamation and flux recovery, chemical soaking was an effective method for the irreversible fouling removal and ceramic membrane flux recovery.

Physical backwash and chemical soaking were conducted to remove reversible and irreversible fouling, respectively. While backwashing was conducted at more regular intervals, chemical soaking was done only when necessary. Chemical soaking was generally necessary for ceramic membrane filtration systems when

periodic backwashing to restore system productivity reached a point of diminishing returns.

Chemical dose and soaking time were investigated in chemical soaking. In this study, there are 16 fouled ceramic membranes performed under 16 conditions by varied 4 chemical dosages and 4 soaking times. THMs were investigated and found in every condition in chemical soaking water.

The THMs value at 2,000 mg/L NaOCl and 6 h soaking time was the lowest; 206.19  $\mu\text{g/L}$ . And the THMs value at 5,000 mg/L NaOCl and 12 h soaking time was the highest; 887.59  $\mu\text{g/L}$ .

For fouled ceramic membrane reclamation and flux recovery, the most effective condition is 5,000 mg/l of NaOCl concentration at soaking time 12 h in chemical soaking which provided 69.68% of flux recovery. The increasing of NaOCl concentration during chemical soaking was higher increased of flux recovery than the increasing of soaking time. From the results, it can be concluded that the chemical concentration of chemical soaking was highly affected the flux recovery of fouled ceramic membrane.

## CHAPTER VI

### RECOMMENDATIONS FOR FUTURE WORK

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

1. The effect of seasonal variation in raw water, Ping River, should be studied.
2. The other chlorine reagent in chemical soaking should be also considered.
3. The fouling causes by inorganic matter should be investigated.
4. From this study, THMs formed in every condition, so chemical soaking water could be treated or should be studied for appropriate treatment technology.
5. Circulation should be conducted together with chemical cleaning to increase chemical contact effectively for enhance flux recovery.

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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย  
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APPENDIX A  
EXPERIMENTAL DATA

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Table A. 1 Initial Flux (m/d) Measurement

Ceramic Membrane No.	Filtration Lap (Every 200 ml)									
	1	2	3	4	5	6	7	8	9	10
1	68.57	68.46	68.80	68.12	67.23	67.89	68.57	68.69	68.34	68.57
2	68.46	68.12	68.57	68.92	67.56	67.45	68.34	68.80	67.78	68.57
3	68.69	68.57	68.23	68.46	67.78	67.78	67.89	68.23	68.80	68.34
4	68.57	67.45	68.23	68.12	68.00	68.46	67.78	68.00	67.67	68.00
5	67.45	68.34	67.45	68.80	67.89	67.89	67.56	67.45	68.57	68.46
6	67.78	68.23	68.34	68.34	68.23	67.89	68.12	67.56	67.45	67.78
7	68.12	68.34	68.69	68.46	67.89	67.45	68.23	67.67	68.12	68.34
8	67.89	67.67	67.78	68.00	68.69	68.12	67.89	67.45	67.78	67.89
9	68.23	68.46	68.34	68.23	67.89	68.57	68.46	67.56	68.00	68.23
10	68.46	68.46	67.89	67.56	68.12	67.78	68.69	68.00	67.56	67.89
11	68.34	68.80	68.12	68.00	68.80	68.34	67.89	68.00	68.46	67.67
12	67.78	68.57	68.69	67.45	67.78	67.89	68.23	68.00	67.56	67.45
13	67.45	67.89	68.80	68.80	67.78	67.78	68.00	68.46	67.78	67.89
14	68.57	67.45	68.23	68.12	68.00	68.46	67.78	68.00	67.67	68.00
15	67.45	68.34	67.45	68.80	67.89	67.89	67.56	67.45	68.57	68.46
16	67.78	68.23	68.34	68.34	68.23	67.89	68.12	67.56	67.45	67.78

Table A. 2 Recovery Flux (m/d) Measurement

Ceramic Membrane No.	Filtration Lap (Every 200 ml)									
	1	2	3	4	5	6	7	8	9	10
1	32.09	31.89	31.70	31.92	32.14	32.12	32.07	32.12	31.94	32.07
2	33.48	33.45	33.45	33.64	33.29	33.59	33.42	33.37	33.83	33.61
3	34.57	34.66	34.57	34.57	34.54	34.40	34.46	34.66	34.57	34.46
4	34.84	34.75	35.16	35.02	35.08	35.05	35.16	34.75	34.78	35.07
5	37.99	37.71	38.24	37.92	37.75	38.06	37.88	37.75	38.06	37.78
6	38.38	38.67	38.56	38.92	38.49	38.92	38.56	38.96	38.67	38.63
7	39.37	39.30	39.18	39.81	39.30	39.37	39.45	39.71	39.04	39.52
8	39.45	39.52	39.71	40.14	40.10	39.48	40.10	39.48	39.83	40.10
9	40.66	40.70	41.02	40.74	40.66	41.23	40.78	41.27	40.62	41.18
10	42.11	42.11	41.98	42.20	42.07	42.28	41.94	42.15	41.90	41.98
11	42.20	41.98	42.42	42.50	42.37	42.28	42.42	42.33	42.59	42.15
12	42.33	42.72	42.99	42.50	42.59	42.72	42.42	42.33	42.59	42.15
13	45.61	45.31	45.87	46.02	45.36	45.92	45.87	45.21	45.51	45.66
14	47.13	47.20	43.57	47.67	47.97	47.56	47.56	46.97	46.75	46.81
15	47.90	47.40	47.18	47.79	47.90	47.40	47.35	47.02	47.84	47.56
16	47.79	47.95	47.51	47.12	47.79	47.84	47.29	47.73	47.01	47.73







Table A. 5 Average Total Filtration Time

Filtration Lap	Times	
	Second	Minute
1	2371.00	39.52
2	1673.18	27.89
3	1414.54	23.58
4	1124.07	18.73
5	1050.92	17.52
6	859.51	14.33
7	684.13	11.40
8	495.51	8.26
9	287.64	4.79
10	104.22	1.74
Total	10064.72	167.75

Table A. 6 DOC after Ceramic Membrane Filtration

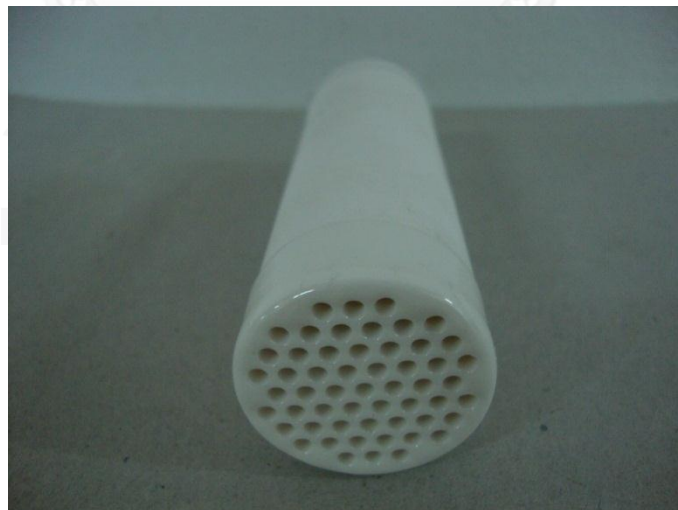
Ceramic Membrane No.	Filtration Lap									
	1	2	3	4	5	6	7	8	9	10
1	3.628	3.542	3.533	3.533	3.326	3.318	3.31	3.287	3.269	3.214
2	3.611	3.544	3.512	3.512	3.445	3.389	3.332	3.276	3.219	3.163
3	3.645	3.525	3.467	3.467	3.409	3.351	3.293	3.235	3.177	3.135
4	3.71	3.61	3.523	3.523	3.436	3.349	3.262	3.221	3.203	3.121
5	3.672	3.566	3.561	3.561	3.489	3.354	3.312	3.244	3.176	3.108
6	3.598	3.54	3.412	3.412	3.331	3.311	3.281	3.277	3.273	3.269
7	3.661	3.599	3.467	3.467	3.335	3.302	3.287	3.267	3.247	3.227
8	3.612	3.523	3.472	3.472	3.421	3.37	3.319	3.268	3.217	3.166
9	3.587	3.476	3.441	3.441	3.406	3.371	3.336	3.301	3.266	3.231
10	3.633	3.485	3.457	3.457	3.429	3.356	3.283	3.21	3.137	3.112
11	3.702	3.537	3.489	3.489	3.441	3.393	3.345	3.297	3.249	3.201
12	3.675	3.552	3.52	3.52	3.488	3.456	3.424	3.392	3.36	3.328
13	3.627	3.438	3.421	3.421	3.404	3.387	3.37	3.353	3.336	3.319
14	3.654	3.445	3.438	3.438	3.431	3.424	3.417	3.355	3.241	3.162
15	3.644	3.502	3.491	3.491	3.48	3.378	3.332	3.31	3.288	3.266
16	3.634	3.521	3.453	3.453	3.385	3.317	3.302	3.266	3.23	3.194
Avg.	3.643	3.525	3.479	3.416	3.364	3.325	3.285	3.243	3.201	3.166



APPENDIX B

Ceramic Membrane Filtration Experiment Overview

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**Figure B. 1** Clean Ceramic Membrane before filtration



Figure B. 2 Fouled Ceramic Membrane after filtration

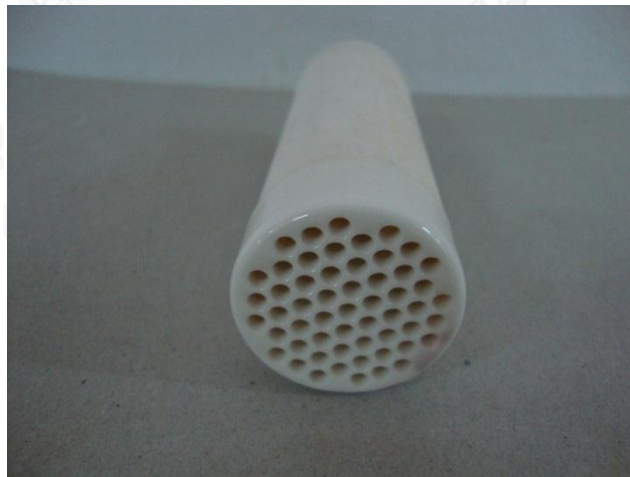


Figure B. 3 Ceramic Membrane after Recovery



Figure B. 4 Batch type Ceramic Membrane filtration pilot



Figure B. 5 Pressure Tank



Figure B. 6 Raw water sampling point





Figure B. 7 The Ceramic Membrane Research Center for Potable Water

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