

ผลกระทบของสารอินทรีย์ละลายน้ำและไบโอฟิล์มต่อศักยภาพการเกิดสารพลอยด์จากการฆ่าเชื้อ  
โรคในน้ำประปา



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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Effects of dissolved organic matters and biofilm on disinfection by-products  
formation potential in tap water

Miss Rina Heu



A Thesis Submitted in Partial Fulfillment of the Requirements  
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รินา ฮู : ผลกระทบของสารอินทรีย์ละลายน้ำและไบโอฟิล์มต่อศักยภาพการเกิดสารพลอยได้จากการฆ่าเชื้อโรคในน้ำประปา (Effects of dissolved organic matters and biofilm on disinfection by-products formation potential in tap water) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ปฎิภาณ ปัญญาพลกุล, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ศ. ดร.ชาโตชิ ทากิซาวา, หน้า.

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาผลกระทบของไบโอฟิล์มในระบบสูบน้ำประปาต่อการลดลงและการดูดซับของสารอินทรีย์ละลายน้ำรวมถึงวิเคราะห์ศักยภาพในการเกิดสารพลอยได้จากกระบวนการฆ่าเชื้อโรคซึ่งมีสาเหตุมาจากสารอินทรีย์ละลายน้ำหรือไบโอฟิล์ม รวมถึงการมีอยู่ร่วมกันระหว่างสารอินทรีย์ละลายน้ำและไบโอฟิล์มในระบบสูบน้ำประปา

ผลการทดลองแสดงให้เห็นว่าทั้งไบโอฟิล์มชนิดแอกทิฟและไบโอฟิล์มชนิดอินแอกทิฟต่างมีศักยภาพในการลดและดูดซับสารอินทรีย์ละลายน้ำชนิดผสม สารอินทรีย์ละลายน้ำชนิดชอบน้ำ และสารอินทรีย์ละลายน้ำชนิดไม่ชอบน้ำ นอกจากนี้จากการเปรียบเทียบข้อมูลของการลดลงของสารอินทรีย์ละลายน้ำทุกชนิดระหว่างไบโอฟิล์มชนิดแอกทิฟกับข้อมูลการลดลงจากสภาพไบโอดิกทำให้สามารถยืนยันกิจกรรมทางชีววิทยาได้

จากผลการศึกษาศักยภาพในการเกิดสารพลอยได้จากกระบวนการฆ่าเชื้อโรคโดยอาศัยข้อมูลปริมาณคาร์บอนอินทรีย์พบว่า สารกลุ่มฮาโลไซโตไนด์ ไตรล์ กลุ่มฮาโลอะซิดิกแอซิด และกลุ่มฮาโลลิโตน ยกเว้นคลอโรฟอร์ม มีศักยภาพในการเกิดขึ้นสูงในกรณีที่มีต้นกำเนิดสารคาร์บอนอินทรีย์จากสารอินทรีย์ละลายน้ำทุกชนิด และเริ่มลดลงเมื่อทำการผสมต้นกำเนิดสารคาร์บอนอินทรีย์จากสารอินทรีย์ละลายน้ำกับสารอินทรีย์จากไบโอฟิล์ม ซึ่งอาจมีสาเหตุมาจากการลดลงของสารอินทรีย์ละลายน้ำและสารพลอยได้จากกระบวนการฆ่าเชื้อโรคที่เกิดขึ้นโดยกิจกรรมของไบโอฟิล์ม สารกลุ่มฮาโลไซโตไนด์ ไตรล์มีศักยภาพการเกิดสูงถ้าคำนวณโดยอาศัยปริมาณสารไนโตรเจนอินทรีย์ที่มีอยู่ในตัวอย่าง จากผลการทดลองที่ได้กล่าวไว้ว่า การมีอยู่ของไบโอฟิล์มในระบบสูบน้ำประปาอาจช่วยลดศักยภาพในการเกิดสารพลอยได้จากกระบวนการฆ่าเชื้อโรคในกลุ่มฮาโลไซโตไนด์ ไตรล์ กลุ่มฮาโลอะซิดิกแอซิด และกลุ่มฮาโลลิโตนที่เกิดจากปฏิกิริยาระหว่างคลอรีนและสารอินทรีย์ละลายน้ำที่คงเหลือ นอกจากนี้สารไดคลอโรไซโตไนด์ ไตรล์สามารถถูกดูดซับได้ดีกว่าสารคลอโรฟอร์มในตัวอย่างดูดซับชนิดกัมมันต์ชนิดเกร็ด



ภาควิชา วิศวกรรมสิ่งแวดล้อม

สาขาวิชา วิศวกรรมสิ่งแวดล้อม

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# # 5670556021 : MAJOR ENVIRONMENTAL ENGINEERING

KEYWORDS: DISINFECTION BY-PRODUCTS FORMATION POTENTIAL/ DISSOLVED ORGANIC MATTER/ BIOFILM/ TAP WATER/ ADSORPTION

RINA HEU: Effects of dissolved organic matters and biofilm on disinfection by-products formation potential in tap water. ADVISOR: ASSOC. PROF. PATIPARN PUNYAPALAKUL, Ph.D., CO-ADVISOR: PROF. SATOSHI TAKIZAWA, D.Eng., pp.

This study aims to investigate the effects of biofilm in drinking water distribution system on dissolved organic matter (DOM) consumption and adsorption and to analyze the disinfection by-products formation potential (DBPsFP) which caused by DOM or biofilm and the combination of DOMs and biofilm in treated water distribution system. Also, the objective of this research is to evaluate the adsorption efficiency of occurred DBPs by using granular activated carbon (GAC).

The results showed that active and inactivated biofilm has capacity to consume and adsorb mixed DOM, hydrophilic DOM (HPI) and hydrophobic DOM (HPO) fraction. Biological consumption of all kind of DOMs was confirmed by comparing DOM consumption data of active biofilm with abiotic data.

For the result of formation potential based on organic carbon content, Haloacetonitriles (HANs), Haloacetic acids (HAAs), and Haloketones (HKs), except Chloroform (CF), have high formation potentials in individual samples of DOM and DOM fractions but started to decrease formation potential in mixed DOM or DOM fractions with biofilm. That might be caused by the consumption of DOM and occurred DBPs (excepted CF) by biofilm's activities. HANs seem to have high formation potential which calculated based on the amount of dissolved organic nitrogen (DON). From obtained results, the existing of re-growth biofilm in distribution system might reduce DBPsFP of HANs, HAAs and HKs that occurred from the reaction of chlorine and remained DOM. Also, dichloroacetonitrile (DCAN) seems easier to be adsorbed by granular activated carbon (GAC) than CF.



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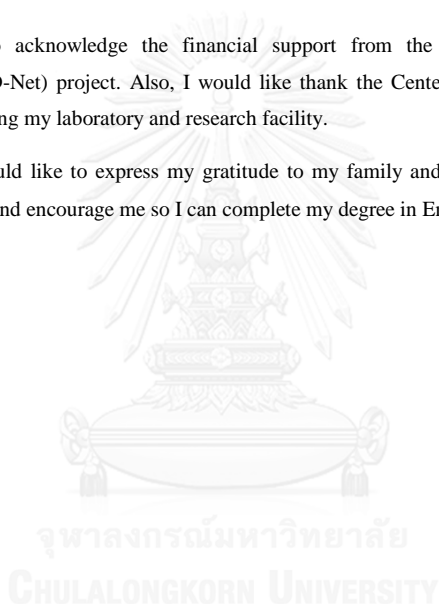
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# CHAPTER I

## INTRODUCTION

### 1.1 Keywords

- Disinfection by-products Formation Potential  
ศักยภาพการเกิดสารพลอยได้จากการฆ่าเชื้อโรค
- Dissolved organic matter  
สารอินทรีย์ละลายน้ำ
- Biofilm  
ไบโอฟิล์ม
- Tap water  
น้ำประปา
- Adsorption  
การดูดซับ

### 1.2 Introduction

Water is essential to sustain life and a satisfactory supply must be available to all. As the world population has been growing rapidly, the drinking water demand also has been increasing. To strengthen public health standard, the various treatment processes has developed such as, disinfection by chlorination, which help to reduce the waterborne pathogen-induced diseases over the past decades.

Chlorination is the most economic and effective method of drinking water disinfection in comparison with another methods such as ozonation and ultra-violet. But one of the disadvantages of water chlorination process is the production of disinfection by-products products (DBPs). The reaction between natural organic matters (NOMs) and disinfectants, and combination effect of organic matter from biofilm communities in pipe line system are supposed to be the main source for disinfection by-products (DBPs) formation in tap water. Once before being consumed, the treated water has to spend some time in the distribution system which can cause the possibility to increase of disinfection by-products (DBPs). It's not surprising to see levels of these DBPs in the tap water that can increase to one or two times higher than what they are found in water treatment plant.

The existences of DBPs in the drinking water is very dangerous to the human health because it can cause variety of disease such as cancer or pose adverse effect on reproductive systems, urinary organs, digestive and nervous system, and so on. Based on the report of the U.S Council of Environmental Quality claimed that people drinking chlorinated water can face a cancer risk about 93% higher than who drink water without containing of chlorine.

In Thailand, most people do not drink water directly from tap because of their low reliability of tap water as well as a high concentration of chlorine residuals and its nature like smell and taste. Disinfection method by using chlorination process is widely operated at water treatment plant in Bangkok Metropolitan area. All of treatment facilities nearby Bangkok Metropolitan area convey the raw water from Chao Phraya and Mae Klong River. There are four treatment plants which is Bangkok WTP (3.6 MCM/D), Mahasawat WTP (1.2 MCM/D), Samsen WTP (550,000 CM/D), and Thonburi WTP (170,000 CM/D) which are responsible for water supply in three joining areas : Bangkok, Nonthaburi, and Samut Prakan (MWA,2009). Base on previous research, (Kruawal K. et al., 2005) revealed that the raw water quality parameters from Chao Praya river in the average rate are: temperature (29°C), pH (7.45), Conductivity (260µS/cm), turbidity (60NTU), DO (3.03mg/l), and BOD (1.5mg/l).

**Table 1.1** The parameters of water qualities in Chao Praya and Mae Klong rivers (Kruawal K. et al., 2005)

River	Flow rate (m <sup>3</sup> /s)	River reaches	pH	Temp (°C)	Turb (NTU)	DO (mg/l)	BOD (mg/l)
Chao Praya	917	Upper	7.51	29.9	54.3	4.45	0.9
		Middle	7.54	29.8	91.7	3.34	0.8
		Lower	7.32	27.8	34.7	1.3	2.8
Mae Klong	550		7.98	28.2	10	6.08	1.0

Up to date, even though the Metropolitan Waterworks Authority (MWA) has promoted that tap water already met the World Health Organization standard and criteria which is suitable for drinking in some areas of Bangkok, point of use devices (POU devices) as well as boiling water are still popular in Thailand. Water quality standards of MWA are followed the regulations of WHO in 2006 for drinking water quality which concerning following parameters: turbidity not more than 5 NTU, color not more than 15 color units, total dissolved solids not more than 1,000 mg/l, manganese not more than 0.4 mg/l, iron not more than 0.3 mg/l, chloride not more than 250 mg/l, fluoride not than 1.5 mg/l, sulfate not more than 250 mg/l, no taste odor and E.coli. However, little is known about maximum limitation of some trihalomethane, pesticides, heavy metals, and radioactive substances.

**Table 1.2** The parameters of drinking water and their limit regulation (MWA, 2014)

<b>Parameters</b>	<b>Unit</b>	<b>Limit Regulation</b>
<b>True Color</b>	TCU	<15
<b>Taste</b>		Absence
<b>Turbidity</b>	NTU	<5
<b>Total Dissolved Solids</b>	mg/l	<1000
<b>Manganese</b>	mg/l	<0.4
<b>Iron</b>	mg/l	<0.3
<b>Chloride</b>	mg/l	<250
<b>Fluoride</b>	mg/l	<1.5
<b>Sulfate</b>	mg/l	<250
<b>E.coli</b>	P-A/100ml	Absence

According to the document of MWA in fiscal year 2014, the water quality parameters of four water treatment plants in the average level including: Color (2 CU), turbidity (0.63 NTU), Conductivity (370.25  $\mu\text{mho/cm}$ ), dissolved solids (229.25 mg/l), Odor (Chlorine), free chlorine (1mg/l), total alkalinity (84.5 mg/l), total solids (229.75mg/l), total hardness (111.75 mg/l), total bacteria (1 CFU/ml), TOC (2.925 mg/l), and THMs (0.22).

However, according to the information of water quality that report by MWA, the concentration of DBPs (Trihalomethane) have a trend to increase after passing the water distribution network and re-add chlorine maintain the chlorine residue until with water is reached the consumer. Although the concentration of trihalomethane that was found at the end of water network is still lower that the regulated standard of WHO, but the increasing of those concentration can imply that the distribution system (network) might be contaminated with external organic matters which can interact with the re-added chlorine in network system. Moreover, the existing of biofilm in old water plumbing system is also have to be investigated that biofilm and released organic matter from biofilm can be one of the main factors of the increasing of trihalomethane at the end of network or not. Moreover, The MWA report the concentration of DBPs just only for trihalomethane group, hence, another groups of DBPs such as haloacetic acids (HAAs), haloacetonitrile (HANs) and haloketone (HKs) also have a high potential to be increased by the same precursors. Hence, this research would like to focus on the study of DBPs formation potential of four DBPs base on the combination of biofilm and remain NOMs in tap water. Moreover, obtained information of DBPs formation potentials will be applied to investigate the efficiency of adsorption process by activated carbon for point of use (POU) unit in household.

### **1.3 Problem Statements**

Many researches pointed out that the major groups of DBPs from individual NOMs and biofilm which existed in chlorinated drinking water were trihalomethans (THMs) and haloacetic acids (HAAs). They identified separately between how DOM effect on DBPs formation potential and how biofilm effect on DBPs formation potential. However, little is known about the combination effects of DOM and biofilm on



DBPs formation potential and what types of DBP groups that are produced by those combination effects. Moreover, the activities of biofilm that related to the consumption and/or release of DOM also cannot be understood yet.

Many researchers tried to propose adsorption method by using many types of adsorbents to remove DBP precursors from raw water and DBP groups from tap water. They recommended some adsorbents to reduce the DBP formation potential by adsorb the DBPs precursors such as NOMs (Uyak V. et al., 2007). Moreover, some researchers proposed the application of carbonaceous and hybrid inorganic adsorbents to remove DBPs, but the removal efficiencies were varied by the type of DBPs. Hence, the appropriate adsorbent to remove DBPs from the combined DBPs effect between NOMs and biofilm should be studied based on the obtained DBPs formation potential data.

#### **1.4 Objective of Research**

This study aims to investigate the effects of biofilm in drinking water distribution system on dissolved organic matter (DOM) consumption and adsorption and to analyze the DBPs formation potential (DBFPs) which caused by the combination of NOMs and biofilm in treated water distribution system. The research also focuses to evaluate the adsorption efficiency of occurred DBPs by using commercial activated carbon.

#### **1.5 Scope of Research**

1. This research focused on analyses of DBP formation potential of tap water from distribution systems in Bangkok metropolitan area, Thailand.
2. The contributions of dissolved organic matters (DOM) in treated water and biofilm in distribution system on DBP formation potential was determined.
3. DOM was sampled from real treated water and was fractionated to be hydrophobic and hydrophilic in order to apply in this study.
4. Chlorination by sodium hypochlorite was applied in this study.
5. Adsorption of DOM in biofilm structure was determined in this study.
6. Granular activated carbon (GAC) was applied in adsorption process.
7. The main target groups of DBPs that were studied are:
  1. Trihalomethane (THM)

- ✚ Chloroform (CF)
- 2. Haloacetic acids (HAAs)
  - ✚ Chloroacetic acid (MCAA)
  - ✚ Dichloroacetic acid (DCAA)
  - ✚ Trichloroacetic acid (TCAA)
- 3. Haloacetonitrile (HKs)
  - ✚ 1,1 Dichloro-1-propanone (1,1-DCP)
  - ✚ 1,1,1 Trichloroacetonitrile (1,1,1-TCA)
- 4. Haloacetonitriles (HANs)
  - ✚ Chloroacetonitrile (MCAN)
  - ✚ Dichloroacetonitrile (DCAN)
  - ✚ Trichloroacetonitrile (TCAN)
  - ✚ Bromochloroacetonitrile (BCAN)
  - ✚ Dibromoacetonitrile (DBAN)
- 8. The four groups of DBPs were analyzed by the method that recommended by USEPA 5551.1 and USEPA 552.2 then measured by gas chromatography with electron capture detector (GC/ECD).
- 9. Experiment was done at department of environmental engineering, Chulalongkorn University.

### 1.6 Expected Outcome and Contribution

After completing this research, we expect to get following outcomes:

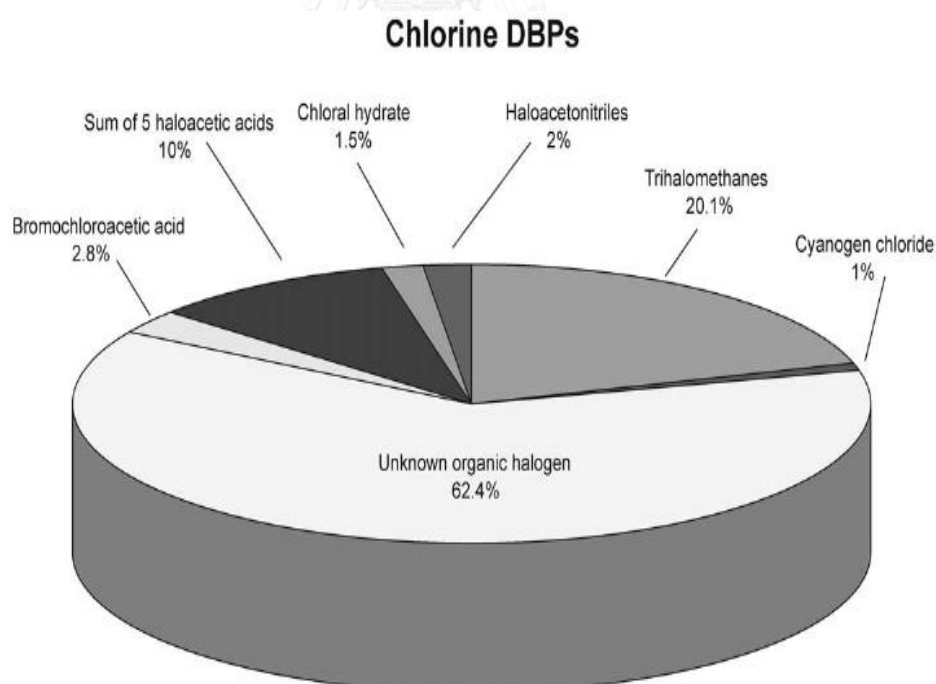
1. Enable to provide information to evaluate the risk of DBPs in tap water especially in distribution water network, by recognizing the types of DBP groups such as HAAs, HANs, HKs and THMs from combination of NOM and biofilm in treated water.
2. Enable to prove whether biofilm has much influent on DOM absorption and consumption as well as DBPs absorption and consumption or not.
3. Enable to choose the best adsorbent and adsorption condition to remove DBPs in the treated water.

## CHAPTER II

### LITERATURE REVIEWS

#### 2.1 DBPs Formation Potential (DBPsFP)

Disinfection by-product formation potential (DBPsFP) is frequently credit to the reaction between natural organic matters (NOM) and disinfectants but few have examined the contribution from disinfecting bacteria in the important process of water disinfection. DBPsFP could be analyzed by using EPA 551.1 and EPA 552.2 methods, followed by gas chromatography-electron capture detector (GC-ECD). There are two main groups of DBPs including DBPs from carbon source (C-DBPs) which are trihalomethans (THMs), haloacetic acids (HAAs), as well as haloketones, and DBPs from nitrogen source such as haloacetonitriles (HANs) and trichloronitromethane (TCNM).



**Figure 2.1** The main groups of DBPs in chlorinated tap water  
(Richardson S.D., 2003) .

In Thailand, based on the studies of Kruawal (2005) revealed that by following the European standard procedure EN 1484 using a TOC-5,000A Total Organic Carbon

Analyzer, the total organic carbon in tap water and drinking water produced from raw water of Chao Praya River was about 2.66 mg/l. The three groups of disinfection by-product (DBPs) were detectable: trichloromethane, bromodichloromethane (BDCM), and dibromochloromethane (DBCM) and total DBPs in tap water and bottled drinking water produced from Chao Praya water source was around 75 $\mu$ g/l and from Mae Klong River as source was about 30 $\mu$ g/l which such a high level.

Chlorine and THMs have been linked to various types of cancer, kidney and liver damage, disorders of the nervous system, immune system dysfunction, birth defects and hardening of the arteries. THMs increase the production of free radicals in the body and are highly cancer causing while drinking chlorinated water for long period tended to be increased the risk of developing bladder cancer as much as 80 percent which about 45,000 Americans are suffered every year, based on the report published in the Journal of the National Cancer Institute. More seriously, women who suffered from breast cancer tend to have 50 to 60% higher levels of these disinfection by-products of THMs group in their fat tissue than women without breast cancer. According to Health Freedom News (1987) which has completed on a study of colon cancer and non-cancer patients concluded that drinking of chlorinated water for 15 years or more seemed to increase a high rate of colon cancer.

**Table 2.1** The components of DBPs in drinking water, their toxicity and health effects

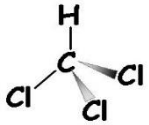
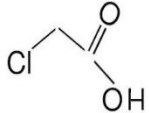
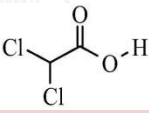
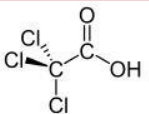
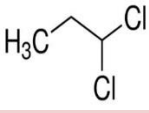
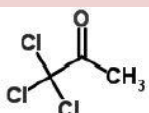
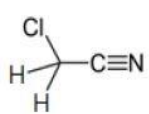
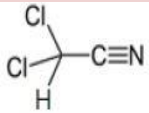
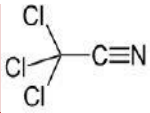
<b>Main Group</b>	<b>Compounds</b>	<b>Toxicity (mg/kg day)</b>	<b>Health Effect</b>
<b>Trihalomethane (THMs)</b>	Chloroform (CF)	0.01	Carcinogen B-2, liver tumors
	Bromoform (BF)	0.02	Carcinogen B-2, Colon tumors
<b>Haloacetic acids (HAAs)</b>	Bromochloacetic acid (BCAA)	-	Liver tumors
	Dichloroacetic acid (DCAA)	0.004	Carcinogen B-2, Liver tumors
	Trichloroacetic acid (TCAA)	-	Carcinogen C, liver tumors
<b>Haloacetonitriles (HANs)</b>	Dibromoacetonitrile (DBAN)	-	Skin tumors
	Dichoroacetonirile (DCAN)	-	Embryo death
	Trichloroacetonitrile (TCAN)	-	Embryo death
<b>Haloketone (HKs)</b>	1,1-dichloropropanone (1,1-DCP)	-	Reproductive effects

Source: Chowdhury.S., Champagne P., and McLellan P. J. (2009). Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review. *Sci Total Environ* 407 (14): 4189-4206.

### 2.1.1 Physical and Chemical Properties of DBP Groups

The physical and chemical properties of the four groups of DBPs: trihalomethane (CF), haloacetic acids (MCAA, DCAA, and TCAA), halo ketone (1,1-DCP and 1,1,1-TCP) and haloacetonitrile (MCAN, DCAN, and TCAN) are summarized in **table 2.2**.

**Table 2.2** The physical and chemical properties of some groups of DBPs

Main group	Compound	Molecular structure	MW (g mol <sup>-1</sup> )	BP (°C)	Density g ml <sup>-1</sup>
<b>Trihalomethane</b>	Chloroform (CF): CHCl <sub>3</sub>		119.377	61.17	1.4888 (25°C)
<b>Haloacetic acids (HAAs)</b>	Chloroacetic acid (MCAA): C <sub>2</sub> H <sub>3</sub> ClO <sub>2</sub>		94.5	189	1.58
	Dichloroacetic acid (DCAA): C <sub>2</sub> Cl <sub>2</sub> HO <sub>2</sub>		128.94	194	1.56
	Trichloroacetic acid (TCAA): C <sub>2</sub> Cl <sub>3</sub> HO <sub>2</sub>		163.39	197	1.63
<b>Haloketone (HKs)</b>	1,1-dichloropropanone (1,1-DCP): CCl <sub>2</sub> H <sub>3</sub> O		119.37	61	1.488
	1,1,1-Trichloroacetone (1,1,1-TCA): CCl <sub>3</sub> H <sub>3</sub> O		161.41	149	1.43
<b>Haloacetonitriles (HANs)</b>	Chloroacetonitrile (MCAN): CNCIH <sub>2</sub>		94.5	189	1.58
	Dichloroacetonitrile (DCAN): CCl <sub>2</sub> HN		109.94	112	1.369
	Trichloroacetonitrile (TCAN): CNCI <sub>3</sub>		144.39	84	1.44

Bromochloroacetonitrile (BCAN): C <sub>2</sub> HBrClN	$\begin{array}{c} \text{Cl} \\   \\ \text{Br}-\text{CH}-\text{C}\equiv\text{N} \end{array}$	154.39	152	1.722
Dibromoacetonitrile (DBAN): C <sub>2</sub> HBr <sub>2</sub> N	$\begin{array}{c} \text{Br} \\   \\ \text{Br}-\text{CH}-\text{C}\equiv\text{N} \end{array}$	198.85	170	2.29

### 2.1.2 DBPs Standard Regulations in Some Organization and Countries

The guideline of the World Health Organization (WHO, 2004) regulated the maximum level of trihalomethanes (THMs) groups: chloroform (TCM), bromodichloromethane (BDCM), bromoform (DBCM), dibromochloromethane (TBM) was 300µg/l, 60µg/l, 100µg/l, and 100µg/l, respectively. In the case of haloacetic acids groups (HAAs), standard limitation was 50µg/l for dichloroacetic acid (DCAA) as well as trichloroacetic acid (TCAA) was 100µg/l. For haloacetonitriles group (HANs): dibromoacetonitrile (DCAN) and trichloroacetonitrile (TCAN) were 70µg/l and 20µg/l, respectively. According to US Environmental Protection Agency (USEPA, 2006), trihalomethanes (THMs) was limited more than 80 µg/l while haloacetic acids (HAAs) must less than 60 µg/l as annual average that contain in the chlorinated drinking water.

In Australia and New Zealand drinking water (2004), a regulation standard was assigned total THMs in maximum concentration of 250µg/l, follow by HAA groups such as dichloroacetic acid (DCAA) at 100µg/l, monochloroacetic acid (MCAA) at 150µg/l and trichloroacetic acid (TCAA) at 100µg/l.

Based on health Canada (2006), maximum concentration of total THMs in chlorinated drinking water which measured at the end of distribution system was 100µg/l and Bromate standard which was produced during ozone disinfection was 10µg/l.

The standard regulation of DBPs in United Kingdom (UK, 2000) was about 250µg/l for total THMs and other concentration standard of DBP groups seems to be unknown.

In Thailand, the standard regulation of drinking water (TH, 2014) concerning only THMs species about  $\leq 1$  sum of ration which based on drinking water regulations of WHO, 2011.

**Table 2.3** The components of DBPs in drinking water and their limit regulations

Main Group	Compound	Canada, 2007 (mg/l)	USEPA, 2006 (mg/l)	WHO, 2004 (mg/l)	Aus-NZ, 2004 (mg/l)	UK, 2000 (mg/l)	TH,2014 (ration,W HO,2011)
THMs	TCM			0.3			
	BDCM	0.016		0.06			
	DBCM			0.01			
	TBM			0.01			
<b>Total THMs</b>		0.1	0.08	0.14	0.25	0.1	1
HAAs	DCAA			0.05	0.1		
	MCAA				0.15		
	TCAA			0.1	0.1		
<b>Sum of HAA5</b>			0.06				
HANs	DBAN			0.07			
	DCAN			0.02			

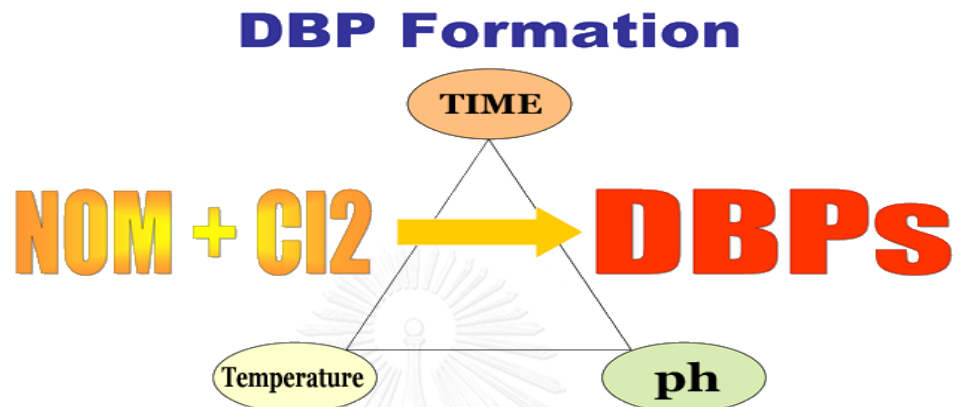
## 2.2 Disinfection By-Product Formation Potential (DBPsFP) by NOM

### 2.2.1 NOM's Characteristic on DBPs

NOM acts as important precursor of disinfection by-products (DBPs) and enables the microorganisms to grow in the treatment unit or distribution system (Khan E. et al., 1998). It is clear that DBP formation potential highly depends on NOM concentration as a main contributor, however, NOM composition and water



treatment methods are also other factors effect on DBPs formations. NOM is a mixture of allochthonous which is produced from degradation of plant tissues and leaching of organic detritus in the soils and autochthonous which is from photosynthetic input of bacterial and algae growth in water.



**Figure 2.2** The influence of NOM as precursors on formation of DBPs in chlorinated tap water (Thomas F.C., 2008)

Nowadays, the NOM's properties come from autochthonous and allochthonous, and relationship with DBPs yields have been deeply consideration. For instant, during chlorination, allochthonous NOM which mostly existed in hydrophobic fractions can contribute to THMs, TCAA and other carbonaceous DBPs in the high yield while autochthonous NOM is more hydrophilic, can gave lower levels of THMs, TCAA but higher or similar yield of DCAA. Concerning to this point, there are some information gap regarding the NOM's characteristics from sediment and its connection with DBPs formation potential. While substantial NOM can be released from sediment and might become DBPs precursors.

NOM molecules that have diameter less than 0.45  $\mu\text{m}$  are considered as dissolved organic matters (DOM) which consist of five components such as hydrophilic acids, hydrophobic humid substances, some carbohydrates, amino acids, and hydrocarbons (Thurman E.M, 1985). Dissolved organic carbon (DOC) as a part of DOM had influence on formation potential of carbonated DBPs (C-DBPs) whereas dissolved organic nitrogen (DON) which also is of DOM play an important

role in nitrogenated DBPs (N-DBPs). Because DON is hard to remove by conventional water and wastewater treatment so it can be stayed as precursor of N-DBPs during disinfection process. A few studies had identified that between surface water and treated wastewater gave the differences of DON compositions. Normally, DON in raw water contains urea, free and dissolved hydrolysable amino acid nitrogen, hexosamine and algae derived nitrogen. For wastewater treatment, 5 to 25 mg-N/L were found in the secondary treated wastewater and less than 4 mg-N/L can be found in tertiary treated wastewater (Westerhoff P. et al., 2002).

### **2.2.2 DOM Fractionation and Analyze Methods**

It's important to extensively investigate the fractionation of NOM and associate with DBPs formation. The previous studies tried to separate the dissolved natural mater (DOM) in hydrophilic and hydrophobic fraction. By using resin adsorption, e.g. DAX-8 resin, DOM was classified in six fractions such as hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophobic neutral (HPON), and, hydrophilic base (HPIB), hydrophilic acid (HPIA) and hydrophilic neutral (HPIN). Then to characterize NOM in the fractioned sample, it's popular to use UV absorbance at 254 nm ( $UV_{254}$ ), specific UV at 254 nm ( $SUV_{254}$ ) and total organic carbon (TOC). The past research claimed that 76% of dissolved organic matter tends to be hydrophobic and hydrophilic acids and got a low concentration of total organic carbon (TOC), less than 5 mg/l. The purpose of the fractionation is to allow in investigation of DBPs formation potential from the natural organic matter in raw water source.

### **2.2.3 Development of NOM Characterization and Removal Efficiency**

This section reviews the research results concerning about NOM characterizations in four countries: United Kingdom (UK), China, South Korea, and Thailand.

#### **2.2.3.1 NOM Concentration and Removal Efficiency in WTP of UK**

According to (Gough R. et al., 2014) who work on DOC removal of a potable WTW in an upland area of the UK claimed that the highest concentration of DOC was 16.2 mg/l and lowest concentration at 9.0mg/l in the raw water. The average of DOC removal rate was 76% whereas maximum rate was 83% and minimum rate was 62%.

### **2.2.3.1 NOM Characterization from Drinking Water Reservoir in China**

The fractionations of the sediment elutriate which was collected from a drinking water reservoir in South China performed by using XAD-8 and XAD-4 resin (Hong H. C. et al., 2013). Quantity and characteristics of NOM were analyzed by DOC, UV absorbance at 254 nm ( $UV_{254}$ ), and specific UV at 254 nm ( $SUV_{254}$ ). The research revealed that for DOC analysis obtained a high hydrophilic fractions and low hydrophobic fractions so that it was concluded that the natural organic matter in water sample was more likely to autochthonous origin and hydrophilic in nature. Also, the hydrophobic fractions could produce more chloroform (TCM) and trichloroacetonitrile (TCAA) than hydrophilic fractions. In the contrast, hydrophilic fractions contain a highest yield and a better predictor for its yields compared to the hydrophobic fractions.

### **2.2.3.2 NOM Characterization and Removal Efficiency from Han River in South Korea**

US standard methods and USEPA methods were conducted in this research and raw water sample was taken from Han River in South Korea. Experimental results revealed that hydrophobic NOM fraction was lower than hydrophilic NOM fraction which range from 55% to 70% for all waters. Through conventional treatment process, about 34% of DOC was removed comparing 70% of NOM removal by the GAC process. It also claimed that the removal efficiency of hydrophobic NOM was higher than hydrophilic NOM removal, that's why hydrophilic NOM demonstrated that HAAFP than in hydrophobic NOM.

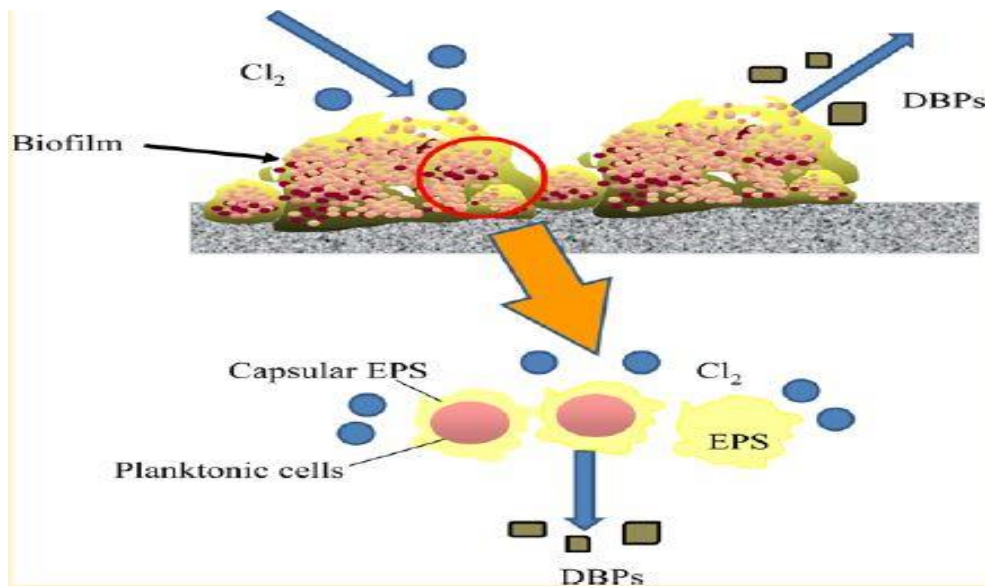
### **2.2.3.3 NOM Characterization and Removal Efficiency from WTP in Thailand**

According to (Panyapinyopol B. et al., 2005), the raw water from Bangkok water treatment plant in Bangkok was characterized by using resin adsorption such as e.g. DAX-8, AG-MP-50, and WA-10. The results of DOC from water sample analysis and fractionation demonstrated that the crucial component in the water sample was HPIN (45%) follow by HPOA (34%), HPIA (18%), HPON (6%), HPIB (3%) and HPOB (3%). The major precursors of trihalomethane formation potential (THMFP) was ranged from high to low level: HPIN (32%), HPOA (21%), and HPIA, HPOB, HPON around 13-15% whereas HPON was the smallest quantity. These conclusion results

are based on the quality of the water sources during the collection period in the August, 2003.

## 2.3 Disinfection By-Product Formation Potential (DBPsFP) by Biofilm

### 2.3.1 Effect of Microorganisms on DBP Formation Potentials (DBPsFP)



**Figure 2.3** The influence of EPS on Formation of DBP in Chlorinated tap water  
(Wang Z. et al., 2012)

During disinfection process the reactions between disinfectants and pathogens or microorganisms can produce DBP formation potential. The important part in water disinfection is the breaking down of bacterial cells and dissolved organic materials like polysaccharides, proteins, and nucleic acids, were released (Wang Z. et al., 2012). Frequently, it was reported that bacterial contamination happened in source waters (Ruecker N.J. et al., 2007) as well as water distribution systems (Batte M. et al., 2006). The bacteria from variety sources grew in different planktonic cells and biofilms in the drinking water distribution system. Planktonic usually found in the untreated source water while biofilms are frequently formed on the pipeline walls along the water supply system. Both planktonic cells and biofilm can grow fast and might change the DBP formation potential (DBPsFP). Even though, the same species, the biofilm cell covered by extracellular polymeric substance (EPS) are different from

planktonic cells and lead to different contributions of quality and quantity of DBP formation.

### **2.3.2 DBP Formation Potentials (DBPsFP) by Pure Bacteria**

By using pure bacteria *Escherichia coli* (Wang J. J. et al., 2013), the experimental result shows that some pure bacterial stains produced three groups of DBPs: THMs (6.1-37.6 $\mu\text{g}/\text{mg-C}$ ), HANs (3.2-16.3 $\mu\text{g}/\text{mg-C}$ ), and CHD (0.65-1.98 $\mu\text{g}/\text{mg-C}$ ) so it was clear that the bacteria could serve as important precursors in water treatment. Also, THMs HANs and CHD could be reduced 46, 61, and 13%, respectively, by using 1mg/l of chloramine instead of 1mg/l chlorine. Moreover, the pipe surface materials effect on DBP formation of bacteria as well. The result showed that approximate 4-28% of bromine for biofilm on poly-vinyl chloride is greater than those on galvanized zinc. The different bacteria phenotypes also result in different DBP formation for *P.aeruginosa*, for example, THMs were formed in planktonic cells about 7-11 times higher than those in biofilm cells. This research can be concluded that up to  $10^5$  to  $10^7$ cfu/cm<sup>2</sup> of biofilm were found in pipeline which was a huge amount, whereas the water distribution systems contain large contact areas. Therefore the contribution from biofilms to overall DBPsFP in finished drinking water cannot be ignored where the residual chlorine exists.

### **2.3.3 DBP Formation Potentials (DBPsFP) by EPS from Biofilm**

According to previous study (Wang Z. et al., 2012), which concern about the influence of the major biomolecules such as proteins, polysaccharides, and lipids in EPS on DBP formations, demonstrated that extracellular polymeric substances (EPS) of biofilm may exist of similar chemical composition to the DBP precursor and cause the disinfectant increasing. However, by increasing concentration of chlorine residual to eliminate biofilm and its EPS may be contributor to DBP formation in distribution system. The DBP yield experiments were conducted with both extracted total EPS and surrogate EPS in order to detector the influence of biomolecule and their structures on DBP formations. *P.aeruginosa* and *P.putida* which were the EPS composition from single species bacteria strains as well as mixed species biofilm got from water utilities were used to determined bimolecular composition of their EPS. As the result, C-DBP and N-DBP yields of extracted EPS.*P.putida* EPS contained

HAA(72.5 $\mu\text{g}/\text{mgC}$ ), HAN, HK, TCNM and CF (62.9 $\mu\text{g}/\text{mgC}$ ) yields higher than those in the regrown and the isolated *P.aeruginosa* and biofilm EPS. In the isolated biofilm, the highest HAN and HK yields were 4.0 $\mu\text{g}/\text{mgC}$  and 7.1 $\mu\text{g}/\text{mgC}$  respectively. Among all tested EPS, isolated biofilm EPS produced very high concentrations of HAN and HK. Addition, isolated biofilm EPS contained 6 times of polysaccharide concentration higher than EPS from regrown biofilm and it also associated with various NOM which was described to contribute to high DBP yields like N-DBP precursors.

#### **2.3.4 Impact Factors on DBP Formation Potentials (DBPsFP)**

By using excessive biomass, stains with different EPS quantity and composition didn't effect on DBP formation because of limited amount of  $\text{Cl}_2$  for preferential reactions with biomass. For example, at pH= 5.5, chloroform (TCM) and haloacetic acids (HAAs) was analyzed about (1-5 $\mu\text{g}/\text{l}$ ) whereas  $\text{Cl}_2$  does had a little influence on TCM but when pH increase to 7.5 the TCM also keep increasing. By using 5mg/l of  $\text{Cl}_2$ , TCM formation was produced about 25 $\mu\text{g}/\text{l}$  for all the tested stains. Also, the formation of HAAs at pH=5.5 was higher than at pH=7.5. In contrast, the research concerning about HAA formation upon chlorination of NOM claimed that HAA formation decreased at higher pH. From the experimental result of (Wang J. J. et al., 2013) showed that highest of HAA and TMC formation by biomass and EPS can be up to one-third of regulated DBP concentrations. Moreover, there are varieties of factors such as temperature, pH, precursor, disinfectant residual, pipe material, water age and etc, which impact on biofilm as well as DBP formation in the distribution system.

#### **2.3.5 The effect of DBPs Consumption and Adsorption by Biofilm**

Based on the research of Limtrakul.K.,2015 who studied on the effect of DBPs consumption and adsorption by biofilm showed that activated and inactivated biofilm can consume and adsorb DBPs. DCAN is the most biological consumable followed by 1,1 DCP, therefore it might cause the reduction of DCAN and 1,1 DCP concentration in drinking water distribution system. In contrast, CF and DCAA were slightly consumed by physical attachment on biofilm surface.

## **2.4 DBPs Removal Methods**

This part recalls the previous study results regarding DBPs removal methods in two cases: DBPs precursor removal methods (before disinfection process) and DBPs removal methods (After disinfection process).

### **2.4.1 DBPs Precursor Removal Methods**

Removing precursors before they react with disinfectants are the most economical and effective methods in order to control DPBs in conventional water treatment plants. The main DBPs precursor in chlorinated water is natural organic matter (NOM) which represents in TOC content, according to (Singer P.C., 1994). In this section will be discussed four of the DBPs precursor removal methods: enhanced coagulation behavior, granular activated carbon (GAC), ozonation and advance oxidation process (AOP).

#### **2.4.1.1 Enhanced Coagulation Behavior**

The USEPA Disinfectant/DBP rule of 1998 identified that enhanced coagulation is the best available technology. The aim of enhanced of coagulation is to maximized TOC removal which is the main DBPs precursor. Based on (Wang D. S. et al., 2013) who worked on the four types of coagulants (Polyaluminum chloride PACI, high performance polyaluminum chloride HPAC ,  $\text{Al}_2(\text{SO}_4)_3$ , and  $\text{FeCl}_3$ ) in treatability efficiency of DOM, found out that HPAC was recommended for removing DOM because of its high utilization efficiency. Metal salts coagulant exhibited higher removal efficiency at high dosage while Al based polymeric were low efficiency at a little dosage.

#### **2.4.1.2 Granular Activated Carbon (GAC)**

Granular activated carbon (GAC) is one of best technologies for the control of DBPs, based on United State Environmental Protection Agency (US EPA). GAC as well as powdered activated carbon (PAC) were used to remove turbidity, taste, odor, especially NOM which is the principle of DBPs precursor. But the disadvantage of PAC is that its practical ability is limited to the low concentration of NOM due to short contact time even though the capital cost is low (Najm I.N. et al., 1991) There

are two choices in GAC adsorption: building a GAC absorber after the sand filter and retrofitting a sand filter to a GAC filter-adsorber (GAC-FA).

#### **2.4.1.3 Ozonation**

In drinking water treatment, oxidation processes could bring to get improvements in the water quality. Ozone is known as a powerful pre-oxidant which could be carried out to reduce the DBP formation effectively. The study of (Kleiser G. et al., 2000) which concerning about differences between ozone and OH-radical-induced oxidation showed that using ozone to decrease halogenated organics is more effective than OH-radicals. According to Criegee (1975), Ozone reacts with organic material by an electrophilic addition to double bonds.

#### **2.4.1.4 UV-H<sub>2</sub>O<sub>2</sub> Based Advanced Oxidation Process**

UV-H<sub>2</sub>O<sub>2</sub> based advanced oxidation process give a high potential because it's already been accepted and applied of UV as effective disinfectant. There are two processes that UV-H<sub>2</sub>O<sub>2</sub> based AOP might eliminate the formation of DBP in drinking water including oxidation or mineralization of natural organic matter to CO<sub>2</sub> and decrease the TOC content. However, UV-H<sub>2</sub>O<sub>2</sub> based AOP is effective for reducing formation of DBPs whereas high UV and initial concentration of H<sub>2</sub>O<sub>2</sub> is greater than 23mg/l, based on (Toor R. et al., 2007).

### **2.4.2 DBPs Removal Methods**

In this section will be discussed two of the DBPs removal methods: ultrafiltration, and adsorption processes.

#### **2.4.2.1 Ultrafiltration**

Ultrafiltration has been used for drinking water treatment over past decades. Also, it was used to fractionate DOM in various molecular weights. By adsorbing or interacting with membrane surfaces, solute properties of dipole moment and hydrophobic also affect the separation efficiency (Katsuki Kimura et al., 2003; C. Visvanathan et al., 1998). Because of its high permeate flux and less operation cost, ultrafiltration membrane plays an important role in removal of algal cells, algal organic matters as well as DBPs formation.



#### **2.4.2.2 Adsorption by Hexagonal Mesoporous Silicate (HMS)**

Because of its large surface area, big pore volume and small pore size distribution, hexagonal mesoporous silicate (HMS) give a high potential as adsorbents. Although activated carbon is available and have a high removal efficiency, it has a low adsorption selective nature and difficult to regenerate. The study of (Prarat P., 2011) which considered about removal HANs by adsorption claimed that the adsorption capacity by using HMS is greater than that using powder activated carbon.

#### **2.4.3 DBPs Removal by Adsorption Method**

By recommended from the US Environmental Protection Agency (USEPA), adsorption method is considered as one of the best available technologies to control DBPs. The popular sorbent materials were divided into three main groups including activated carbon, inorganic adsorbents, and synthesized organic resin.

##### **2.4.3.1 Adsorption by Activated Carbon**

Because it has a high surface area, activated carbon becomes a universal adsorbent. Activated carbon is separated into two major types which are powdered activated carbon (PAC) and granular activated carbon (GAC). According to (Kim J. et al., 2008) GAC filter-absorber (GAC FA) was used to investigate TOC, DOC, DBPs, turbidity and manganese removal by comparing with a sand filter at a full scale WTP which had retrofitted a sand filter with a GAC FA. Based on 3 years of investigation, the study found out that at the early stage of operation, we got a high removal efficiency of THMs and HAAs but started to decrease after 3 months for THMs and 3.5 months for HAAs. Removal was occurred by physical adsorption at the early GAC FA operation but later on it was major caused by biodegradation. It shows that earlier breakthrough was found out in THMs than HAAs and THMs were harder adsorbed to GAC than HAAs.

##### **2.4.3.2 Adsorption by Inorganic Adsorbents**

Inorganic adsorbents including silicate materials, magnesium oxide, zeolite, etc, consist of uniform surface functional group and modification recyclable by thermal method. Based on (Prarat P., 2011) which studied on HANs removal by using

Hexagonal mesoporous silicate (HMS) revealed that for kinetic adsorption study, the adsorption process was dependent on the boundary layer as well as the intraparticle diffusion. Hydrophobic surface of the adsorbent may decrease the film resistance of water to mass transfer surrounding the adsorbent particle and the boundary layer thickness was affected pore size of the adsorbent. For the studies of adsorption isotherm show that the surface functional groups, porosity and crystalline structure affected the adsorption capacity of five-HANs whereas adsorption selectivity indicated that the molecular structure of HANs have influence on the adsorption capacity and selectivity over M-HMS.

#### **2.4.3.3 Adsorption by Synthesized Organic Resin**

In many research used synthesized organic resin which were ion exchange resin, regeneration by salt and ionic species in order to remove dissolved organic matter (DOM) and bromide for controlling disinfection by-products (DBPs). The studies of (Phetrak A. et al., 2014) who worked on DOM and bromide removal by anion exchange resin reveal that even though coagulation, activated carbon adsorption, ultrafiltration and nanofiltration membrane offered a good efficiency of DOM removal but not effectively remove bromide. The use of anion exchange resin is the effective method to get rid of DBP precursors and bromide. The result demonstrated that a polyacrylic macropore-type resin is the most effective removal of DOC because of the small bead size but polystyrene anion exchange resin was more effective in bromide removal. The anion exchange resin treatments lowered the DBPsFP level with HAAs removal efficiency range from 47% to 89% whereas THM removal rate from 52% to 77%.

### **2.5 Summary**

Disinfection by-product formation potential (DBPsFP) is the reaction between natural organic matters (NOM) and disinfectants but few have examined the contribution from disinfecting bacteria which can be identified by the measurement procedure from EPA 551.1 and EPA 552.2 methods by using gas chromatography-electron capture detector (GC-ECD). THMs and HAAs are the major groups of DBPs that normally were found in chlorinated drinking water. Because of its toxicity, DBPs

were limited the maximum concentration in treated water for many countries in the world.

Natural organic matters (NOM) play an important role in DBPsFP. Dissolved organic carbon (DOC) as a part of DOM had influence on formation potential of carbonated DBPs (C-DBPs) whereas dissolved organic nitrogen (DON) which also is of DOM play an important role in nitrogenated DBPs (N-DBPs).

The microorganisms effect on DBPsFP in two ways. First, by pure bacteria which stay along the distribution system because it may contribution DPBs in finished drinking water where the residual chlorine exists. Second, by biofilm EPS including proteins, polysaccharides, and lipids and it may exist of similar chemical composition to the DBP precursor and cause the DBPsFP increasing during disinfection process.

To reduce DBPsFP, it is recommended to control DPB precursors before disinfection process in the raw water and to remove DPBs after disinfection process of treated water. In order to remove DPBs in treated water, adsorption is one of the most economical and effective methods. In selective adsorbent issue, activated carbon was well known for THMs and HAAs removal whereas Silicate was used as adsorbent to remove HANs.

Moreover, the knowledge gap of the previous studies is in the combination effects between DOMs and biofilm especially in water distribution network, which have to maintain the chlorine residue. The combination effects are included the DBPsFP and fate and transportation of DOM after contacting with biofilm which can be increased or decreased base of the DOC consumption for biofilm, DOC release from biofilm and adsorption (absorption) mechanism in water network. Beside, occurred DBPs is also suggested that they also might be consumed by biofilm as the carbon source. These combination effects are still unclear and strongly needed to be investigated to understand the DBPs related phenomena in water network system.

## CHAPTER III

### RESEARCH METHODOLOGY

#### 3.1 Chemical Reagents

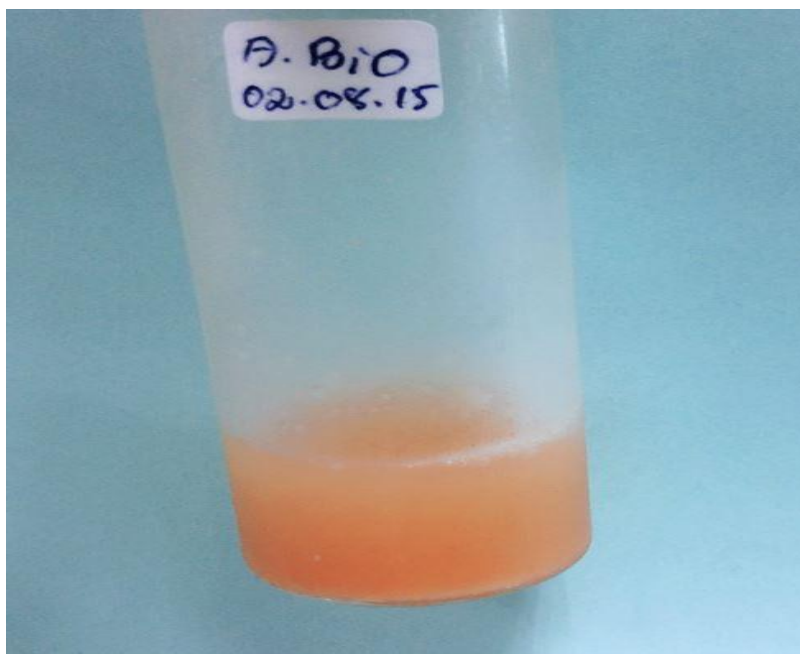
Chemical reagents are used in this experimental work include in following list:

- Acetic acid glacial ( $C_2H_4O_2$ )
- Copper (II) sulfate pentahydrate ( $CuSO_4 \cdot 5H_2O$ )
- Methanol (MeO)
- Methyl tert-butyl ether (MTBE)
- Monopotassium phosphate ( $KH_2PO_4$ )
- Potassium hydrogen phosphate ( $K_2HPO_4$ )
- Potassium hydrogen phthalate (KHP)
- Potassium iodide (KI)
- Potassium nitrate ( $KNO_3$ )
- Sodium bicarbonate ( $Na_2HCO_3$ )
- Sodium carbonate ( $Na_2CO_3$ )
- Sodium chloride (NaCl)
- Sodium hydroxide (NaOH)
- sodium hypochlorite (NaHOCl)
- Sodium sulfate ( $Na_2SO_4$ )
- Sodium thiosulfate ( $Na_2S_2O_3$ )
- Sulfuric acids ( $H_2SO_4$ )
- 2,3-dibromopropionic acid

#### 3.2 Biofilm Sample and characterization

Biofilm sample was scraped from the tap water reservoir tank and placed in tubes which contain 15 ml of DI water controlled ionic strength at 0.01 M (or near real tap water's IS). Then the sample was analyzed the carbon and nitrogen components by solid TOC and TN measurement. For inactivated biofilm, the active biofilm was

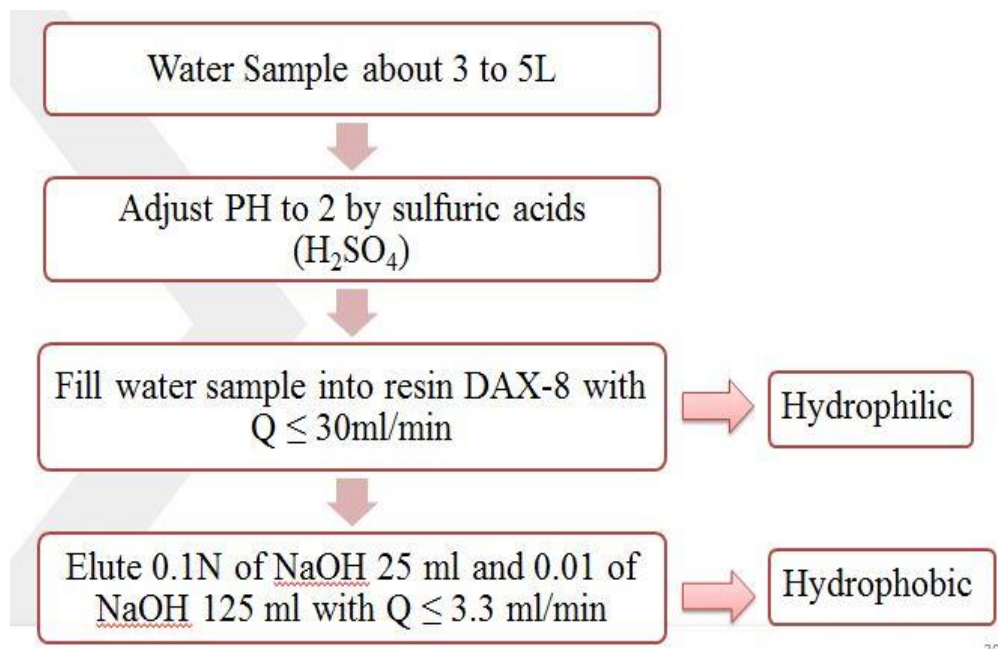
heated by autoclave at 105 °C for 20 mins before washing with phosphate buffer. After 7 days the plate did not has any colony (duplicate), therefore it can be concluded that the biofilm was completely deactivated.



**Figure 3.1** The active biofilm from water distribution system

### 3.3 DOM Fractionation

As show in **figure 3.2**, 3 to 5 liters of tap water sample was adjusted with sulfuric acids ( $H_2SO_4$ ) to get pH=2. Next, the water sample was filled into resin DAX-8 with a flow rate less than or equal to 30ml/min. Hydrophilic NOM component was released from column in the first time. 0.1 N of NaOH 25 ml and 0.01 N of NaOH 125 ml were used to elute hydrophobic NOM component with the flow rate 3.3 ml/min.



**Figure 3.2** The summary works of DOM fractionation process

### 3.4 DOM Characterization

Dissolved organic matters (DOM), hydrophobic (HPO) and hydrophilic (HPI) fractions were tested in TOC analyzer in order to measure dissolved organic carbon (DOC) and dissolved organic nitrogen (DON). For dissolved organic carbon (DOC) measurement, TOC analyzer can measure directly by following equation (**Eq 3.1**). On the other hands, DON was determined by subtracting TDN concentration with sum of DIN (NH<sub>3</sub>-N + NO<sub>2</sub>-N + NO<sub>3</sub>-N) concentrations as shown in **Eq 3.2**.

$$\text{DON (mg/L as N)} = \text{TDN} - (\text{NH}_3\text{-N} + \text{NO}_2\text{-N} + \text{NO}_3\text{-N}) \quad (\text{Eq 3.2})$$

Where:

(i) Ammonia (NH<sub>3</sub>) was measured by phenate method and ammonium chloride was used to prepare standard ammonia solutions (APHA et al., 2005). The procedure was described following;

- 1) 25 mL of samples were used
- 2) Add 1 mL of phenol solution follow by 1 mL sodium nitroprusside.
- 3) Add 2.5 mL alkaline hypochlorite solution to the samples and leave it for 1 hour.

4) After 1 hour, UV absorbance at wavelength of 640 nm of solution was measured using spectrophotometer (DR-3000, HACH, USA).

(ii) Nitrite ( $\text{NO}_2^-$ ) in the samples was analyzed by a Standard Method 4500- $\text{NO}_2$ , B colorimetric method (APHA et al., 2005) following;

- 1) 25 mL samples were add in Erlenmeyer flask.
- 2) Add 2 mL color reagent was pipetted into a samples.
- 3) Incubated in the dark for 10 min.
- 4) The UV absorbance of the solution was measured at 540 nm.
- 5) Sodium nitrite was used for preparation of nitrite standard.

(iii) Nitrate ( $\text{NO}_3^-$ ) was by following procedures ((Jones, 1984):

- 1) 25 mL of sample was added into 50 mL centrifuge tube
- 2) Add 5 mL of 0.7 M ammonium chloride was added follow by 1 g of wet spongy cadmium.
- 3) The mixture was shaken at 200 rpm for 90 min at room temperature.
- 4) Pipetted samples 10 mL and add 2.5 mL of color reagent, incubated in the dark for 10 min.
- 5) The solution was measured for absorbance at 540 nm.

The value obtained in this step was the nitrite concentration (reduced from nitrate plus original nitrite). The concentration of nitrate was subtracted with original nitrite concentration that was determined separately.

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### 3.5 Experimental Procedure

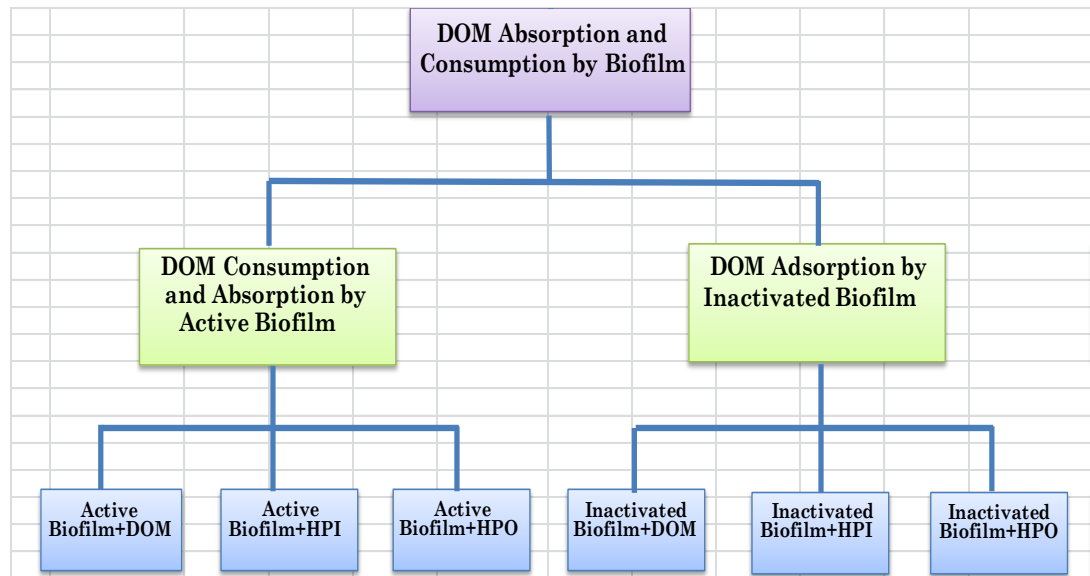
In this research, the experimental works were divided into three processes which were:

- DPB formation potentials (DBPsFP)
- DOM absorption and consumption by biofilm.
- DBP removal by absorption method.

#### 3.5.1 DOM absorption and consumption by Biofilm

DOM (total DOM, HPO, and HPI) were mixed with inactivated and active biofilm and keep for a period of time (2 days) under pH 7 and IS 0.01 M (as shown in **figure 3.2**). Then the mixed sample was filtered by GF/C and then the filtrated was injected

into TOC to analyze carbon concentration of DOM mgC/l. The comparison of carbon concentration of DOM before and after mixing was applied to analyze the role of biofilm on DOM adsorption and consumption. Experimental framework and parameters (fixed and varied) of this topic were shown in **figure 3.3** and **Table 3.1**, respectively.



**Figure 3.3** The summary works of DOM adsorption and consumption study

**Table 3.1** The parameters in DOM adsorption and consumption by biofilm experiment

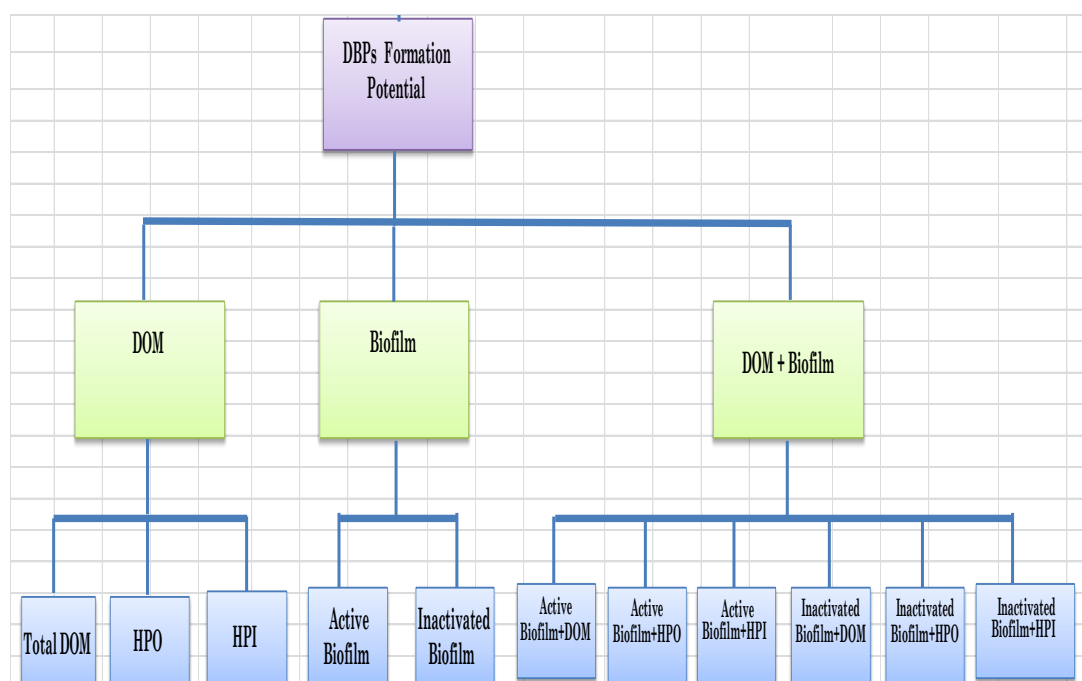
Fixed Parameters	Varied Parameters	Measured Parameters	No. Replicate
pH=7	Active biofilm =25, 50, 100 mg-SS/l	HPO	3* for all sample
IS=0.01M	Inactivated biofilm =25, 50, 100 mg-SS/l	HPI	
Contact time=24hrs	Total DOM= 2.09 mg-C/l	Total DOM	
Temperature=25°C	HPO=0.47 mg-C/l		
Volume=50 ml	HPI=1.59 mg-C/l		



\*Depend on the adsorption isotherm shape, sometime, changing concentration can give better results.

### 3.5.2 DBP Formation Potential

DBPs formation potential (DBPsFP) was analyzed base on this followed organic sources as concluded in following **figure 3.4**:



**Figure 3.4** The summary works of DBPs formation potentials analysis

#### 3.5.1.1 DBPsFP of DOM in Single Solute

Total DOM as well as DOM fractions (HPO, HPI) were added individually into different bottles containing phosphate buffer and mixed with  $\text{Cl}_2$  to reach the target concentration. After keeping the reaction for 24 hours in the dark at  $25^\circ\text{C}$  chlorinated water sample was transferred to analyze DBPs immediately.

**Table 3.2** The parameters in DBPsFP of DOM in single solute experiment

<b>Fixed Parameters</b>	<b>Varied Parameters</b>	<b>Measured Parameters</b>	<b>No. Replicate</b>
<b>NaOCl=20mg-Cl/mg-C</b>	<b>DOM=2.09mg-C/l</b>	<b>THM (CF)</b>	<b>3</b>
<b>pH=7</b>	<b>HPO=0.47mg-C/l</b>	<b>HAAs (MCAA, DCAA, TCAA)</b>	<b>3</b>
<b>IS=0.01M</b>	<b>HPI=1.59mg-C/l</b>	<b>HKs (1,1-DCP, 1,1,1-TCA)</b>	<b>3</b>
<b>Contact time=24hrs</b>		<b>HANs (MCAN, DCAN, TCAN, BCAN, DBAN)</b>	<b>3</b>
<b>Temperature=25 °C</b>			
<b>Volume=350ml</b>			

### 3.5.2.2 DBPsFP of active and inactivated Biofilm

Biofilm was collected from distribution system (tap water reservoir) was washed twice with phosphate buffer (pH 7 and IS 0.01 M as same as in Tap water), then the sample was centrifuged to obtain cells and added into bottles containing phosphate buffer to reach the target concentration. For inactivated biofilm, the active biofilm was heated by autoclave at 105 °C for 20 mins before washing with phosphate buffer. Both inactivated and active biofilm were mixed with NaOCl and keep the reaction for 24 hours in the dark at 25°C. Then chlorinated water sample was transferred to analyze DBPs immediately.

**Table 3.3** The parameters in DBPFP of active and inactivated biofilm experiment

Fixed Parameters	Varied Parameters	Measured Parameters	No. Replicate
$\text{Cl}_2=5 \text{ mg/l}$	Active biofilm =10mg-C/l	THM (CF)	3
$\text{pH}=7$	Inactivated biofilm =10mg-C/l	HAAs (MCAA, DCAA,TCAA)	3
$\text{IS}=0.01\text{M}$		HKs (1,1-DCP, 1,1,1-TCA)	3
<b>Contact time=24hrs</b>		HANs (MCAN, DCAN, TCAN, BCAN, DBAN)	3
<b>Temperature=25°C</b>			
<b>Volume=350 ml</b>			

### 3.5.2.3 DBPsFP of DOM and Biofilm in Mixed Solute

For DBPsFP experiments as shown in **table 3.4** and **3.5**, the combination of DOM and DOM fractions with biofilm (active and inactivated biofilm) sample was added sodium hypochlorite ( $\text{NaClO}$ ) (20 mg-Cl/mg-C at initial concentration) as disinfectant during chlorination process and kept reaction for a period of time (24 hrs). The chlorine residual concentration was checked every 2 hours to ensure that the chlorine is enough for chemical reaction. After finishing the reaction, the mixture was filtered by GF/C and filtrate was used to analyze the DBPs concentration.

Finally, the filtrate was prepared and analyzed DBPs base on the recommended analytical methods of USEPA methods. THMs, HANs and HKs were measured by USEPA 551.1 and HAAs were analyzed by USEPA 552.2 method. These two methods required gas chromatograph with an electron capture detector GC/EDC.

**Table 3.4** The parameters in DBPsFP of DOM and active biofilm in mixed solute experiment

<b>Fixed Parameters</b>	<b>Varied Parameters</b>	<b>Measured Parameters</b>	<b>No. Replicate</b>
<b>NaOCl=20mg-Cl/mg-C</b>	Total DOM= 2.09 mg-C/l	THM (CF)	3
<b>pH=7</b>	HPO=0.47 mg-C/l	HAA <sub>s</sub> (MCAA, DCAA, TCAA)	3
<b>IS=0.01M</b>	HPI=1.59 mg-C/l	HK <sub>s</sub> (1,1-DCP, 1,1,1-TCA)	3
<b>Contact time =24hrs</b>		HAN <sub>s</sub> (MCAN, DCAN, TCAN, BCAN, DBAN)	3
<b>Temperature=25°C</b>			
<b>Volume=500 ml</b>			
<b>Active biofilm =10mg-C/L</b>			

**Table 3.5** Parameters in DBPsFP of DOM and inactivated biofilm in mixed solute experiment

<b>Fixed Parameters</b>	<b>Varied Parameters</b>	<b>Measured Parameters</b>	<b>No. Replicate</b>
<b>NaOCl=20mg-Cl/mg-C</b>	Total DOM= 2.09 mg-C/l	THM (CF)	3
<b>pH=7</b>	HPO=0.47 mg-C/l	HAAs (MCAA, DCAA,TCAA)	3
<b>IS=0.01M</b>	HPI=1.59 mg-C/l	HKs (1,1-DCP, 1,1,1-TCA)	3
<b>Contact time=24hrs</b>		HANs (MCAN, DCAN, TCAN, BCAN, DBAN)	3
<b>Temperature=25°C</b>			
<b>Volume=350 ml</b>			
<b>Inactivated biofilm conc. =10mg-C/L</b>			

### 3.5.3 DBPs Removal Method

In this research, adsorption method was applied to remove DBPs which have high formation potential due to the remaining DOM and biofilm in water supply distribution system. Since trihalomethanes (CF) is the major group of C-DBPs and haloacetonitrile (DCAN) is one of the major groups of N-DBPs, they were selected to be studied in this experiment. Granular activated carbon (GAC) is effective adsorbents for end-tap used for removing a wide range of compounds, especially for toxic organic compounds. In this study commercial GAC was used as the model to remove high formation potential DBPs from synthetic water.

### 3.5.3.1 Adsorption Isotherm

After the kinetic experiment, the adsorption isotherm study was conducted for investigating the adsorption capacity of CF and DCAN on commercial GAC. Adsorption isotherms of THMs and HAAs were conducted under following batch experiment process.

First, stock solutions of CF and DCAN in DI water were prepared and adjusted pH at 7 and 0.01 M of ionic strength (IS) by using phosphate buffer. 0.025 g of adsorbent (GAC) is mixed with 500mL of CF and DCAN solution by varying concentration from 50-800  $\mu\text{g/L}$  in a 50 mL of flask covered with a glass stopper. After that, stir the slurry in a rotary shaker at 200 rpm at 25 °C until equilibrium state about 10 hours for CF and 12 hours for DCAN (obtained data from kinetic experiment). The solids were removed by a glass microfiber filter (GF/C). Finally, the final concentration of CF and DCAN were analyzed by a gas chromatograph equipped with an electron capture detector (GC/ECD) according to the EPA method 551.1 and 552.2 for THMs and HAAs respectively. The parameters that were applied in this experiment were concluded in the following table.

**Table 3.6** The parameters in adsorption isotherm experiments

Fixed Parameters	Varied Parameters	Measured Parameters	No. Replicate
GAC=1g	CF=50-800 $\mu\text{g/L}$	CF	-
IS=0.01M	DCAN=50-800 $\mu\text{g/L}$	DCAN	-
pH=7			-
Temperature=25°C			-
Contact time=8hrs (CF), 12hrs (DCAN)			-
Speed=200rpm			-
Volume=500 ml			-

## 3.6 DBPs Analysis Methods

### 3.6.1 HAAs Determination

Determination of haloacetic acids (HAAs) in water by used of acidic methanol esterification and followed by gas chromatography-electron capture detector (GC/ECD) which described in USA EPA 552.2 method with just a little modifications.

#### 3.6.1.1 Derivatization Process

The 15ml of sample was poured into 40 ml glass vial and with a polypropylene screw cap and PTFE faced septum. 60 ml of Std surrogate at 10mg/l was added into sample (final conc. of surrogate is 40 µg/L) and shake. Then added 0.5 ml of conc. H<sub>2</sub>SO<sub>4</sub> to obtain PH around 2 and shake. Continue to add 4g of Na<sub>2</sub>SO<sub>4</sub> and shaken until dissolved and quickly adding 1.5g of CuSO<sub>4</sub>.5H<sub>2</sub>O and shake. The sample was added 2.5 ml of MTBE shake by hand for 2 min and let it stand by for 5 min.

#### 3.6.1.2 Methylation Process

Transferring 1650 µm (550 µm x 3 times) of MTBE into 14 ml glass vial contained 2 ml of 10% H<sub>2</sub>SO<sub>4</sub> / MeOH and incubated in water at 50 °C for 2 hr. After incubation, the sample was cooled down in refrigerator at 4 °C for 3 min and then added 4 ml of NaHCO<sub>3</sub><sup>(4)</sup>, shake for 2 min (release CO<sub>2</sub> by open tap frequently) and stood for 5 min. Finally, the sample was transferred 1 ml of organic layer to GC- vial.

#### 3.6.1.3 GC/EDC Analytical Process

The analysis was carried out using an HP 5890 Series II Gas Chromatograph with a 63Ni Electron Capture Detector (ECD). A fused silica capillary HP-1 column 30m x 0.32mm i.d. x 0.25 µm film thickness was used. Injections were made in splitless mode, with helium (1.6ml/min) as carrier gas and nitrogen (46ml/min) as makeup gas. The oven temperature program started at 35°C for 7 min with 5 °C/min, to 55°C for 3 min with 7.5°C/min to 110°C for 10 min as well as the injector and detector temperatures are 200°C and 290°C, respectively.

**Table 3.7** The gas chromatographic conditions for THM, HANs and HKs determinations

<b>Gas Chromatograph</b>	<b>HP 5890 Series II</b>
<b>Column</b>	HP-1 column 30m x 0.32mm i.d. (0.25 $\mu$ m film thickness)
<b>Injection mode</b>	Splitless
<b>Carrier gas</b>	1.6ml/min
<b>Makeup gas</b>	46ml/min
<b>Oven temperature program</b>	35°C (7 mins), with 5 °C/min to 55°C (3 mins), with 7.5°C/min to 110°C (10 min)
<b>Injector temperature</b>	200°C
<b>Detector temperature</b>	290°C

### 3.6.2 HKs, THMs and HANs Determination

Trihalomethan groups (THMs) as well as haloacetonitriles (HANs), and haloketones groups (HKs) were determined by USEPA 55.1.1 method with slightly modification.

#### 3.6.2.1 Extraction Process

The 30ml of sample was poured into 40 ml glass vial and with a polypropylene screw cap and PTFE faced septum. Next 5g of Na<sub>2</sub>SO<sub>4</sub> 60 was added into sample to increase the ionic strength in the aqueous solution. After that, added 2ml of MTBE and shaking for 2 min and standing for 3 min. Then 550  $\mu$ l of the MTBE was placed into 2 ml GC vial. Afterward, 1 $\mu$ l organic layer was injected into a gas chromatograph with an electron capture detector (GC/ECD).

#### 3.6.2.2 GC/EDC Analytical Process

The analysis was carried out using a Gas Chromatograph with an Electron Capture Detector (ECD). Injections were made in splitless mode, with helium (1.6ml/min) as carrier gas and nitrogen (46ml/min) as makeup gas. A fused silica capillary DB-1 column 30m x 0.32mm i.d. x 0.25  $\mu$ m film thickness was used. The oven temperature program started at 30°C for 5.5 min with 10 °C/min, to 35°C for 4 min with 10°C/min



to 40°C for 3 min with 10 °C/min, to 150°C with 15 °C/min. The injection temperature is at 200°C and detector temperature is at 300°C.

**Table 3.8** The gas chromatographic conditions for HAAs determination

<b>Gas Chromatograph</b>	<b>HP 5890 Series II</b>
<b>Column</b>	VF-X column 30m x 0.32mm i.d. (0.10 µm film thickness)
<b>Injection mode</b>	Splitless
<b>Carrier gas</b>	1.6ml/min
<b>Makeup gas</b>	46ml/min
<b>Oven temperature program</b>	30°C (5.5 mins) with 10 °C/min, to 35°C (4 mins) with 10°C/min, to 40°C (3 min) with 10°C/min, to 150°C with 15 °C/min
<b>Injector temperature</b>	200°C
<b>Detector temperature</b>	300°C

## CHAPTER IV

### RESULTS AND DISCUSSIONS

#### 4.1 DOM Characterization

Natural organic matter (NOM) that had diameter less than  $0.45\mu\text{m}$  were considered as dissolved organic matters (DOM). Tap water was sampled at Bangkok metropolitan area, and was fractionated to be hydrophobic-like and hydrophilic-like DOM. Then, DOM concentration was measured by TOC and TN analyzer. Dissolved organic matters (DOM) were divided into two main components including dissolved organic carbon (DOC) which was the main precursor of C-DBPs and dissolved organic nitrogen (DON) which was the main precursor of N-DBPs.

##### 4.1.1 DOC Characterization

The result from the analysis of DOC in the tap water samples and from DOM fractionations were shown in **Table 4.1**. In tap water, the concentrations of DOC were about 1.82 to 2.09 mg-C/l. There were two components to separate which were hydrophobic (HPO) and hydrophilic (HPI) fractions. The highest concentration of DOC which got from HPI fraction is about 1.309 to 1.59 mg-C/l, follow by HPO fraction was about 0.245 to 0.47 mg-C/l.

**Table 4.1** The concentration of dissolved organic carbon (DOC)

Sample	DOM (mg-C/l)	HPI (mg-C/l)	HPO (mg-C/l)	± Mass Balance (mg-C/l)
1	2.09	1.59	0.47	- 0.03
2	1.82	1.39	0.245	- 0.185
Average	1.955	1.49	0.357	--

#### 4.1.2 DON Characterization

The result from the analysis of DON in the tap water samples and from DOM fractionations were shown in **Table 4.2**. In tap water, the concentration of DON was about 0.591 mg-N/l whereas HPI fraction seemed contain DON in higher concentration than those in HPO fraction about 0.512 and 0.0388 mg-N/l, respectively.

**Table 4.2** The concentration of dissolved organic nitrogen (DON)

Sample	Unit	TDN	NH <sub>3</sub>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	DON
Tap water 1	mg-N/l	0.986	0.038	0.002	0.355	0.591
Tap Water 2	mg-N/l	0.918	0.007	0.002	0.138	0.771
<b>Average</b>		<b>0.952</b>	<b>0.022</b>	<b>0.002</b>	<b>0.246</b>	<b>0.681</b>
HPI fraction 1	mg-N/l	0.873	0.02	0.002	0.34	0.512
HPI fraction 2	mg-N/l	1.09	0.012	0.001	0.173	0.904
<b>Average</b>		<b>0.981</b>	<b>0.016</b>	<b>0.0015</b>	<b>0.256</b>	<b>0.708</b>
HPO fraction 1	mg-N/l	-	-	-	-	-
HPO fraction 2	mg-N/l	0.0428	0.0028	0.0001	0.001	0.0388
<b>Average</b>		<b>0.0428</b>	<b>0.0028</b>	<b>0.0001</b>	<b>0.001</b>	<b>0.0388</b>

#### 4.2 Biofilm Characterization

Biofilm was sampling from reservoir tank of treated water. Then active biofilm and inactivated biofilm were analyzed the total organic carbon (TOC) and total nitrogen (TN) through TOC analyzer and suspended solids (SS). The results of average concentration of TOC, TN and SS in active and inactivated were summarized in **Table 4.5**.

#### 4.2.1 Active Biofilm Characterization

In active biofilm, the result of total organic carbon (TOC), total nitrogen (TN), suspended solids (SS), and percentages of TOC and TN components in biofilm were presented as in **Table 4.3**. Average concentration of suspended solid in active biofilm was about 10.23 g/l while the average of total organic carbon was around 3.236 g-C/l which was equal to 31.145% of suspended solid. The average concentration of TN was 0.153 g-N/l which was equal to 0.07 % of total components of biofilm lower than TOC component about 1.81 %.

**Table 4.3** The concentration of SS, TOC and percentages of TOC and TN components in active biofilm

Active biofilm	SS (g/l)	TOC (g-C/l)	TN (g-N/l)	%TOC/Biofilm (% g-C/g-Biofilm)	%TN/Biofilm (% g-N/g-Biofilm)
1	11.2	3.956	0.24	1.3	0.08
2	9.26	2.516	0.066	2.31	0.06
<b>Average</b>	<b>10.23</b>	<b>3.236</b>	<b>0.153</b>	<b>1.81</b>	<b>0.07</b>

#### 4.2.2 Inactivated Biofilm Characterization

Total organic carbon (TOC), suspended solids (SS) and percentages of TOC component in biofilm results were presented as in **Table 4.4**. In inactivated biofilm, average concentration of suspended solid was about 10.23 g/l whereas the average of total organic carbon was around 3.236 g-C/l which was equal to 31.145% of suspended solid.

**Table 4.4** The concentration of SS, TOC and percentages of TOC component in inactivated biofilm

Inactivated biofilm	SS (g/l)	TOC (g-C/l)	%TOC/Biofilm (% g-C/g-Biofilm)
1	11.2	4.092	1.3
2	9.26	2.602	2.31
<b>Average</b>	<b>10.23</b>	<b>3.347</b>	<b>1.805</b>

**Table 4.5** Concentration of SS, TOC, and percentages of TOC and TN components in biofilm

Biofilm	SS (g/l)	TOC (g-C/l)	TN (g-N/l)	%TOC/Biofilm (%g-C/ g-Biofilm)	%TN/Biofilm (%g-N/ g-Biofilm)
<b>Activated</b>	10.23	3.236	0.153	1.805	0.07
<b>Inactivated</b>	10.23	3.347	-	1.805	-

### 4.3 DOM and DOM Fractions Consumption and Adsorption by Biofilm

From the **figure 4.1 and 4.2** pointed out that biofilm was able to consume and adsorb DOM and DOM fractions which remain in the treated water. The result of average concentration of total DOM, HPI and HPO fraction that were consumed and adsorbed by active and inactivated biofilm were summarized in **Table 4.7**.

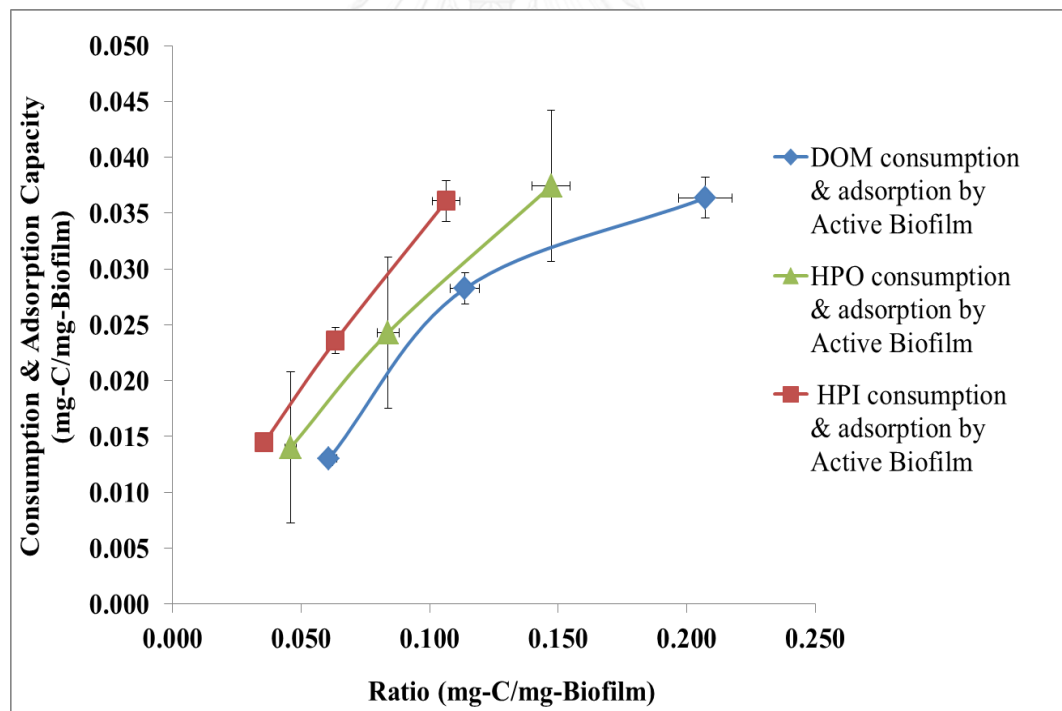
#### 4.3.1 DOM and DOM Fractions Consumptions by Active Biofilm

The varying ratios of organic carbon and active biofilm revealed that active biofilm could consume total DOM, HPI fraction and HPO fraction in different levels as shown in **figure 4.1**. In the low ratio (0.07 mg-C/mg-Biofilm), HPI fraction seemed

to be consumed by active biofilm higher than HPO fraction which was about 0.025 mg-C/mg-Biofilm, following by HPO was 0.020 mg-C/mg-Biofilm.

In moderate ratio (0.08 mg-C/mg-Biofilm), HPI fraction still trended to be consumed higher than HPO fraction about 0.031 mg-C/mg-Biofilm whereas HPO fraction was around 0.024 mg-C/mg-Biofilm. In high ratio (0.11 mg-C/mg-Biofilm), active biofilm still could consume HPI fraction in high level compare to HPO fraction. So it could be concluded that HPI fraction had higher biological consumption and physical adsorption capacity by active biofilm than HPO fraction.

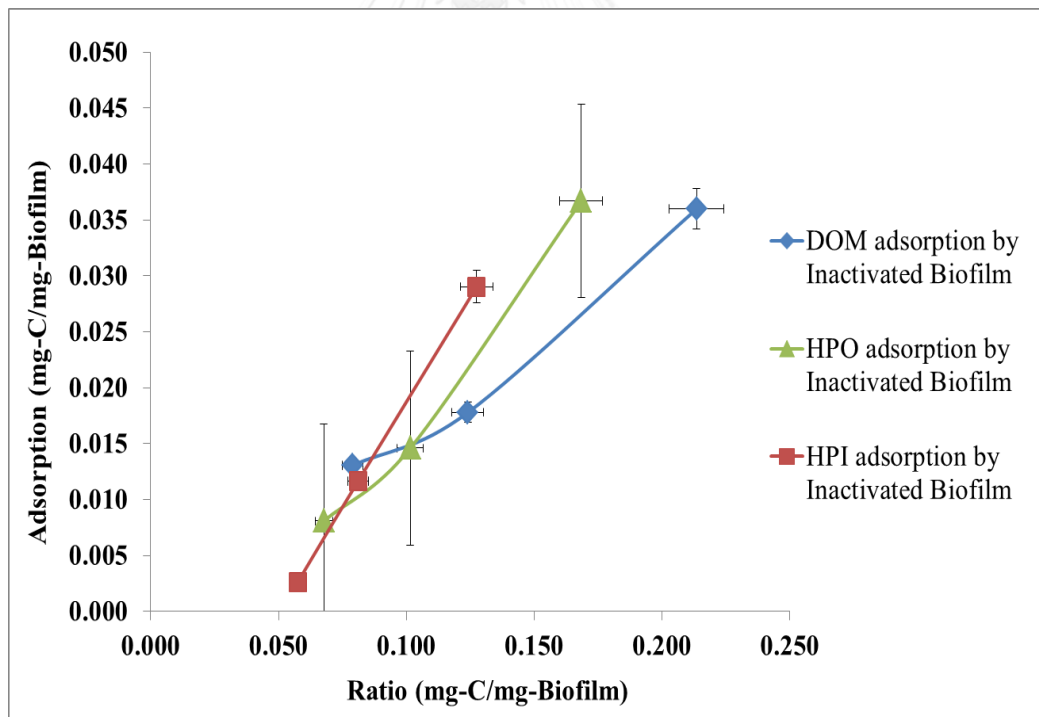
For total DOM, the capacity of consumption and adsorption were ranged from lowest ratio (0.06 mg-C/mg-Biofilm) to highest ratio (0.21 mg-C/mg-Biofilm): 0.013, 0.028, 0.036 mg-C/mg-Biofilm, respectively. It was clear that active biofilm in water distribution system also had an ability to consume and adsorb remain DOM in treated water.



**Figure 4.1** The summary results of DOM and DOM fractions consumption and adsorption by active biofilm

#### 4.3.2 DOM and DOM Fractions Adsorption by Inactivated Biofilm

From **figure 4.2**, HPI and HPO fractions could be adsorbed by vary ratios of inactivated biofilm in different concentrations. Not different from the results of HPI and HPO fractions consumption and adsorption by active biofilm, inactivated biofilm seemed adsorb HPI fraction in higher capacity than HPO fractions in low (0.08 mg-C/mg-Biofilm), moderate (0.10 mg-C/mg-Biofilm) and high (0.13 mg-C/mg-Biofilm) ratio. It showed that both active and inactivated biofilm tend to play more important role in biological consumption and physical adsorption capacity of HPI fraction than from HPO fraction. Adsorption capacities of total DOM were ranged from lowest ratio (0.08 mg-C/mg-Biofilm) to highest ratio (0.21 mg-C/mg-Biofilm): 0.013, 0.018, 0.036 mg-C/mg-Biofilm, respectively. Similar to active biofilm, inactivated biofilm in water distribution system also had an ability to adsorb remained DOM in treated water.

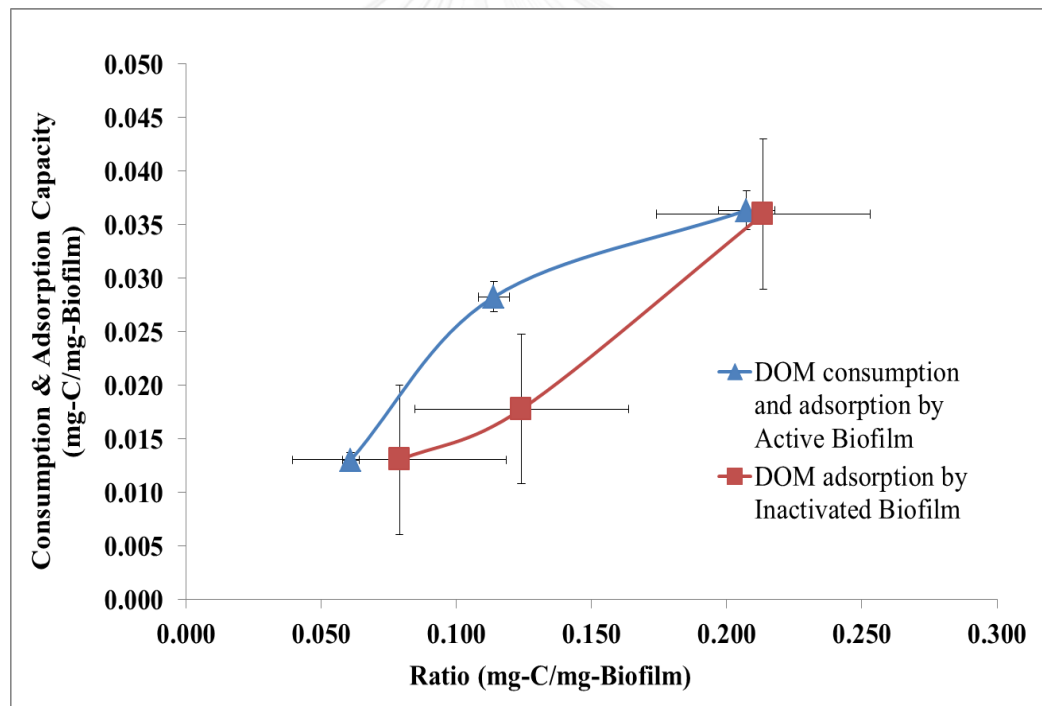


**Figure 4.2** The summary results of DOM and DOM fractions adsorption by inactivated biofilm

### 4.3.3 DOM Consumptions and Adsorption by Active and Inactivated Biofilm

The results of DOM consumption and adsorption capacity by active and inactivated biofilm were shown in **Figure 4.3**. From the table showed that the capacity of DOM consumption and adsorption by active biofilm from the lowest to highest were: 0.013, 0.028, and 0.036 mg-C/mg-Biofilm, respectively whereas the capacity of DOM adsorption capacity by inactivated biofilm from the lowest to highest, respectively, were: 0.013, 0.018, and 0.036 mg-C/mg-Biofilm.

From the result, the capacity of DOM consumption and adsorption by active biofilm was higher than those by inactivated biofilm. It could be concluded that DOM was easier to be adsorbed by active biofilm than inactivated biofilm. It also could be emphasized that DOM which remained in treat water could be degraded by biofilm in water distribution system.



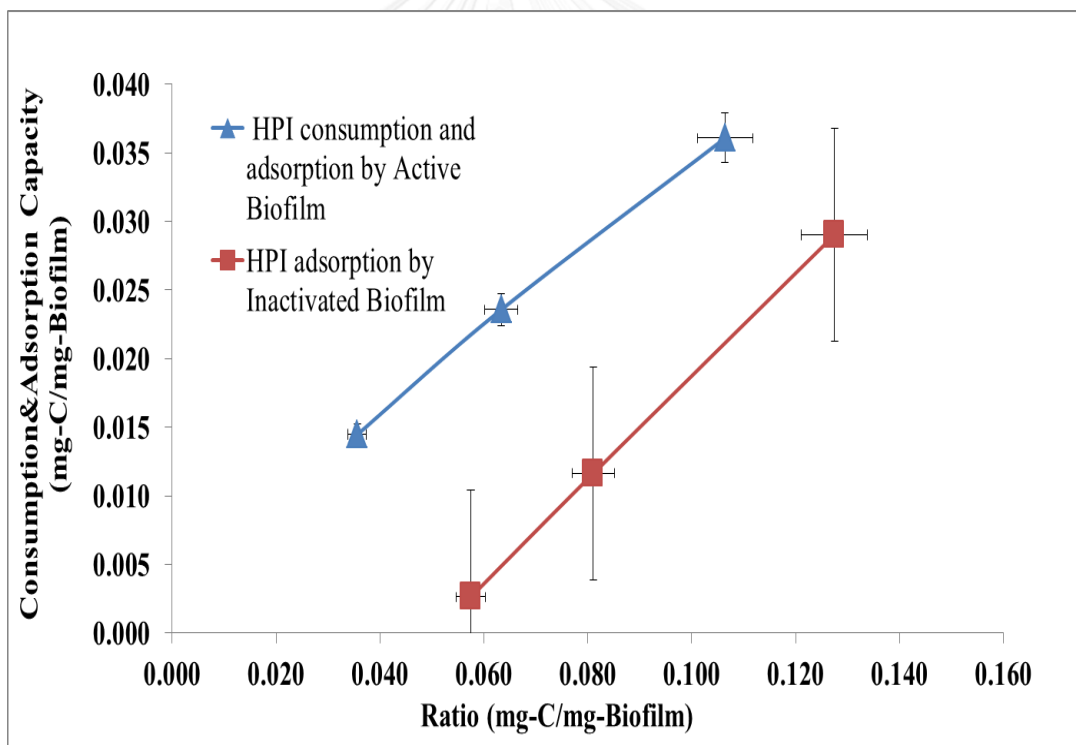
**Figure 4.3** The summary results of DOM consumption and adsorption by active and inactivated biofilm



#### 4.3.4 HPI Fraction Consumptions and Adsorption by Active and Inactivated Biofilm

**Figure 4.4** showed the capacity of HPI fraction consumption and adsorption by active and inactivated biofilm. From the result, the highest capacity that active biofilm could consume and adsorb HPI fraction was about 0.036 mg-C/mg-Biofilm, following by 0.024 mg-C/mg-Biofilm and the lowest was around 0.015 mg-C/mg-Biofilm. For inactivated biofilm, the adsorption capacities of HPI fraction were ranged from low to high were: 0.003, 0.012, 0.029 mg-C/mg-Biofilm, respectively.

For both, active and inactivated biofilm, at the higher ratio gave higher consumption and adsorption capacities so it meant that higher ratio provided higher driving force for consumption and adsorption of HPI fraction. Active biofilm still played more important role than inactivated biofilm in consumption and adsorption of HPI fraction.



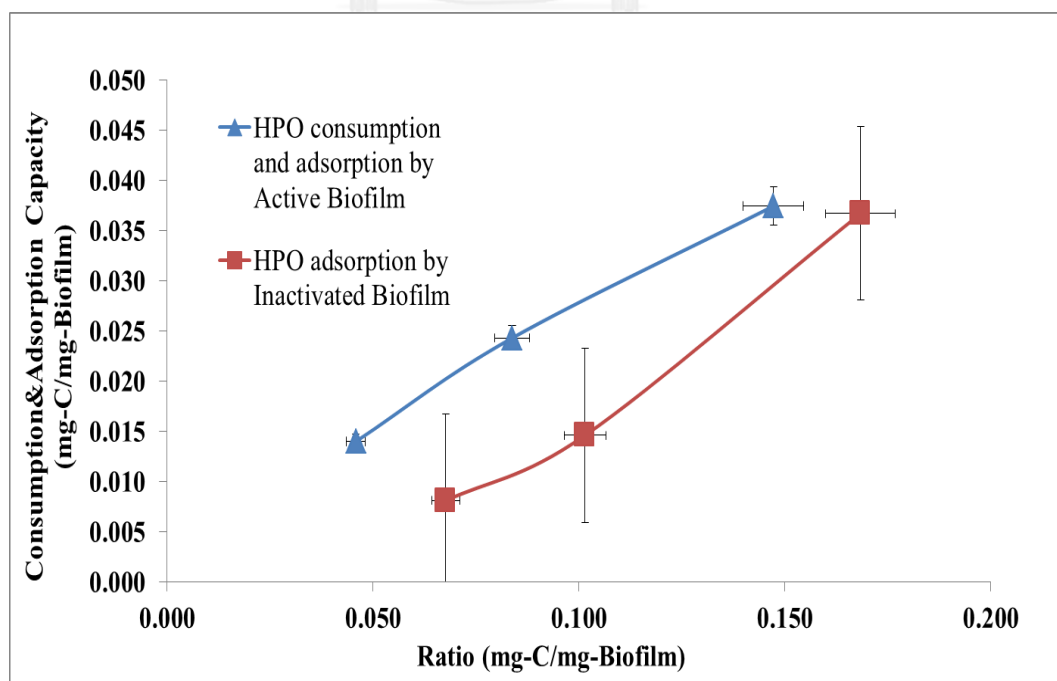
**Figure 4.4** The summary results of HPI consumption and adsorption by active and inactivated biofilm

#### 4.3.5 HPO Fraction Consumptions and Adsorption by Active and Inactivated Biofilm

The results of HPO fraction consumption and adsorption capacity by active and inactivated biofilm were shown in **Figure 4.5**. The result showed that the capacity of HPO consumption and adsorption by active biofilm from the lowest to highest were: 0.014, 0.024, and 0.037 mg-C/mg-Biofilm, respectively whereas the capacity of HPO adsorption capacity by inactivated biofilm from the lowest to highest, respectively, were: 0.008, 0.015, and 0.037 mg-C/mg-Biofilm.

Similar to the results of total DOM and HPI fraction consumption and adsorption capacities, the capacities of active biofilm in HPI fraction consumption and adsorption was higher than those by inactivated biofilm. At the higher ratio of carbon component and active and inactivated biofilm gave higher consumption and adsorption capacities so it meant that higher ratio provided higher driving force for consumption and adsorption of DOM, HPI and HPO fractions.

It indicated that total DOM, HPI and HPO fractions which were the main precursors of C-DBPs and N-DBPs could be biological consumption or physical adsorption by biofilm in pipeline. Also, it could be implied that biofilm in pipeline could reduce the precursors of DBPs in treated water.



**Figure 4.5** The summary results of HPO adsorption by activated and inactivated biofilm

#### 4.4 Disinfection By-Products Formation Potential

After keeping sample 24 hours in incubation, the free chlorine residue still remained in each sample (7-9 mg/L). Then disinfection by-products formation potential (DBPsFP) in water sample was measured through gas chromatograph/electron capture detector (GC/ECD) and results were showed in following tables and figures.

##### 4.4.1 Chloroform Formation Potential from Carbon Source

**Table 4.6** and **figure 4.6** presented the results of chloroform formation potential from DOM, biofilm and combination of DOM and biofilm. For DOM including total DOM, HPI and HPO fractions showed that total HPI fraction gave the highest CF potential about 56.89  $\mu\text{g}/\text{mg-C}$  following by HPO fraction at 55.13  $\mu\text{g}/\text{mg-C}$  and the lowest potential got from DOM. Similar to Panyapinyopol.B's report in 2005 that studied about effect of organic fraction on THM potential, CF potential from HPI fraction was higher than those from HPO fraction. This result showed that DOM and HPI fraction tended to be higher reactive with free residual chlorine than HPO fraction in forming CF formation potential.

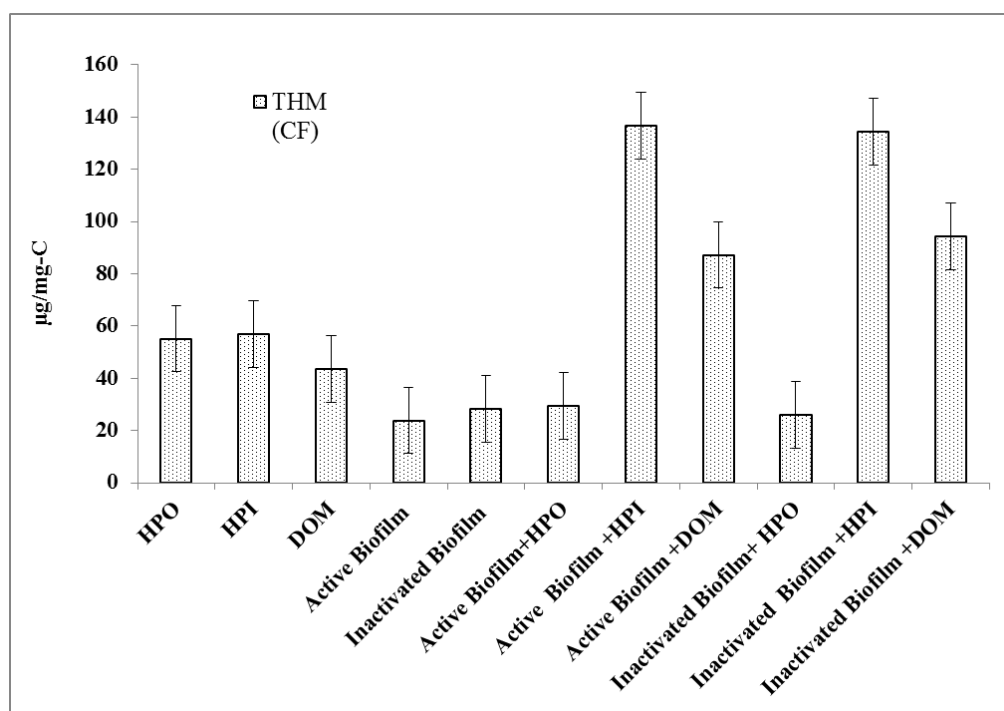
CF formation potential got from biofilm which focused on both active and inactivated biofilm was about 23.86  $\mu\text{g}/\text{mg-C}$  and 28.35  $\mu\text{g}/\text{mg-C}$ , respectively. It was clear that CF potential from active and inactivated biofilm were not different significantly. This result was about twice times higher than the result of Limtrakul.K who also worked on effect of biofilm on DBPs potential.

From the result of combination between active or inactivated biofilm and total DOM or DOM fraction presented their capacity in forming CF formation potential. The highest CF potentials were found in the combinations of active and inactivated biofilm with HPI fraction, following by the combinations of active and inactivated biofilm with total DOM and lowest potential was from the combinations of active and inactivated biofilm with HPO fraction.

**Table 4.6** The summary result of chloroform formation potential

<b>Samples</b>	<b>Averaged THM (CF) (<math>\mu\text{g} / \text{mg-C}</math>) (n=3)</b>
<b>HPO</b>	55.13
<b>HPI</b>	56.89
<b>DOM</b>	43.65
<b>Active Biofilm</b>	23.86
<b>Inactivated Biofilm</b>	28.35
<b>Active Biofilm +HPO</b>	29.52
<b>Active Biofilm +HPI</b>	136.75
<b>Active Biofilm +DOM</b>	87.28
<b>Inactivated Biofilm +HPO</b>	25.91
<b>Inactivated Biofilm +HPI</b>	134.49
<b>Inactivated Biofilm +DOM</b>	94.31

The overall result in this experiment could be concluded that the combination of active and inactivated biofilm with total DOM and HPI fraction samples gave the highest formation potential of CF, following by total DOM and DOM fractions and then was combination of active and inactivated biofilm with HPO fraction samples. The lowest CF potentials got from active and inactivated biofilm samples. Based on the study of the effect of biofilm on DBPs consumption and adsorption (Limtrakul.K., 2015), CF was slightly consumed by physical attachment on biofilm surface. It could be a reason that CF formation potential was still high in combination of active and inactivated biofilm with total DOM and DOM fraction.



**Figure 4.6** The summary result of chloroform potential from carbon source (n=3)

#### 4.4.2 Haloacetic acids Formation Potential from Carbon Source

The summary result of haloacetic acids (HANs) which focus on MCAA, DCAA, and TCAA from biofilm, DOM or DOM fraction, and combination of biofilm with DOM or DOM fractions were shown in **Table 4.7** and **figure 4.7**.

In DOM, HPI and HPO fractions, DCAA formation potential wasn't detectable, exhibited that total DOM, HPI and HPO fractions had poor free chlorine reactivity in forming DCAA whereas MCAA wasn't detectable in HPI fraction. The highest MCAA potential was observed in the total DOM sample (21.92 µg /mg-C) and the least in HPO fraction (8.81 µg /mg-C). The major precursor of TCAA potential was total DOM (704.75 µg /mg-C); following by HPI (248.98 µg /mg-C) and HPO fractions (258.37 µg /mg-C). Different from MCAA and DCAA results, DOM, HPI and HPO fractions had high free chlorine reactivity and formed high level of TCAA formation potential (Hong et al., 2013).

The result got from table 4.10 and figure 4.6 demonstrated that MCAA, DCAA, and TCAA formation potentials which obtained from active and inactivated biofilm were not quite differences. Because of effect of active and inactivated biofilm on HAAs consumption and adsorption (Limtrakul.K., 2015) were the same, it could be the reason that active and inactivated biofilm give the similar result of HAAs potential.

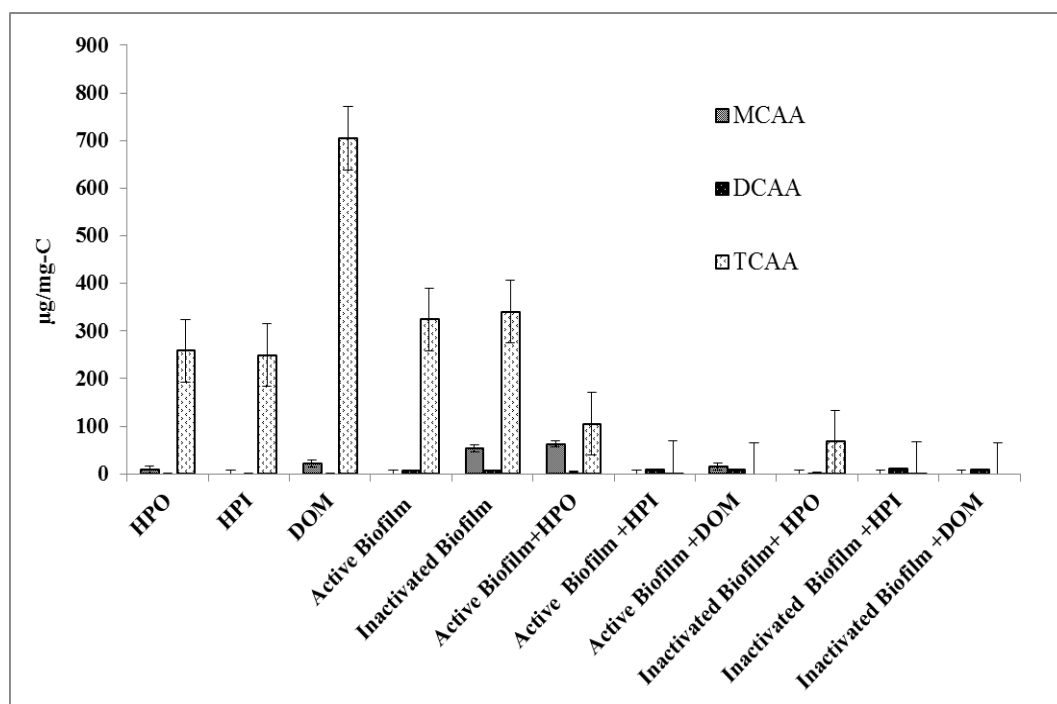
**Table 4.7** The summary results of haloacetic acids formation potential

<b>Sample</b>	<b>MCAA (<math>\mu\text{g}/\text{mg-C}</math>)</b>	<b>DCAA (<math>\mu\text{g}/\text{mg-C}</math>)</b>	<b>TCAA (<math>\mu\text{g}/\text{mg-C}</math>)</b>
<b>HPO</b>	8.81	N/A	258.37
<b>HPI</b>	N/A	N/A	248.98
<b>DOM</b>	21.92	N/A	704.75
<b>Active Biofilm</b>	N/A	6.72	324.16
<b>Inactivated Biofilm</b>	53.32	7.37	340.75
<b>Active Biofilm +HPO</b>	62.69	4.68	105.30
<b>Active Biofilm +HPI</b>	N/A	8.99	2.53
<b>Active Biofilm +DOM</b>	15.53	8.22	N/A
<b>Inactivated Biofilm +HPO</b>	N/A	2.92	67.62
<b>Inactivated Biofilm +HPI</b>	N/A	10.25	0.91
<b>Inactivated Biofilm +DOM</b>	N/A	9.27	N/A

From the combination of active and inactivated biofilm with total DOM and DOM fractions, the formation potential of TCAA was very low comparing to only total DOM, HPI or HPO and only active or inactivated biofilm. It could be because active and inactivated biofilm had ability to consume and adsorb DOM and DOM fractions which were the major precursor of TCAA potential. Also, active and inactivated could consume and adsorb TCAA itself (Limtrakul.K.,2015). That was why it could reduce the potential of TCAA when biofilm mix together with DOM or DOM fractions.

DCAA formation potential could't find in the presence of only DOM or DOM fraction but in the presence of only biofilm or combination of biofilm with DOM or DOM fraction, DCAA had higher potential than MCAA and TCAA.

The presence of MCAA was so limited that it was detectable only in HPO (8.81  $\mu\text{g} / \text{mg-C}$ ), DOM (21.92  $\mu\text{g} / \text{mg-C}$ ), inactivated biofilm (53.32  $\mu\text{g} / \text{mg-C}$ ), and active biofilm with DOM (15.53  $\mu\text{g} / \text{mg-C}$ ) and active biofilm with HPO (62.69  $\mu\text{g} / \text{mg-C}$ ).



**Figure 4.7** The summary results of haloacetic acids potentials from carbon source

#### 4.4.3 Haloketones Formation Potential from Carbon Source

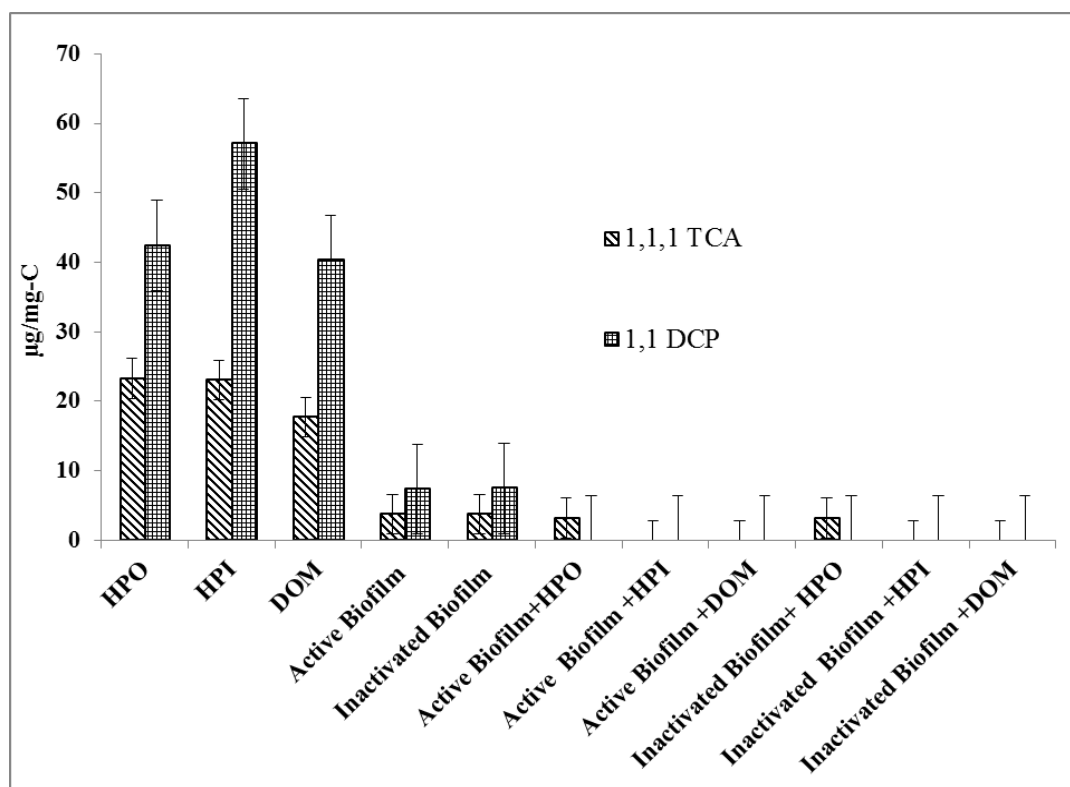
From **table 4.8** and **figure 4.8** which presented the result of HKs formation potential (1, 1-DCP and 1, 1, 1-TCA) pointed out that only total DOM, HPI and HPO fractions gave the highest formation potential of 1, 1-DCP and 1, 1, 1-TCA while the lowest got from only active and inactivated biofilm. However, 1, 1-DCP and 1, 1, 1-TCA could't find any formation potential in combination of active and inactivated biofilm with total DOM and HPI fraction, except active and inactivated biofilm with HPO fraction that gave about 6  $\mu\text{g} / \text{mg-C}$  and 3.2  $\mu\text{g} / \text{mg-C}$  of 1, 1-DCP and 1, 1, 1-TCA formation potential, respectively.

**Table 4.8** The summary results of haloketones formation potential

<b>Samples</b>	<b>1,1-DCP (<math>\mu\text{g} / \text{mg-C}</math>)</b>	<b>1,1,1-TCA (<math>\mu\text{g} / \text{mg-C}</math>)</b>
<b>HPO</b>	45.294	24.84
<b>HPI</b>	N/A	24.597
<b>DOM</b>	43.081	18.971
<b>Active Biofilm</b>	7.333	3.789
<b>Inactivate Biofilm</b>	7.475	3.780
<b>Active Biofilm +HPO</b>	6.088	3.227
<b>Active Biofilm +HPI</b>	N/A	N/A
<b>Active Biofilm +DOM</b>	N/A	N/A
<b>Inactivated Biofilm +HPO</b>	6.101	3.189
<b>Inactivated Biofilm +HPI</b>	N/A	N/A
<b>Inactivated Biofilm +DOM</b>	N/A	N/A

The 1,1-DCP and 1,1,1-TCA formation potentials in combinations of DOM and DOM fractions with active and inactivated biofilm were quite lower than those in only DOM and DOM fractions but had similar potential to only active and inactivated biofilm. There were two reasons to interpret this result. First reason was that active and inactivated biofilm be able to consume and adsorb DOM and DOM's fractions which were the main precursor of DBPs. Second, the past study also pointed out that biofilm also had biological consumption and physical adsorption capacities of DBPs (Limtrakul.K., 2015). So it was clear that DOM and DBPs could reduce while mixing with biofilm. As the result biofilm in water distribution system could decrease 1,1-DCP and 1,1,1-TCA formation potential in treated water while traveling in pipeline.





**Figure 4.8** The summary results of halo ketones formation potential from carbon source

#### 4.4.4 Haloacetonitriles Formation Potential from Carbon Source

The result of five HANs including MCAN, DCAN, TCAN, BCAN, and DBAN were summarized in **table 4.9** and **figure 4.9**.

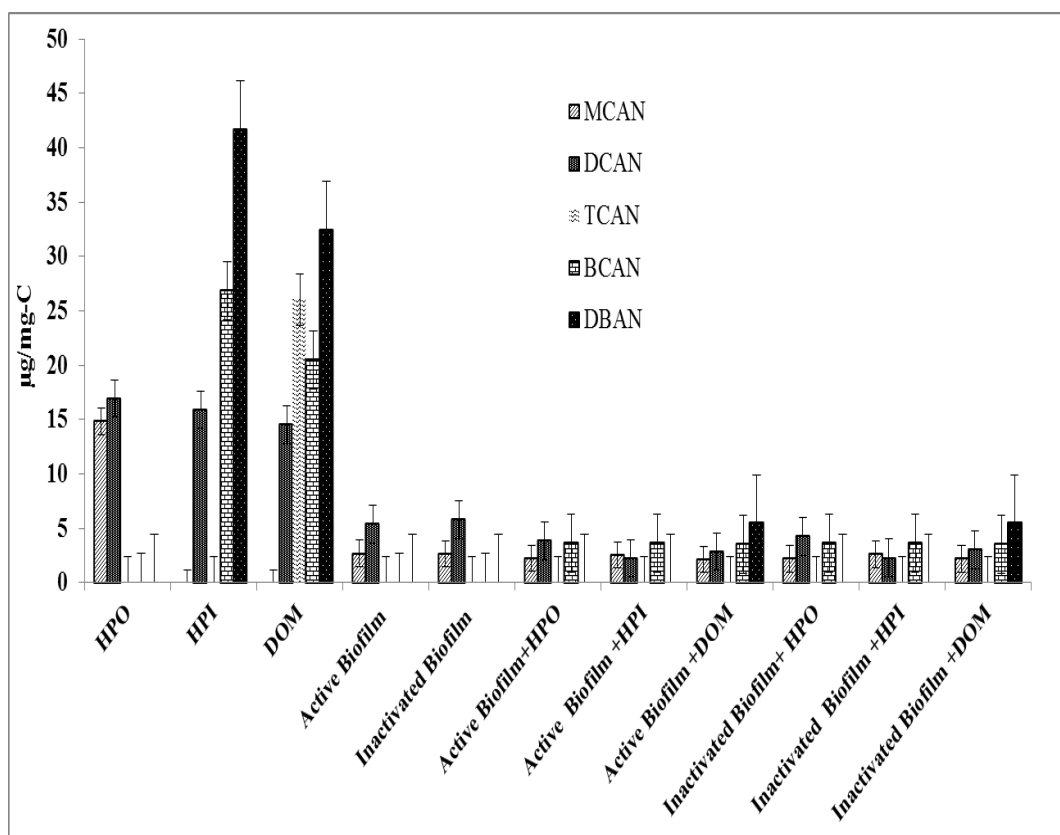
In total DOM sample gave the potential of DBAN > TCAN > BCAN > DCAN whereas MCAN could't be detected. In HPI fraction, DBAN got the highest potential among group (41.66 µg /mg-C), following by BCAN (26.4 µg /mg-C) and lowest one was DCAN potential (15.92 µg /mg-C) and MCAN and TCAN potential still could't find in HPI water sample. HPO fraction was main precursor of MCAN (14.87 µg /mg-C) and DCAN (16.95 µg /mg-C) while TCAN, BCAN, and DBAN could't be detectable.

In active and inactivated biofilm only MCAN and DCAM could be found but formation potential was very low compare to MCAN and DCAN in DOM and DOM fractions. It was clear that total DOM and DOM fractions had high reactive with free residual chlorine in forming HANs.

**Table 4.9** The summary results of haloacetonitriles formation potential

<b>Samples</b>	<b>MCAN (<math>\mu\text{g}/\text{mg-C}</math>)</b>	<b>DCAN (<math>\mu\text{g}/\text{mg-C}</math>)</b>	<b>TCAN (<math>\mu\text{g}/\text{mg-C}</math>)</b>	<b>BCAN (<math>\mu\text{g}/\text{mg-C}</math>)</b>	<b>DBAN (<math>\mu\text{g}/\text{mg-C}</math>)</b>
<b>HPO</b>	14.87	16.95	N/A	N/A	N/A
<b>HPI</b>	N/A	15.92	N/A	26.4	41.66
<b>DOM</b>	N/A	14.53	26.08	20.49	32.48
<b>Active Biofilm</b>	2.69	5.42	N/A	N/A	N/A
<b>Inactivated Biofilm</b>	2.66	5.83	N/A	N/A	N/A
<b>Active Biofilm +HPO</b>	2.24	3.88	N/A	3.68	N/A
<b>Active Biofilm +HPI</b>	2.55	2.25	N/A	3.68	N/A
<b>Active Biofilm +DOM</b>	2.17	2.88	N/A	3.55	5.48
<b>Inactivated Biofilm +HPO</b>	2.23	4.28	N/A	3.68	N/A
<b>Inactivated Biofilm +HPI</b>	2.61	2.26	N/A	3.68	N/A
<b>Inactivated Biofilm +DOM</b>	2.20	3.05	N/A	3.56	5.50

Not quite different from only active and inactivated biofilm, the combination of active and inactivated biofilm with total DOM and DOM fractions gave a very low formation potential of 5 species of HANs comparing to HAN potential in only total DOM and DOM fractions. It exhibited that effect of active and inactivated biofilm on consumption and adsorption of DOM and DBPs played very important role in reduce formation potential of HANs.



**Figure 4.9** The summary results of haloacetonitriles potential from carbon source

#### 4.4.5 Haloacetonitriles Formation Potential from Nitrogen Source

**Table 4.10** and **figure 4.10** presented the results of five HANs formation potential such as MCAN, DCAN, TCAN, BCAN, and DBAN formation potentials from nitrogen source in biofilm, DOM and DOM's fractions, and combination of biofilm with DOM and DOM's fractions.

Total HPO sample gave a very high MCAN and DCAN potential formations whereas TCAN, BCAN, and DBAN could not be found. Quite different from DCAN and MCAN formation potential in HPO fraction from carbon source, DCAN and MCAN potential in HPO fraction from nitrogen source was about 100 times higher than those from carbon source. It was because the carbon component was about 10 times higher than nitrogen component in HPO fraction.

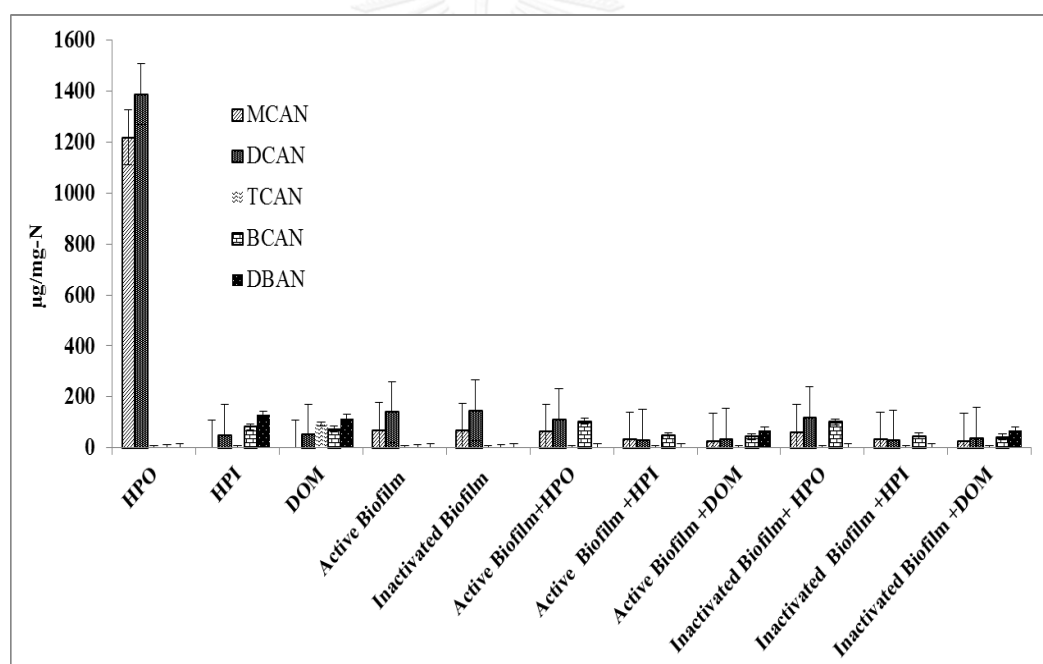
In HPI fraction, from the highest to lowest potential are DBAN (129.37  $\mu\text{g}/\text{mg-N}$ ), BCAN (83.35  $\mu\text{g}/\text{mg-N}$ ), and DCAN (49.43  $\mu\text{g}/\text{mg-N}$ ) while MCAN and TCAN could not detectable. Comparing to DCAN and MCAN formation potential in HPI fraction from carbon source, DBAN, BCAN and DCAN potential in HPO fraction from nitrogen source was about three times higher than those from carbon source. For total DOM, only DBAN (114.88  $\mu\text{g}/\text{mg-N}$ ), TCAN (92.23  $\mu\text{g}/\text{mg-N}$ ), BCAN (72.46  $\mu\text{g}/\text{mg-N}$ ), and DCAN (51.39  $\mu\text{g}/\text{mg-N}$ ) could be detected and about four times higher than those from carbon source.

**Table 4.10** The summary results of haloacetonitriles formation potential from nitrogen sources

Samples	MCAN ( $\mu\text{g}/\text{mg-N}$ )	DCAN ( $\mu\text{g}/\text{mg-N}$ )	TCAN ( $\mu\text{g}/\text{mg-N}$ )	BCAN ( $\mu\text{g}/\text{mg-N}$ )	DBAN ( $\mu\text{g}/\text{mg-N}$ )
HPO	1218.96	1388.86	N/A	N/A	N/A
HPI	N/A	49.43	N/A	83.35	129.37
DOM	N/A	51.39	92.23	72.46	114.88
Active Biofilm	69.67	140.44	N/A	N/A	N/A
Inactivated Biofilm	66.75	146.18	N/A	N/A	N/A
Active Biofilm +HPO	64.02	111.04	N/A	105.15	N/A
Active Biofilm +HPI	32.93	29.08	N/A	47.48	N/A
Active Biofilm +DOM	26.80	35.61	N/A	43.96	67.84
Inactivated Biofilm +HPO	61.89	118.46	N/A	101.89	N/A
Inactivated Biofilm +HPI	33.21	28.79	N/A	46.80	N/A
Inactivated Biofilm +DOM	26.90	37.19	N/A	43.44	67.12

Only DCAN (140.44  $\mu\text{g}/\text{mg-N}$ ) and MCAN (69.67  $\mu\text{g}/\text{mg-N}$ ) could be found in active biofilm and similar to active biofilm, in inactivated biofilm sample only DCAN (146.18  $\mu\text{g}/\text{mg-N}$ ) and MCAN (66.75  $\mu\text{g}/\text{mg-N}$ ) could be detected. But it was logical reason to see DCAN and MCAN potentials from nitrogen source were so much higher than those from carbon source about 30 times whereas the carbon component in biofilm was higher than nitrogen component about 20 times.

Similar to total DOM, DOM fractions, active and inactivated biofilm, the formation potential of five HANs in the combination of active and inactivated biofilm with DOM and DOM fractions from nitrogen source was much higher than HANs potentials from carbon source.



**Figure 4.10** Summary results of haloacetonitriles formation potential from nitrogen source

#### 4.5 Disinfection By-Products Removal by GAC Adsorption

Chloroform (CF) come from trichloromethans group (THMs) which was carbonaceous disinfection by-products (C-DBPs) and dichloroacetonrile (DCAN) come from haloacetonitriles group (HANs) which was nitrogenous disinfection by-

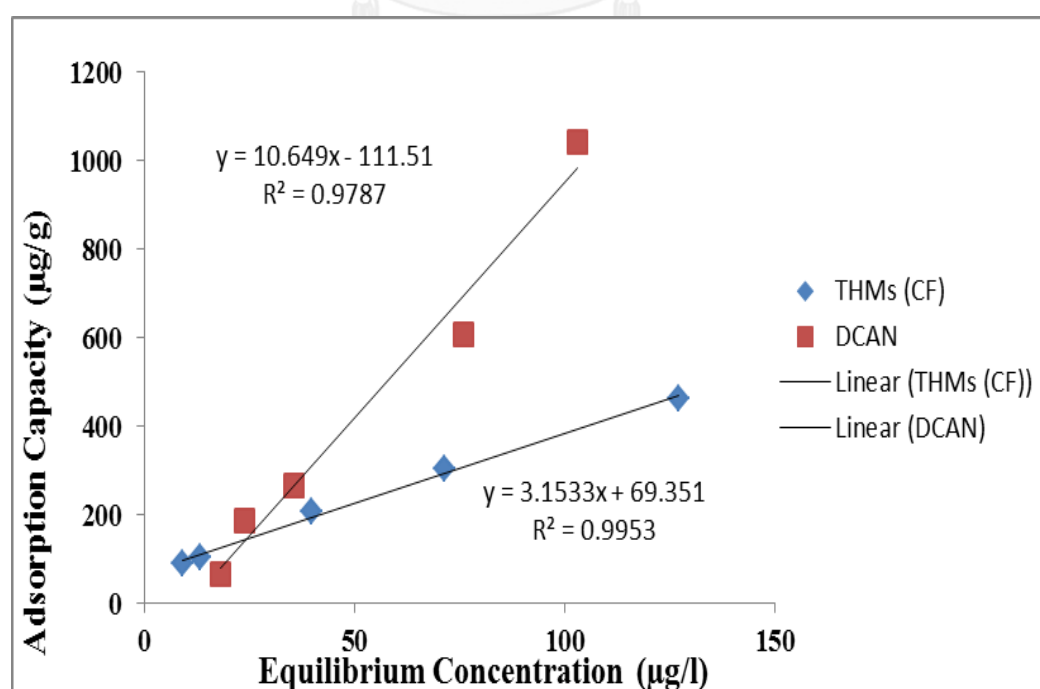
products (N-DBPs) were selected to study on adsorption kinetic and isotherm whereas granular activated carbon (GAC) was selected as an adsorbent.

#### 4.5.1 Adsorption Kinetic

Based on the report of Buaoui.D,2015 who also worked on DBPs removal by GAC showed that the equilibrium state of chloroform (CF) was at 10 hours and dichloroacetonitrile (DCAN) was at 12 hours of retention time.

#### 4.5.2 Adsorption Isotherm

The results of adsorption capacity of CF and DCAN were summarized in **figure 4.11**. From the figure showed that at the low initial concentrations (50, 100, 200 µg/l) of CF and DCAN, the adsorption capacity of CF and DCAN had similar results. In contrast, DCAN had adsorption capacity a bit higher than CF from moderate to high initial concentration (400, 600 µg/l). Not quite different to the result of Kim.J.,2008 who also worked on THMs and HAAs removal by GAC filter-absorber (GAC-FA) revealed that the removal efficiency of HAAs were much higher than that of THMs and THMs were harder adsorbed to GAC than HAAs. It could be concluded that THMs seemed to have a low adsorption capacity comparing to other groups of DBPs.



**Figure 4.10** The summary results of adsorption capacities of CF and DCAN

## CHAPTER V

### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

The study of 'Effects of Dissolved Organic Matters and Biofilm on Disinfection By-Products Formation Potential in Tap Water' aimed to investigate the effect of biofilm in drinking water distribution system on dissolved organic matter (DOM) consumption and adsorption and to analyze the DBPs formation potential (DBPFP) which caused by DOMs, biofilm and the combination of DOMs and biofilm in treated water distribution system. Also, the objective of this research was to evaluate the adsorption efficiency of occurred DBPs by using granular activated carbon (GAC).

For the study of DOM consumption and adsorption by biofilm, total DOM, HPO, and HPI were mixed with inactivated and active biofilm and kept for a period of time (24 hours) under pH 7 and IS 0.01 M. Then the mixed sample was filtered by GF/C and then the filtrate was injected into TOC to analyze carbon concentration of DOM. The comparison of adsorption capacity between active and inactivated biofilm showed that active biofilm had a higher capacity of adsorption of total DOM, HPI and HPO fractions than inactivated biofilm. In total DOM, the adsorption capacity of these two types of biofilm wasn't quite different but in HPI and HPO fractions, active biofilm seemed consume HPI and HPO twice time higher than inactivated biofilm. Also, HPI fraction seemed to be consumed and adsorbed by active and inactivated biofilm easier than HPO fraction.

To analyze the DBPs formation potential (DBPFP), DOMs, biofilm and the combination of DOMs and biofilm was added individually into different bottles containing phosphate buffer and mixed with NaOCl to reach the target concentration. After keeping the reaction for 24 hours in the dark at 25°C chlorinated water sample was transferred to analyze DBPs immediately by using methods of USEPA 551.1 and USEPA 552.2 and following gas chromatograph with an electron capture detector (GC/ECD). The result showed that the combination of active and inactivated biofilm with total DOM and HPI fraction samples gave the highest formation potential of CF, following

by total DOM and DOM fractions and then was combination of active and inactivated biofilm with HPO fraction samples. The lowest CF potentials got from active and inactivated biofilm samples. For haloacetic acids (HAAs), MCAA and TCAA seemed to have a high potential in DOMs and biofilm but started to decrease potential in combination of DOMs and biofilm. In contrast, DCAA had a similar potential in biofilm and combination of DOMs and biofilm but could't be detectable in DOM and DOM fractions. In haloketone (HKs) and haloacetonitrile (HANs), the highest potential obtained from DOMs, and the lowest ones got from biofilm and the combination of DOMs and biofilm. It was clear that DOMs had high reactive with free residual chlorine in forming HKs and HANs. The result also showed that HANs formation potential from nitrogen source was much higher than HANs potentials from carbon source.

To evaluate the adsorption efficiency of occurred DBPs, chloroform (CF) come from trichloromethans group (THMs) which was carbonaceous disinfection by-products (C-DBPs) and dichloroacetonitrile (DCAN) came from haloacetonitriles group (HANs) which was nitrogenous disinfection by-products (N-DBPs) were selected to study on adsorption kinetic and isotherm whereas granular activated carbon (GAC) was selected as an adsorbent. From adsorption kinetic result, the equilibrium state of chloroform (CF) was for 10 hours and dichloroacetonitrile (DCAN) was for 12 hours. The adsorption capacities of CF and DCAN had similar results at the low initial concentrations but from moderate to high initial concentration, DCAN had adsorption capacity higher than CF.

## **5.2 Engineering Significance**

Formation potentials of CF were low in individual samples of DOM, DOM fractions and biofilm but start to increase in combinations of DOM and DOM's fractions with biofilm. There were two reasons to emphasize this result. First, based on the past studies, CF was harder to consume and adsorb by biofilm than other groups of DBPs. Second, based on report of primary survey in 2014 showed that the concentration of THMs at the ending point of pipeline is about one or two times higher than those at the starting point (at water treatment plant), so it means that the level of DBPs trend to



increase while traveling through pipeline by interaction with biofilm and external contamination of DOM. In contrast, HANs, HAA, and HF<sub>s</sub> had high formation potentials in individual samples of DOM, DOM fractions and biofilm but started to decrease formation potential in mixed DOM or DOM fractions with biofilm samples. There were two reasons to interpret this result. First reason was that active and inactivated biofilm be able to consume and adsorb DOM and DOM's fractions which were the main precursor of DBPs. Second, the past study also pointed out that biofilm also had biological consumption and physical adsorption capacities of DBPs.

So it was clear that DOM and DBPs could be increased and reduced while mixing with biofilm. As the result biofilm in water distribution system played very important role in increasing CF formation potentials but in decreasing HANs, HAAs, and HK<sub>s</sub> formation potential in treated water while traveling in pipeline.

### **5.3 Recommendation and Future Work**

The targets of this research focused on only formation potentials of chlorinated DBPs whereas the chlorine was selected as disinfectant. But bromide DBPs also had a high concentration in drinking water (Richardson S.D., 2003). So that, the future works needs to investigate the effect of DOM and biofilm on bromide DBPs formation potential.

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**APPENDICES**





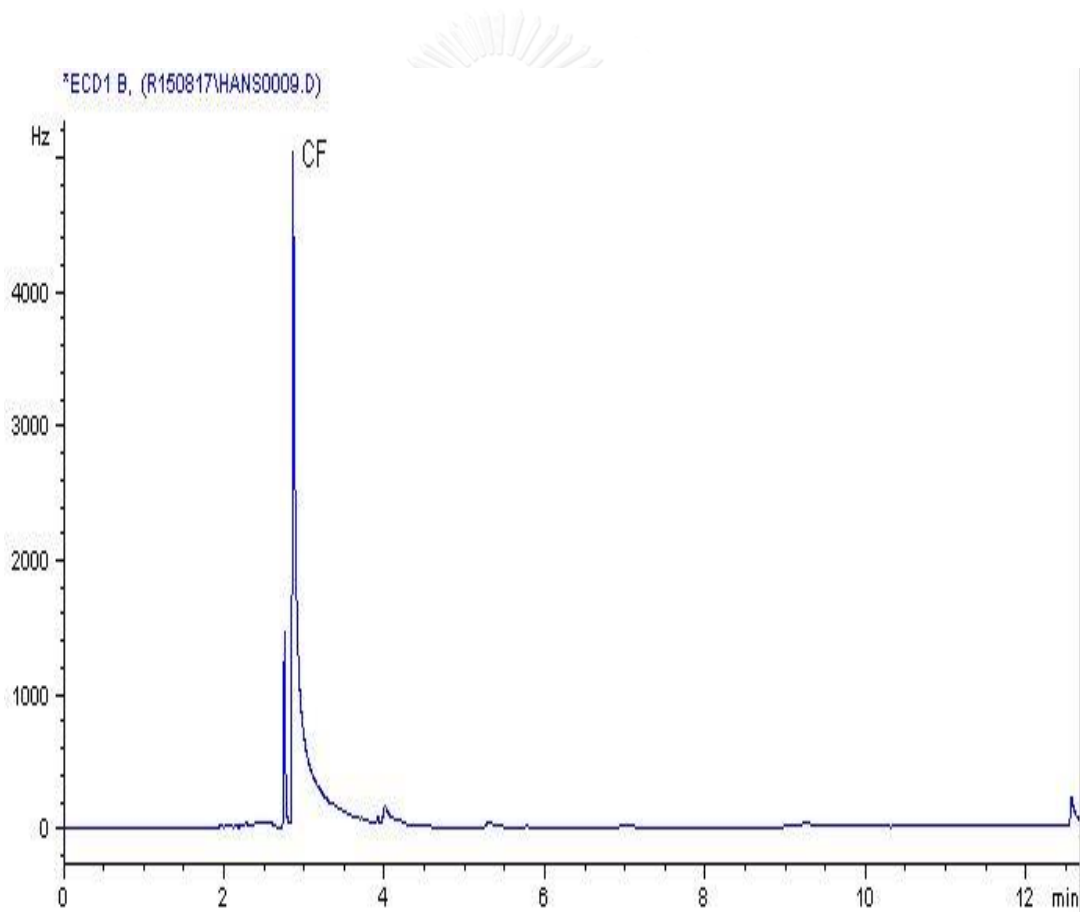
**APPENDIX A**

**GC Chromatogram of THM, HANs, HKs and HAAs**

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**Table A-1** THM analyses by the USEPA Method 551.1 followed by gas chromatograph (Column VFX, GC/ECD)

THM	CF
Retention time (min)	2.85
Detection Limit	0.05-0.10 ppb

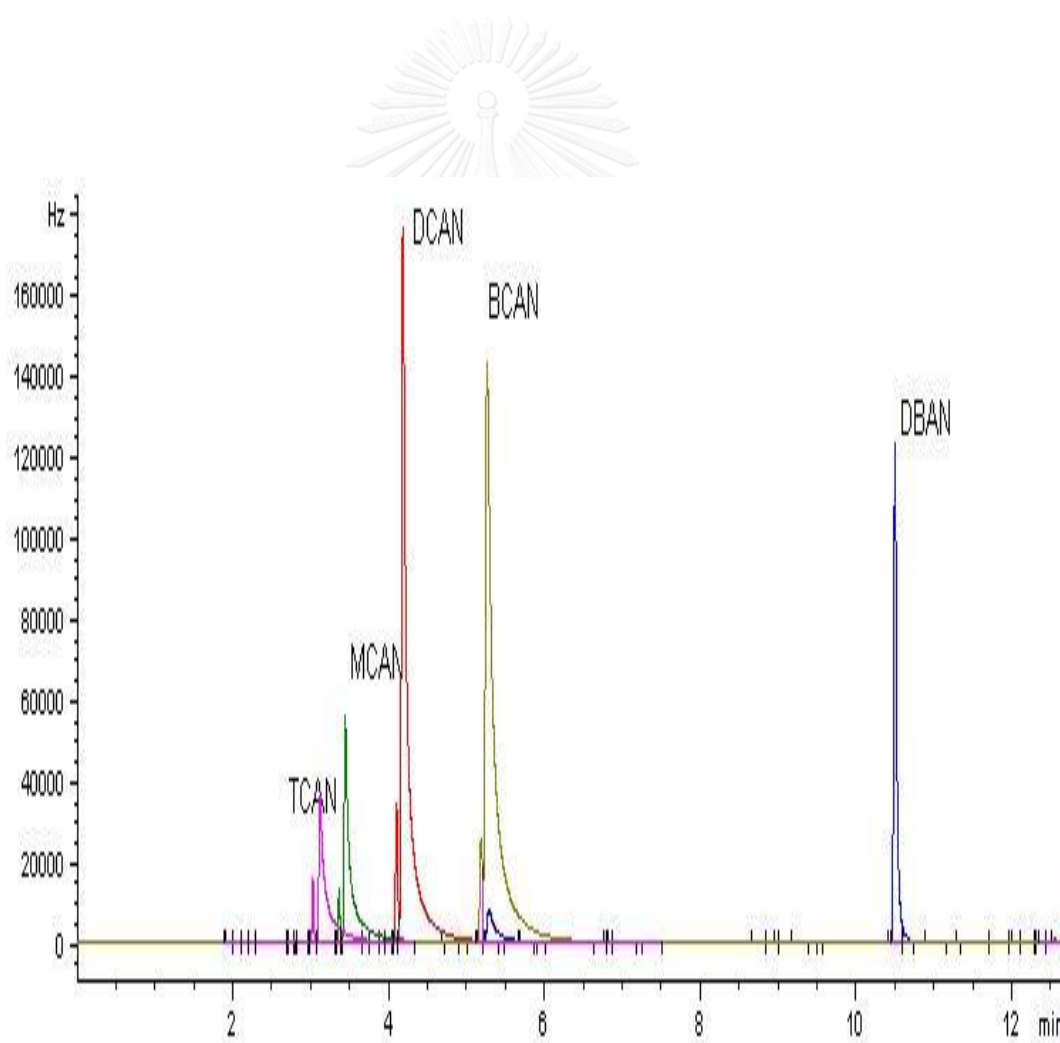


**Figure A-1** Chromatogram of CF



**Table A-2** Five-HANs analyses by the USEPA Method 551.1 followed by gas chromatograph (Column VFX, GC/ECD)

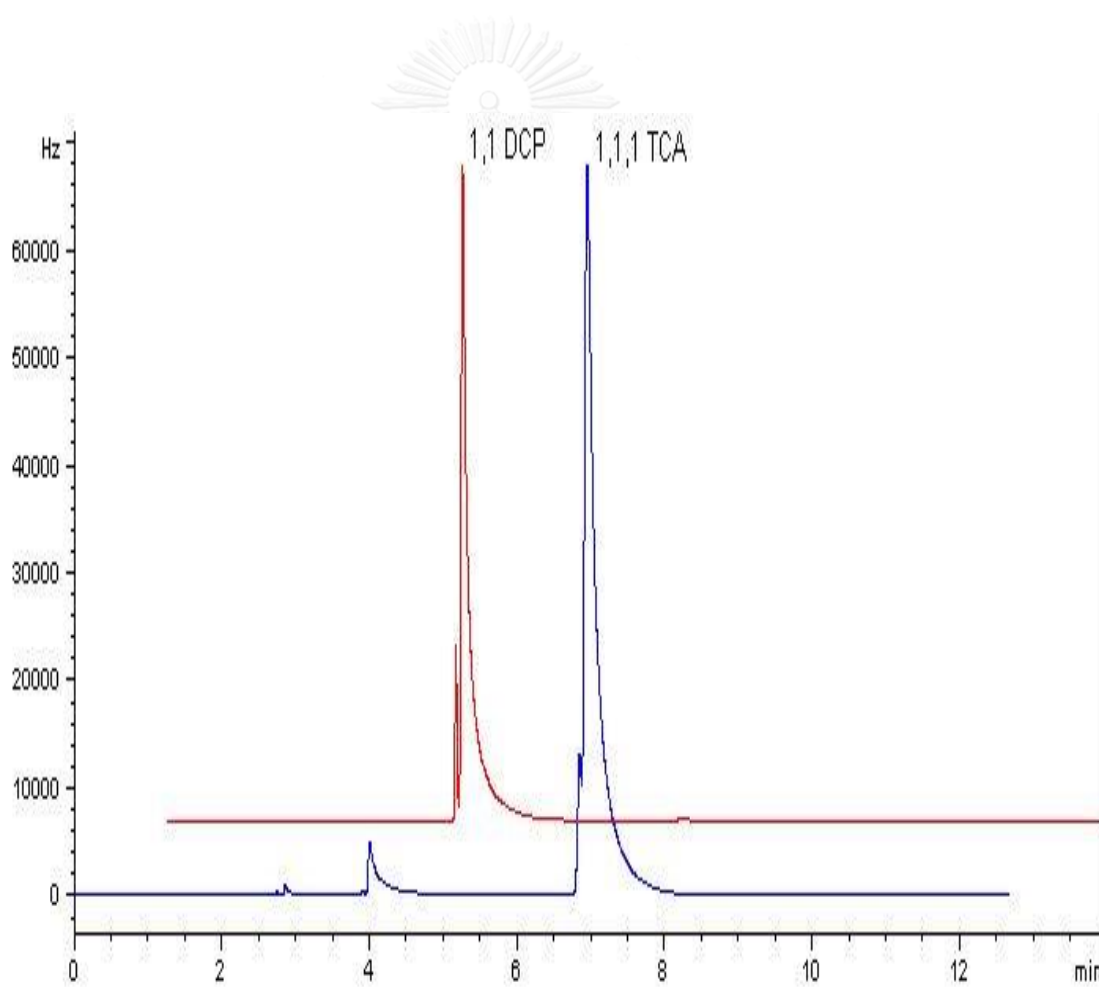
HANs	MCAN	DCAN	TCAN	BCAN	DBAN
<b>Retention time (min)</b>	3.43	4.17	3.11	5.28	10.49
<b>Detection Limit</b>	0.05-0.10 ppb				



**Figure A-2** Chromatogram of Five-HANs

**Table A-3** HKs analyses by the USEPA Method 551.1 followed by gas chromatograph (Column VFX, GC/ECD)

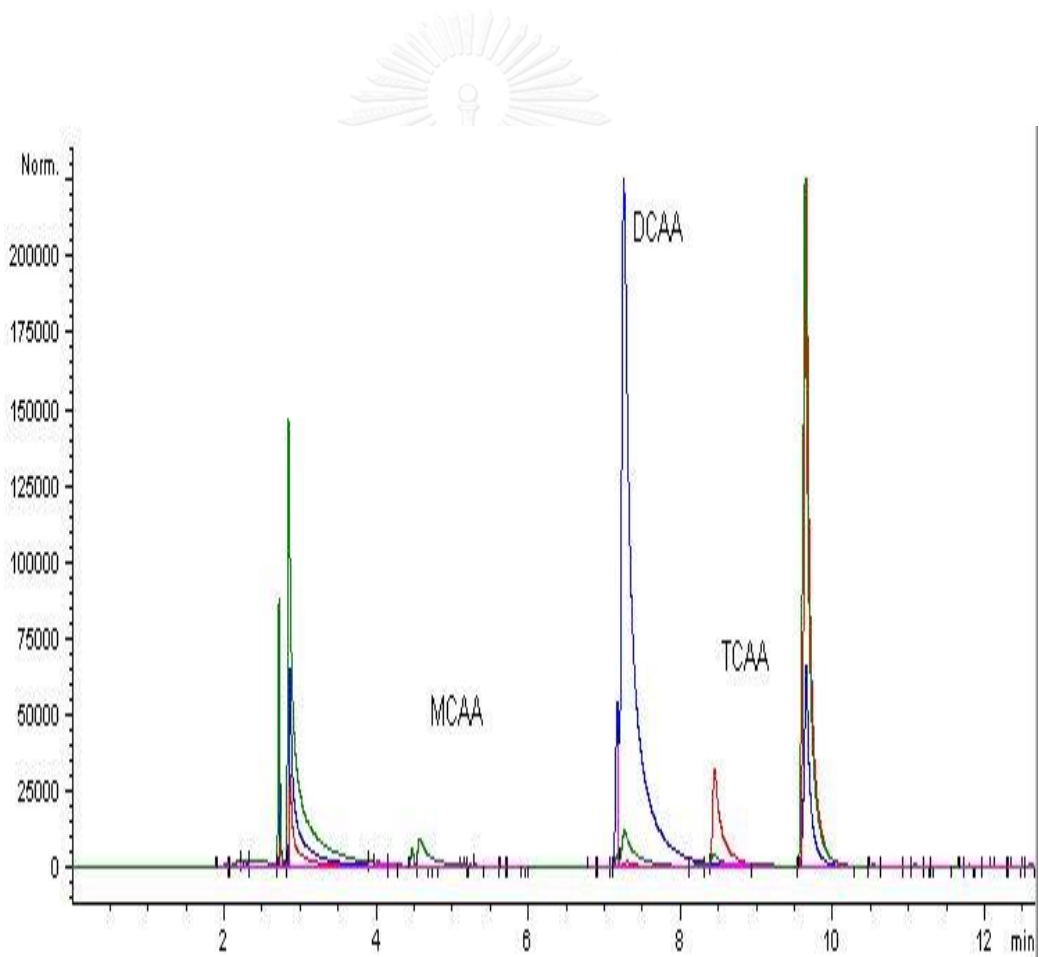
HKs	1,1,1- TCA	1,1- DCP
Retention time (min)	6.95	3.99
Detection Limit	0.05-0.10 ppb	



**Figure A-3** Chromatogram of HKs

**Table A-4** HAAs analyses by the USEPA Method 552.2 followed by gas chromatograph (Column VFX, GC/ECD)

HAAs	MCAA	DCAA	TCAA
<b>Retention time (min)</b>	4.58	7.26	8.21
<b>Detection Limit</b>	0.05-0.10 ppb		



**Figure A-4** Chromatogram of HAAs

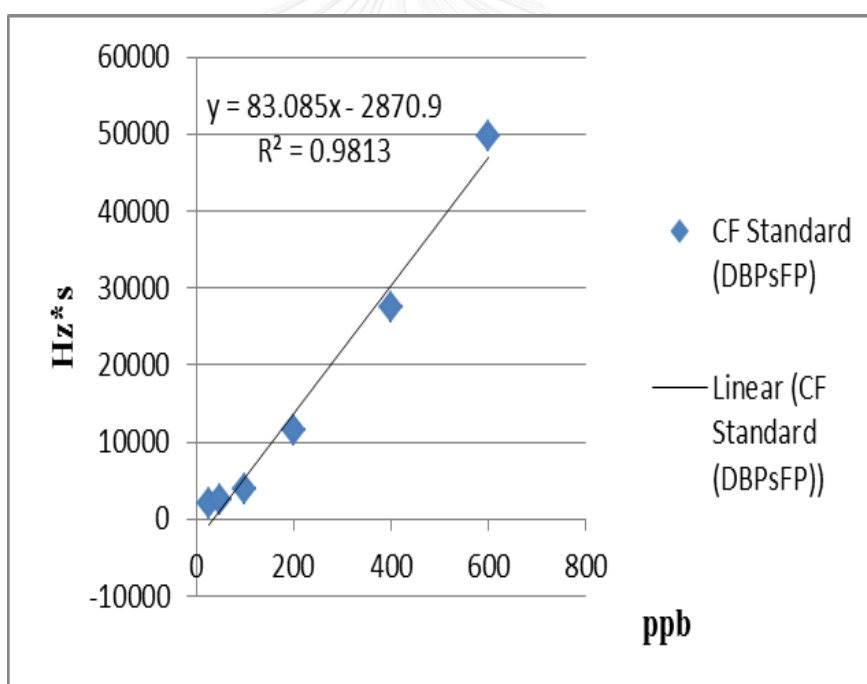
## **APPENDIX B**

### **Calibration Curve of THM, HANs, HKs and HAAs Standards**



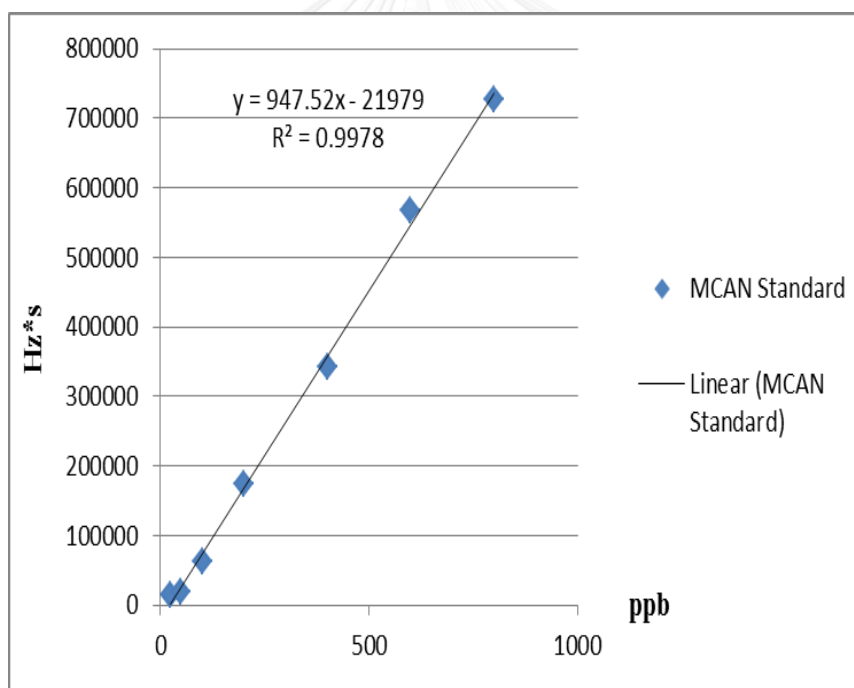
**Table B-1** Concentrations and areas of THM (CF) standard

CF (ppb)	RT (min)	Areas (Hz*s)
25	2.857	2031.5
50	2.857	2517.7
100	2.855	3857.7
200	2.855	11449.1
400	2.855	27389.4
600	2.854	49770.9

**Figure B-1** Calibration curve of CF standard

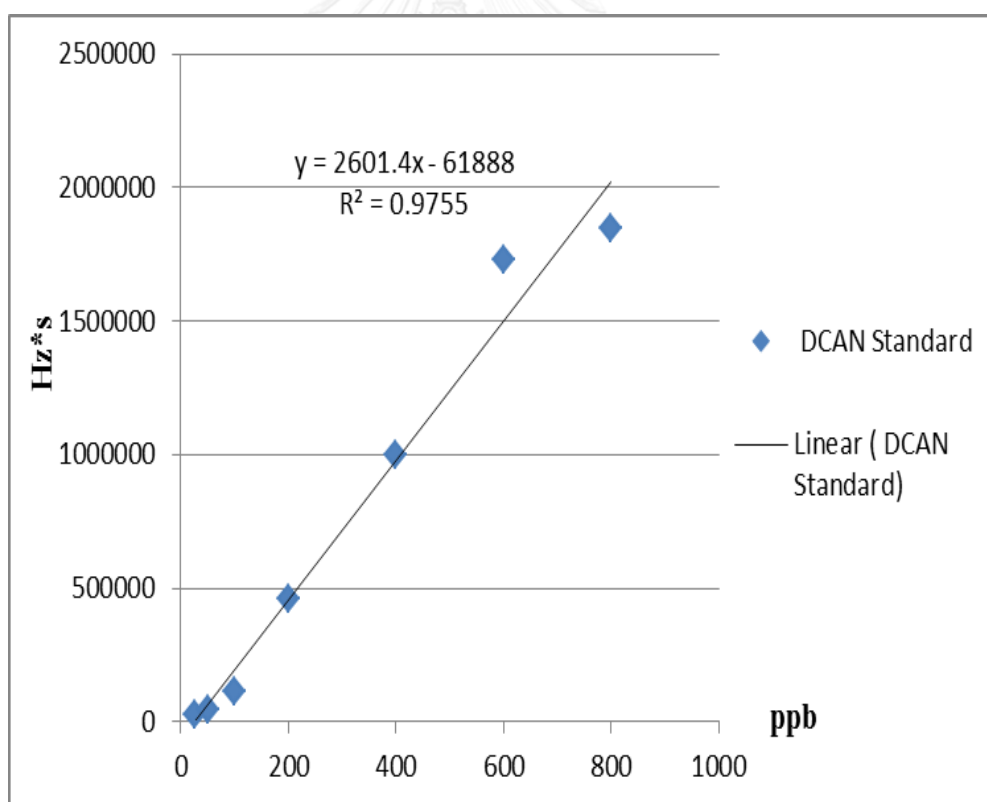
**Table B-2** Concentrations and areas of MCAN standard

MCAN (ppb)	RT (min)	Areas (Hz*s)
25	3.439	13597.8
50	3.439	18862.6
100	3.442	63353.7
200	3.438	174125.7
400	3.437	342329
600	3.437	567516.3
800	3.438	727207.1

**Figure B-2** Calibration curve of MCAN standard

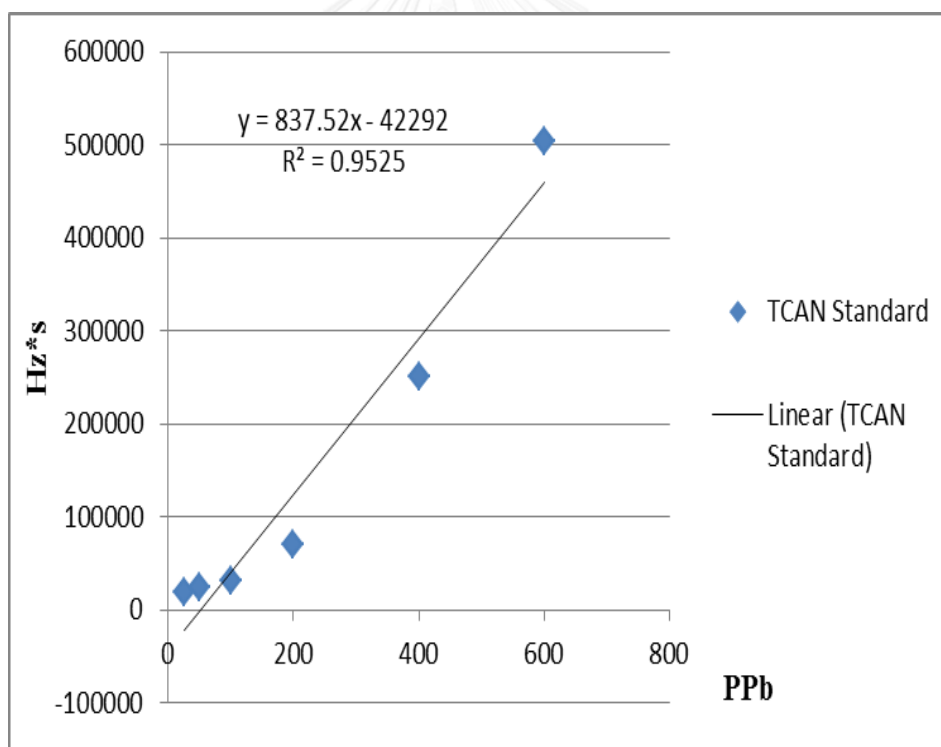
**Table B-3** Concentrations and areas of DCAN standard

DCAN (ppb)	RT (min)	Areas (Hz*s)
25	4.173	28818
50	4.173	45665.6
100	4.174	114787.8
200	4.173	460223.6
400	4.176	999199.4
600	4.173	1729457.6
800	4.172	1846653.4

**Figure B-3** Calibration curve of DCAN standard

**Table B-4** Concentrations and areas of TCAN standard

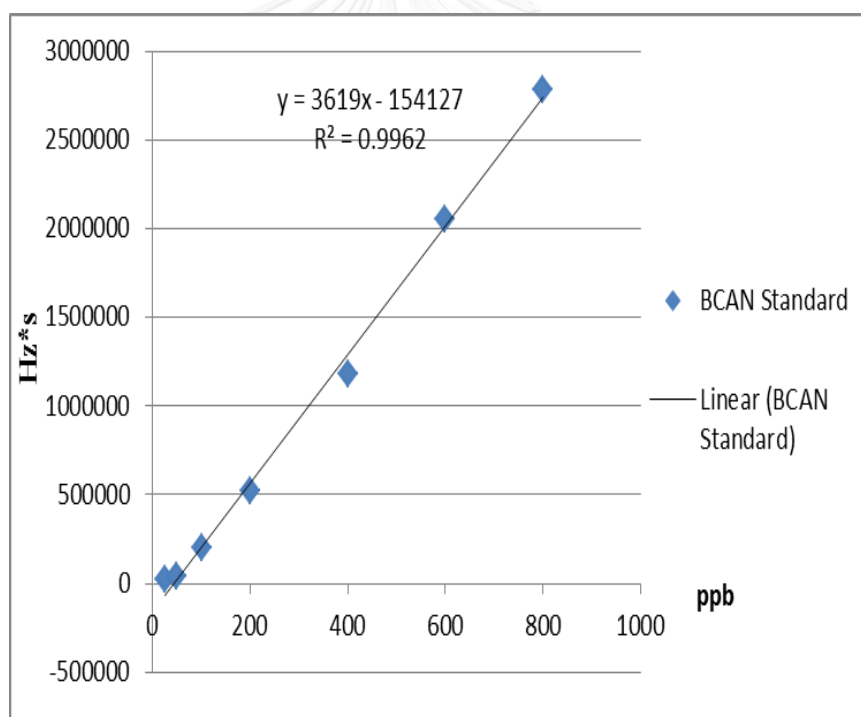
TCAN (ppb)	RT (min)	Areas (Hz*s)
25	3.112	18248.9
50	3.112	23391.8
100	3.111	30846.3
200	3.112	69522.1
400	3.112	251295.5
600	3.113	504527.9

**Figure B-4** Calibration curve of TCAN standard



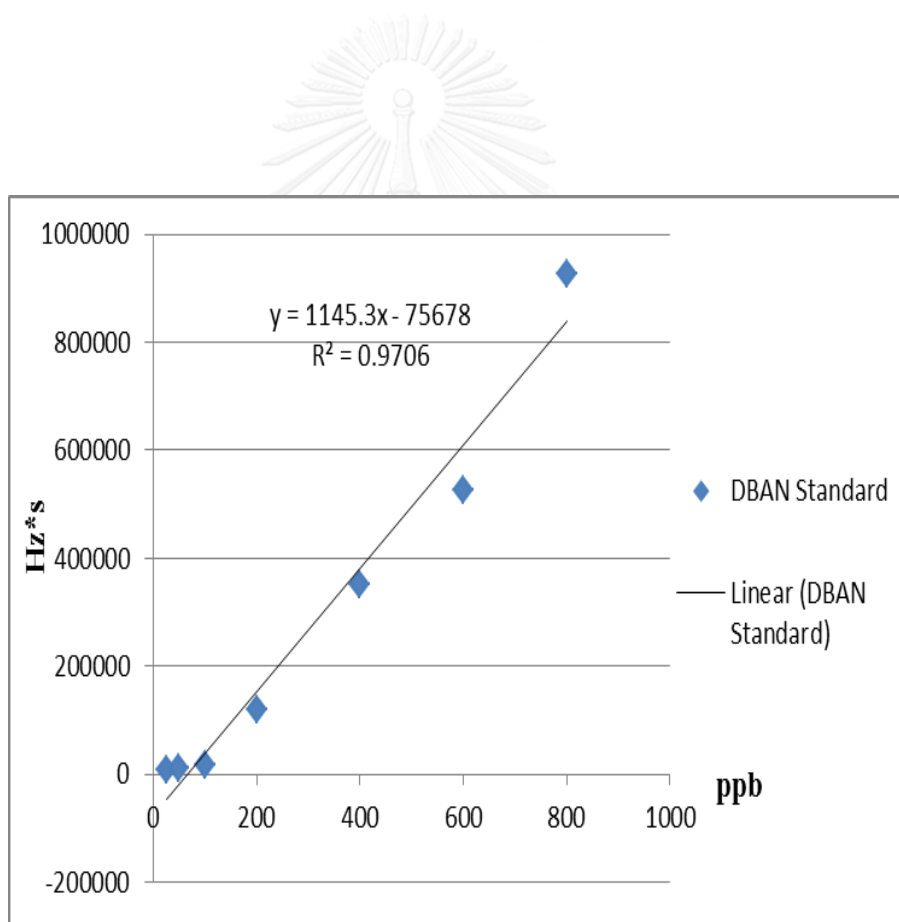
**Table B-5** Concentrations and areas of BCAN standard

BCAN (ppb)	RT (min)	Areas (Hz*s)
25	5.282	24508.6
50	5.281	37039.9
100	5.271	198826.6
200	5.265	520991.9
400	5.258	1176283
600	5.255	2048982.5
800	5.25	2785730.8

**Figure B-5** Calibration curve of BCAN standard

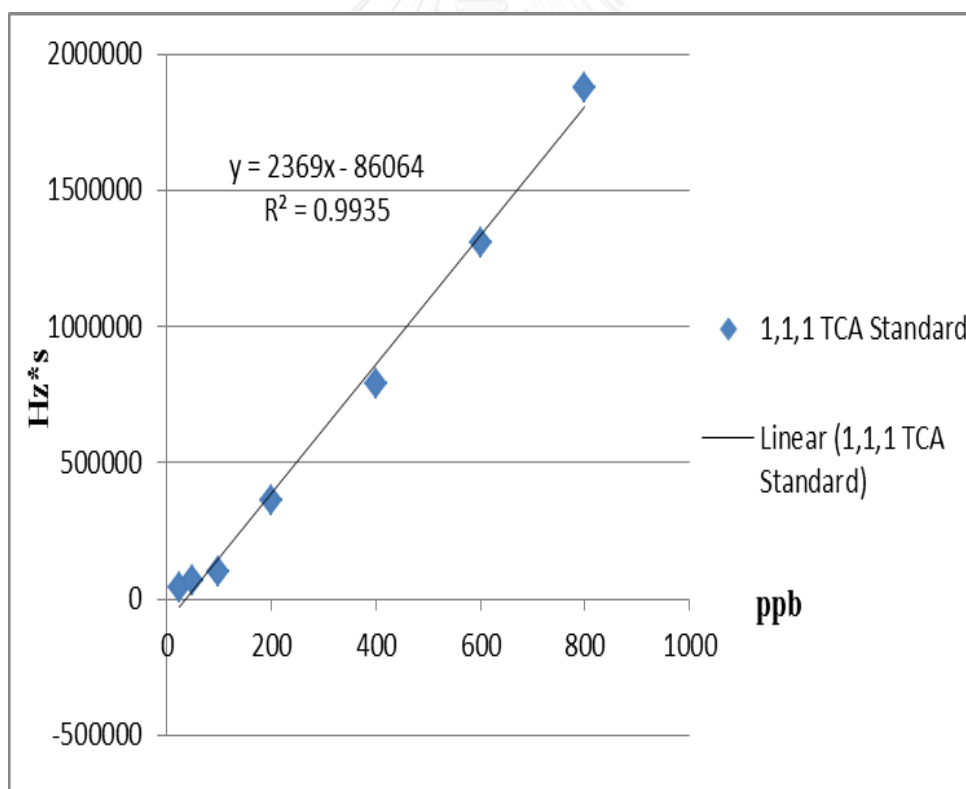
**Table B-6** Concentrations and areas of DBAN standard

DBAN (ppb)	RT (min)	Areas (Hz*s)
25	10.497	7667.9
50	10.497	10331.1
100	10.496	18296
200	10.495	119719
400	10.494	352013.2
600	10.493	525436.3
800	10.491	927771.3

**Figure B-6** Calibration curve of DBAN standard

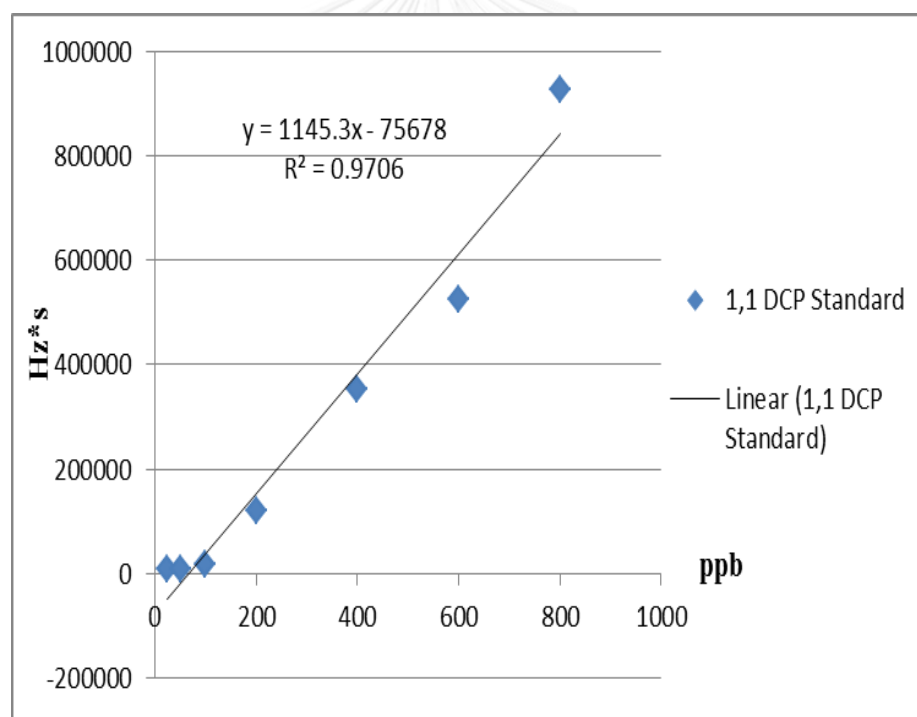
**Table B-7** Concentrations and areas of 1,1,1-TCA standard

1,1,1 TCA (ppb)	RT (min)	Areas (Hz*s)
25	6.951	44731.6
50	6.951	70236.1
100	6.951	101340
200	6.947	362589.9
400	6.945	790656.1
600	6.944	1306381.6
800	6.942	1874097.1

**Figure B-7** Calibration curve of 1,1,1-TCA standard

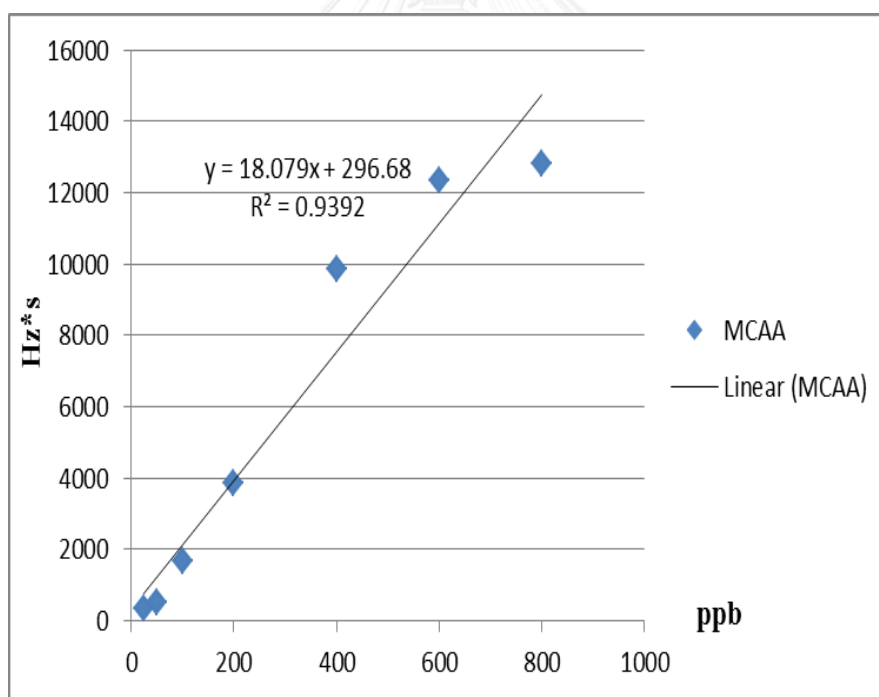
**Table B-8** Concentrations and areas of 1,1-DCP standard

1,1 DCP (ppb)	RT (min)	Areas (Hz*s)
25	4	7667.9
50	3.999	10331.1
100	3.999	18296
200	4	119719
400	3.999	352013.2
600	3.999	525436.3
800	3.999	927771.3

**Figure B-8** Calibration curve of 1,1-DCP standard

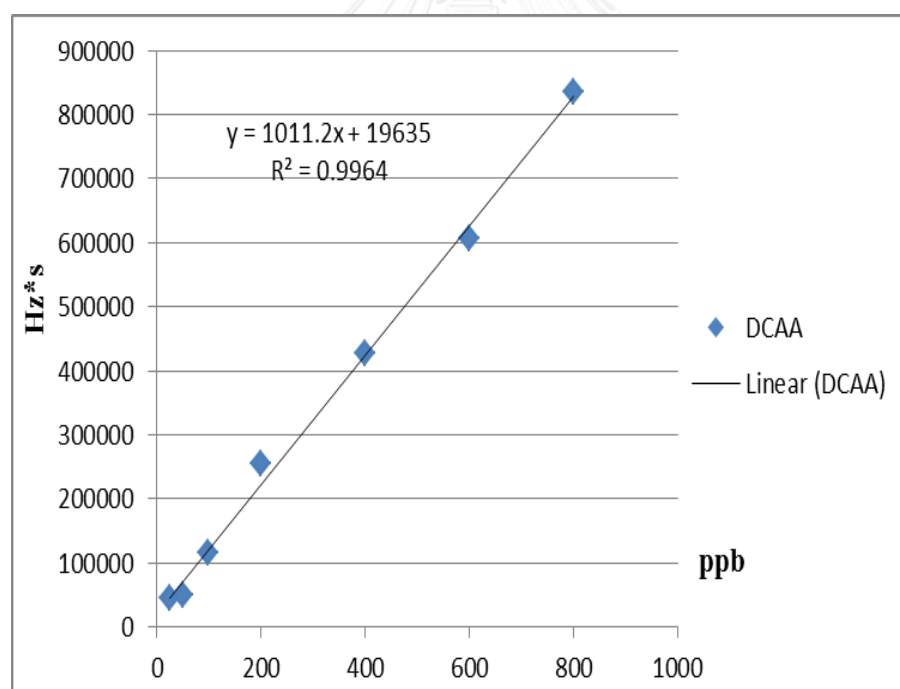
**Table B-9** Concentrations and areas of MCAA standard

MCAA (ppb)	RT (min)	Area (Hz*s)
25	4.586	356.5
50	4.588	501.5
100	4.586	1684.5
200	4.585	3840.1
400	4.584	9838.2
600	4.584	12352.3
800	4.583	12824.9

**Table B-9** Concentrations and areas of MCAA standard

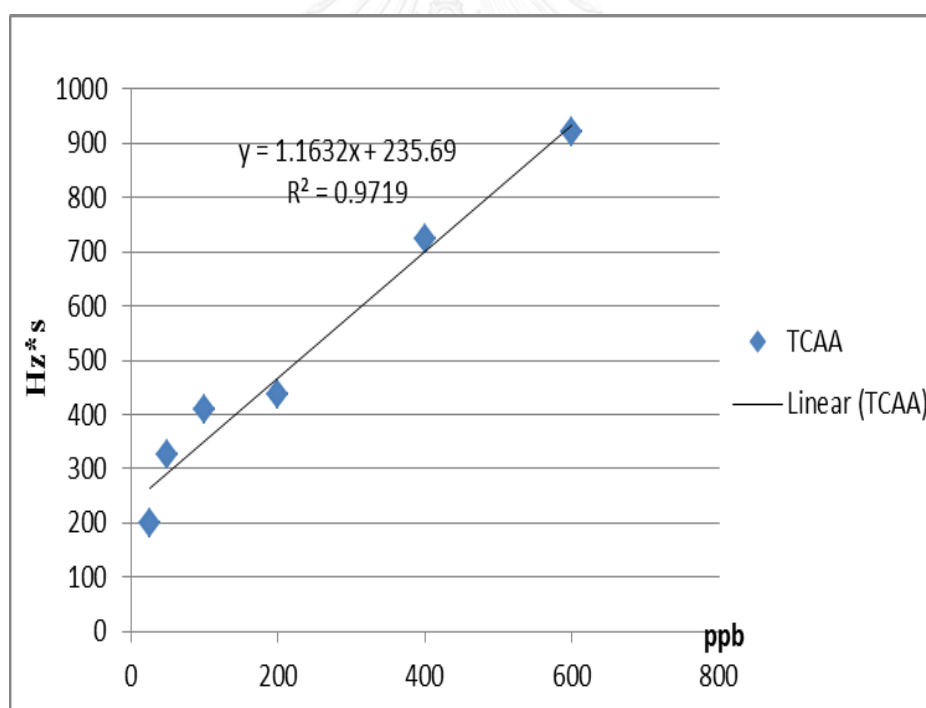
**Table B-10** Concentrations and areas of DCAA standard

DCAA (ppb)	RT (min)	Area (Hz*s)
25	7.265	45337.8
50	7.267	50416.2
100	7.265	116840.9
200	7.26	255269.9
400	7.254	427317.5
600	7.253	606074.3
800	7.25	835609

**Figure B-10** Calibration curve of DCAA standard

**Table B-11** Concentrations and areas of TCAA standard

TCAA (ppb)	RT (min)	Areas (Hz*s)
25	8.21	199.6
50	8.203	325.5
100	8.203	408.5
200	8.198	436.8
400	8.194	723.1
600	8.196	920

**Figure B-10** Calibration curve of TCAA standard

## APPENDIX C

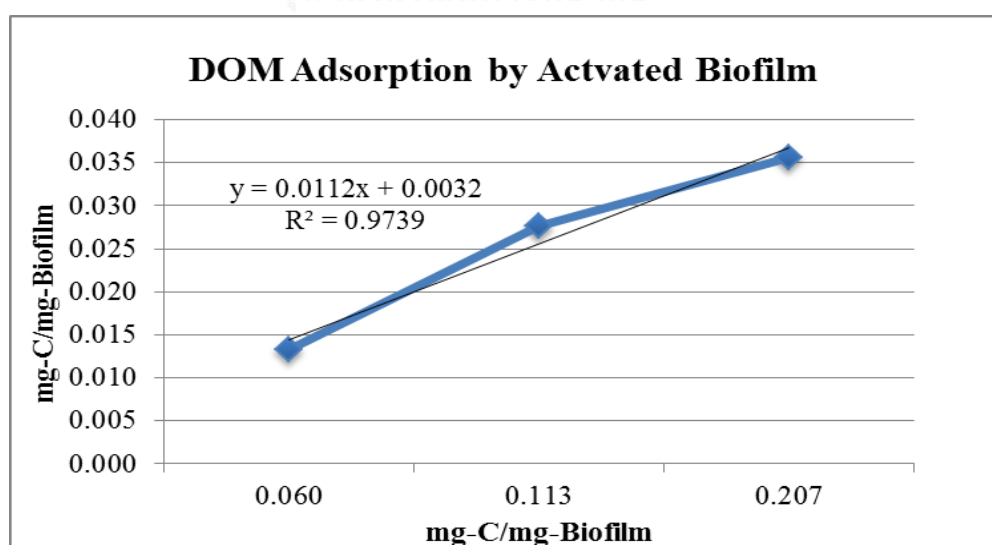
### Data of DOM, HPI, and HPO Consumption and Adsorption by Active and Inactivated Biofilm Experiments





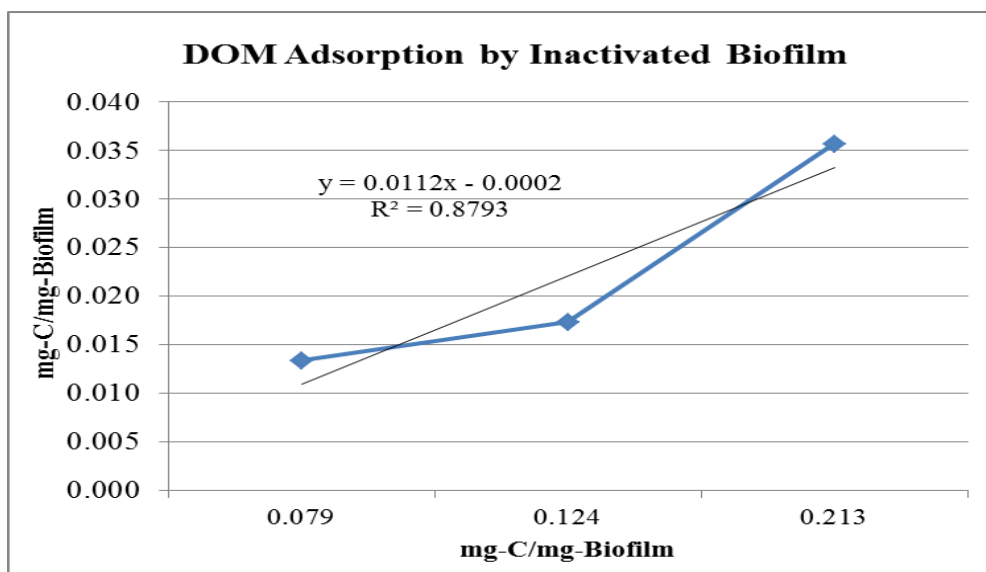
**Table C-1** Data of DOM consumption and adsorption by active biofilm experiments

Sample	RT (hours)	TOC (mg-C/l)	Ration (mg-C/mg-Biofilm)	Carbon Adsorption (mg-C/mg-Biofilm)
<b>DOM+ Active Biofilm at 25mg/l</b>				
Rep 1	24h	4.268	0.205	0.035
Rep 2	24h	4.163	0.204	0.033
Rep 3	24h	4.401	0.212	0.039
<b>Average</b>	<b>24h</b>	<b>4.277</b>	<b>0.207</b>	<b>0.036</b>
<b>DOM+ Active Biofilm at 50mg/l</b>				
Rep 1	24h	4.279	0.111	0.026
Rep 2	24h	5.038	0.115	0.029
Rep 3	24h	4.318	0.112	0.028
<b>Average</b>	<b>24h</b>	<b>4.545</b>	<b>0.113</b>	<b>0.028</b>
<b>DOM+ Active Biofilm at 100mg/l</b>				
Rep 1	24h	5.237	0.080	0.016
Rep 2	24h	4.948	0.070	0.014
Rep 3	24h	4.164	0.030	0.010
<b>Average</b>	<b>24h</b>	<b>4.783</b>	<b>0.060</b>	<b>0.013</b>

**Figure C-1** Curve of DOM consumption and adsorption by active biofilm

**Table C-2** Data of DOM adsorption by inactivated biofilm experiments

Sample	RT (hours)	TOC (mg-C/l)	Ration (mg-C/mg-Biofilm)	Carbon Adsorption (mg-C/mg-Biofilm)
<b>DOM+ Inactivated Biofilm at 25mg/l</b>				
Rep 1	24h	4.220	0.211	0.035
Rep 2	24h	4.172	0.210	0.033
Rep 3	24h	4.753	0.218	0.039
<b>Average</b>	<b>24h</b>	<b>4.382</b>	<b>0.213</b>	<b>0.036</b>
<b>DOM+ Inactivated Biofilm at 50mg/l</b>				
Rep 1	24h	5.616	0.128	0.021
Rep 2	24h	5.410	0.124	0.018
Rep 3	24h	4.907	0.121	0.013
<b>Average</b>	<b>24h</b>	<b>5.311</b>	<b>0.124</b>	<b>0.017</b>
<b>DOM+ Inactivated Biofilm at 100mg/l</b>				
Rep 1	24h	7.024	0.085	0.018
Rep 2	24h	5.916	0.071	0.010
Rep 3	24h	6.835	0.082	0.012
<b>Average</b>	<b>24h</b>	<b>6.592</b>	<b>0.079</b>	<b>0.013</b>



**Figure C-2** Curve of DOM adsorption by inactivated biofilm

**Table C-3** Data of HPI consumption and adsorption by active biofilm experiments

Sample	RT (hours)	TOC (mg-C/l)	Ration (mg-C/mg-Biofilm)	Carbon Adsorption (mg-C/mg-Biofilm)
<b>HPI+ Active Biofilm at 25mg/l</b>				
Rep 1	24h	1.599	0.103	0.034
Rep 2	24h	1.821	0.106	0.036
Rep 3	24h	1.855	0.108	0.038
<b>Average</b>		<b>1.758</b>	<b>0.106</b>	<b>0.036</b>
<b>HPI+ Active Biofilm at 50mg/l</b>				
Rep 1	24h	1.972	0.062	0.021
Rep 2	24h	1.980	0.063	0.024
Rep 3	24h	2.013	0.065	0.026
<b>Average</b>		<b>1.988</b>	<b>0.063</b>	<b>0.024</b>
<b>HPI+ Active Biofilm at 100mg/l</b>				
Rep 1	24h	2.072	0.034	0.012
Rep 2	24h	2.155	0.038	0.015
Rep 3	24h	2.120	0.036	0.016
<b>Average</b>		<b>2.116</b>	<b>0.036</b>	<b>0.014</b>

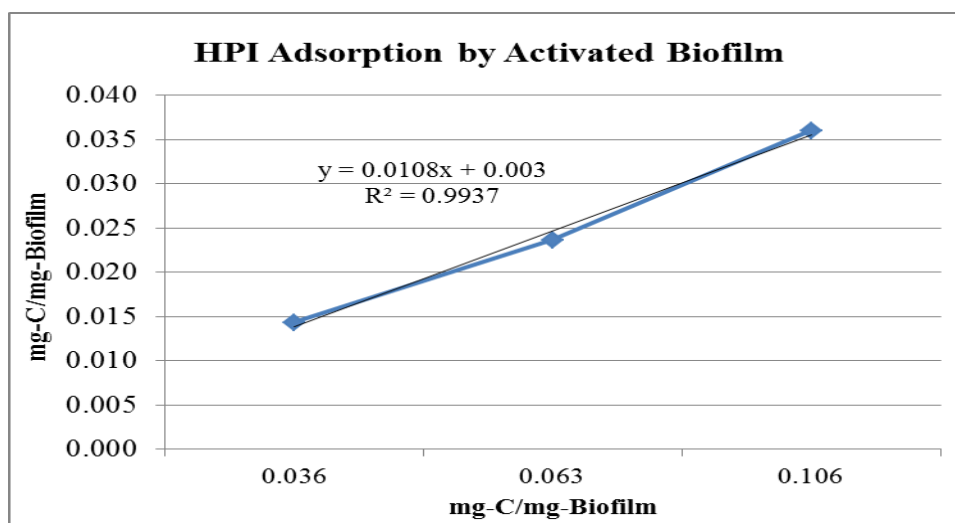


Figure C-3 Curve of HPI consumption by activated biofilm

Table C-4 Data of HPI adsorption by inactivated biofilm experiments

Sample	RT (hours)	TOC (mg-C/l)	Ration (mg-C/mg-Biofilm)	Carbon Adsorption (mg-C/mg-Biofilm)
<b>HPI+ Inactivated Biofilm at 25mg/l</b>				
Rep 1	24h	2.301	0.123	0.026
Rep 2	24h	2.564	0.129	0.031
Rep 3	24h	2.517	0.129	0.029
<b>Average</b>		<b>2.461</b>	<b>0.127</b>	<b>0.029</b>
<b>HPI+ Inactivated Biofilm at 50mg/l</b>				
Rep 1	24h	2.668	0.075	0.009
Rep 2	24h	3.973	0.086	0.015
Rep 3	24h	3.772	0.082	0.013
<b>Average</b>		<b>3.471</b>	<b>0.081</b>	<b>0.012</b>
<b>HPI+ Inactivated Biofilm at 100mg/l</b>				
Rep 1	24h	5.830	0.058	0.004
Rep 2	24h	5.887	0.059	0.002
Rep 3	24h	4.734	0.054	0.001
<b>Average</b>		<b>5.484</b>	<b>0.057</b>	<b>0.002</b>

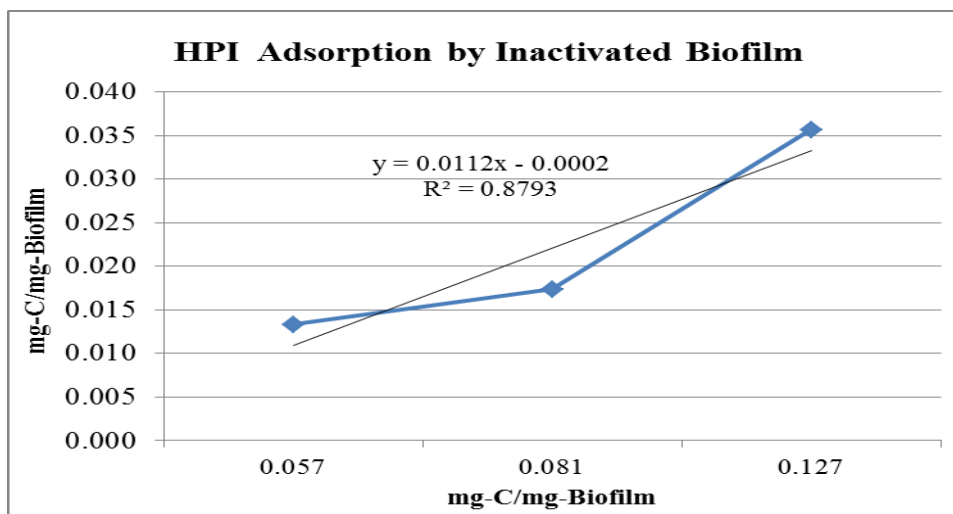


Figure C-4 Curve of HPI adsorption by inactivated biofilm

Table C-5 Data of HPO consumption and adsorption by active biofilm experiments

Sample	RT (hours)	TOC (mg-C/l)	Ration (mg-C/mg-Biofilm)	Carbon Adsorption (mg-C/mg-Biofilm)
<b>HPO+ Active Biofilm at 25mg/l</b>				
Rep 1	24h	2.733	0.146	0.035
Rep 2	24h	2.758	0.148	0.039
<b>Average</b>		<b>2.746</b>	<b>0.147</b>	<b>0.037</b>
<b>HPO+ Active Biofilm at 50mg/l</b>				
Rep 1	24h	3.053	0.086	0.026
Rep 2	24h	2.929	0.082	0.022
Rep 3	24h	2.946	0.084	0.024
<b>Average</b>		<b>2.976</b>	<b>0.084</b>	<b>0.024</b>
<b>HPO+ Active Biofilm at 100mg/l</b>				
Rep 1	24h	3.210	0.049	0.018
Rep 2	24h	3.110	0.046	0.015
Rep 3	24h	3.094	0.042	0.010
<b>Average</b>		<b>3.138</b>	<b>0.046</b>	<b>0.014</b>

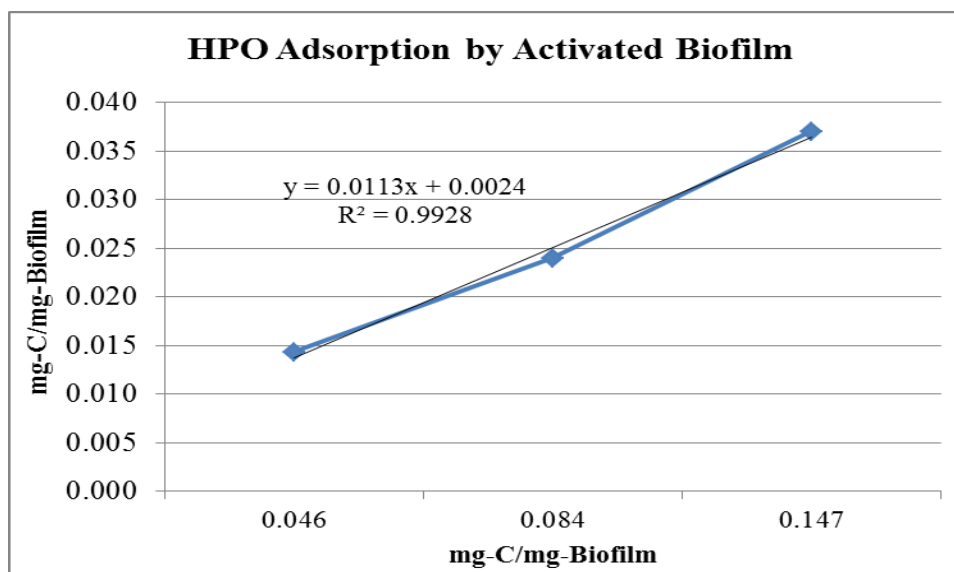
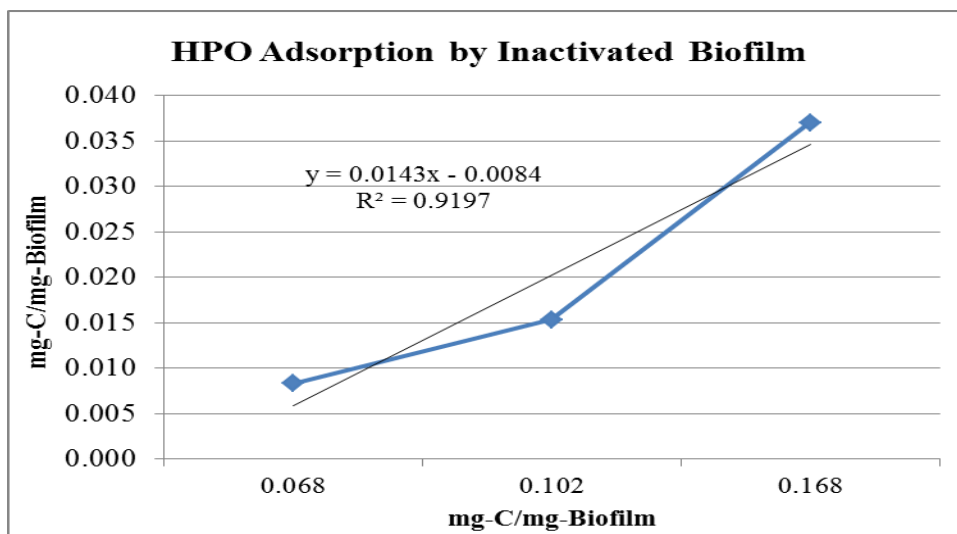


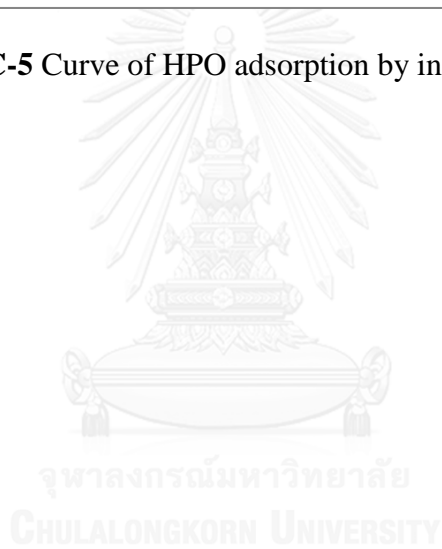
Figure C-5 Curve of HPO consumption by activated biofilm

Table C-6 Data of HPO adsorption by inactivated biofilm experiments

Sample	RT (hours)	TOC (mg-C/l)	Ration (mg-C/mg-Biofilm)	Carbon Adsorption (mg-C/mg-Biofilm)
<b>HPO+ Inactivated Biofilm at 25mg/l</b>				
Rep 1	24h	3.250	0.169	0.038
Rep 2	24h	3.109	0.162	0.033
Rep 3	24h	3.520	0.173	0.040
<b>Average</b>		<b>3.293</b>	<b>0.168</b>	<b>0.037</b>
<b>HPO+ Inactivated Biofilm at 50mg/l</b>				
Rep 1	24h	4.668	0.106	0.018
Rep 2	24h	4.280	0.104	0.016
Rep 3	24h	4.090	0.095	0.012
<b>Average</b>		<b>4.346</b>	<b>0.102</b>	<b>0.015</b>
<b>HPO+ Inactivated Biofilm at 100mg/l</b>				
Rep 1	24h	5.920	0.068	0.009
Rep 2	24h	6.109	0.071	0.010
Rep 3	24h	5.880	0.066	0.006
<b>Average</b>		<b>5.970</b>	<b>0.068</b>	<b>0.008</b>



**Figure C-5** Curve of HPO adsorption by inactivated biofilm



## APPENDIX D

### Data of DBPs Formation Potential Experiments





**Table D-1** Data of THM (CF) formation potential experiments

Sample	Unit	THM (CF)	1,1,1 TCA	1,1 DCP
<b>DOM</b>				
Area	(Hz*s)	4708.29	1796.18	20875.70
Rep 1	(Hz*s)	4760.20	3587.73	25501.10
Rep 2	(Hz*s)	5037.59	1299.54	16250.30
Rep 3	(Hz*s)	4327.08	501.28	N/A
Concentration	(µg/l)	91.22	37.09	84.30
Formation Potential	(µg /mg)	43.65	17.75	40.34
<b>HPI</b>				
Area	(Hz*s)	4644.20	759.73	28221.75
Rep 1	(Hz*s)	4820.40	1002.50	N/A
Rep 2	(Hz*s)	4752.10	757.80	27997.60
Rep 3	(Hz*s)	4360.10	518.90	28445.90
Concentration	(µg/l)	90.45	36.65	90.72
Formation Potential	(µg /mg)	56.89	23.05	57.06
<b>HPO</b>				
Area	(Hz*s)	4412.15	1618.00	1616.75
Rep 1	(Hz*s)	4972.90	2578.40	1290.70
Rep 2	(Hz*s)	3851.40	657.60	1942.80
Concentration	(µg/l)	87.66	37.01	67.49
Formation Potential	(µg /mg)	55.13	23.28	42.45
<b>Active Biofilm</b>				
Area	(Hz*s)	16950.23	3692.57	8309.20
Rep 1	(Hz*s)	21771.90	5035.30	8650.90
Rep 2	(Hz*s)	6981.50	2173.00	8236.70
Rep 3	(Hz*s)	22097.30	3869.40	8040.00
Concentration	(µg/l)	238.56	37.89	73.33
Formation Potential	(µg /mg)	23.86	3.79	7.33
<b>Inactivated Biofilm</b>				
Area	(Hz*s)	20684.47	3482.53	9936.47
Rep 1	(Hz*s)	22049.90	3801.20	9871.00
Rep 2	(Hz*s)	20549.80	3798.80	10476.00
Rep 3	(Hz*s)	19453.70	2847.60	9462.40
Concentration	(µg/l)	283.51	37.80	74.75
Formation Potential	(µg /mg)	28.35	3.78	7.48

<b>Active Biofilm +DOM</b>				
Area	(Hz*s)	84800.60	N/A	N/A
Rep 1	(Hz*s)	85699.90	N/A	N/A
Rep 2	(Hz*s)	90600.20	N/A	N/A
Rep 3	(Hz*s)	78101.70	N/A	N/A
Concentration	(µg/l)	1055.20	N/A	N/A
Formation Potential	(µg /mg)	87.28	N/A	N/A
<b>Inactivated Biofilm +DOM</b>				
Area	(Hz*s)	91865.63	N/A	N/A
Rep 1	(Hz*s)	86307.10	N/A	N/A
Rep 2	(Hz*s)	94300.10	N/A	N/A
Rep 3	(Hz*s)	94989.70	N/A	N/A
Concentration	(µg/l)	1140.24	N/A	N/A
Formation Potential	(µg /mg)	94.31	N/A	N/A
<b>Active Biofilm +HPI</b>				
Area	(Hz*s)	128815.53	N/A	N/A
Rep 1	(Hz*s)	130451.00	N/A	N/A
Rep 2	(Hz*s)	117951.00	N/A	N/A
Rep 3	(Hz*s)	138044.60	N/A	N/A
Concentration	(µg/l)	1584.96	N/A	N/A
Formation Potential	(µg/mg)	136.75	N/A	N/A
<b>Inactivated Biofilm +HPI</b>				
Area	(Hz*s)	126637.77	N/A	N/A
Rep 1	(Hz*s)	133619.20	N/A	N/A
Rep 2	(Hz*s)	131564.70	N/A	N/A
Rep 3	(Hz*s)	114729.40	N/A	N/A
Concentration	(µg/l)	1558.75	N/A	N/A
Formation Potential	(µg /mg)	134.49	N/A	N/A
<b>Active Biofilm +HPO</b>				
Area	(Hz*s)	25555.55	1782.40	N/A
Rep 1	(Hz*s)	28292.00	1758.50	N/A
Rep 2	(Hz*s)	22819.10	1806.30	N/A
Concentration	(µg/l)	342.14	37.08	N/A
Formation Potential	(µg /mg)	29.52	3.20	N/A

<b>Inactivated Biofilm+ HPO</b>				
Area	(Hz*s)	22077.90	1470.30	N/A
Rep 1	(Hz*s)	19389.10	1225.20	N/A
Rep 2	(Hz*s)	24766.70	1715.40	N/A
Concentration	(µg/l)	300.28	36.95	N/A
Formation Potential	(µg /mg)	25.91	3.19	N/A

**Table D-2** Data of HANs formation potential from carbon source experiments

<b>Sample</b>	<b>Unit</b>	<b>MCAN</b>	<b>DCAN</b>	<b>TCAN</b>	<b>BCAN</b>	<b>DBAN</b>
<b>DOM</b>						
Area	(Hz*s)	N/A	18855.65	3359.86	850.32	2078.60
Rep 1	(Hz*s)	N/A	17113.70	N/A	433.50	432.70
Rep 2	(Hz*s)	N/A	931.08	5593.00	850.40	1914.72
Rep 3	(Hz*s)	N/A	20597.60	1126.71	1267.05	3888.39
Concentration	(µg/l)	N/A	30.37	54.51	42.82	67.89
Formation Potential	(µg /mg)	N/A	14.53	26.08	20.49	32.48
<b>HPI</b>						
Area	(Hz*s)	N/A	3888.38	N/A	317.11	186.51
Rep 1	(Hz*s)	N/A	3954.93	N/A	339.74	194.12
Rep 2	(Hz*s)	N/A	3556.30	N/A	293.70	165.40
Rep 3	(Hz*s)	N/A	4153.90	N/A	317.90	200.00
Concentration	(µg/l)	N/A	25.31	N/A	42.68	66.24
Formation Potential	(µg /mg)	N/A	15.92	N/A	26.84	41.66
<b>HPO</b>						
Area	(Hz*s)	427.70	8204.00	N/A	N/A	N/A
Rep 1	(Hz*s)	506.50	6823.70	N/A	N/A	N/A
Rep 2	(Hz*s)	348.90	9584.30	N/A	N/A	N/A
Concentration	(µg/l)	23.65	26.94	N/A	N/A	N/A
Formation Potential	(µg /mg)	14.87	16.95	N/A	N/A	N/A
<b>Active Biofilm</b>						
Area	(Hz*s)	3501.90	73740.63	N/A	N/A	N/A
Rep 1	(Hz*s)	2944.20	79130.90	N/A	N/A	N/A
Rep 2	(Hz*s)	3057.00	72483.70	N/A	N/A	N/A
Rep 3	(Hz*s)	4504.50	69607.30	N/A	N/A	N/A

Concentration	( $\mu\text{g/l}$ )	26.89	54.21	N/A	N/A	N/A
Formation Potential	( $\mu\text{g /mg}$ )	2.69	5.42	N/A	N/A	N/A
<b>Inactivated Biofilm</b>						
Area	( $\text{Hz*s}$ )	3257.77	89838.40	N/A	N/A	N/A
Rep 1	( $\text{Hz*s}$ )	3476.40	89790.60	N/A	N/A	N/A
Rep 2	( $\text{Hz*s}$ )	3049.40	94211.40	N/A	N/A	N/A
Rep 3	( $\text{Hz*s}$ )	3247.50	85513.20	N/A	N/A	N/A
Concentration	( $\mu\text{g/l}$ )	26.63	58.32	N/A	N/A	N/A
Formation Potential	( $\mu\text{g /mg}$ )	2.66	5.83	N/A	N/A	N/A
<b>Active Biofilm + DOM</b>						
Area	( $\text{Hz*s}$ )	2828.13	28610.97	N/A	1305.17	236.20
Rep 1	( $\text{Hz*s}$ )	3034.60	30287.70	N/A	1380.70	270.70
Rep 2	( $\text{Hz*s}$ )	2953.00	27788.40	N/A	1252.90	179.00
Rep 3	( $\text{Hz*s}$ )	2496.80	27756.80	N/A	1281.90	258.90
Concentration	( $\mu\text{g/l}$ )	26.18	34.79	N/A	42.95	66.28
Formation Potential	( $\mu\text{g /mg}$ )	2.17	2.88	N/A	3.55	5.48
<b>Inactivated Biofilm +DOM</b>						
Area	( $\text{Hz*s}$ )	3255.63	33899.50	N/A	1525.40	421.70
Rep 1	( $\text{Hz*s}$ )	3330.50	33853.30	N/A	1489.60	375.20
Rep 2	( $\text{Hz*s}$ )	3470.50	36425.70	N/A	1635.00	490.20
Rep 3	( $\text{Hz*s}$ )	2965.90	31419.50	N/A	1451.60	399.70
Concentration	( $\mu\text{g/l}$ )	26.63	36.82	N/A	43.01	66.45
Formation Potential	( $\mu\text{g /mg}$ )	2.20	3.05	N/A	3.56	5.50
<b>Active Biofilm +HPI</b>						
Area	( $\text{Hz*s}$ )	6037.35	6040.53	N/A	178.83	N/A
Rep 1	( $\text{Hz*s}$ )	6322.60	5830.00	N/A	177.90	N/A
Rep 2	( $\text{Hz*s}$ )	5752.10	5633.70	N/A	180.70	N/A
Rep 3	( $\text{Hz*s}$ )	N/A	6657.90	N/A	177.90	N/A
Concentration	( $\mu\text{g/l}$ )	29.57	26.11	N/A	42.64	N/A
Formation Potential	( $\mu\text{g /mg}$ )	2.55	2.25	N/A	3.68	N/A
<b>Inactivated Biofilm +HPI</b>						
Area	( $\text{Hz*s}$ )	6690.80	6334.50	N/A	172.73	N/A

Rep 1	(Hz*s)	6766.90	6404.80	N/A	32.00	N/A
Rep 2	(Hz*s)	6614.70	5951.80	N/A	191.90	N/A
Rep 3	(Hz*s)	5835.40	6646.90	N/A	294.30	N/A
Concentration	(µg/l)	30.26	26.23	N/A	42.64	N/A
Formation Potential	(µg /mg)	2.61	2.26	N/A	3.68	N/A
<b>Active Biofilm+HPO</b>						
Area	(Hz*s)	2614.15	55212.85	N/A	148.95	N/A
Rep 1	(Hz*s)	2904.70	60774.20	N/A	160.50	N/A
Rep 2	(Hz*s)	2323.60	49651.50	N/A	137.40	N/A
Concentration	(µg/l)	25.96	45.01	N/A	42.63	N/A
Formation Potential	(µg /mg)	2.24	3.88	N/A	3.68	N/A
<b>Inactivated Biofilm+HPO</b>						
Area	(Hz*s)	2557.10	67045.75	N/A	155.20	N/A
Rep 1	(Hz*s)	2232.20	55374.00	N/A	135.00	N/A
Rep 2	(Hz*s)	2882.00	78717.50	N/A	175.40	N/A
Concentration	(µg/l)	25.90	49.56	N/A	42.63	N/A
Formation Potential	(µg /mg)	2.23	4.28	N/A	3.68	N/A

**Table D-3** Data of HAAs formation potential experiments

Sample	Unit	MCAA	DCAA	TCAA
<b>DOM</b>				
Area	(Hz*s)	1124.80	16158.13	1949.00
Rep 1	(Hz*s)	1124.80	16848.20	3840.00
Rep 2	(Hz*s)	N/A	16353.70	N/A
Rep 3	(Hz*s)	N/A	15272.50	58.00
Concentration	(µg/l)	45.81	-3.44	1472.93
Formation Potential	(µg /mg)	21.92	-1.65	704.75
<b>HPI</b>				

Area	(Hz*s)	N/A	12581.20	525.30
Rep 1	(Hz*s)	N/A	13932.40	553.50
Rep 2	(Hz*s)	N/A	11840.10	481.40
Rep 3	(Hz*s)	N/A	11971.10	541.00
Concentration	(µg/l)	N/A	-6.98	248.98
Formation Potential	(µg /mg)	N/A	-4.39	156.59
<b>HPO</b>				
Area	(Hz*s)	549.90	15139.75	713.55
Rep 1	(Hz*s)	444.50	13875.90	891.70
Rep 2	(Hz*s)	655.30	16403.60	535.40
Concentration	(µg/l)	14.01	-4.45	410.81
Formation Potential	(µg /mg)	8.81	-2.80	258.37
<b>Active Biofilm</b>				
Area	(Hz*s)	N/A	87552.40	4006.27
Rep 1	(Hz*s)	N/A	71510.00	1662.90
Rep 2	(Hz*s)	N/A	93743.30	5142.80
Rep 3	(Hz*s)	N/A	97403.90	5213.10
Concentration	(µg/l)	N/A	67.17	3241.55
Formation Potential	(µg DBPs/mg Biofilm)	N/A	6.72	324.16
<b>Inactivated Biofilm</b>				
Area	(Hz*s)	9936.47	94126.03	4199.27
Rep 1	(Hz*s)	9871.00	104243.20	3813.40
Rep 2	(Hz*s)	10476.00	94659.30	3691.80
Rep 3	(Hz*s)	9462.40	83475.60	5092.60
Concentration	(µg/l)	533.20	73.67	3407.48
Formation Potential	(µg /mg)	53.32	7.37	340.75
<b>Active Biofilm +DOM</b>				
Area	(Hz*s)	3692.10	120147.93	N/A
Rep 1	(Hz*s)	3692.10	139023.10	N/A

Rep 2	(Hz*s)	N/A	113645.30	N/A
Rep 3	(Hz*s)	N/A	107775.40	N/A
Concentration	(µg/l)	187.81	99.40	N/A
Formation Potential	(µg /mg)	15.53	8.22	N/A
<b>Inactivated Biofilm +DOM</b>				
Area	(Hz*s)	N/A	132960.87	N/A
Rep 1	(Hz*s)	N/A	143489.90	N/A
Rep 2	(Hz*s)	N/A	125838.90	N/A
Rep 3	(Hz*s)	N/A	129553.80	N/A
Concentration	(µg/l)	N/A	112.07	N/A
Formation Potential	(µg /mg)	N/A	9.27	N/A
<b>Active Biofilm +HPI</b>				
Area	(Hz*s)	152.53	124976.53	269.77
Rep 1	(Hz*s)	145.30	130128.40	283.20
Rep 2	(Hz*s)	162.70	121774.20	306.50
Rep 3	(Hz*s)	149.60	123027.00	219.60
Concentration	(µg/l)	-7.97	104.17	29.30
Formation Potential	(µg /mg)	-0.69	8.99	2.53
<b>Inactivated Biofilm +HPI</b>				
Area	(Hz*s)	203.67	139733.17	247.90
Rep 1	(Hz*s)	182.90	148462.50	309.90
Rep 2	(Hz*s)	137.20	125059.50	215.50
Rep 3	(Hz*s)	290.90	145677.50	218.30
Concentration	(µg/l)	-5.14	118.77	10.50
Formation Potential	(µg /mg)	-0.44	10.25	0.91
<b>Active Biofilm +HPO</b>				
Area	(Hz*s)	13433.35	74445.05	1655.35

Rep 1	(Hz*s)	18080.00	89200.20	2200.70
Rep 2	(Hz*s)	8786.70	59689.90	1110.00
Concentration	(µg/l)	726.63	54.20	1220.48
Formation Potential	(µg /mg)	62.69	4.68	105.30
<b>Inactivated Biofilm+ HPO</b>				
Area	(Hz*s)	160.05	53901.05	1147.25
Rep 1	(Hz*s)	182.90	52485.20	1117.60
Rep 2	(Hz*s)	137.20	55316.90	1176.90
Concentration	(µg/l)	-7.56	33.89	783.67
Formation Potential	(µg /mg)	-0.65	2.92	67.62

**Table D-5** Data of HANs formation potential from nitrogen source experiments

Sample	Unit	MCAN	DCAN	TCAN	BCAN	DBAN
<b>DOM</b>						
Area	(Hz*s)	N/A	18855.65	3359.86	850.32	2078.60
Rep 1	(Hz*s)	N/A	17113.70	N/A	433.50	432.70
Rep 2	(Hz*s)	N/A	931.08	5593.00	850.40	1914.72
Rep 3	(Hz*s)	N/A	20597.60	1126.71	1267.05	3888.39
Concentration	(µg/l)	N/A	30.37	54.51	42.82	67.89
Formation Potential	(µg/mg)	N/A	51.39	92.23	72.46	114.88
<b>HPI</b>						
Area	(Hz*s)	N/A	3888.38	N/A	317.11	186.51
Rep 1	(Hz*s)	N/A	3954.93	N/A	339.74	194.12
Rep 2	(Hz*s)	N/A	3556.30	N/A	293.70	165.40
Rep 3	(Hz*s)	N/A	4153.90	N/A	317.90	200.00
Concentration	(µg/l)	N/A	25.31	N/A	42.68	66.24
Formation Potential	(µg/mg)	N/A	49.43	N/A	83.35	129.37



<b>HPO</b>						
Area	(Hz*s)	427.70	8204.00	N/A	N/A	N/A
Rep 1	(Hz*s)	506.50	6823.70	N/A	N/A	N/A
Rep 2	(Hz*s)	348.90	9584.30	N/A	N/A	N/A
Concentration	(µg/l)	23.65	26.94	N/A	N/A	N/A
Formation Potential	(µg/mg)	1218.96	1388.86	N/A	N/A	N/A
<b>Active Biofilm</b>						
Area	(Hz*s)	3501.90	73740.63	N/A	N/A	N/A
Rep 1	(Hz*s)	2944.20	79130.90	N/A	N/A	N/A
Rep 2	(Hz*s)	3057.00	72483.70	N/A	N/A	N/A
Rep 3	(Hz*s)	4504.50	69607.30	N/A	N/A	N/A
Concentration	(µg/l)	26.89	54.21	N/A	N/A	N/A
Formation Potential	(µg/mg)	69.67	140.44	N/A	N/A	N/A
<b>Inactivated Biofilm</b>						
Area	(Hz*s)	3257.77	89838.40	N/A	N/A	N/A
Rep 1	(Hz*s)	3476.40	89790.60	N/A	N/A	N/A
Rep 2	(Hz*s)	3049.40	94211.40	N/A	N/A	N/A
Rep 3	(Hz*s)	3247.50	85513.20	N/A	N/A	N/A
Concentration	(µg/l)	26.63	58.32	N/A	N/A	N/A
Formation Potential	(µg/mg)	66.75	146.18	N/A	N/A	N/A
<b>Active Biofilm +DOM</b>						
Area	(Hz*s)	2828.13	28610.97	N/A	1305.17	236.20
Rep 1	(Hz*s)	3034.60	30287.70	N/A	1380.70	270.70
Rep 2	(Hz*s)	2953.00	27788.40	N/A	1252.90	179.00
Rep 3	(Hz*s)	2496.80	27756.80	N/A	1281.90	258.90
Concentration	(µg/l)	26.18	34.79	N/A	42.95	66.28
Formation Potential	(µg/mg)	26.80	35.61	N/A	43.96	67.84
<b>Inactivated Biofilm +DOM</b>						
Area	(Hz*s)	3255.63	33899.50	N/A	1525.40	421.70
Rep 1	(Hz*s)	3330.50	33853.30	N/A	1489.60	375.20
Rep 2	(Hz*s)	3470.50	36425.70	N/A	1635.00	490.20
Rep 3	(Hz*s)	2965.90	31419.50	N/A	1451.60	399.70

Concentration	( $\mu\text{g/l}$ )	26.63	36.82	N/A	43.01	66.45
Formation Potential	( $\mu\text{g/mg}$ )	26.90	37.19	N/A	43.44	67.12
<b>Active Biofilm +HPI</b>						
Area	(Hz*s)	6037.35	6040.53	N/A	178.83	N/A
Rep 1	(Hz*s)	6322.60	5830.00	N/A	177.90	N/A
Rep 2	(Hz*s)	5752.10	5633.70	N/A	180.70	N/A
Rep 3	(Hz*s)	N/A	6657.90	N/A	177.90	N/A
Concentration	( $\mu\text{g/l}$ )	29.57	26.11	N/A	42.64	N/A
Formation Potential	( $\mu\text{g/mg}$ )	32.93	29.08	N/A	47.48	N/A
<b>Inactivated Biofilm +HPI</b>						
Area	(Hz*s)	6690.80	6334.50	N/A	172.73	N/A
Rep 1	(Hz*s)	6766.90	6404.80	N/A	32.00	N/A
Rep 2	(Hz*s)	6614.70	5951.80	N/A	191.90	N/A
Rep 3	(Hz*s)	5835.40	6646.90	N/A	294.30	N/A
Concentration	( $\mu\text{g/l}$ )	30.26	26.23	N/A	42.64	N/A
Formation Potential	( $\mu\text{g/mg}$ )	33.21	28.79	N/A	46.80	N/A
<b>Active Biofilm +HPO</b>						
Area	(Hz*s)	2614.15	55212.85	N/A	148.95	N/A
Rep 1	(Hz*s)	2904.70	60774.20	N/A	160.50	N/A
Rep 2	(Hz*s)	2323.60	49651.50	N/A	137.40	N/A
Concentration	( $\mu\text{g/l}$ )	25.96	45.01	N/A	42.63	N/A
Formation Potential	( $\mu\text{g/mg}$ )	64.02	111.04	N/A	105.15	N/A
<b>Inactivated Biofilm + HPO</b>						
Area	(Hz*s)	2557.10	67045.75	N/A	155.20	N/A
Rep 1	(Hz*s)	2232.20	55374.00	N/A	135.00	N/A
Rep 2	(Hz*s)	2882.00	78717.50	N/A	175.40	N/A
Concentration	( $\mu\text{g/l}$ )	25.90	49.56	N/A	42.63	N/A
Formation Potential	( $\mu\text{g/mg}$ )	61.89	118.46	N/A	101.89	N/A



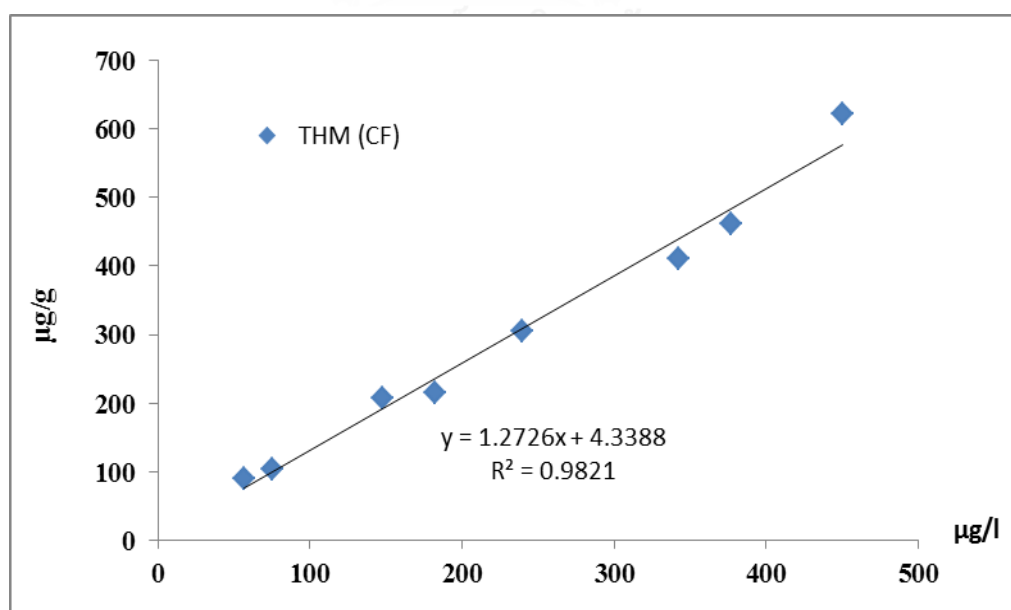
**APPENDIX E**

**Data of CF and DCAN Adsorption by Granular Activated Carbon  
Experiments**

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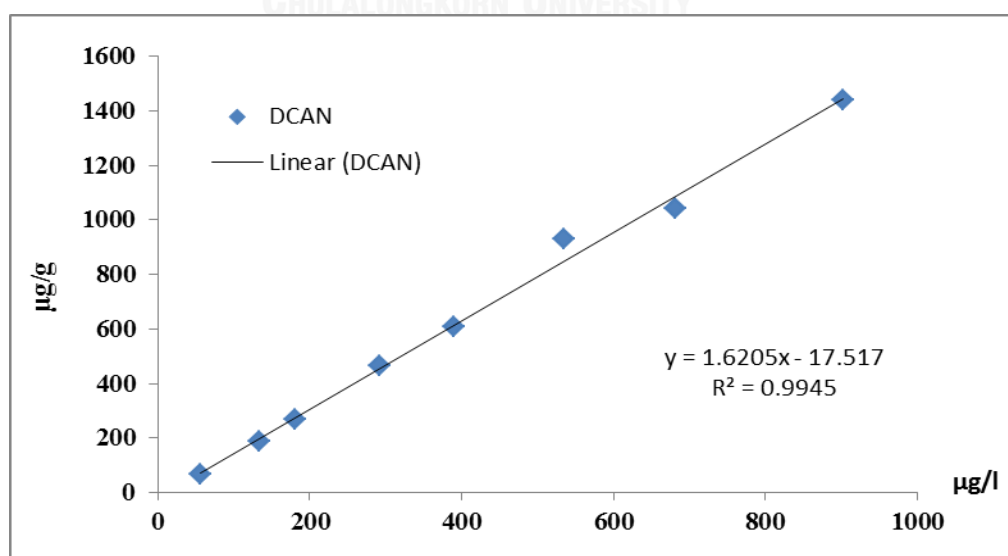
**Table E-1** Data of CF adsorption by granular activated carbon experiments

Sample	Initial Concentration ( $\mu\text{g/l}$ )	Final Concentration ( $\mu\text{g/l}$ )	Carbon Weight (g)	Volume (L)	Q Capacity Adsorption ( $\mu\text{g/g}$ )
CF 50 ppb	56.68	9.10	0.0262	0.05	90.811
CF 100 ppb	75.37	13.14	0.0301	0.05	103.366
CF 200 ppb	147.79	39.76	0.0260	0.05	207.742
CF 300 ppb	182.13	58.04	0.0288	0.05	215.441
CF 400 ppb	240.00	71.34	0.0277	0.05	304.436
CF 500 ppb	342.52	98.29	0.0297	0.05	411.164
CF 600 ppb	377.14	127.03	0.0271	0.05	461.453
CF 700 ppb	450.02	136.49	0.0252	0.05	622.099

**Figure D-1** Curve of CF adsorption by granular activated carbon experiments

**Table E-2** Data of DCAN adsorption by granular activated carbon experiments

Sample	Initial Concentration ( $\mu\text{g/l}$ )	Final Concentration ( $\mu\text{g/l}$ )	Carbon Weight (g)	Volume (L)	Capacity Adsorption ( $\mu\text{g/g}$ )
DCAN 50 ppb	56.00	18.05	0.0285	0.05	66.583
DCAN 100 ppb	133.15	23.72	0.0292	0.05	187.394
DCAN 200 ppb	181.42	35.67	0.0273	0.05	266.944
DCAN 300 ppb	292.13	32.13	0.0280	0.05	464.286
DCAN 400 ppb	389.45	75.79	0.0258	0.05	607.871
DCAN 500 ppb	535.56	50.59	0.0261	0.05	929.068
DCAN 600 ppb	681.59	102.87	0.0278	0.05	1040.872
DCAN 700 ppb	902.87	86.39	0.0284	0.05	1437.465

**Figure D-2** Curve of DCAN adsorption by granular activated carbon experiments



## VITA

Miss Rina Heu was born in 20th of December, 1990 in Takeo province, southern province of Cambodia. After she graduated from high school, she continued her studied at Institute of Technology of Cambodia (ITC), Phnom Penh capital city, in majoring of Rural Engineering for academic year 2008-2013. In 22nd of October, 2013 she got a scholarship under the sponsored by AUN/SEED-Net program to pursue master degree in Environmental Engineering Department, Chulalongkorn University, Thailand for academic year 2013-2015.



