

REMOVAL OF DISSOLVED ORGANIC MATTER IN SHALLOW WELL LOCATED NEAR
ABANDON LANDFILL BY POWDER ACTIVATED CARBON WITH CERAMIC MEMBRANE



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จุฬาลงกรณ์มหาวิทยาลัย

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การศึกษานี้มีวัตถุประสงค์เพื่อกำจัดสารอินทรีย์ละลายน้ำในน้ำบ่อตื้นปนเปื้อนน้ำชะขยะโดยการผสมผสานการดูดติดผงถ่านกัมมันต์และการกรองเซรามิกเมมเบรน ถ่านกัมมันต์ชนิดผงใช้ในกระบวนการดูดติดและเซรามิกเมมเบรนที่มีรูพรุน 0.1 ไมโครเมตร ใช้ในกระบวนการกรอง น้ำบ่อตื้นปนเปื้อนเก็บจากพื้นที่เทกองขยะมูลฝอยที่ไม่ถูกหลักสุขาภิบาลที่ปิดดำเนินการแล้วในจังหวัดเชียงใหม่ ประเทศไทย จากการศึกษาพบว่า น้ำบ่อตื้นปนเปื้อนมีสารอินทรีย์คาร์บอนละลายน้ำเท่ากับ 11.4-12.6 มิลลิกรัม/ลิตร และค่าการดูดกลืนแสง UV254 เท่ากับ 1.577 เซนติเมตร-1 การทดลองจลนพลศาสตร์การดูดติดพบว่า เวลาที่สมดุลในการทำปฏิกิริยาคือ 6 ชั่วโมง และการเพิ่มปริมาณผงถ่านกัมมันต์สามารถเพิ่มประสิทธิภาพในการกำจัดสารอินทรีย์คาร์บอนละลายน้ำได้ อย่างไรก็ตาม การผสมผสานการดูดติดผงถ่านกัมมันต์และการกรองเซรามิกเมมเบรนมีประสิทธิภาพในการกำจัดสารอินทรีย์คาร์บอนละลายน้ำต่ำกว่าการดูดติดถ่านกัมมันต์เพียงอย่างเดียว ซึ่งอาจเนื่องมาจากการอุดตันของเซรามิกเมมเบรนและการคายสารอินทรีย์คาร์บอนละลายน้ำที่ดูดติดบนผิวผงถ่านกัมมันต์ นอกจากนี้ น้ำบ่อตื้นปนเปื้อนมีค่าความเข้มข้นของสารไตรฮาโลมีเทนทั้งหมดเท่ากับ 10.84 ไมโครกรัม/ลิตร หลังจากที่น้ำบ่อตื้นปนเปื้อนผ่านการผสมผสานการดูดติดผงถ่านกัมมันต์และการกรองเซรามิกเมมเบรนพบว่า ค่าความเข้มข้นของสารไตรฮาโลมีเทนทั้งหมดลดลงเหลือ 3.06 ไมโครกรัม/ลิตร

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This study aimed to remove dissolved organic matter from shallow well water contaminated with landfill leachate by powder activated carbon (PAC) adsorption and ceramic microfiltration (CM) membrane hybrid process. PAC was utilized as adsorbent. CM membrane with nominal pore size 0.1 μm was applied. Contaminated shallow well water was collected from a closed unsanitary landfill in Chiang Mai, Thailand. It was found that the contaminated shallow well water contained 11.4-12.6 mg/L of dissolved organic carbon (DOC) and 1.545-1.577 cm^{-1} of UV₂₅₄. For the kinetic adsorption experiment, equilibrium time was 6 hours. It was proven that increasing in PAC dosage could enhance DOC removal efficiency. The hybrid process showed lower DOC removal efficiency when compared with that of the sole PAC adsorption process. It could be the result of membrane fouling and desorption of DOC from PAC during a course of ceramic membrane filtration. For chlorination process, total trihalomethane in shallow well water was reduced from 10.84 $\mu\text{g/L}$ to 3.06 $\mu\text{g/L}$ in treated water by the hybrid process.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Shallow well water is one of the most important water sources that support human life, animals, and environments. People as consumers used water in households and agricultures. From the information of national statistical office reported in 2012 that approximate 18 percent of using water in Thailand (National statistical office, 2014: online).

The dumping site of wastes has been used as landfill site. For disposal municipal wastes, degradation in term of anaerobic part of solid waste was taken a very long time in the production of leachate and landfill gas (Huo *et al.*, 2008). Leachate and landfill gas were the inherent pollution sources for the surrounding environments, and it has an environmental impacts in long-term and several decades (Cossu *et al.*, 2003; Bilgili *et al.*, 2007).

The open dumping at the Mae-Hia site for waste disposal was operated for over 30 years until it was closed in May 1989 because of the unacceptable environmental impacts on shallow well water and groundwater nearby the site. Dissolved organic matter (DOM), hereafter called disinfection by product (DBP) precursors in term of dissolved organic carbon was presented in groundwater in that

area (Karnchanawong *et al.*, 1993). DBPs occurred in water supply process when chlorine was added into the water and reacted with organic matters.

Treatment technologies for water contaminated with landfill leachate were introduced e.g., electro-coagulation with aluminum plate electrodes, aerobic biological treatment, air stripping, adsorption by activated carbon, coagulation-flocculation, oxidation process with $\text{Fe}^{2+}/\text{H}_2\text{O}$, and membrane filtration (Gotvajn *et al.*, 2009; Top *et al.*, 2011).

This study aimed to measure and characterizes shallow well water at Mae-Hia open dumping site. Powder activated carbon adsorption combined with ceramic membrane filtration was applied to remove DBP precursors.

1.2 Objectives:

1. To measure DBP precursors in shallow well water contaminated with landfill leachate.
2. To characterize DBP precursors in contaminated shallow well water.
3. To remove DBP precursors by powder activated carbon adsorption and ceramic membrane filtration
4. To study a formation of DBP during treatment process

1.3 Hypotheses:

1. Powder activated carbon adsorption hybridized with ceramic membrane filtration can reduce DBP precursors, as well as, DBP formation during a chlorination process.

1.4 Scope of the Study:

1. Shallow well water contaminated with landfill leachate from Mae-Hia open dumping site, Chiang Mai, Thailand, was used in this study.
2. Organic matters were fractionated into two parts including hydrophilic and hydrophobic groups
3. Powder Activated Carbon (PAC) was utilized as an adsorbent.
4. Ceramic microfiltration (CM) membrane with pore size 0.1 μm was tested.
5. Sodium hypochlorite was employed during a chlorination process in a formation of DBP experiment.

1.5 Benefit of this study:

1. The characteristics of the shallow well water contaminated with landfill leachate were explored.
2. Knowledge of removal DBP precursors by powder activated carbon adsorption and ceramic membrane filtration was carried out.

3. The removal efficiency of DBP precursors by powder activated carbon adsorption hybridized with ceramic membrane filtration was found out.



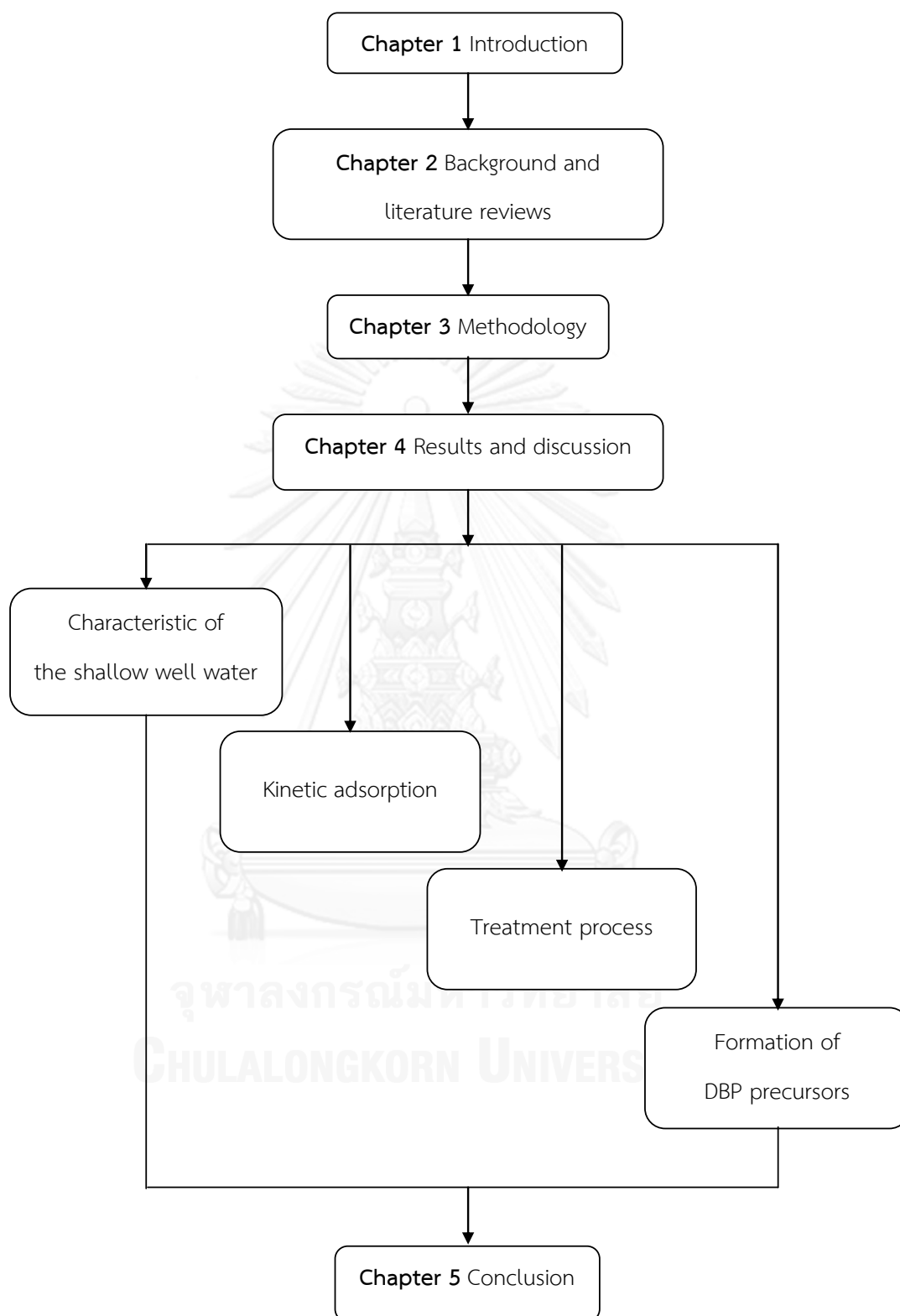


Figure 1. 1 The schematic of this study.

The schematic of this study was illustrated in **Figure 1.1**. The Chapter 1 was presented the introduction including the motivation, objectives, hypotheses, scope, and benefit of this study. Chapter 2 described about the earlier researches in the same field of disinfection by products removal by powder activated carbon and ceramic membrane filtration. Chapter 3 source and located of water sample, materials, experimental methods, and chemical reagents and instruments in this study were described. Chapter 4 reported the results of this study, i.e. characteristics of shallow well water, kinetic adsorption experiment, and the treatment process by powder activated carbon and ceramic membrane. In addition, organic fractionation and the flux measurement of ceramic membrane were reported in this part. Furthermore, this chapter was reported the results of disinfection by-product formation. Chapter 5 summarized the results of this study and provided recommendation for the further studies.

CHAPTER 2

LITERATURE REVIEWS

2.1 Ceramic Membrane filtration

Currently, membrane filtration has been increasingly applied in water and wastewater treatments. The chemical and mechanical properties of ceramic membranes gave them significant advantages over polymeric membranes in many applications. Ceramic membranes have an excellent resistance against abrasion and chemically aggressive fluids. Furthermore, they have high mechanical strength, good thermal resistance and high separation efficiency (Heidenreich and Michell, 2011). These made ceramic membranes suitable for many applications where polymeric and other inorganic membranes cannot be used.

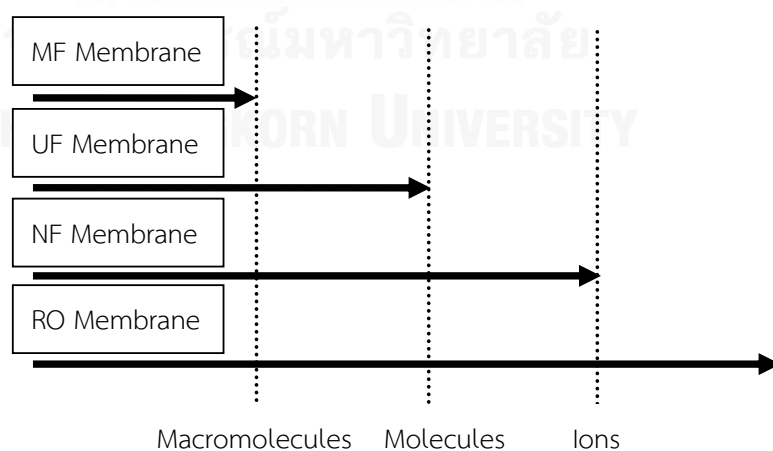


Figure 2. 1 Type of membrane and size of substance.

Types of membrane filtration can be categorized into 4 types including reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) (Luque *et al.*, 2008; Tomaszewska *et al.*, 2002). **Figures 2.1 and 2.2** present the relationship between type of membrane and size of substance. The UF and MF membrane processes were considered when large particles, macromolecules, and large molecules need to be removed. For removals of ions, RO and NF were considered.

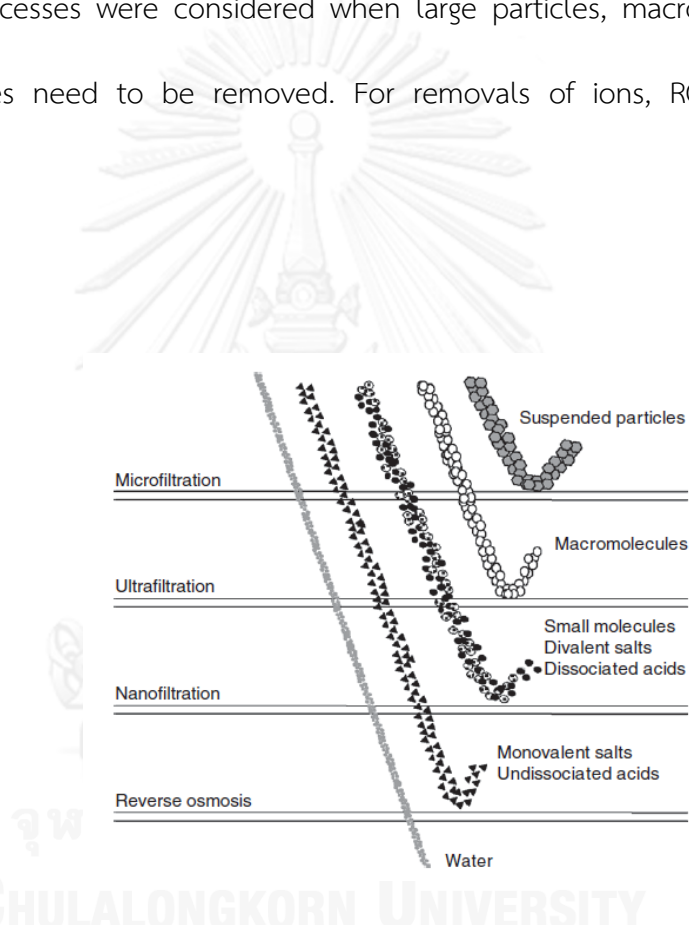


Figure 2. 2 Type of membrane and their applications (Luque *et al.*, 2008).

The most common advantages of ceramic membranes mentioned by Luque *et al.* (2008), when compared with other membrane types used in pressure-driven membrane processes including:

- Long and reliable working lifetime and high fluxes.
- Resistance to high temperatures (up to 300°C, though that also depends on the gaskets) across the entire pH range.
- Excellent chemical stability (i.e., organic solvents, oxidants, and hydrocarbons).
- Bacteria resistant and, frequently, bio inert.
- Compatibility with highly viscous fluids.
- Enhanced ease of cleaning and backwash is also possible.

Ceramic membrane filtration was an effective way to remove the pollutants; in addition, it was not a complicate process and easy to use. It was suitable to remove suspended solids from highly turbid water (Kimura *et al.*, 2004). Furthermore, when the ceramic membrane filtration process was combined with coagulation, it was able to effectively remove suspended solids from several river water samples in Southeast Asia. **Figure 2.3** shows examples of ceramic membranes.

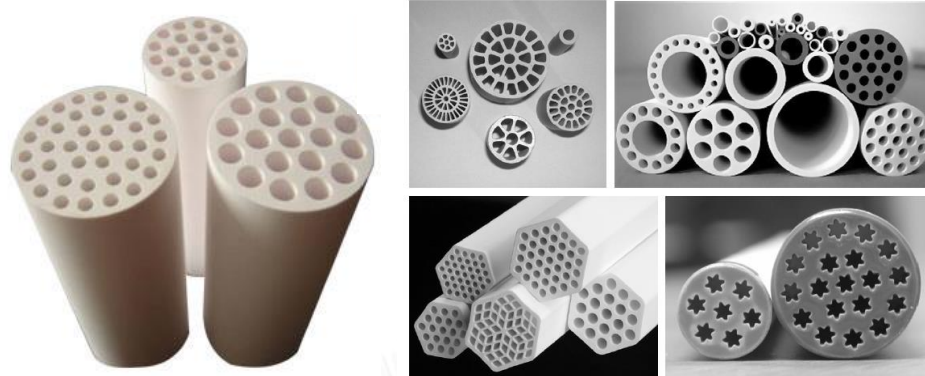


Figure 2. 3 Examples of ceramic membranes (Photographies courtesy of TAMI Industries, Inopor, PallMembralox, and Fairey Industrial Ceramics).

2.2 Activated carbon adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process.

Activated carbon, also called activated charcoal or activated coal, is a general term that includes carbon material mostly derived from charcoal. Activated carbon was frequently used in everyday life, such as in industry, food production, medicines, and even by the military. For instance, activated charcoal was considered to be the most effective single agent available as an emergency decontaminant in the gastrointestinal tract (Kopecky *et al.*, 1996).



Figure 2. 4 Types of activated carbon: GAC (left) and PAC (right).

There are two types of activated carbons: powdered activated carbon (PAC) and granular activated carbon (GAC). Both types, PAC and GAC, were effective adsorbents because they had large surface areas and were highly porous (Punyapalakul, 2009) as can be seen in **Figure 2.4**.

The characteristics of activated carbon were consists of physical structure and chemical structure. A porous carbon structure contains amounts of heteroatoms such as oxygen, hydrogen, and carbon. Some activated carbons also contained some mineral matter (ash content). It depended on the nature of the raw material. The porous structure of activated carbon was one of the most physical properties that defined the efficiency of activated carbons (Sing *et al.*, 1985). According to IUPAC recommendations, it can be classified into three groups that were macropores, mesopores, and micropores. Macropores has pore width larger than 50×10^9 m., mesopores has pore from 2.0 to 50×10^9 m., and micropores with a pore width of less

than 2×10^9 m. High surface area and large pore size which were the important factors for the researcher to select the activated carbon as an adsorbent for their studies.

For chemical structure of activated carbon, carbon atoms located at the boundary of unsaturated zone of carbon atoms, which unpaired electrons. These sites were usually bonded to heteroatoms giving rise to surface groups. In particular, some activated carbons had a relatively large area, which resulted in a strong tendency for oxygen chemisorption. Therefore, oxygen molecule could separate into atoms that reacted with carbon atoms to form oxygen surface compounds. The reaction was increased while the temperature was high.

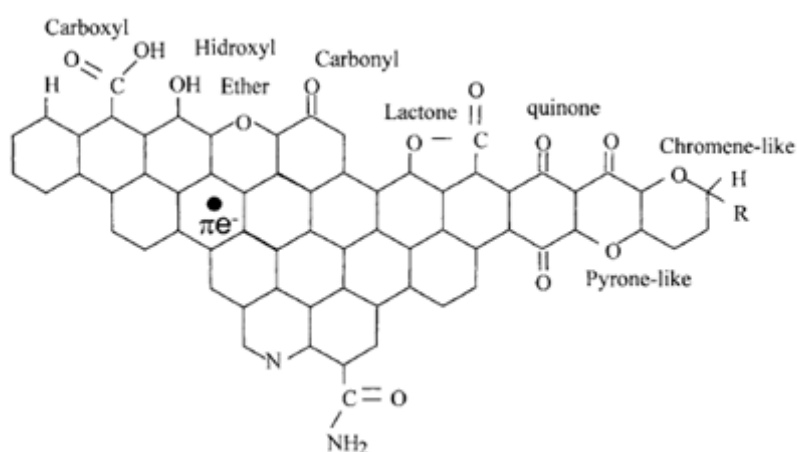


Figure 2. 5 Types of surface groups that presented on carbon surface areas (Leon *et al.*, 1985).

Oxygen-containing surface groups were not only formed with oxygen atoms but could also react with other oxidizing gases or solutions such as ozone, carbon dioxide, nitric acid, hydrogen peroxide, etc. Thus, the surface chemistry of activated carbons could be improved by oxidation with acid-base agents or by heat treatment to remove them either selectively depends on the temperatures used (Leon *et al.*, 1985). **Figure 2.5** shows the important types of surface groups that might be presented on carbon surfaces.

The analysis of isotherm experiment as mention by Kannan and Sundaram (2001); Hyung and Kim (2008), C_e was determined, the equilibrium concentration of DOC adsorbed on the unit mass of PAC adsorbent, q_e (mg C/g PAC), was obtained by the following the equation:

$$(q_e) = (C_0 - C_e)/M$$

; where C_0 (mg/L) the initial concentration of DOC, C_e (mg/L) the final concentration and M (g PAC/L) dosage of PAC.

The adsorption isotherm was followed the linear forms of Langmuir and Freundlich isotherms (Kannan and Sundaram, 2001):

Langmuir isotherm: $1/q_e = 1/(K_L q_m C_e) + 1/q_m$

Freundlich isotherm: $\log q_e = \log K_f + (1/n) \log C_e$

; where q_m is the maximum adsorption capacity (mg/g), q_e is the amount of adsorbate adsorbed at equilibrium (mg/L), and K_L is the Langmuir constant (L/mg).

For the Freundlich constant is $\log K_f$ and $1/n$ is an indicator of adsorption effectiveness.

2.3 Hybrid membrane process

Hybrid membrane processes can be described as processes where “one or more membrane process was coupled with another unit process such as adsorption, ion exchange, coagulation, bioconversion, catalysis, etc. (Fane, 1996).

Previous researches have been studied many types of adsorbents to combine with membrane. The research of Kim *et al.* (2009) was studied the hybrid microfiltration combined with the long contact time of granular activated carbon system as treatment process. They found that the hydrophobic NOM and trihalomethane precursors were decreased by using the applied treatment process. In addition, the removal efficiencies of DOC, COD, TN, total phosphorus and turbidity were slightly higher than those obtained from the only microfiltration process (Kim *et al.*, 2009).

Recently, researchers have also investigated the use of PAC in biological mode, which could lead to the removal of the biodegradable organic substances and reduce the costs related to PAC regeneration (Markarian *et al.*, 2010). Khan *et al.* (2009) used a high concentration (40g/L of reactor) of PAC combined with membrane microfiltration to removed THMs and TOC from the river water. The results of their

study were 18% and 5% removal of THMs and TOC without PAC process, while the combination process were 65% and 95% removal of THMs and TOC respectively.

Kim *et al.* (2005) studied the combination process between different PAC dosages (PAC-0 g/L, PAC-10 g/L, and PAC-40 g/L) and bench-scale immersed membrane separation system. They found that increasing in the concentration of PAC, the filtrate quality and the performance efficiency were improved.

Other researchers investigated about different concentrations of PAC combined with MBR to treat slightly polluted surface water (SPSW) at low temperatures. It was found that the effluent quality, performance efficiency, resistance of shock load were all enhanced and chemical irreversible membrane fouling was reduced with increasing dosages of PAC in MBR. 50 g/L of PAC was the optimal dosage in MBR for stable and extended operation. Under this condition, mean removal efficiencies of ammonia nitrogen (NH₃-N), dissolved organic carbon (DOC) and UV₂₅₄ were 93%, 75%, and 85%, respectively (Ma *et al.*, 2012).

Furthermore, the hybrid process or combination process between adsorption and membrane filtration have been both of advantage and disadvantage. Thus the combination process can caused the membrane fouling because of the particles of PAC/GAC as an adsorbent can be attached with membrane surface as cake layer and also affected to the removal efficiency. The research from Khan *et al.* (2011) used the 40 g/L of PAC combined with membrane filtration. And they mentioned that the

larger particles of PAC reduced the effects of membrane fouling, causing higher transmembrane pressure (TMP) and increasing the fouling frequency (Khan *et al.*, 2011).

2.4 Dissolve organic carbon (DOC)

Dissolve organic carbon (DOC) is defined as the ratio of total organic carbon while filtrated by the 0.7 μm GF/F filter paper. There are two fraction of organic carbon that are particulate organic carbon (POC) and dissolve organic carbon (DOC). From the research of Thurman (1985) mentioned the surface water, DOC was around 50-60% of humic substance. Biodegradable dissolved organic carbon (BDOC) was dissolved organic carbon (DOC) that was biodegradable. DOC that can be divided into two types: DOC that moves horizontally with soil particles and DOC that moves vertically on the surface of water.

DOC is an example of DBPs precursor. The organic matters combined with free chlorine, it can form THMs HAAs HANs CH and other DBPs in disinfection process. The organic compound in raw water was the main factor to form THMs (Panyapinyopol *et al.*, 2005). It depended on different area, different season, different consume.

2.5 Dissolve organic nitrogen (DON)

Dissolved organic nitrogen (DON) is an important precursor of carcinogenic substances like nitrogenous disinfection by-products (N-DBPs) such as haloacetonitriles (HANs) and N-nitrosodimethylamine (NDMA) (Lee *et al.*, 2007). DON was presented at a low percentage (about 0.5–10.0% by weight) in natural organic matters (NOM) (Westerhoff and Mash, 2002) and consisted of nitrogen containing functional groups, such as NH classes, the amino category, and nitrile compounds. Usually, drinking water treatment used chlorine to eliminate pathogenic microbes and warranted the microbiological safety of drinking water (Ates *et al.*, 2007). Nevertheless, these nitrogenous organic compounds can react with chlorine during the disinfection process or water treatment process to form nitrogenous disinfection by-products (Westerhoff and Mash, 2002; Lee *et al.*, 2007).

There are two types of dissolved organic nitrogen (DON): one is biodegradable dissolved organic nitrogen and the other is bioavailable dissolved organic nitrogen. Due to recent advances in technology, wastewater treatment facilities were able to remove high inorganic nitrogen content, leading to dissolved organic nitrogen (DON) being a major nitrogen form (>50%) of the effluent (total dissolved nitrogen or TDN). Dissolved organic nitrogen can be removed by activated sludge and a trickling filter (Simsek *et al.*, 2013). A study showed that the TF process can remove 65% of BDON and 63% of ABDON, while AS removed 68% of BDON and 56% of ABDON. Then TF was used to remove 62% BDON and 71% ABDON 26% and 47% of effluent DON in

AS wastewater treatment plant. In addition, DON utilization was the highest when the bacteria and algae were used as a co-inoculum in the samples. (Simsek *et al.*, 2013)

2.6 Disinfection by-products (DBPs)

Since the discovery of disinfection by-products (DBPs) in drinking water in the 1970s and with increasing understanding about their occurrence and health effects, the control of DBP formation has become one of the major issues for the water that people use. In addition to other measured DBPs, the sum of known DBPs has accounted for 30 to 60% of the total organic halogen (TOX) detected during chlorination, which was the oldest and the most commonly used disinfection technique in water treatment around the world (Karanfil *et al* 2008 cited in Gan *et al.*, 2013).

The direct incorporation of chloramines and dissolved organic nitrogen (DON) might provide the nitrogen for nitrogenous disinfection byproducts (N-DBPs). The results supported the hypothesis that THMs, DXAAs, and DXANs were mainly derived from similar precursors upon chloramination. In addition, the precursor of HANs was approximately 10% (on a molar basis) of that of THMs and HAAs combined. The N-nitrosodimethylamine (NDMA) formation potential was correlated with DON/DOC in hydrophilic and transphilic fractions. Isotope ^{15}N -labeled monochloramine coupled with LC-electrospray ionization-tandem mass spectrometry was used to explore the

nitrogen source of NDMA formed in chloraminated organic fractions (Chuang *et al.*, 2013).

Sandrucci *et al.* (1995) used the differences PAC adsorption to removed precursors from Po River in Italy. They added hypochlorite to the samples for chlorination process after that kept 1 h to imitated actual treatment and another sample kept 1 d in the darkness and accept 1 mg/L of free chlorine residual. They found that the PAC was effective to remove the organic precursors and reduced DBPs. In addition the lower 10 mg/L with a contact time 60 min of PAC was found 20% DBP precursor removal, which was the most efficiency for this application. Moreover, ozonation and flocculation can be applied with PAC (Sandrucci *et al.*, 1995). Another study found that 20 mg/L of chlorine and allowed to react 1 d in the darkness for chlorination process and also used 10 mg/L of chlorine to react for 3 d in the darkness too. The results showed ClO_2 was destroyed the aromatic and conjugated structure of natural organic matter. Moreover, ClO_2 was transformed large organic structures of aromatic and aliphatic to small and hydrophilic organics. Furthermore, ClO_2 preoxidation reduced the THMs, HAA, CH and HANs formation after the chlorination process (Yang *et al.*, 2013).

NOM contained many precursors for the disinfection by-product formation that were used in the water supplies. Furthermore, they used organic content such

as TOC, and UV absorbance at 254 nm to characterize the NOM and the potential of THMs (Marhaba and Washington. 1998).

Nitrogenous DBPs have attracted much attention because chloramination favors the formation of certain nitrogenous DBPs such as cyanogen chloride and N-nitrosodimethylamine (NDMA) (Mitch *et al.*, 2003). Chen and Valentine (2006) developed a kinetic model to approve proposed reactions and to predict NDMA formation in chloraminated water. The results indicated that NDMA formation was limited by the oxidation of NOM by the protonated chlorine species or HOCl. Schreiber and Mitch (2005) reported on the critical importance of dichloramine and dissolved oxygen in nitrosamine formation and proposed a new nitrosamine formation pathway. Lee and colleagues (2007) reported the destruction or transformation of NDMA precursors using ozone and chlorine dioxide. Also, Charrois and Hrudey (2007) found that prechlorination minimized NDMA formation during subsequent chloramination.

Other than evaluating the formation and control of NDMA, various researchers have studied the source of NDMA precursors. Krasner and colleagues (2007) found treated wastewater to be a major source of NDMA precursors. Moreover, they found that wastewater treatment plants can reduce the level of precursors for NDMA. Some cationic polymers contained NDMA precursors; therefore, it was important to not overdose the polymers used in the coagulation process.

2.6.1 Trihalomethanes

Trihalomethanes (THMs) are mono-carbon compounds with halogen substituted which occur with bromine, chlorine, fluorine, etc. Natural organic matters can be combined with chlorine in water supplies and form the THMs and other DBPs (Panyapinyopol *et al.*, 2005) as shown in equation below.



Four THM species that actually occur in water supplies: Chloroform (CHCl_3), Bromodichloromethane (CHBrCl_2), Dibromochloroform (CHBr_2Cl) and Bromoform (CHBr_3).

Chloroform was not only causes the depression on the central nervous system, but also hepatotoxicity, nephrotoxicity, teratogenicity and carcinogenicity (USEPA, 1997). The basic chemical and physical characteristics of forth of trihalomethanes are shown in **Table 2.1**, and **Table 2.2** shows its chemical structure.

Table 2. 1 Basic chemical and physical characteristics of trihalomethanes

Empirical Formula	Molecular weight (g/mol)	Specific gravity (g/cm ³)	Boiling point (°C)	Melting point (°C)	Solubility in water (g/L)
CHCl ₃	119.37	1.472	61	-63	8.1
CHCl ₂ Br	163.82	1.472	90.1	-57.1	Insoluble
CHClBr ₂	208.29	2.38	120	-63	4.75
CHBr ₃	257.73	2.894	150	8.3	Insoluble

(Source: Ghazali, 1989)

Table 2. 2 Chemical structure of trihalomethanes

Disinfection by-product (DBPs)	Formula	Chemicals structure
Chloroform	CHCl ₃	$\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}-\text{H} \\ \\ \text{Cl} \end{array}$
Bromodichloromethane	CHCl ₂ Br	$\begin{array}{c} \text{Cl} \\ \\ \text{Br}-\text{C}-\text{H} \\ \\ \text{Cl} \end{array}$
Dibromochloromethane	CHClBr ₂	$\begin{array}{c} \text{Br} \\ \\ \text{Cl}-\text{C}-\text{H} \\ \\ \text{Br} \end{array}$
Bromoform	CHBr ₃	$\begin{array}{c} \text{Br} \\ \\ \text{Br}-\text{C}-\text{H} \\ \\ \text{Br} \end{array}$

(Source: Ghazali, 1989)

2.6.2 Possible Reaction Pathway of THMs in Water Treatment

The National Environmental Board (1984) demonstrated a series of reactions of chloroform that might be produced during water treatment as shown in

Figure 2.6.

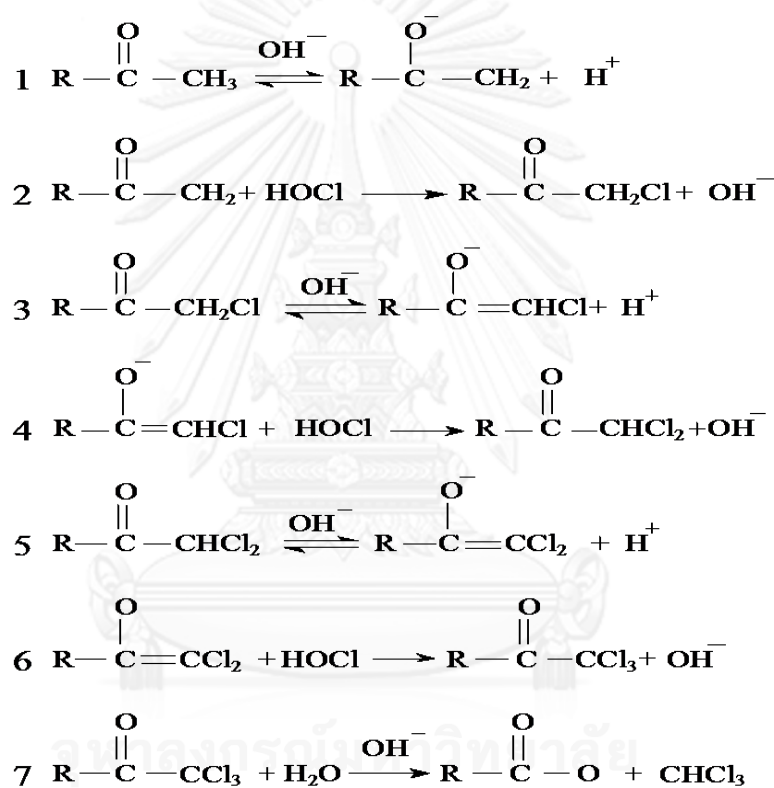


Figure 2. 6 Reaction steps of chloroform produced during water treatment.

2.6.3 Toxicity of disinfection by-products

The chemical risk of disinfection by-product can be exposed to human in several routes such as oral ingestion of DBP precursors in drinking water, inhalation of volatile DBP precursors during hand washing or showering and dermal

absorption (Wang *et al.*, 2007). THMs precursors have been effected both of carcinogenic and genotoxic in the organism of human life (kidney and liver).

In raw water, bromide can be formed of brominated-THMs, including bromodichloromethane, chlorodibromomethane, and bromoform. However, water treatment systems or water supplies could remove the bromide and organic precursors which was precursor to form DBPs. After chlorination, disinfection process in water supplies, this would result in the shift of THM species from chlorinated-THMs to brominated-THMs.

The previous research has shown that higher bromide and organic carbon concentrations have higher levels of DBPs risks with chlorination of raw water (Black *et al.*, 1996). For the research of Lee *et al.* (2004), they calculated and reported the cancer risks and hazard index of THMs in different exposure routes in Hong Kong. The oral ingestion exposed had highest risk with the dermal absorption and inhalation. Like a result was reported by Tokmak *et al.* (2004), which concluded that the highest risk was from the exposure to chloroform through oral ingestion too.

Other researchers found that the level of individual exposure to trihalomethanes depended on the routes and time of exposure to THMs by ingestion, inhalation and dermal absorption that people exposed (Villanueva *et al.*, 2006). They also mentioned that evaluation of one single exposure route such as ingestion might lead to misclassification of the total THMs (TTHMs) exposure. Some

another reported that THMs could be absorbed, metabolized, and eliminated by mammals after oral or inhalation exposure (IPCS, 2000).

The U.S. EPA computed human uptake levels of THMs in milligrams per year from air, food and drinking water employing as number of assumption. Chloroform were 64 mg/L in drinking water exposure, 9 mg/L in food exposure, and 20 mg/L in air exposure. Besides, the trihalomethanes was 85 mg/L in drinking water exposure.

United States Environmental Protection Agency (USEPA) fixed a maximum contaminant level (MCL) for total THMs (TTHMs) at 0.10 mg/L (USEPA, 1997). This standard applied to systems serving over 10,000 people. Owing to wide occurrence and potential health risks of DBPs, the USEPA proposed the Disinfectants/Disinfection By-Products (D/DBP) Rule in two points. The first one was 0.080 mg/L TTHM (MCLs of D/DBP Rule was proposed in 1994). Another one was 0.040 mg/L TTHM (MCLs of D/DBP Rule was proposed in 1994). Both required even lower MCLs for DBPS (USEPA, 1994).

Table 2. 3 Natural Primary Drinking Water Regulations establishing MCLs and MCLGs related to DBPs

Compound	MCLG (mg/L)	MCL (mg/L)	Potential Health Effects	Sources of Water Contamination
Chloroform	Zero ^a	see TTHMs	Cancer, liver, kidney, Reproductive effects	Drinking water chlorination and chloramination by-product
Bromodichloromethane	Zero ^b	see TTHMs	Cancer, liver, kidney, Reproductive effects	Drinking water chlorination and chlorination by-product
Dibromochloromethane	0.06 ^a	see TTHMs	Nervous system, liver, kidney, reproductive	Drinking water chlorination and chloramination by-product
Bromoform	Zero ^a	see TTHMs	Cancer, nervous system, liver, kidney effects	Drinking water ozonation, chloramination, and chlorination by-product
Total trihalomethanes ^c (TTHMs)	N/A	0.08 ^b	Cancer and other effects	Drinking water chlorination and chloramination by-product

(Source: 63 Federal Register 69390)

^a Finalized on December 16, 1998 (63 federal Register 69390) as established in 40 CFR 141.53.

^b Finalized on December 16, 1998 (63 federal Register 69390) as established in 40 CFR 141.64.

^c. Total trihalomethanes are the sum of the concentrations of chloroform, bromodichloromethane, dibromochloromethane and bromoform in mg/L

2.7 Fractionation

Many researchers have investigated the characteristics of dissolved organic matter (DOM) in leachate of landfills of different ages through chemical, spectroscopic, and elemental analyses. Humic acid (HA), fulvic acid (FA), and hydrophilic (Hyl) fractions were isolated and purified by the XAD-8 resin combined with the cation exchange resin method. The nitrogen contents in these isolated fractions were as follows: HA >Hyl> FA. (Shouliang *et al.*, 2008) Dissolved organic matter in water was characterized into two types that are hydrophilic and hydrophobic which are carbohydrates, protein, amino functional groups and fulvic-humic acids (Marhaba *et al.*, 2003).

The DOM fractionation and elemental analysis of isolated fractions showed that the aromatic components and the degree of humification increases with the age of the landfill. Berthe, Redon and Feuillade (2007) investigated the fractionations that were carried out using (i) XAD resins in order to divide the organic matter into several fractions according to the hydrophobic character of the molecules and (ii) an ultrafiltration protocol to divide the organic matter into several fractions according to the apparent molecular weight of molecules.

Leenheer *et al.* (2007) used xad-1 to absorb hydrophobic dissolved organic nitrogen; 0.5L xad-4 to absorb amphiphilic dissolved organic nitrogen, and 1L xad-4 to absorb hydrophilic bases and the fractionation process as shown in **Figure 2.7**.

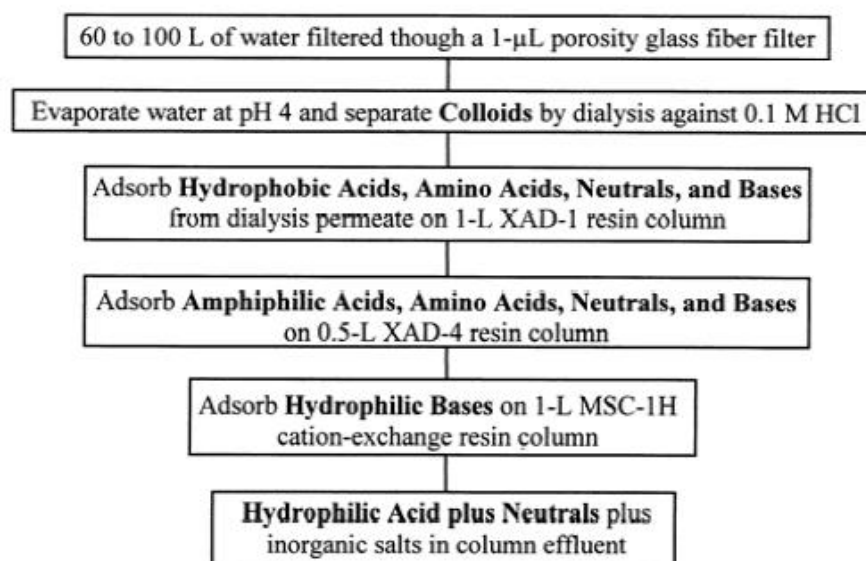


Figure 2. 7 The schematic of DOM fractionation.

For that, the method proposed by Aiken *et al.* (1992) and Croue *et al.* (1993) depending on the solubility of the organic compounds was applied. The protocol allowed the separation of the organic matter into three different fractions; each fraction grouping together molecules, which presented the same physicochemical properties. The fractionation of the dissolved organic matter was carried out using non-ionic resins in a series (DAX-8 and XAD-4). The DAX-8 resin has an acrylic nature and is slightly polar, whereas the XAD-4 resin has a similar structure to the styrenedivinybenzene type and was regarded as non-polar. The sample was successively passed through the DAX-8 resin and then through the XAD-4 resin as shown in **Figure 2.8**.

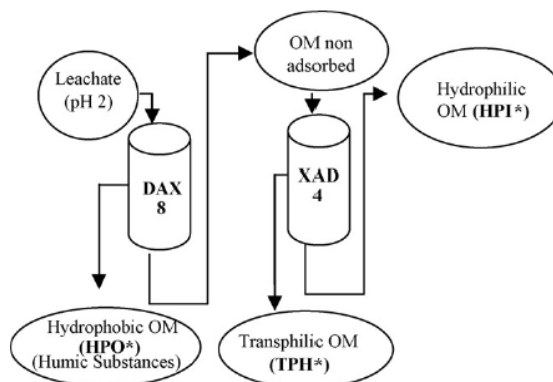


Figure 2. 8 Protocol of OM fractionation according to the hydrophobic character of molecules. (Berthe *et al.*, 2007)

This protocol allowed for the determination of hydrophobic-like substances (HPO*) adsorbed on DAX-8 resin. HPO* represented by the humic-like substances that was to say by the fulvic-like acids. The transphilic-like substances (TPH*) are adsorbed on XAD-4 resin. The hydrophilic-like substances (HPI*), which included the dissolved organic carbon were not adsorbed on these resins. The higher the percentage of hydrophobic-like substances, the more the leachate has an advanced state of humification. These different fractions of organic matter represented families of molecules whose structures were not well defined (Berthe *et al.*, 2007)

CHAPTER 3

METHODOLOGY

3.1 Source of Raw water

Chiang Mai is the largest and most culturally significant city in northern Thailand. It is located 700 km north of Bangkok, among the highest mountains in the country. The way of life of this province is influenced by its location along the Ping River, a major tributary of the Chao Phraya River.

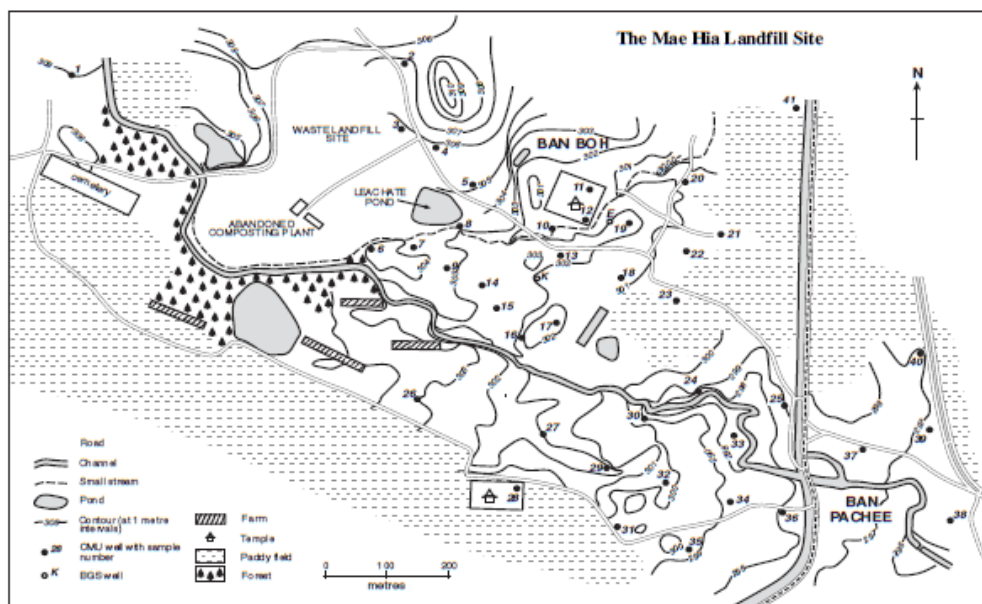


Figure 3. 1 A detailed sketch of the site and the location of the sampling wells
(Karnchanawong *et al.*, 1993).

The city relied on open dumping at the Mae-Hia site for waste disposal for over 30 years until it was closed in May 1989 because of the unacceptable environmental impacts on shallow groundwater wells in the locality of the site. Mae-Hia landfill site lied about 10 km southwest of the city of Chiang Mai and covers an area of approximately 0.21 km², of which 0.12 km² has been used for waste dumping (Klinck and Stuart, 1999). Nearby water sources has been contaminated with organic matters and hazardous substances (Karnchanawong *et al.*, 1993). **Figure 3.1** illustrates the detail of Mae-Hia landfill site and sampling location.

3.2 Sample collection

Shallow well water at the Mae-Hia open dumping landfill in Chiang Mai, Thailand, was collected. The sampling point was located downstream of the groundwater flow as shown in **Figure 3.2**. The area around the dumping site was used for residential housing and agricultures. This study concerned about impacts of the landfill on shallow well water quality and its consumption.

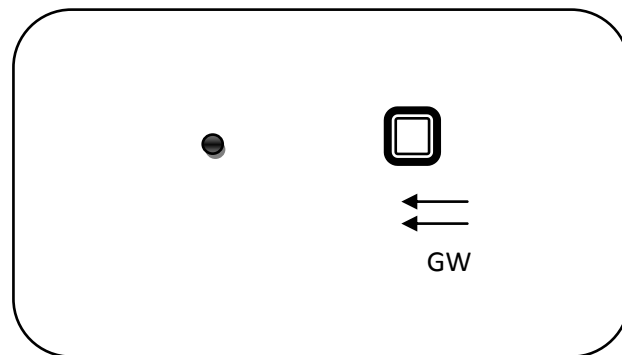



Figure 3. 2 Sampling point (downstream of the groundwater flow).

NOTE:

 = open dumping landfill
 = collection point

3.3 Experimental procedure



Figure 3. 3 Shallow well in the study.

Figure 3.3 illustrates the shallow well in Mae-Hia dumping site. The water samples were collected from this shallow well. Then, it was measured and utilized in a series of experiments in this study as shown in **Figure 3.4**.

- Firstly, the water samples were collected from contaminated shallow well water at Mae-Hia landfill site and then it was measured for pH and temperature.
- UV_{254} , ammonia, DOC, and TN were measured in water sample which was filtered by 0.7 GF/F and followed by 0.45 μm filter (PTFE).
- Water samples were passed through 0.7 GF/F filter paper and which were treated by two processes; (1) PAC adsorption process and (2) the hybrid process of PAC adsorption and ceramic membrane filtration.
- Organic matters in raw water, treated water by PAC adsorption, and treated water by hybrid process further fractionated in term of hydrophilic and hydrophobic fractions.
- Finally, sodium hypochlorite was employed during a chlorination process in a formation of DBP experiment. 0.1-0.2 mg/L of chlorine residual in 24 h were preferred.

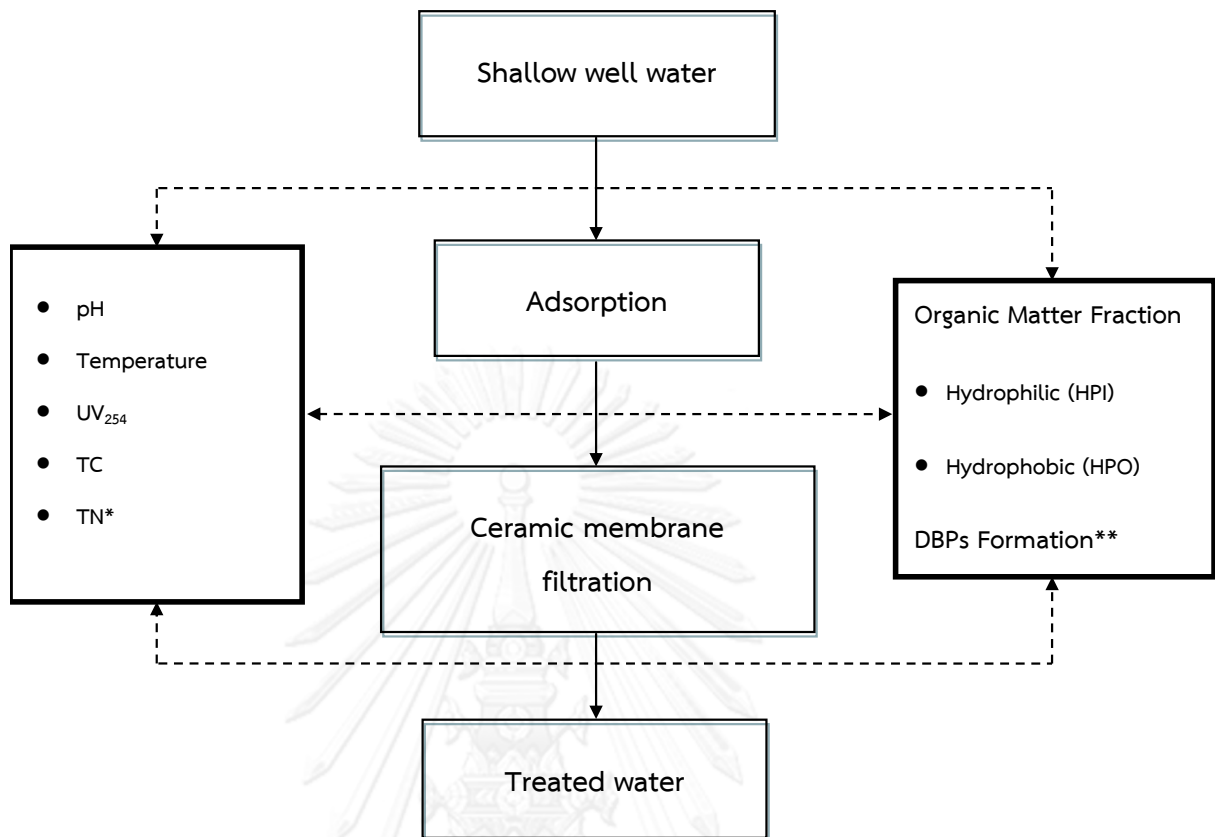


Figure 3. 4 The flow chart of the experimental framework of this study.

*only measured in kinetic process.

**measured in shallow well water and hybrid process treated water.

3.4 Kinetic Adsorption Experiment

The powder activated carbon (PAC) was investigated in this study has been characterized by Prarat et al (2011). They mentioned the physiochemical characteristics of PAC adsorbent as shown in Table 3.1.

Table 3. 1 Characteristics of PAC adsorbent

Adsorbent	Surface functional group	Surface characteristic	Pore size as diameter (nm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	pH_{PZC}	Contact angle (Θ)
PAC	Carboxyl, phenyl and oxygen-containing groups	Hydrophobic	1.90	980	9.5	58.34

(Source: Punyapalukul, 2009).

The kinetic adsorption used PAC as adsorbent to removed organic matters, i.e. dissolved organic carbon (DOC) from shallow well water contaminated with landfill leachate. The PAC was prepared by washing it with pure water and baking 48 h at a temperature of 105°C, then it was kept in a desiccator. The water samples were passed through 0.7 GF/F filter paper before kinetic adsorption process.

The equilibrium contact time for DOC adsorption was varied (0 min., 10 min., 30 min., 1 h, 6 h, 12 h, and 24 h). The adsorption process was carried out by placing shallow well water into 500 mL flasks. Each flask contained 350 mL of shallow well water and 0.0070 g of PAC (20 mg/L) and they were shaken with a rotary shaker at 200 rpm, at a temperature of 25°C. After that, they were filtered by 0.45 μm filter (PTFE) for measured UV_{254} , DOC.

The further various dosages of PAC was prepared as similar as the equilibrium contact time process including 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 500

mg/L, and 1000 mg/L, respectively. The adsorption process was carried out by placing shallow well water into 500 mL flasks. Each flask was contained 200 mL of water samples. They were shaken with a rotary shaker at 200 rpm, at a temperature of 25°C until it reached equilibrium contact time. After that, they were filtered by 0.45 µm filter (PTFE) for UV₂₅₄, DOC measuring.

3.5 Treatment process

(1) PAC adsorption process

PAC adsorption process was followed the kinetic adsorption experiment. After finding the equilibrium contact time, the shallow well water samples contaminated with landfill leachate of 3.5 liters were treated by PAC and they were fractionated into hydrophilic fraction and hydrophobic fractions by DOM fractionation process.

(2) Hybrid process of PAC adsorption and ceramic membrane filtration

Hybrid process of PAC adsorption and ceramic membrane filtration was examined with 3.5 liters of the shallow well water contaminated with landfill leachate. Ceramic membrane filtration of the water sample was done without PAC separation. Moreover, ceramic membranes have been used for separating the large particles, colloidal materials (Luque *et al.*, 2008; Tomaszewska *et al.*, 2002). Hence, the PAC adsorbent this study was separated by ceramic membrane microfiltration.



Figure 3. 5 Ceramic membrane with pore size diameter of 0.1 μm .

Advanced ceramic membrane with 0.1 μm pore size diameter, total surface area of 0.042 m^2 , 3 centimeters in diameter, 10 centimeters height and 55 tubular channels was tested as **Figure 3.5**. It was utilized under up flow mode of operation and controlled pressure of 100 kPa. The hybrid process of PAC adsorption and ceramic membrane filtration was demonstrated in **Figure 3.6**. The treated water was fractionated into hydrophilic fraction and hydrophobic fractions by DOM fractionation process.

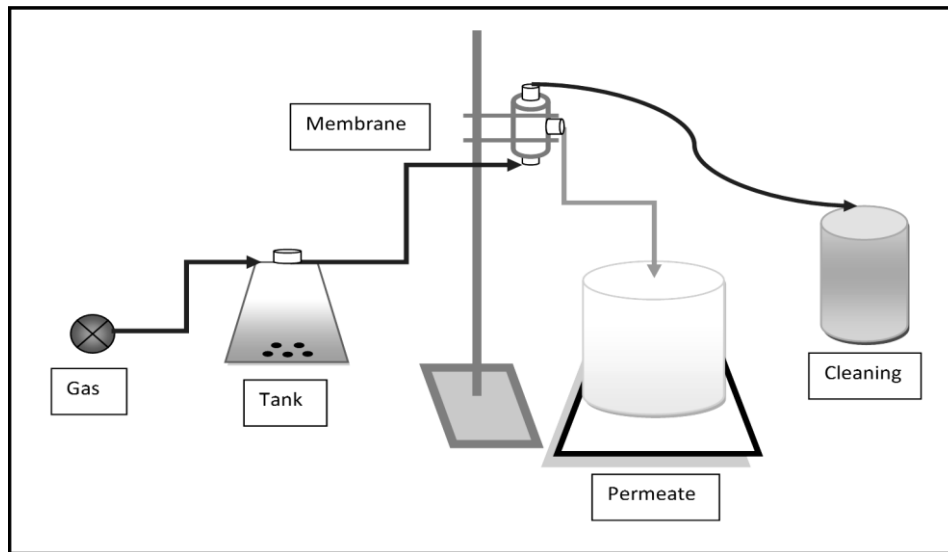


Figure 3. 6 The schematic of the hybrid process with PAC adsorption and CM membrane filtration process of this study.

3.6 DOM Fractionation using resin fractionation

The DOM fractionation procedure that was used in this study are based on a procedure used by Leenheer, 1981; Leenheer, 2007. The preparation of the DAX-8 resin and fractionation procedure is described below.

Preparation of DAX-8 Resin

- Put DAX-8 resin into beaker with 0.1N NaOH for 24 h and 24 h of milli-Q water
- Extraction with 24 hours of Acetone and Hexane respectively for in a set of Soxhlet extraction instrument.

- The refined DAX-8 resin was transferred into columns in slurry of Methanol.
- The packed resin was rinsed with two times 250 mL of 0.1 N each NaOH and HCl, respectively. Finally finished with milli-Q water until the conductivity and dissolve organic carbon (DOC) of each column were below 10 us/cm and 0.2 mg/L, respectively.

For the resin adsorption procedure, 3.0 liters of the filtered water sample was categorized the organic matter into the two organic fractions, the hydrophilic (HPI) and hydrophobic (HPO) fractions by using DAX-8 resin (Leenheer, 1981). The water sample was filtrated by 0.7 μm GF/F and hydrophilic sample that was acidic (pH 2) by H_2SO_4 then it was passed through the columns containing DAX-8 resin and come out at the bottom of columns. After samples were run through the columns, they were rinsed with 100 mL milli-Q water and eluted with 250 mL of 0.1 NaOH first, and follow by 50 mL 0.01 N NaOH. The solution eluted from the DAX-8 resin was defined as hydrophobic (HPO). A diagram of the resin fractionation procedure was presented in **Figure 3.7**. The samples were analyzed for their DOC by using UV_{254} and a TOC analyzer.

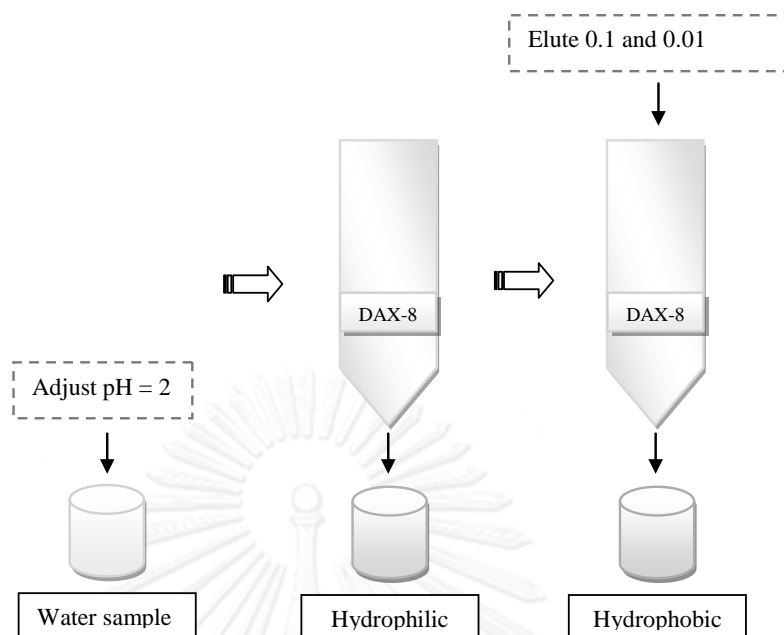


Figure 3. 7 Diagram of the fractionation process.

3.7 Formation of DBP precursors

The water samples, raw water; treated water by PAC adsorption; and treated water by hybrid process needed the fractionation process. Moreover, sodium hypochlorite was employed during a chlorination process in a formation of DBP experiment. 0.1-0.2 mg/L of chlorine residual in 24 h were preferred. Furthermore, all of samples were filtered by 0.45 μm filter tubes (PTFE) before measured THMs by Agilent 6890 Series Gas Chromatographic with ECD detector in accordance with standard method 5710.

The THMs species detected during the experiment are shown in **Table 3.2**. In addition to analyzed THMs the details are described below. Furthermore, the analytical methods and instrument for all parameters are shown in **Table 3.3**.

Table 3. 2 Detected THMs species during the experiment.

Parameter	Detected THMs Compounds
TTHM	Chloroform, Bromodichloroform, Chlorodibromoform, and Bromoform

Table 3. 3 Analytical methods and Instruments.

Parameters	Instrument	Note
pH	pH meter	Model F-21 Horiba
Temperature (°c)	Thermometer	-
Alkalinity (mg/L)	Titration	-
Turbidity (FAU)	EC/HACH turbidity meter	Model 2000
UV ₂₅₄	Spectro Photometer UV/VIS spectrophotometer	Perkin-Elmer model lambda 25
NH ₃ -N (mg/L)	DR/890 colorimeter	
TN	TOC analysis	TOC-V _{CPH}
DOC	TOC analysis	TOC-V _{CPH}
THMs	GC/ECD detector	Agilent 6890 Series

3.8 Analytical method

1. TOC/TN analysis

DOC and TN were measured by using TOC analyzer (TOC-V_{CPH}, Shimadzu, Japan).

2. UV₂₅₄ analysis

The UV procedure following method 415.3 from USEPA that the samples were passed through a 0.45- μ m filter tube (PTFE) and transferred to a quartz cell. The water samples were placed in a spectrophotometer or UV-VIS spectrometer, model-Lambda 25 (Perkin-Elmer, USA) to measure the UV absorbance at 254 nm and reported in 1/cm.

3. Trihalomethanes (THMs)

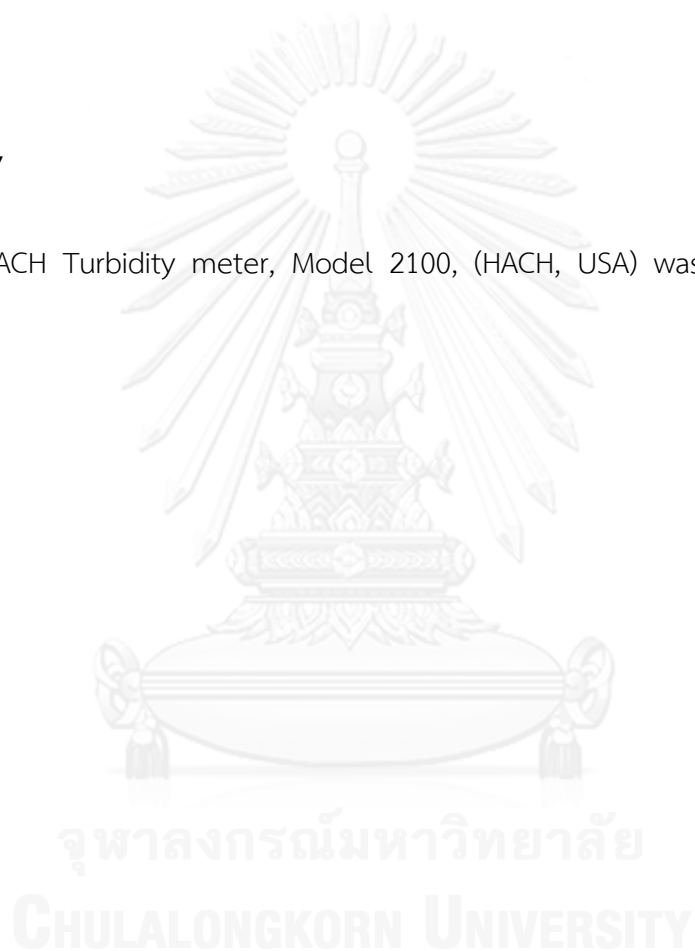
THMs were measured by Agilent 6890 Series Gas Chromatographic with ECD detector in accordance with standard method 5710, formation of THMs and other DBPs.

4. pH

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

5. Turbidity

A HACH Turbidity meter, Model 2100, (HACH, USA) was used for turbidity measuring.



CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characteristics of shallow well water

Shallow well water in this study was selected and observed in the area of closed dumping landfill at Mae-Hia in Chiang Mai Province, Thailand. Water parameters of shallow well water in this study and water quality of other researches are shown in **Table 4.1**.

4.1.1 pH and Alkalinity

pH of shallow well water was observed at 7.7-8.0, which was a weak base. The Mae-Hia landfill has been closed almost 25 years. Shallow well water, as well as, groundwater nearby the landfill has been contaminated from landfill leachate (Jiarisikul, 2003). In the previous study, pH of the shallow well water was found in a range of 7.43-7.92. The degradation process increased the solubility of chemical substances and decreased in the amount of wastes. It was reported that in a couple years of dumping, the pH of landfill leachate was acidic because the degradation in anaerobic process. For old landfill, the destruction of fatty acids resulted in increasing of pH and alkalinity (Andreottola *et al.*, 1990).

In case of alkalinity, the shallow well water was observed at 1230-1290 mg/L as CaCO₃ that represented the compounds in the water such as a

carbonate, bicarbonate and hydroxide that could be reacted with acid. The bicarbonate was the most of functional group which was a source of alkalinity (Hem, 1985). Like another research in the same field, they found alkalinity in a range of 32-1500 mg/L as CaCO_3 for water samples nearby Mae-Hia landfill (Karnchanawong *et al.*, 1993).

4.1.2 Electrical Conductivity

Electric conductivity (EC) of shallow well water in this study was 4.26-5.61 ms/cm. Karnchanawong *et al.* (1993) observed EC in a range of 0.8-11.0 ms/cm for water samples nearby Mae-Hia landfill. High EC could be due to a contamination of the shallow well water from landfill leachate.

4.1.3 Color and Turbidity

Color of the shallow well water was 85 Pt-Co. Color of the shallow well water was yellow to slightly brown. It could be due to a presence of organic matters in the shallow well water (Luque *et al.*, 2008).

Turbidity was the cloudiness or haziness of a fluid caused by the particles such as colloids, bacteria, organic and inorganic matters including total suspended or dissolved solids in the water (Luque *et al.*, 2008). Turbidity of the shallow well water in this study was 14-16 FAU.

4.1.4 Dissolved organic carbon (DOC)

DOC concentration was 11.4-12.6 mg/L. It was indicated that the shallow well water could be highly polluted by landfill leachate. It was stated that high DOC concentrations of water samples nearby landfill site were usually polluted by the landfill leachate (Ziyang and Youcai, 2007).

4.1.5 UV absorbance at wavelength 254 nm (UV₂₅₄)

UV absorbance at wavelength 254 nm (UV₂₅₄) was representative the group of aromatic compounds in organic matters (APHA *et al.*, 1995; Ha *et al.*, 2004). Aromatic, carboxyl, carbonyl, methoxly and aliphatic units were compounds of humic molecules and could represent the hydrophobic fraction of natural organic matter (Stevenson, 1982). Thus, that compounds of organic matter in shallow well water was indicated that HPO fraction in the water. UV₂₅₄ of the shallow well water was 1.545-1.577 cm⁻¹. UV₂₅₄ was very high because of the concentration of aromatic compounds presented in the shallow well water.

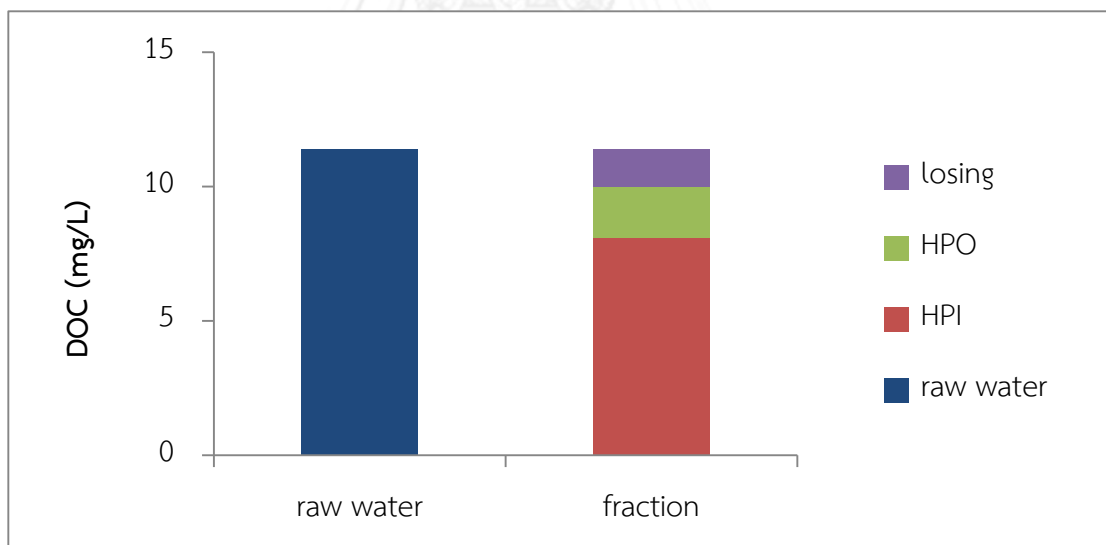
4.1.6 Specific ultraviolet absorbance (SUVA)

Specific ultraviolet absorbance is the ratio of absorbance at 254 nm (UV₂₅₄) divided by the DOC concentration. SUVA of the shallow well water was 12.31-13.83 L/mg-m. This parameter was used to indicate humic content in the water

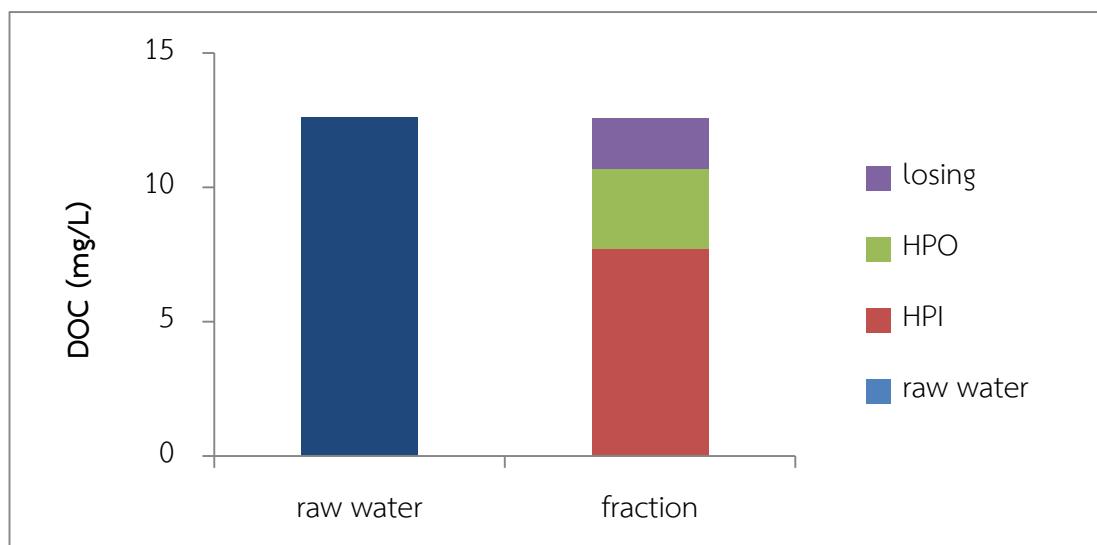
samples (Stevenson, 1982 and Christman *et al.*, 1983).

4.1.7 Organic matter fractionation

From the results of organic matter fractionation, HPI and HPO fractions of the shallow well water were 7.7-8.1 and 1.9-3.0 mg/L, respectively (Recovery was 84.9-87.7%). Therefore, the organic matters contained mainly hydrophilic compounds compared with hydrophobic compounds. Organic fractions in the shallow well water are shown in **Figure 4.1**.



(a)



(b)

Figure 4. 1 Organic fractions in the shallow well water

(a) Organic fraction in December, 2013.

(b) Organic fraction in February, 2014.

Table 4. 1 Water parameters of shallow well water in this study and water quality of other researches.

Water source	Parameters										Reference
	pH	Temp (°C)	UV ₂₅₄ (cm ⁻¹)	EC (ms/cm)	Turbidity (FAU)	Color (Pt-Co)	Alkalinity (mg/L)	DOC (mg/L)	TN (mg/L)	SUVA (L/mg-m)	
Mae-Hia, Chiang Mai, Thailand	8.0	25.0	1.6	5.6	14.0	NA	1230.0	11.4	78.7	13.8	This study (December, 2013)
Mae-Hia, Chiang Mai, Thailand	7.7	25.0	1.5	4.3	16.0	85.0	1290.0	12.6	NA	12.3	This study (February, 2014)
Mae-Hia, Chiang Mai, Thailand	5.9-8.7	23.0-29.5	NA	0.08-11.0	NA	0-1500	32-1500	1.1-630	NA	NA	Karnchanawong <i>et al.</i> , 1993
Beishenshu, Beijing, China	8.0	NA	NA	31.9	NA	NA	15600.0	649.0	NA	1.9	Xu <i>et al.</i> , 2006
Laogang, Shanghai, China	7.1	NA	NA	2.8	NA	1000.0	NA	NA	NA	NA	Ziyang and Youcai., 2007

4.2 Kinetic adsorption

4.2.1 Dissolved organic carbon

A result is shown in **Figure 4.2**. For the optimum contact time of kinetic adsorption process, 20 mg/L of PAC was investigated as an adsorbent. During the first 30 minutes, the adsorption of organic matter in term of DOC was not observed. Then, the adsorption of DOC was increased dramatically and reached the maximum adsorption the contact time of 6 hours (20 mg DOC removal/g PAC). After 6 hours, the adsorption of DOC was decreased. This might be due to desorption of DOC from the PAC surface. Hence, the equilibrium contact time was at 6 hours.

In addition, PAC dosages were further varied at 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 500 mg/L, and 1000 mg/L, respectively, to observe their efficiencies on DOC removal as shown in **Figure 4.3**. At the equilibrium contact time of 6 h, the removal of DOC was increased significantly when PAC dosage increased. The mg DOC removal/g PAC were 80, 100, 180, 180, 240, 1040, and 1400, respectively.

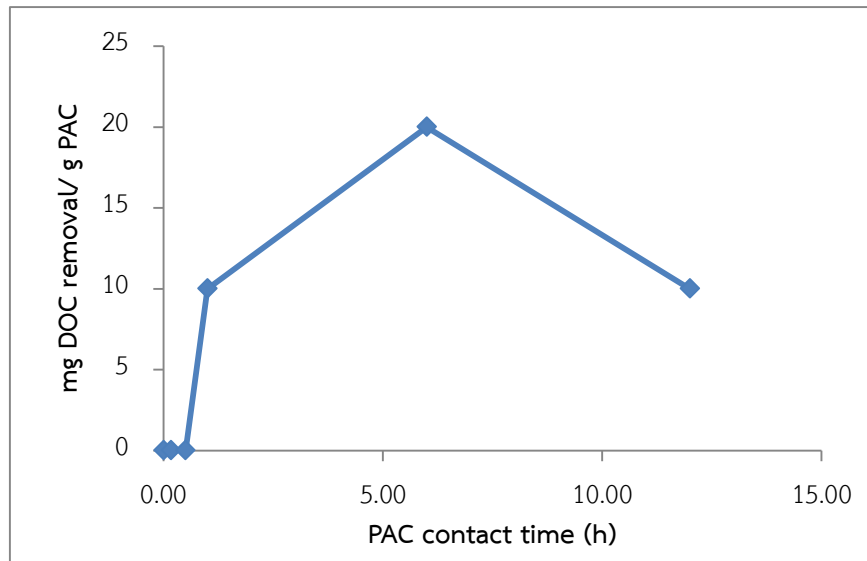


Figure 4. 2 Kinetic adsorption of PAC.

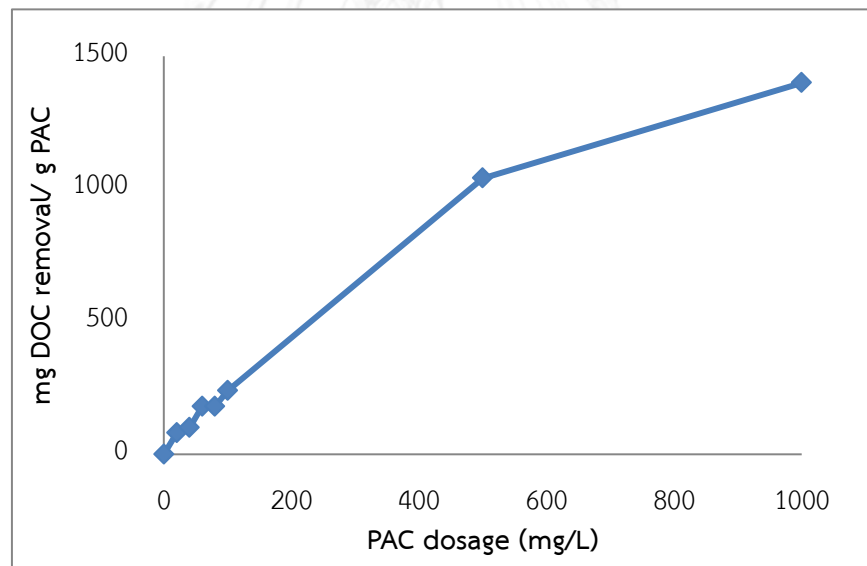


Figure 4. 3 DOC adsorption at various PAC dosages.

4.2.2 UV absorbance at wavelength 254 nm (UV_{254})

At 20 mg/L of PAC, the results of UV_{254} absorbance are shown in

Figure 4.4. During the kinetic adsorption experiment, UV_{254} were decreased from 1.567 to 1.475 cm^{-1} . It meant that the aromatic compounds in the shallow well water were partially adsorbed by PAC and might be due to the degradation of the compounds.

In addition, PAC dosages were further varied at 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 500 mg/L, and 1000 mg/L, respectively, to observe their reduction of UV_{254} as shown in **Figure 4.5**. At the equilibrium contact time of 6 h, the value of UV_{254} was decreased significantly when PAC dosage increased. UV_{254} at PAC dosages of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 500 mg/L, and 1000 mg/L were 1.488, 1.424, 1.380, 1.337, 1.289, 0.720, and 0.471 cm^{-1} respectively. Therefore, it was found the equilibrium dosage at 1000 mg/L of PAC adsorbent.

Therefore, the kinetic adsorption and further varies of PAC dosages could remove the HPO fraction well, when dosage of PAC adsorbent was increased and had the proper of contact time. and it might be due to co-process of the degradation of the aromatic compounds and other substances (Stevenson, 1982).

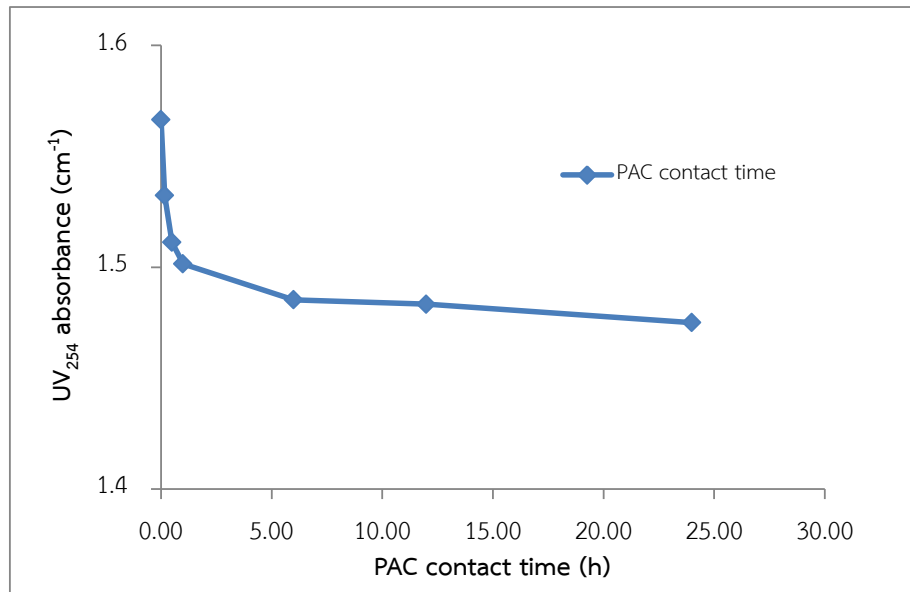


Figure 4. 4 Efficiencies of various contact time of PAC on UV₂₅₄ removal.

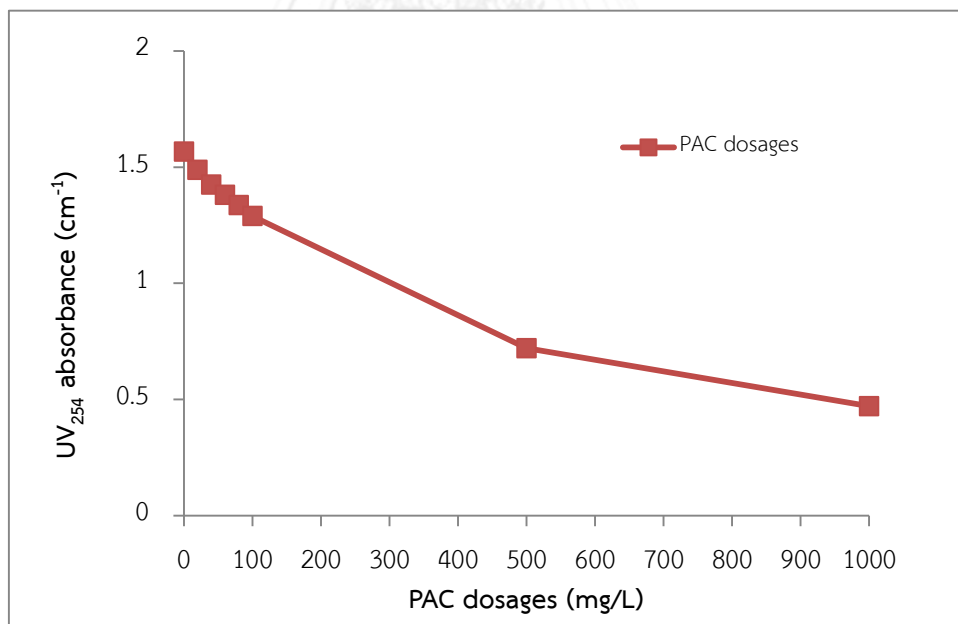


Figure 4. 5 Efficiencies of various dosages of PAC on UV₂₅₄ removal.

4.2.3 Adsorption isotherm

The adsorption isotherm was done with the difference dosages of PAC adsorbent and DOC concentration in each dosage. The result of Langmuir isotherm was illustrated in **Figure 4.6**.

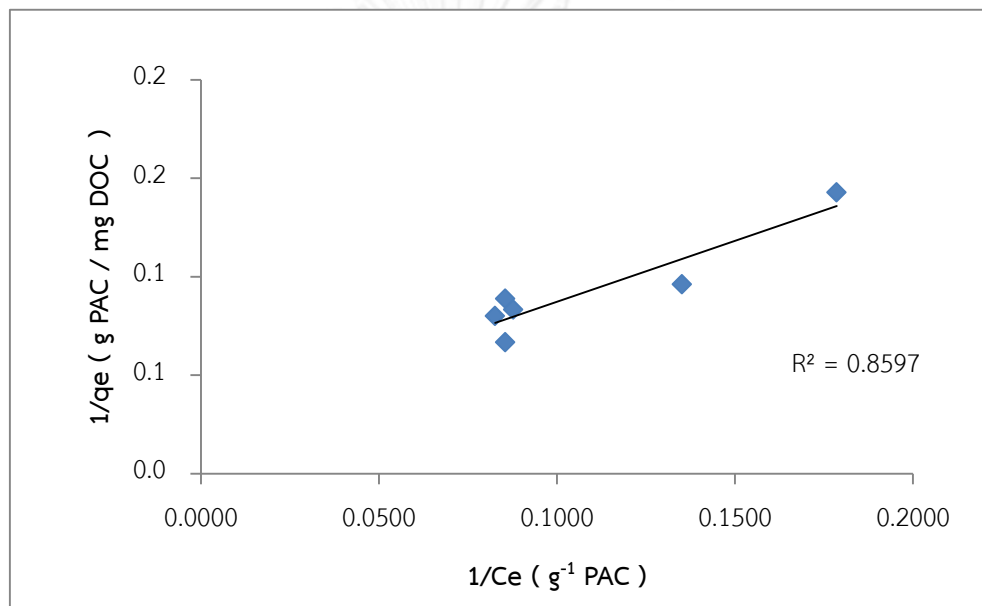


Figure 4. 6 the adsorption isotherm

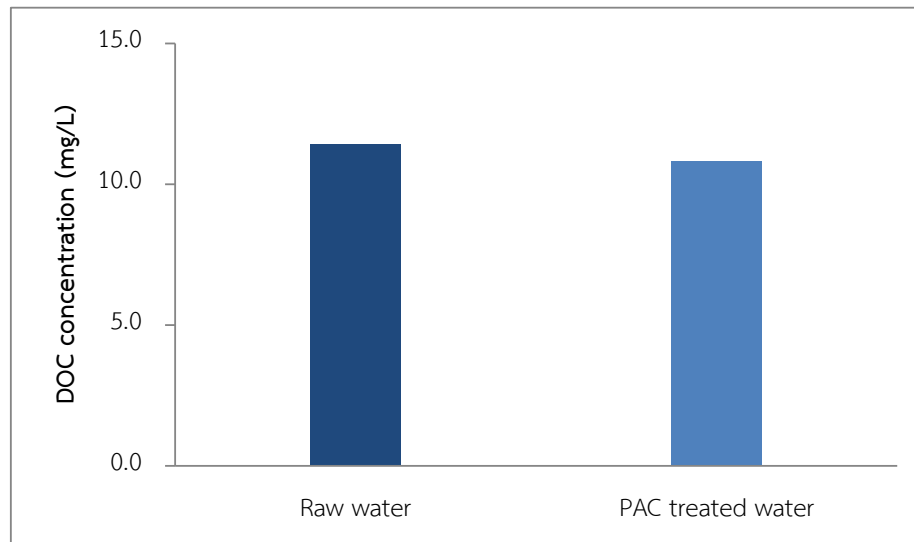
4.3 Treatment processes

4.3.1 PAC adsorption process

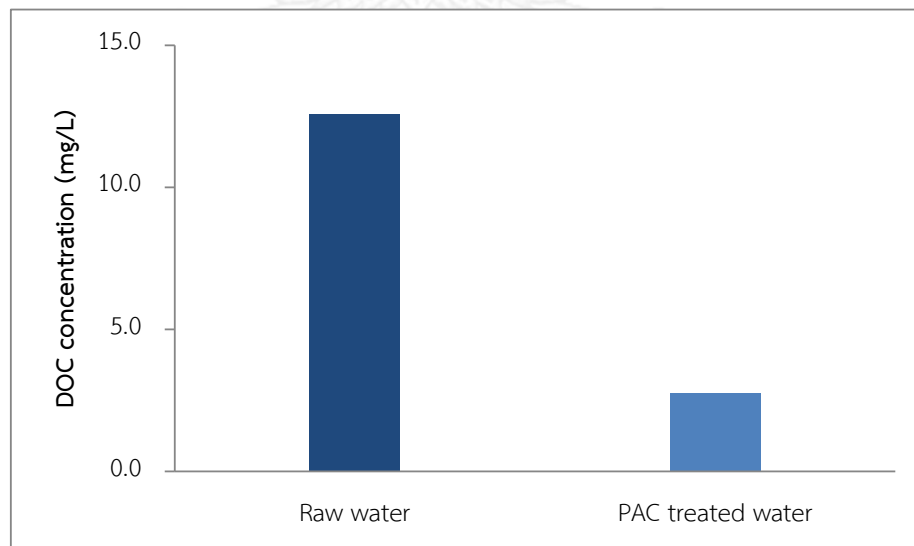
4.3.1.1 Dissolved organic carbon

Dissolved organic carbon (DOC) was investigated in this study. Raw shallow well water contained 11.4-12.6 mg/L of DOC. At PAC dosage of 20 mg/L, DOC in treated water was 10.8 mg/L. It gave poorly removal of DOC (5.3 % DOC removal). In case of PAC dosage of 1000 mg/L, DOC in treated water was 2.8 mg/L (78.1% DOC removal). It was found that the treatment by PAC adsorption at higher

dosage provided significantly high DOC removal efficiency. The results of DOC removal are illustrated in **Figure 4.7**.



(a)



(b)

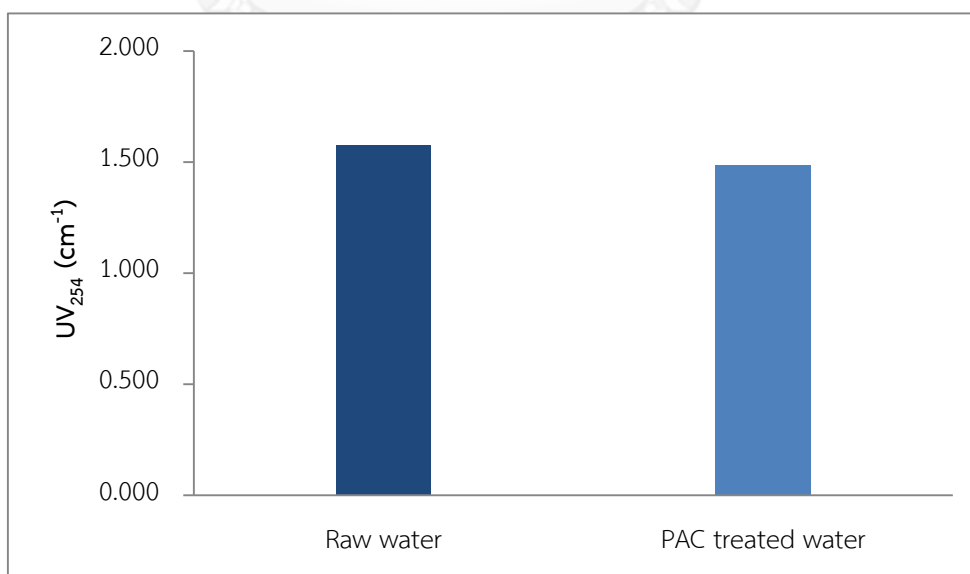
Figure 4. 7 DOC concentrations in water samples.

(a) Low dosage of PAC.

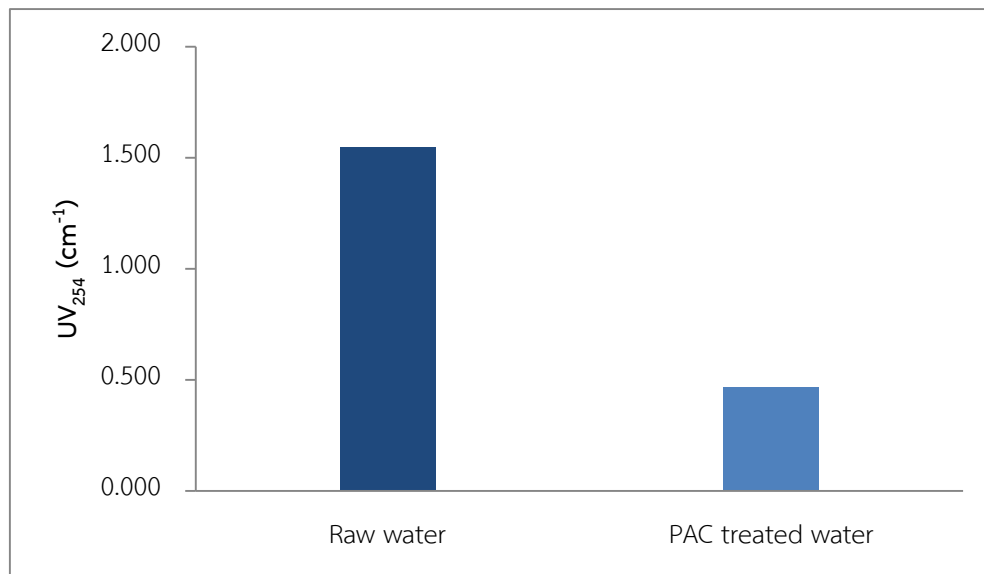
(b) High dosage of PAC.

4.3.1.2 UV absorbance at wavelength 254 nm (UV_{254})

Raw shallow well water was observed with 1.545-1.577 cm^{-1} of UV_{254} . At PAC dosage of 20 mg/L, UV_{254} in treated water was 1.485 cm^{-1} . It contributed very low removal of UV_{254} . In case of PAC dosage of 1000 mg/L, UV_{254} in treated water was 0.467 cm^{-1} . It was found that the aromatic compounds in water sample could be treated by PAC adsorption effectively. Higher PAC dosage provided significantly high UV_{254} removal efficiency. The results of UV_{254} removal are demonstrated in **Figure 4.8**.



(a)



(b)

Figure 4. 8 UV₂₅₄ in water samples.

(a) Low dosage of PAC.

(b) High dosage of PAC.

4.3.1.3 Organic matter fractionation

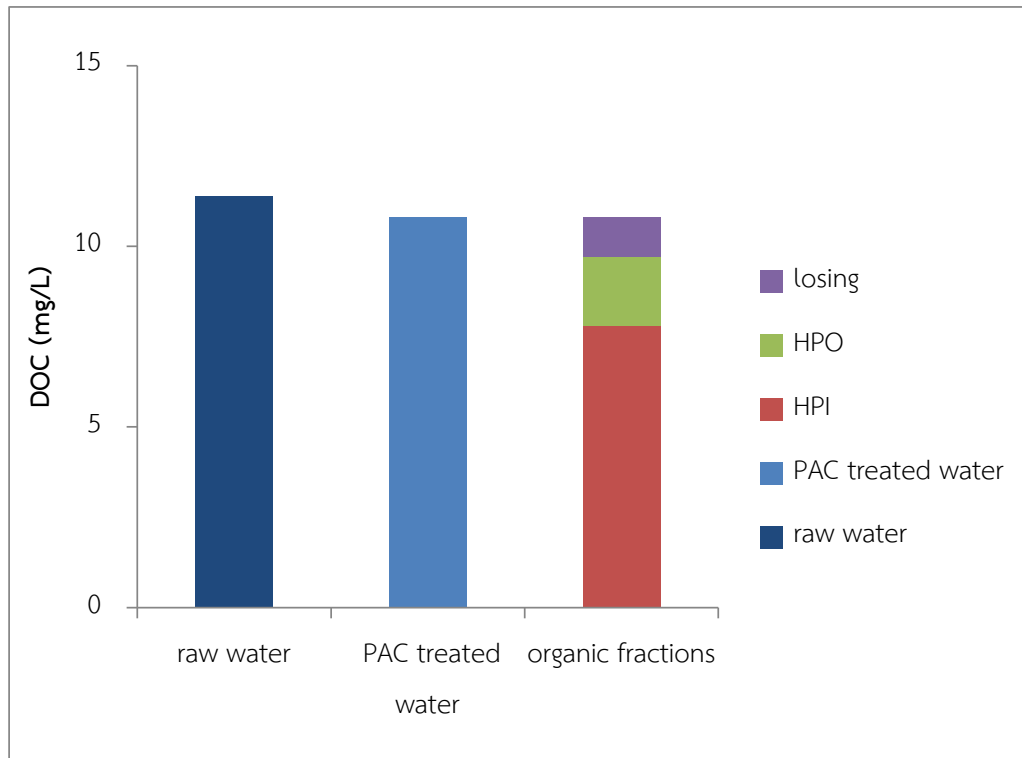
For the results of organic matter fractionation of low PAC dosage (20 mg/L PAC) experiment, HPI and HPO fractions of raw shallow well water were 7.8 and 1.9 mg/L of DOC, respectively. It was found 89.8% DOC recovery in low PAC process that means the percent losing was below 15% (% acceptable). Moreover, it was found that HPI and HPO removals were 3.7% and 0.0%, respectively.

For the results of organic matter fractionation of high PAC

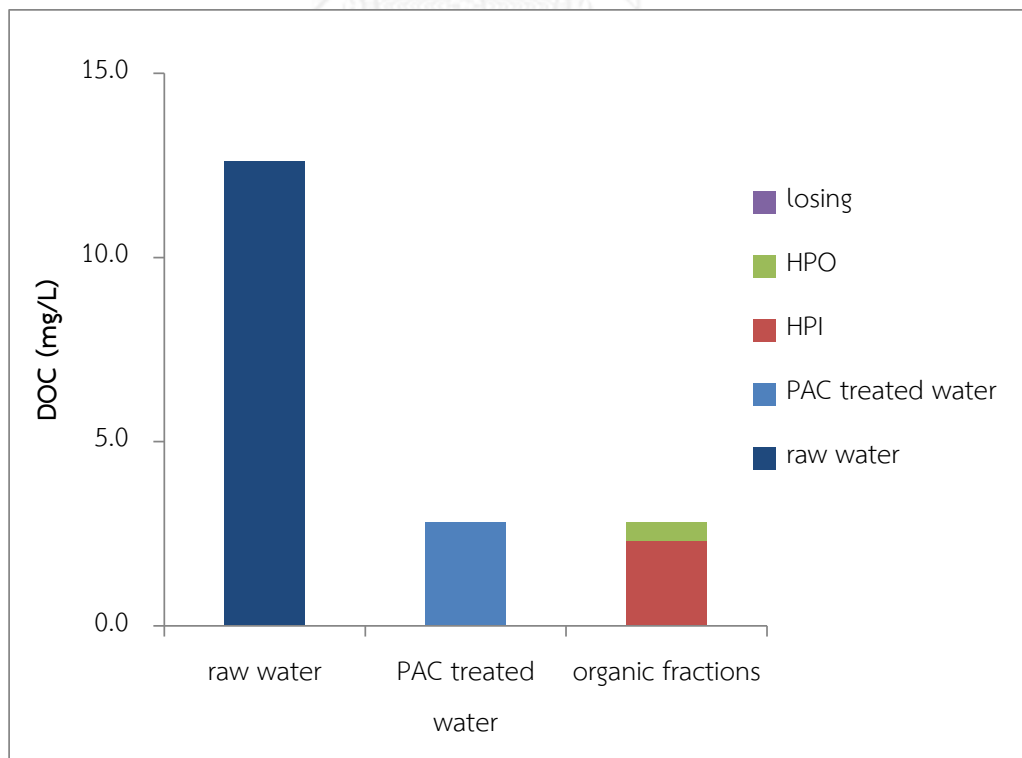
dosage (1000 mg/L PAC) experiment, HPI and HPO fractions of raw shallow well water were 2.3 and 0.5 mg/L of DOC, respectively. It was found 100.0% DOC recovery in high PAC process. Furthermore, it was found that HPI and HPO removals were 70.0% and 83.4%, respectively.

The obtained results related with the study of Jeong *et al* (2011). They found that HPI removal of organic matter fraction was significantly higher than that of HPO at low PAC concentration (<250 mg/L). However, HPO removal could be increased more than HPI removal when the high PAC concentration (>2500 mg/L) was used.

Organic fractions at low and high PAC dosage experiments are shown in **Figure 4.9**.



(a)



(b)

Figure 4. 9 The ratio of DOC fraction in PAC adsorption as treated water.

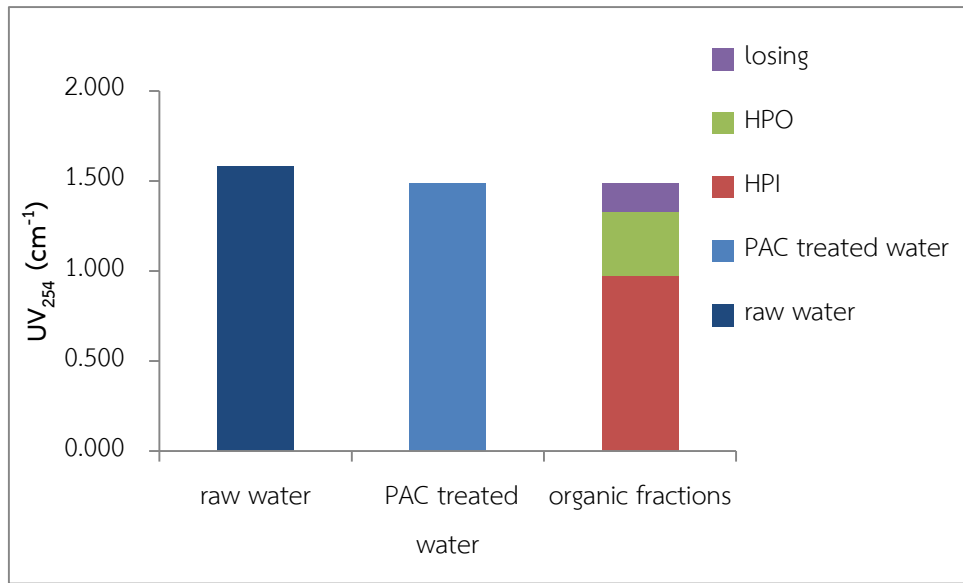
(a) Organic fraction with low dosage of PAC.

(b) Organic fraction with high dosage of PAC.

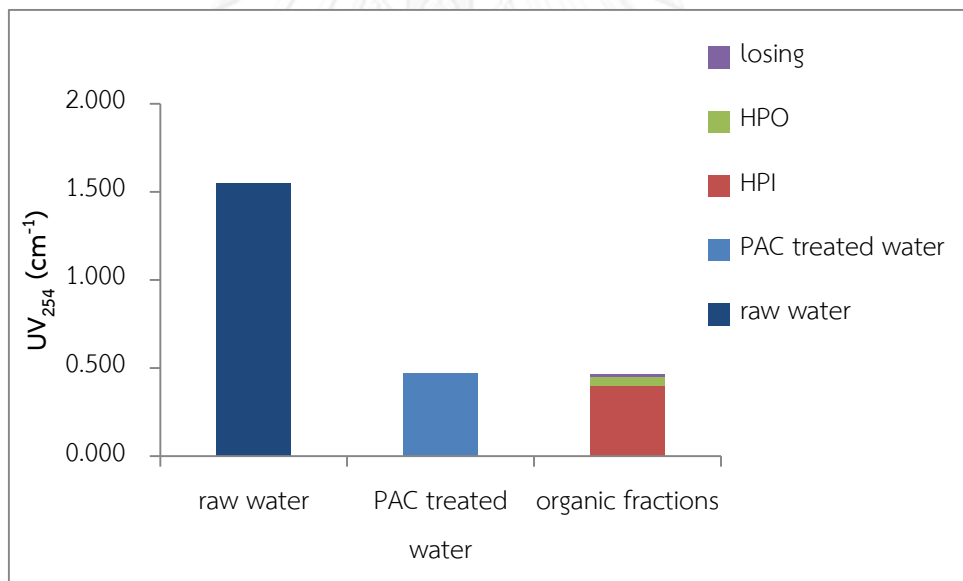
For the results of organic matter fractionation of low PAC dosage (20 mg/L PAC) experiment, UV_{254} values of HPI and HPO fractions of treated water were 0.974 and 0.535 cm^{-1} , respectively. It was found that the organic matter fractions were 5.7 and 6.1% UV_{254} removal in low PAC process, respectively.

Beside the organic matter fractionation of high PAC dosage (1000 mg/L PAC) experiment, HPI and HPO fractions of treated water were 0.400 and 0.053 cm^{-1} , respectively. It was found that the organic matter fractions were 58.2 and 86.0 % UV_{254} removal in high PAC process, respectively.

Organic fractions for UV_{254} at low and high PAC dosage experiments are presented in **Figure 4.10**.



(a)



(b)

Figure 4. 10 The effect on dosages of PAC with UV₂₅₄.

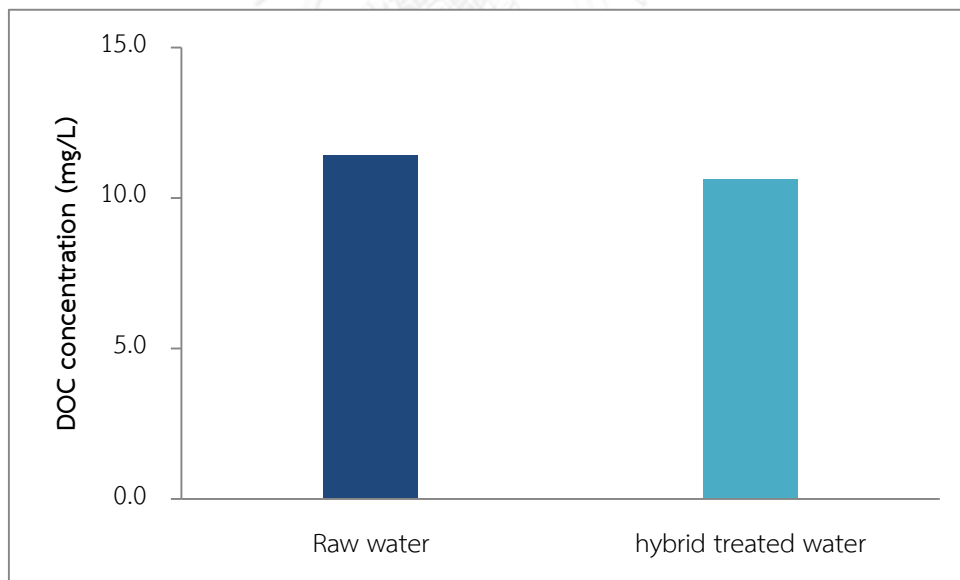
(a) Low dosage of PAC.

(b) High dosage of PAC.

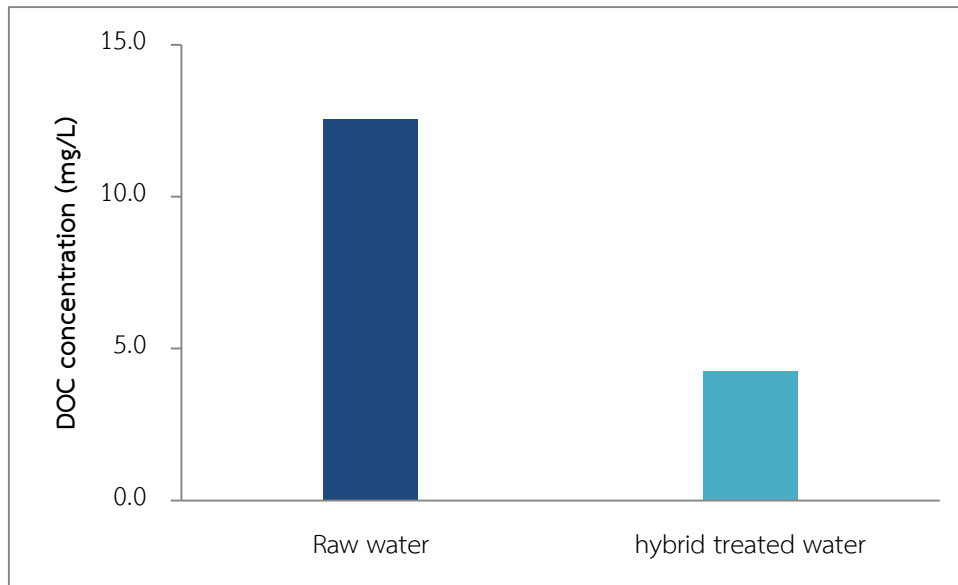
4.3.2 Hybrid process

4.3.2.1 Dissolved organic carbon

Dissolved organic carbon (DOC) was investigated in this study. Raw shallow well water was contained 11.4-12.6 mg/L of DOC. At PAC dosage of 20 mg/L, DOC in treated water by hybrid process was 10.6 mg/L. It gave poorly removal of DOC (7.0 % DOC removal). In case of PAC dosage of 1000 mg/L, DOC in hybrid process treated water was 4.3 mg/L (66.1% DOC removal). It was found that the treatment by PAC adsorption at higher dosage provided significantly high DOC removal efficiency. The results of DOC removal are shown in **Figure 4.11**.



(a)



(b)

Figure 4. 11 DOC concentrations in water samples.

(a) Low dosage of PAC.

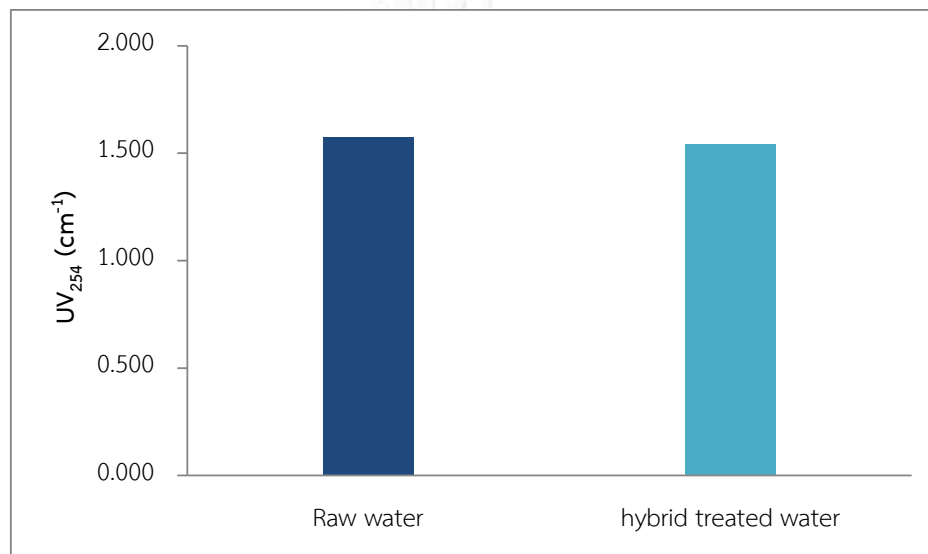
(b) High dosage of PAC.

4.3.2.2 UV absorbance at wavelength 254 nm (UV_{254})

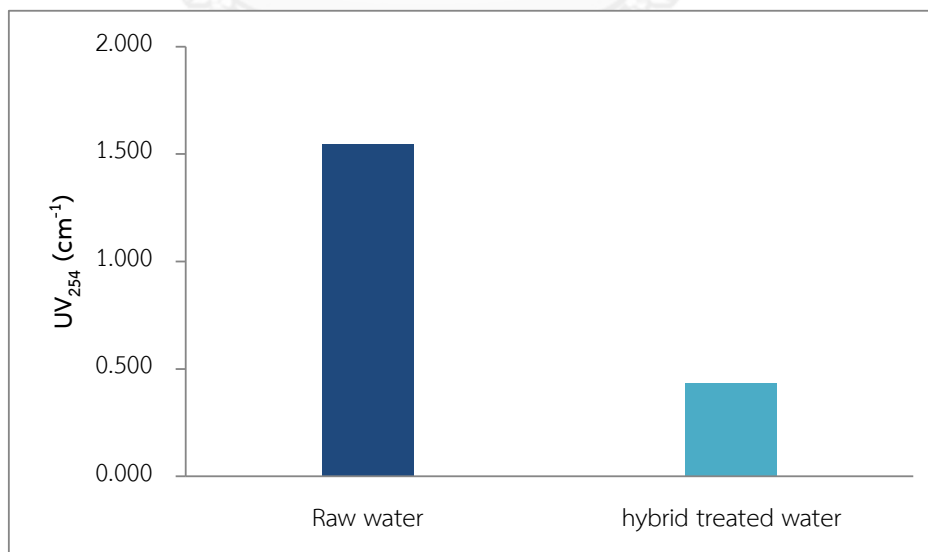
Raw shallow well water was observed with $1.545\text{-}1.577\text{ cm}^{-1}$ of UV_{254} . At PAC dosage of 20 mg/L, UV_{254} in PAC treated water was 1.485 cm^{-1} . It contributed very low removal of UV_{254} . In case of PAC dosage of 1000 mg/L, UV_{254} in treated water was 0.467 cm^{-1} .

For the results of hybrid process, treated water was 1.542 cm^{-1} at low PAC dosage (20 mg/L). The treated water by PAC adsorption and treated water by hybrid process are alike. In case of 1000 mg/L of PAC dosage, UV_{254} in treated

water was 0.436 cm^{-1} . It was found that the aromatic compounds in water sample could be removed by higher PAC dosage of PAC adsorption. The results of UV_{254} removal are demonstrated in **Figure 4.12**.



(a)



(b)

Figure 4. 12 UV_{254} in water samples.

(a) Low dosage of PAC.

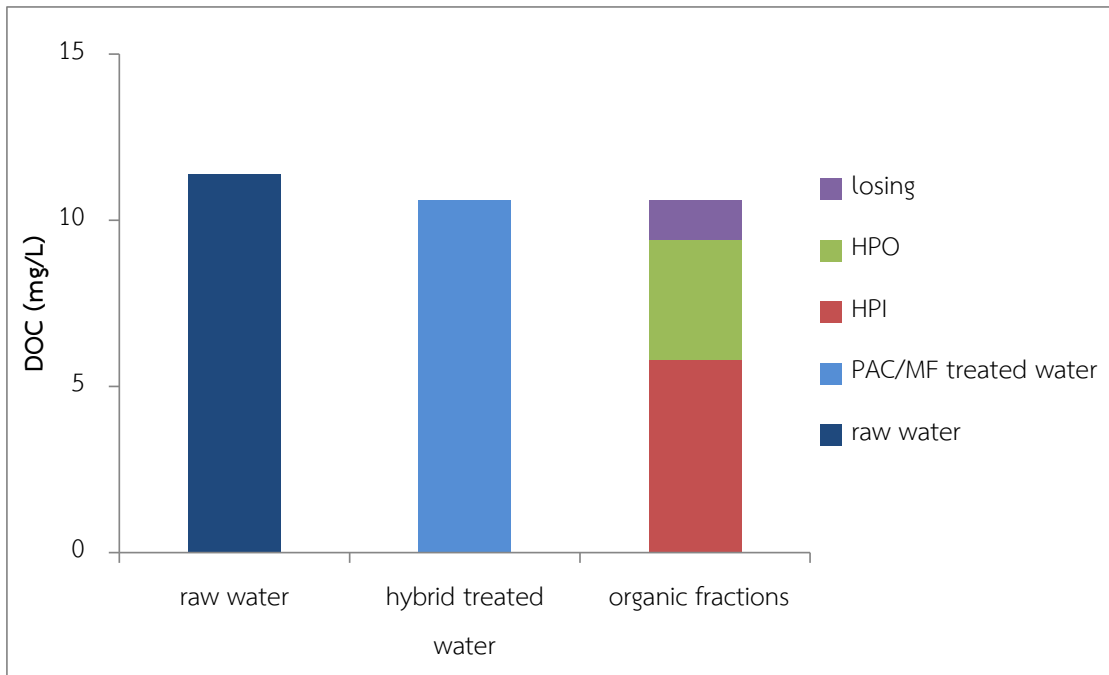
(b) High dosage of PAC.

4.3.2.3 Organic matter fractionation

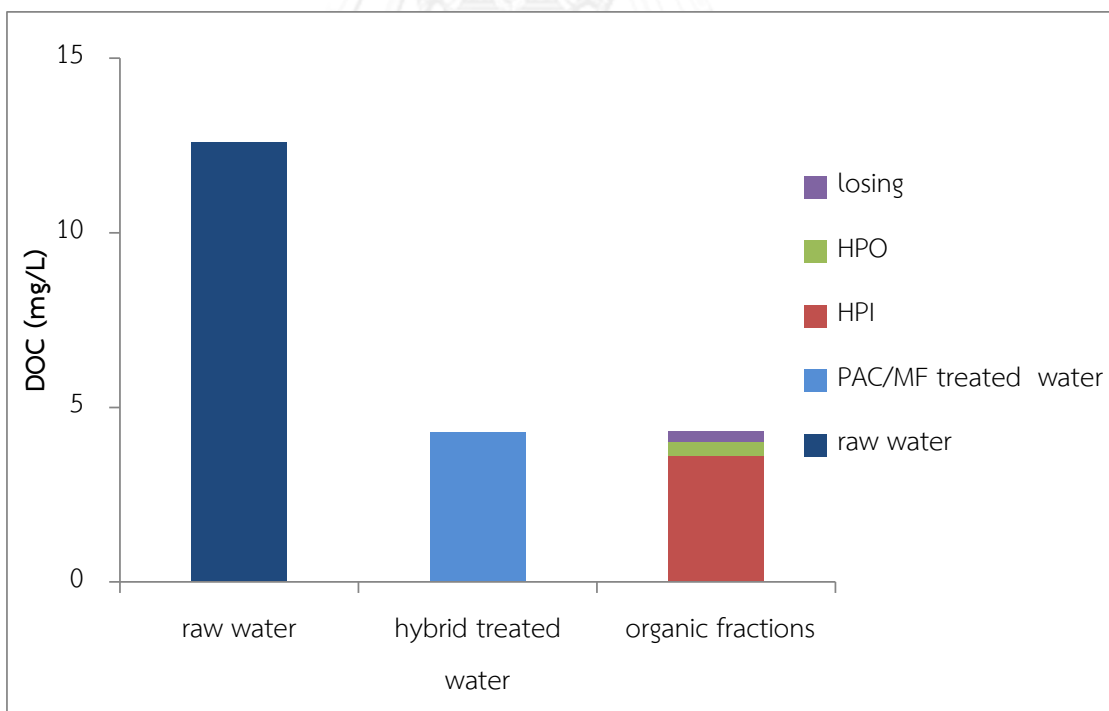
For the results of hybrid process, the organic matter fractionation of low PAC dosage (20 mg/L PAC) experiment, HPI and HPO fractions of raw shallow well water were 7.5 and 1.9 mg/L of DOC, respectively. It was found 88.7% DOC recovery in low PAC process. It was found that HPI and HPO removals were 7.4% and 0.0%, respectively.

At high dosage of PAC for hybrid process, the organic matter fractionation of high PAC dosage (1000 mg/L PAC) experiment, HPI and HPO fractions of raw shallow well water were 3.6 and 0.4 mg/L of DOC, respectively. It was found 94.2% DOC recovery in high PAC process. It was found that HPI and HPO removals were 52.6% and 87.4%, respectively. Discussion among low and high PAC dosages on HPI and HPO removals were mentioned in topic **4.3.1.3**.

Organic fractions at low and high PAC dosage experiments are shown in **Figure 4.13**.



(a)



(b)

Figure 4. 13 The ratio of DOC fraction in hybrid process as treated water.

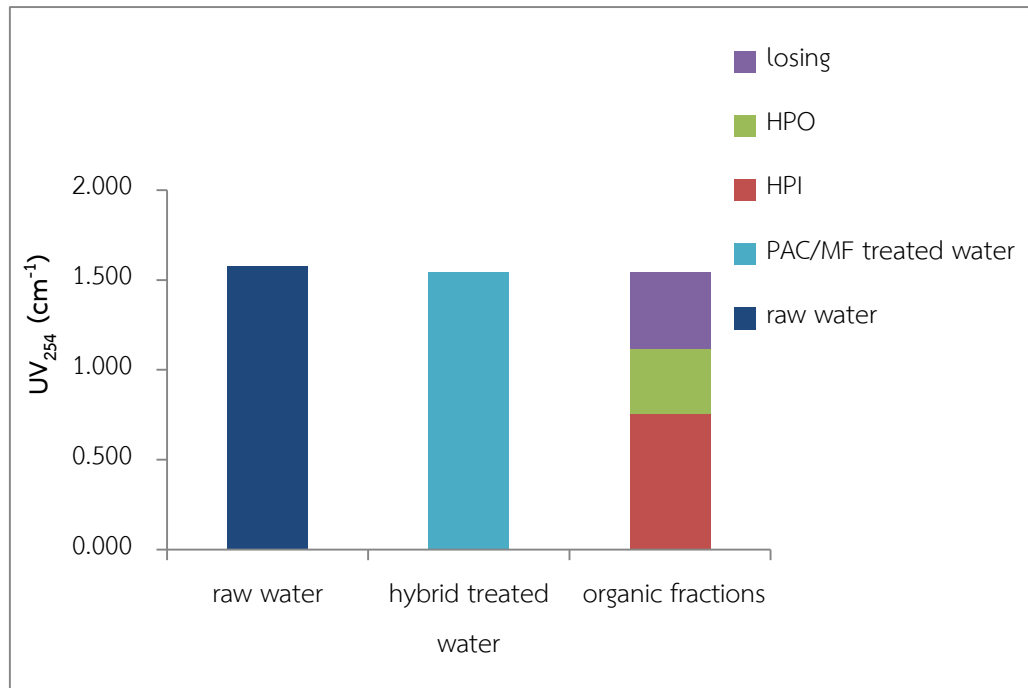
(a) Organic fraction with low dosage of PAC.

(b) Organic fraction with high dosage of PAC.

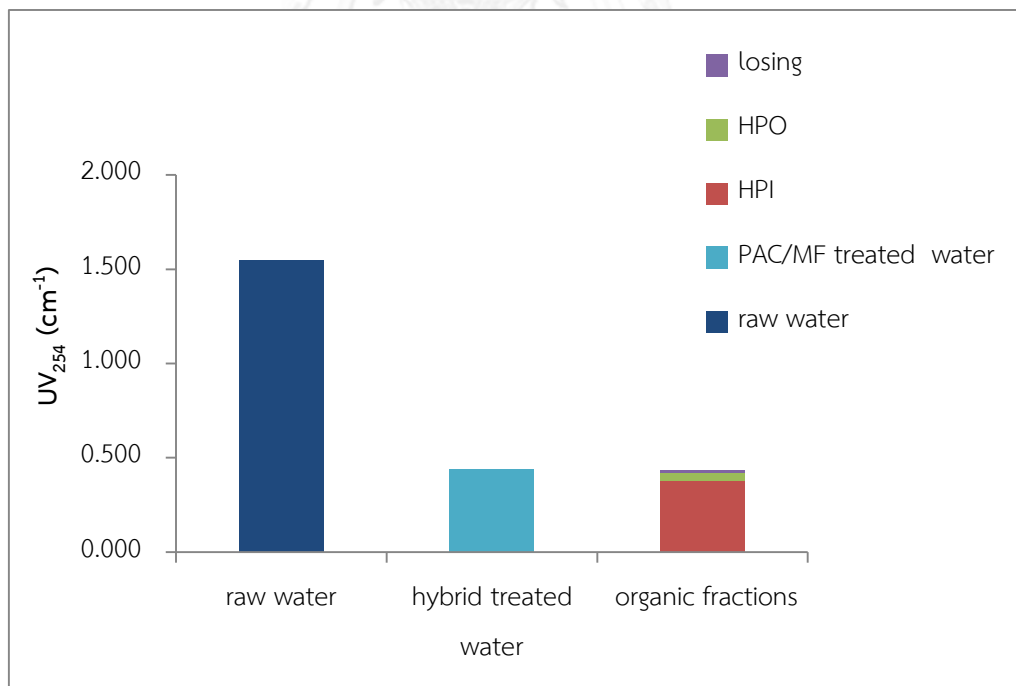
In case of UV_{254} , the results of organic matter fractionation of low PAC dosage (20 mg/L PAC) experiment, UV_{254} values of HPI and HPO fractions of treated water were 0.753 and 0.365 cm^{-1} , respectively. It was found that the organic matter fractions were 27.1 and 2.9% UV_{254} removal in low PAC process, respectively.

Beside the organic matter fractionation of high PAC dosage (1000 mg/L PAC) experiment, HPI and HPO fractions of treated water were 0.378 and 0.044 cm^{-1} , respectively. It was found that the organic matter fractions were 60.4 and 88.3% UV_{254} removal in high PAC process, respectively.

Organic fractions for UV_{254} at low and high PAC dosage experiments are showed in **Figure 4.14**.



(a)



(b)

Figure 4. 14 The effect on dosages of PAC with UV₂₅₄.

(a) Low dosage of PAC.

(b) High dosage of PAC.

4.3.3 Comparison between PAC adsorption process and hybrid process

A comparison between PAC adsorption process and hybrid process was carried out with PAC dosage of 1000 mg/L.

4.3.3.1 Dissolved organic carbon

For the PAC adsorption process, DOC in treated water was 2.8 mg/L (78.1% DOC removal). In case of hybrid process, DOC in treated water was 4.3 mg/L (66.1% DOC removal). **Figure 4.15** shows DOC concentration in each water sample. It was found that PAC adsorption process offered higher DOC removal efficiency. High PAC dosages in both applied processes presented relatively high DOC removal efficiency. The PAC adsorption process showed higher efficiency on DOC removal compared with that of the hybrid process. It might be due to membrane fouling during ceramic membrane filtration. PAC might foul and form cake layer on the ceramic membrane surface. The membrane fouling could be a cause of more DOC pass through the membrane (Khan *et al.*, 2011). Consequently, lower DOC removal efficiency was observed. Owing to the optimum contact time of PAC

adsorption processes, the PAC desorption was occurred after 6 h of contact time. The desorption could cause the DOC came out with treated water. These are the reason that the hybrid process gave lower efficiency of DOC removal than the PAC adsorption process.

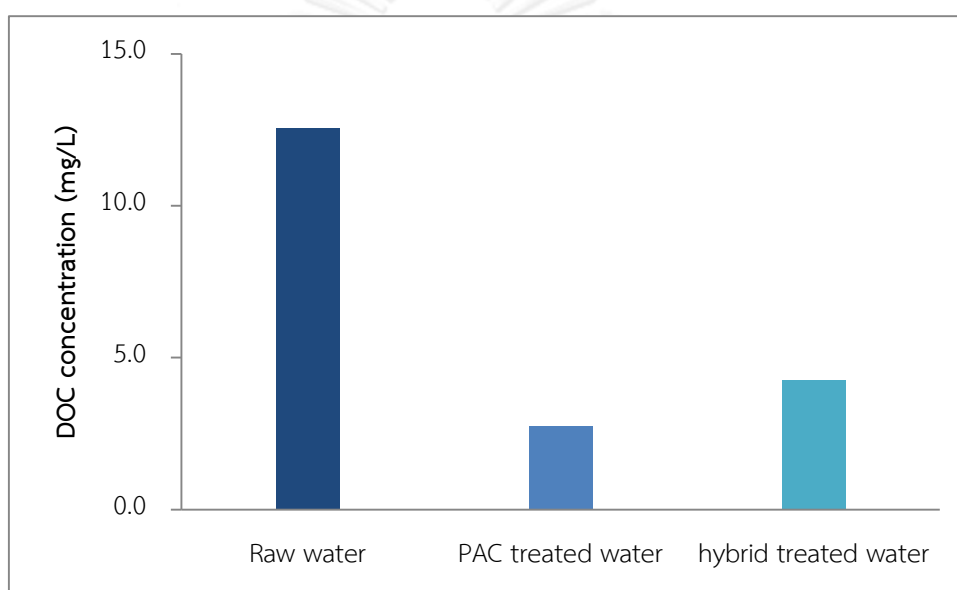


Figure 4. 15 DOC concentrations in each water sample.

4.3.3.2 UV absorbance at wavelength 254 nm (UV_{254})

In case of PAC dosage of 1000 mg/L, UV_{254} in treated water was 0.467 cm^{-1} . While 1000 mg/L of PAC dosage, UV_{254} in treated water was 0.436 cm^{-1} .

The results are shown in **Figure 4.16**.

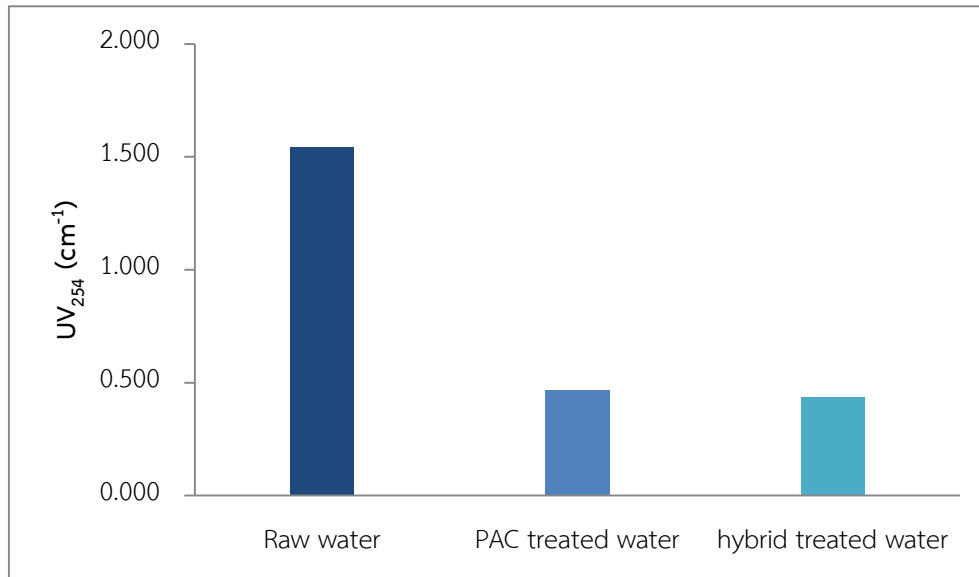


Figure 4. 16 UV₂₅₄ in each water sample.

4.3.3.3 Organic matter fractionation

For the results of organic matter fractionation in PAC adsorption process, HPI and HPO fractions of treated water were 2.3 and 0.5 mg/L of DOC, respectively. For hybrid process, HPI and HPO fractions of treated water were 3.6 and 0.4 mg/L of DOC, respectively. **Figure 4.17** shows organic matter fractionation in each water sample.

For HPO fraction of treated water of hybrid process, the DOC removal was increased from solely PAC adsorption process as a treatment process (83.1% to 87.4% DOC removal). Furthermore, the research of Rakruam in 2014 mention that HPO fraction in shallow well water could form disinfection by-product

(THMs) in chlorination process more than HPI fraction (Rakruam, 2014). Thus, the hybrid process is suitable for reduce HPO fraction.

Considering the DOC removal efficiencies of both processes, it was found that the membrane fouling in the hybrid process enhanced HPI fraction passing through the ceramic membrane. As a result, decreasing in DOC removal efficiency was obtained.

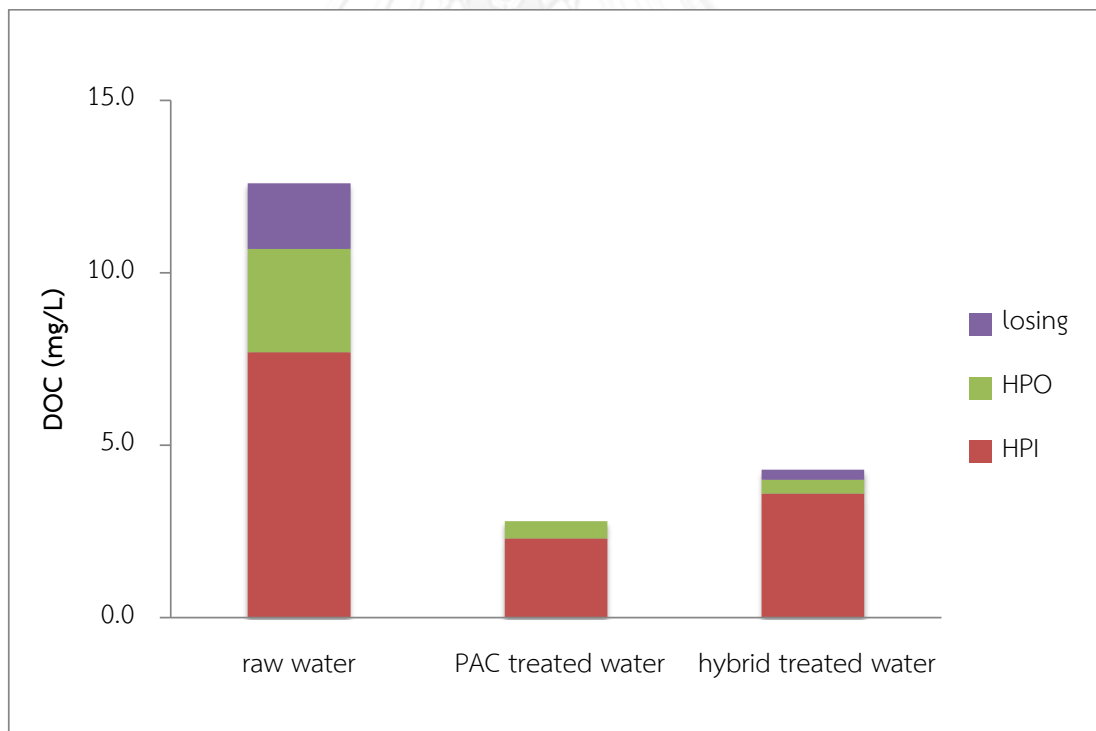


Figure 4. 17 Organic matter fractionation in each water sample.

4.3.4 Flux measurement

Water flux of ceramic membrane filtration is illustrated in **Figure 4.18**. During 3.5 liters of filtered volume, the water flux declined from 47.5 to 43.8 $\text{m}^3/\text{m}^2\text{-day}$ (7.9% reduction). Reduction of the water flux indicated the membrane fouling phenomenon. It could support the effect of membrane fouling on the DOC removal efficiency.

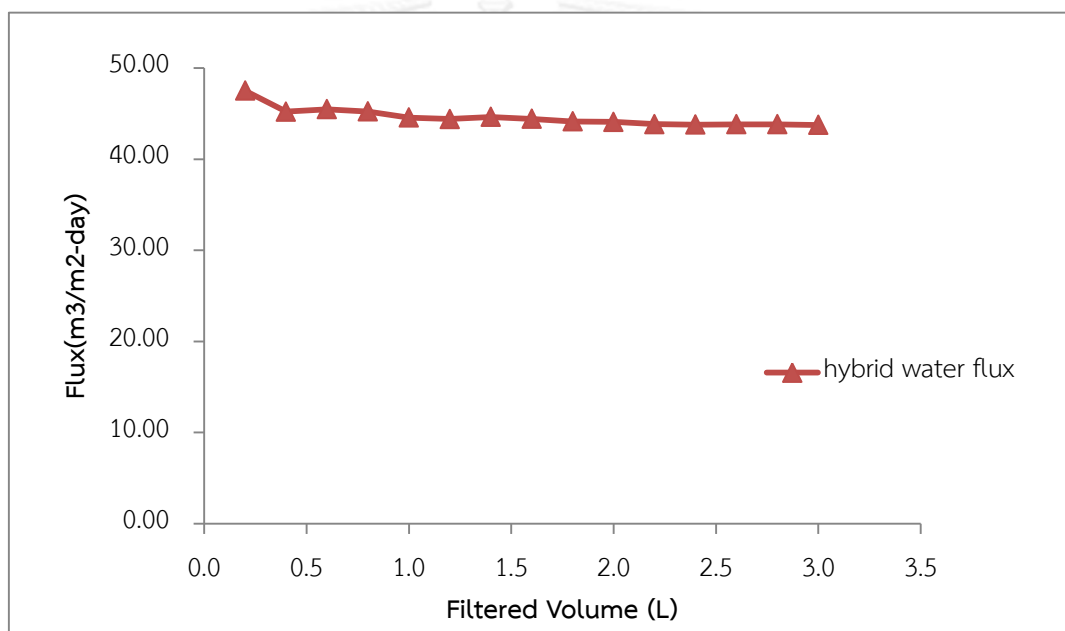


Figure 4. 18 Water flux during a course of filtration.

4.4 DBPs Formation

For the DBPs formation process, 3.0 mg/L of Sodium hypochlorite was dosed into water samples. In this part, the shallow well water and hybrid process treated water were tested. Total THMs in shallow well water was 10.84 $\mu\text{g}/\text{L}$. Total THMs in treated water by hybrid process was 3.06 $\mu\text{g}/\text{L}$. Thus, the hybrid process could

reduce Total THMs by 71.8%. It was effectively removal of DBP precursors. This obtained result motivated us to improve the hybrid process for higher efficiency.

From the study of Tangsuwan in 2014, DBPs formation during treatment process was observed. Ferric chloride coagulation combined with ceramic membrane filtration was utilized. It was showed the decreasing of Total THMs from 10.84 to 4.46 $\mu\text{g/L}$ of Total THMs (58.9% reduction). It was stated that the hybrid process of PAC adsorption and ceramic membrane filtration could remove Total THMs slightly lower than that obtained from the ferric chloride coagulation combined with ceramic membrane filtration.

Table 4. 2 THMs species in contaminated shallow well water and hybrid treated water.

THMs species	Concentration ($\mu\text{g/L}$)			%reduction	
	Raw water	Hybrid treated water		a	b
CHCl_3 ($\mu\text{g/L}$)	1.61	1.30 ^a	1.16 ^b	19.2	28.0
CHBrCl_2 ($\mu\text{g/L}$)	-	-	-	-	-
CHBr_2Cl ($\mu\text{g/L}$)	-	-	-	-	-
CHBr_3 ($\mu\text{g/L}$)	9.23	1.76 ^a	3.30 ^b	80.9	64.2
Total ($\mu\text{g/L}$)	10.84	3.06 ^a	4.46 ^b	71.8	58.9

a=hybrid process between PAC adsorption and ceramic membrane process (this study).

b=hybrid process between ferric chloride coagulation and ceramic membrane process (Tangsuwan, 2014).

CHAPTER 5

CONCLUSIONS

Conclusions of this study were listed as follows;

1. Contaminated shallow well water was collected from an unsanitary landfill in Chiang Mai, Thailand. The shallow well water contaminated from Mae Hia landfill leachate was observed with 11.4-12.6 of DOC. Based on DOC concentration, the organic matter fractionation showed HPI and HPO concentrations of 7.7-8.1 and 1.9-3.0 mg/L, respectively and 1.545-1.577 cm⁻¹ of UV₂₅₄.
2. For a kinetic experiment, 20 mg/L of PAC dosage was used to find the optimum contact time. The optimum contact time was at 6 h.
3. In case of PAC adsorption process, at PAC dosage of 20 mg/L, DOC in treated water was 10.8 mg/L. Whereas PAC dosage of 1000 mg/L, DOC in treated water was 2.8 mg/L. Hence, DOC removal efficiencies of low and high PAC dosages were 5.3% and 78.1% DOC removal, respectively. It was revealed that increasing in PAC dosage could improve the efficiency of the process.
4. For hybrid process of PAC adsorption and ceramic membrane filtration, DOC removal efficiencies of low and high PAC dosages were 7.0% and 66.1%, respectively. It was confirmed that the increasing in PAC dosage could improve the efficiency of the process.
5. In comparison between PAC adsorption process and the hybrid process,

PAC adsorption process showed higher efficiency on DOC removal compared with that of the hybrid process. It could be the result of membrane fouling during the ceramic membrane filtration process. However, HPO fraction in hybrid process was found the highest DOC removal efficiency.

6. Reduction of the water flux could be an indication of the membrane fouling. During 3.5 liters of filtered volume, the water flux declined from 47.5 to 43.8 $\text{m}^3/\text{m}^2 \text{ day}$ (7.9% reduction). It resulted in decreasing of DOC removal efficiency of the hybrid process.

7. Total THMs was formed during chlorination process. Total THMs in shallow well water was 10.84 $\mu\text{g}/\text{L}$. It was reduced to 3.06 $\mu\text{g}/\text{L}$ in treated water by the hybrid process. Thus, the hybrid process could reduce Total THMs well by 71.8%.

8. This study focuses on the PAC adsorption process solely and the combination process of PAC adsorption process and ceramic membrane filtration process. The ceramic membrane process alone or the control system is interesting for further study.

9. For the formation experiment, this study was done with raw water and hybrid process. Thus, the formation in each process and fractionation process should be study.

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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY



APPENDIX

EXPERIMENTAL DATA

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

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