

SYNTHESIS OF MAGNETICALLY-
SEPARABLE POROUS BONE CHAR AS AN EFFECTIVE ADSORBENT FOR DISINFECTION BY-
PRODUCTS PRECURSOR REMOVAL FROM SURFACE WATER

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การสังเคราะห์ถ่านกระดุกูรพูนที่สามารถแยกได้ด้วยแม่เหล็กเพื่อเป็นตัวดูดซับที่มีประสิทธิภาพ
สำหรับการกำจัดสารตั้งต้นของสารก่อมะเร็งจากน้ำผิวดิน



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อลงกรณ์ ศิริ : การสังเคราะห์ถ่านกระดูกพรุนที่สามารถแยกได้ด้วยแม่เหล็กเพื่อเป็นตัวดูดซับที่มีประสิทธิภาพสำหรับการกำจัดสารตั้งต้นของสารก่อมะเร็งจากน้ำผิวดิน (SYNTHESIS OF MAGNETICALLY-SEPARABLE POROUS BONE CHAR AS AN EFFECTIVE ADSORBENT FOR DISINFECTION BY-PRODUCTS PRECURSOR REMOVAL FROM SURFACE WATER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ. ดร. ภาคภูมิ รักร่วม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร. อรรถพงษ์ วงศ์เรือง, 110 หน้า.

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาการสังเคราะห์ถ่านกระดูกหมูและนำไปดูดซับสารอินทรีย์คาร์บอนละลายน้ำกับโอกาสการก่อกำเนิดของสารไตรฮาโลมีเทน (THMFPS) ของน้ำผิวดินจากแม่น้ำปิง จังหวัดเชียงใหม่ ในช่วงเดือนตุลาคม 2559 นอกจากนั้นนำถ่านกระดูกหมูมาสังเคราะห์โดยทำการติดเหล็กไนเตรตด้วยอัตราส่วน 1:1 เพื่อสามารถแยกถ่านกระดูกหมูจากน้ำได้ด้วยแม่เหล็ก กระดูกหมูเผาที่อุณหภูมิ 650 และ 900 องศาเซลเซียสเป็นเวลา 2 ชั่วโมง หลังจากนั้นนำถ่านกระดูกหมูที่ติดเหล็กไนเตรตและไม่ติดเหล็กไนเตรตมาศึกษาคุณสมบัติทางเคมีและกายภาพ ได้แก่ พื้นที่ผิว การศึกษาพื้นผิวดูดซับด้วยเทคนิคจุลทรรศน์อิเล็กตรอนแบบส่องกราด ประจุบนพื้นผิวดูดซับและความหนาแน่นประจุเชิงผิว จากผลการทดลองพบว่าถ่านกระดูกหมูที่ 900 องศาเซลเซียส เป็นตัวดูดซับที่เหมาะสม

การศึกษากลไกการดูดซับแบบจลนพลศาสตร์และไอโซเทอม การดูดซับสารอินทรีย์คาร์บอนละลายน้ำโดยใช้ถ่านกระดูกทั้ง 2 ตัวที่ความเข้มข้น 0.2 0.4 0.6 และ 0.8 กรัม/ลิตร พบว่าจะเข้าสู่สภาวะสมดุลเมื่อเวลาสัมผัสมากกว่า 1 ชั่วโมง อีกทั้งผลการทดลองนี้ยังสามารถสรุปได้ว่าถ่านกระดูกทั้ง 2 ชนิดที่ความเข้มข้นต่างๆ สอดคล้องกับสมการปฏิกิริยาอันดับสองเทียม ในขณะที่ถ่านกระดูกหมูที่ติดเหล็กไนเตรตสมการปฏิกิริยาไอโซเทอมของการดูดซับสอดคล้องกับสมการแบบแลงเมียร์และถ่านกระดูกหมูที่ไม่ติดเหล็กไนเตรตสอดคล้องกับสมการแบบฟรุนดิช

นอกจากนั้นการศึกษากำจัดสารตั้งต้นสารก่อมะเร็งในน้ำผิวดิน โดยศึกษาพารามิเตอร์ สารอินทรีย์คาร์บอนละลายน้ำ (DOC) ค่าการดูดกลืนแสงที่ความยาวคลื่น 254 นาโนเมตร (UV-254) การวิเคราะห์ฟลูออเรสเซนซ์ เอ็กซ์ไซส์เตชัน-อีมิชชัน แมทริกซ์ (FEEM) โอกาสการก่อกำเนิดของสารไตรฮาโลมีเทน (THMFPS) และอัตราการก่อกำเนิดของสารไตรฮาโลมีเทนจำเพาะ STHMFPS ซึ่งพบว่าประสิทธิภาพการกำจัดของถ่านกระดูกที่สามารถแยกได้ด้วยแม่เหล็กที่ความเข้มข้น 0.4 กรัม/ลิตร เป็นตัวดูดซับที่เหมาะสม

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ALONGORN SIRI: SYNTHESIS OF MAGNETICALLY-SEPARABLE POROUS BONE CHAR AS AN EFFECTIVE ADSORBENT FOR DISINFECTION BY-PRODUCTS PRECURSOR REMOVAL FROM SURFACE WATER. ADVISOR: PHARKPHUM RAKRUAM, Ph.D., CO-ADVISOR: ASST. PROF. AUNNOP WONGRUENG, Ph.D., 110 pp.

This research was aims to synthesis pig bone char and apply to adsorb dissolved organic carbon (DOC) and trihalomethane formation potential (THMs) from Ping river water, Chiang Mai on October 2016. In addition, the magnetically-separable porous bone char was synthesized by adding ferrous nitrate at ratio 1:1. Pig bone char was pyrolysis at 650 and 900 degree Celsius for 2 hour. The synthesized bone char including magnetically-separable porous bone char (FPBC) and porous bone char (PBC) was investigated their physical and chemical characteristics including Point of Zero Charge (PZC), Surface charge density, Surface area (BET), Scanning electron microscope (SEM), Fe mapping and Energy-dispersive X-ray spectroscopy (EDX). The result showed that pig bone char that pyrolysis at 900 °c was the optimal adsorbent.

The adsorption kinetics and adsorption isotherms were examined under batch condition. Along with the kinetic study, the adsorption adsorbents reached to the equilibrium after 1 hour of contact time by varied concentration at 0.2, 0.4, 0.6 and 0.8 g/L. The pseudo-second order model was found to fit well with the adsorption kinetic of all adsorbents. From the adsorption isotherm results, the F-PBC-900 °C adsorbent was best fitted with Langmuir isotherm model and the PBC-900 °C adsorbent was best fitted with Freundlich isotherm model.

The DBPs precursor removal experiment were analyzed various parameters including dissolved organic carbon (DOC), UV Absorbance at wavelength 254 nm (UV-254), Fluorescence Excitation-Emission Matrices (FEEM), trihalomethane formation potentials (THMFPS) and Specific Trihalomethanes formation potential (STHMFPS). The results indicated that the pig bone char with adding iron (III) nitrate as magnetically-separable porous bone char at 0.4 g/L concentration can be utilized as low cost absorbent.

Field of Study: Hazardous Substance and
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CHAPTER 1

INTRODUCTION

1.1 Background

The Ping River is an important water resource in Chiang Mai province that use for agriculture and water supply for a long time. Moreover it also uses for fishery, traffic and tourism purposes. Nowadays, the Ping River is faced with various problems that affect to the quality of water such as refuse, discharge induction community, construction and wastewater from factory in several areas where locate near the Ping River. If the problem still continues, Chiang Mai province will risk for water shortage for water supply plant in the future. In general, water supply plant uses several technologies for drinking water processes treatment including coagulation, flocculation and filtration that can reduce flavor, smell and turbidity. However it has a limit of reducing natural organic matter.

Natural Organic Matter (NOM) is precursor for disinfection by-products (DBPs) (Cowman, 1994) and presents in several waters source such as surface, reservoir, lake, soil and ground waters. The NOM can cause many problems in drinking water processes treatment such as oxidation, coagulation, disinfection and adsorption (Owen et al., 1995). NOM can be characterized into 3 groups including Colloidal Organic Matter (COM), Particulate Organic Matter (POM) and Dissolved Organic Matter (DOM). In drinking

water processes treatment generally use chlorine to prevent the potential transmission of pathogenic microorganisms in reclaimed water (USEPA, 2004). DOM is the major problems in water supply and drinking water production due to it very difficult to remove from water sources. Then the reactions between DOM and chlorine create disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (S. Chellam, 2001) that genotoxic and cytotoxic (M.J. Plewa et al., 2010). THMs including Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform were classified as possible carcinogens to humans (USEPA, 2004). In general chloroform is present in surface water more than others. Thus, developed countries published regulation to control disinfection by-products(DBPs) in drinking water for preventing consumer exposure to the potential hazardous chemicals (S.D.Richardson, Plewa, Wagner, Schoeny, & DeMarini, 2007) .

Several methods were used to remove DOM from water sources such as coagulation, ion exchange, advanced oxidation processes, membranes filtration, electrochemical methods and adsorption. All of the methods have different advantages and disadvantages. However, adsorption is one of methods that widely used in many countries for various applications. Adsorption process using activated carbon is a one of the best adsorbents for removing natural organic matter (Bond et al., 2011) due to it has efficient and convenient. Although, the cost for using activated carbon is still high for developing countries.

In Thailand, animals are slaughtered for meeting people demands of eating meat. Amounts of animal bone become to bone wastes that affecting the environment. Hence cattle farms used animal bone to feed their animals but animal bone is still more than demands of feeding. In addition, animal bone has properties to adsorb substances which it has their own surface area and pore volumes. Accordingly, many researches utilized to adsorb many substances including, fluoride (Sawangjang, 2016), arsenic (Yun-Nen Chen, 2007) and chromium (A.H.M.G. Hyder et.al, 2014). Nevertheless, there are a few research on DOM removal by bone char. Various researchers used granular activate carbon (Velten, 2015) and PAC (Fabris, 2008) for removing natural organic matter. Thus, the removal of natural organic matter in surface water by bone char is not well investigated. Consequently, the utilized of bone char for organic matter removal should be investigate.

However, the removal of adsorbent after treatment process is challenging. Bone char is small adsorbent that required filtration process to separate from treated water which it more cost and time consumed. Many researches study the method to separate adsorbents from treated water including using the peanut shell with doping Fe-Ti bimetallic oxide to eliminate fluoride (Zhang et al., 2014) and making oak with doping a soluble ferric Ferrous (Fe^{2+}) for the removal of cadmium and lead in water (Mohan, 2014). So the magnetically-separable porous bone char by adding-iron (III) nitrate to bone char is an interesting method for separating adsorbents from treated

water. However, the effect and efficiency of magnetically-separable porous bone char on DOM removal should be clarify.

1.2 Objectives:

1. To synthesize and characterize porous bone char and magnetically-separable porous bone char
2. To determine the efficiency of synthesized bone char for disinfection by-products (DBPs) precursor removal from surface water

1.3 Hypothesis:

1. Synthesis bone char at higher temperature can provide higher surface areas and pore volume.
2. The magnetically-separable porous bone char can provide higher disinfection by-products (DBPs) precursor removal efficiency.

1.4 Scope of the Study:

1. Pig bone was selected and utilized as synthesis bone char. The synthesis condition was varied with burning temperature at 650 and 900 °C for 2 hour without oxygen for porous bone char and magnetically-separable porous bone char. The magnetically-separable porous bone char was synthesized by adding iron (III) nitrate 20.2 g per 500 mL with 20 g of bone char. After that the characteristics of both porous bone chars were investigated by measured Point of Zero Charge (PZC), Surface Charge Density,

Scanning Electron Microscope (SEM), Surface area (BET) and Energy-Dispersive X-ray spectroscopy (EDX)

2. The adsorption experiments was conducted under a batch condition at temperature 25 °C. The adsorption kinetics and isotherm were determined and fitted with Langmuir and Freundlich models. The rate and mechanisms of adsorption were determined by fitting with pseudo-first-order and pseudo-second-order.

3. Amount 60 L of raw water was collected from the Ping River in rainy season and used for the whole research. The quantity and characteristics of organic matter in raw water were investigated by measured Dissolved organic carbon (DOC), Trihalomethanes formation potential (THMFP), UV Absorbance at wavelength 254 nm (UV_{254}) and Fluorescence excitation-emission matrices (FEEM)

4. The efficiency of synthesis magnetically-separable porous bone char for DOM removal was investigated by conduct a batch adsorption experiment based on the adsorption kinetics and isotherm. The removal of DOM and THMFP from both synthesis bone char was determined and compared.

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1. Dissolved Organic Matter (DOM)

Dissolved Organic Matter (DOM) can be characterized into 2 substance as humic and non-humic substance. Humic substance is hydrophobic including humic and fulvic acid. Meanwhile, non-humic substance is hydrophilic including hydrophilic acids, proteins, amino acids, carbohydrate and carboxylic acids (Thurman, 1985; Amy, 1993). In general, DOM normally found in natural water. The presence of DOM can caused serious problems including negative effect on the water quality, increased coagulant and disinfectant dose requirements and increased the potential harmful disinfection by-products (Jacangelo et al., 1995). DOM react with chlorine during chlorination process to forming disinfection by-products (DBPs) such as trihalomethane (THMs) and Haloacetic acid (HAA) which classified as potential carcinogenic substance pose a cancer risk to humans. DOM is recognized as precursors for disinfection by-product formation during water treatment disinfection operation (Meyn et al., 2012; Marhaba and Washington 1998).

2.1.1. Dissolved Organic Matter Surrogate Parameters

1. Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) is defined as the fraction of TOC that dissolved in water and is able to pass through a filter which range of filter size between 0.7 and 0.22 μm . The term of dissolved are defined as the compound which size lower than 0.45 micrometers. DOC is used to represent the presence of dissolved organic matter such as humic substance and non-humic substance (Julie and Robert, 2004)

2. UV Absorbance at wavelength 254 nm

UV-254 is used to provide an indication of the aggregate concentration of UV-absorbing organic constituents, such as humic substances and various aromatic compounds (APHA, AWWA, WEF, 1995). The first surrogate parameter that utilizes to determine the organic matter in raw water is UV absorbance at a wavelength of 254 nm. Organic matter including humic aromatic compounds and molecules with conjugated double bonds can absorb UV light whereas the simple aliphatic acids, alcohol, and sugars do not absorb (Edzwald et al., 1985). Hence, the UV-254 absorbance can be used to indicate the presence of aromatic compounds of organic matter in natural water. Eaton (1995) found that the UV absorbance of organic matter in water is very useful to indicate the concentration of DOC and THMs in water because the humic substrates strongly absorb ultraviolet radiation.

3. Fluorescence Excitation-Emission Matrices (FEEM)

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

The peaks of Fluorescent excitation-emission wavelengths (Ex/Em) were classified according to the summary data from literatures as shown in Table 1 and shown the location on wavelengths in Figure 1. It reported major pyrolysis fragments of fluorescent organic matter including tyrosine-like, tryptophan-like, fulvic acid-like and humic acid-like substances had been proposed by many researchers.

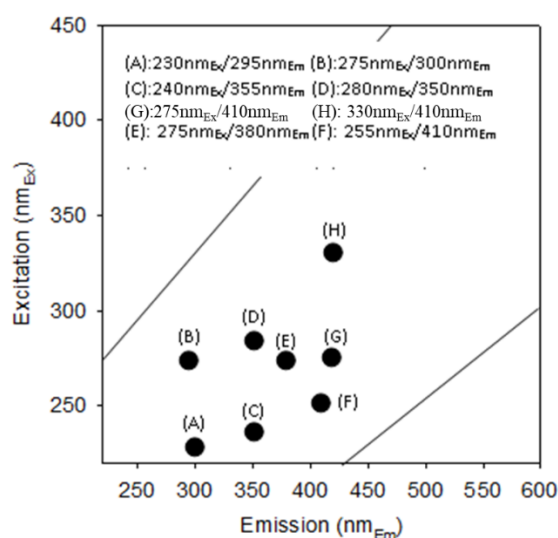



Figure 1 Location of fluorescent peak position

Table 1 Fluorescent peak positions and major pyrolysis fragments of major fluorescent components from literature data

Fluorescent organic matter	Excitation (nm _{Ex})/Emission (nm _{Em})	Majors pyrolysis fragments
Tyrosine-like and protein-like substances	220-275/300-305 (Wolfbeis, 1985), [A] ¹ , [B] 275/310 (Coble, 1996), [B] 270-280/300-320 (Leenheer <i>et al.</i> , 2003), [B] 270-275/300-302 (Yamashita <i>et al.</i> , 2003), [B]	Phenol and p-cresol (phenol, 4 methyl), (Bruchet <i>et al.</i> 1990) Pyridines, pyrroles, indoles, nitriles, phenol and p-cresol (equal quantities from tyrosine), (AWWA, 2000)
Tryptophan-like and protein-like substances	220-275/340-350 (Wolfbeis, 1985), [C], [D] 275/340 (Coble, 1996), [D] 270-280/320-350 (Leenheer <i>et al.</i> , 2003), [D] 280/342-346 (Yamashita <i>et al.</i> , 2003) [D]	Indole (AWWA, 2000), acetronitrile, benzonitrile, phenylacetone, pyridine, methylpyridine, pyrrole, indole and methylindole (Leenheer and Croues, 2003)
Fulvic acids and fulvic-like substances	330-350/420-480 (Coble, 1996), [H] 290-340/395-430 (Baker and Genty 1999), [E], [G] 320-340/410-430 (Baker, 2001), [H] 315/437-441 (Yamashita <i>et al.</i> , 2003) 260/460, 310/440 (Sierra 2005) [F], [H]	Humic substances consist of humic and fulvic acids Humic acids; Bruchet (1986) and Gadel and Bruchet (1987): highly aliphatic.
Humic acids and humic-like substances	250-260/380-460, 330-350/420-480 (Coble, 1996) [E], [F], [G], [H], 235-255/435-465(Nakajima <i>et al.</i> , 2002) [E] 250-260/380-480, 330-350/420-480(Leenheer <i>et al.</i> , 2003) [E], [F] [G], [H] 350-365/446-465 (Yamashita <i>et al.</i> , 2003) 265/525, 360/520 (Sierra, 2005)	Faure <i>et al.</i> 2006: (1) n-alk-1-ene/n-alkane with 8-29 carbon presenting the limited odd over predominance in the C ₂₄ -C ₂₉ range (2) alkyl-benzenes, naphthalene, alkyl-naphthalene (3) phenol. Fulvic acids;

	 <p>จุฬาลงกรณ์มหาวิทยาลัย CHULALONGKORN UNIVERSITY</p>	<p>Bruchet (1986) and Gadel and Bruchet (1987): highly peaks of butenal, acetic acid, 2-fufural, methyl fufural, levoglucosenone, 5-(Hydroxymethyl) 2 fufaral.</p> <p>Croue et al. (1993): large peaks of phenol and cresol</p> <p>Humic substances:</p> <p>Lu et al. 2006: (1) Nitrogen containing compounds (such as pyrrole and pyridine), aliphatic products (such as n-alk-1-ene/n-alkane with 5-29 carbon) (2) aromatic products (such as alkyl-benzenes, naphthalene and alkyl-naphthalene , (4) lignin products (such as o-cresol, m cresol, catechol, dimethylphenol) (5) carbohydrate product (such as furan, 2-methyl proppenal, dimethyfurane, vinyfuran, 2-fufaraldehyde.</p>
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In the Table1, the eight major fluorescent peaks at $230\text{nm}_{\text{Ex}}/295\text{nm}_{\text{Em}}$ (peak A), $275\text{nm}_{\text{Ex}}/300\text{nm}_{\text{Em}}$ (peak B), $240\text{nm}_{\text{Ex}}/355\text{nm}_{\text{Em}}$ (peak C), $280\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$ (peak D), $275\text{nm}_{\text{Ex}}/380\text{nm}_{\text{Em}}$ (peak E), $255\text{nm}_{\text{Ex}}/410\text{nm}_{\text{Em}}$ (peak F), $275\text{nm}_{\text{Ex}}/410\text{nm}_{\text{Em}}$ (peak G), and $330\text{nm}_{\text{Ex}}/410\text{nm}_{\text{Em}}$ (peak H), were detected. It presented that the peaks A and B,

C and D, E, F, G and H were tyrosine-like, tryptophan-like, and humic and fulvic acid-like substances, respectively.

4. Trihalomethanes Formation Potentials (THMFPS)

THMFP₀ or THMFP is the difference between the final TTHMT concentration and the initial TTHM₀ concentration. For samples that do not contain chlorine at the time of sampling, TTHM₀ will be close to zero. Therefore the term THMFP may be used. For samples that contain chlorine at the time of sampling, a TTHM₀ value will be detected. Therefore the term Δ THMFP may be used when reporting the difference between the TTHM concentrations (Standard method, 1995). Total trihalomethanes (TTHMT) is the sum of all four compound concentrations, chloroform, dichlorobromomethane, dibromochloromethane and bromoform, produced at any time T (usually measured in days). TTHM₀ is the total THMs concentration at the time of sampling. It can range between non-detectable to several hundred micrograms per liter if the samples have been chlorinated. TTHM₁ is the total concentration of all four THMs compounds produced during the reactions of the sample precursors with excess free chlorine over a day reaction time at the standard reaction conditions, which were as follows: free chlorine residual at least 3 mg/L and not more than 5 mg/L at the end of a day reaction (incubation) period with sample incubation temperature of $25 \pm 2^\circ\text{C}$, and pH controlled at $7 \pm 0.2^\circ\text{C}$ with phosphate buffer.

2.2 Disinfection By-Products (DBPs)

Disinfection by-products (DBPs) arise on the reaction of disinfection chemicals such as chlorine with Dissolved Organic Matter. It forms Trihalomethanes (THMs) which is carcinogen for human (National Cancer Institute, 1976).

2.2.1 Trihalomethanes (THMs)

Trihalomethanes (THMs) normally are found in water supply and water treatment plant when chlorine reacted with natural organic matter such as humic or fulvic substances. Rook (1974) and Bellar et al. (1974) reported that the disinfection by-products (DBPs) such as THMs are generated from reaction between DOM and chlorine. Trihalomethanes (THMs) have different chemical formulas including Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform.

The standard of THMs in water supply plant for control disinfection by-products (DBPs) in drinking water shown in Table 2.

Table 2 Standard of THMs

Departments	Substances	Maximun contaminant levels (MCLs, $\mu\text{g/L}$)	References
WHO	Total THMs	100	Manlika and Phongsri, 2007
USEPA	Total THMs	80	
	HAAs	60	
EU	Total THMs	10	
THAILAND	CHCl_2Br	60	Metropolitan Waterworks Authority (Thailand),2011
	CHClBr_2	100	
	CHBr_3	100	
	CHCl_3	300	
	Total THMs	560	

1.Factors Influencing THM Formation

Variations in THMs formation reactions include the concentration of the precursor material, chlorine concentration, contact time, temperature, pH and turbidity

2.Toxicity of THMs

THMs induce toxicity in the liver and kidneys of the rodents exposed to doses of about 0.5 mmol/kg of body weight. The THMs have little reproductive and development toxicity, but bromodichloromethane has been shown to reduce sperm motility in rats consuming 39 mg/kg of body weight per day in drinking water. Like chloroform, bromodichloromethane, when administered in corn oil, induces cancer in the liver and kidneys after lifetime exposures to high doses. Unlike chloroform,

bromodichloromethane, dibromochloromethane and bromoform induce tumors of the large intestine in rats exposed by corn oil gavage. Bromodichloromethane induces tumors at all three target sites and at lower doses than the other THMs (ICPS, 2000).

2.2.2. Technique for Disinfection by-products (DBPs) precursor removal

Various technologies used to disinfection by-products (DBPs) precursor removal, the most common and economically feasible method is coagulation and flocculation followed by sedimentation and filtration (Sillanpaa et al, 2010). The coagulation process was able to remove organic matter from water that contained more than 2 mg/L-m of Specific UV Absorbance (SUVA) (USEPA, 1999). Many researches used various types of coagulants for NOM removal such as using aluminium-based coagulant has been alum ($\text{Al}_2(\text{SO}_4)_3$), polyaluminium chloride (PACl), metal salt coagulants (FeCl_3 and AlCl_3) and polyaluminium chloride[Mingquan Yan et al (2009)]. Another research is in-line coagulation [PACl] with ceramic membrane filtration. It has more efficiency to reduce DOM from this water source than using only coagulation process (Rakruam, 2013).

2.3. Adsorption process

The adsorption process is a widely used treatment process because it is a convenient and simple method. The method seems to be more attractive because it presents satisfactory results for removing. In addition, it is an inexpensive method (for design and operation).

2.3.1. Theoretical of adsorption

Adsorption kinetic models

Using mass balance for calculating the amount of dissolved organic carbon of bone chars (mg/g)(C.K. Rojas-M., 2013).

$$q_D = \left(\frac{D_0 - D_f}{m} \right) V \quad \text{—————} \quad \text{Eq (1)}$$

Where D_0 is the initial dissolved organic carbon concentration [mg/L], D_f is the final dissolved organic carbon concentration in the adsorption experiment [mg/L], m is the mass of bone char of each type (mg), T is time (min) and V is the volume of the water sample solution [L].

The pseudo-first-order and pseudo-second-order kinetics used to describing the adsorption rate of the reaction in this study.

Pseudo-first-order kinetics

The pseudo-first-order model is represented by the following equation:

$$\frac{dq_t}{dt} = k_{p1}(q_e - q_t) \quad \text{—————} \quad \text{Eq (2)}$$

where q_t is the adsorption capacity at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), t is time (min), and k_{p1} is the pseudo-first-order rate constant for the kinetic model (min^{-1})(Hui Q, 2009).

The pseudo-first-order equation can be rearranged by integrating with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, and expressed as:

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_{p1}t \quad \text{Eq (3)}$$

which can be rearranged into a logarithmic form as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303}t \quad \text{Eq (4)}$$

A linear plot of $\log(q_e - q_t)$ versus t provides the value of k_{p1} , which is the slope of the line.

Pseudo-second-order kinetics.

The pseudo-second-order kinetic model is based on an assumption related to the process of chemisorption. It consists of valence forces through sharing or exchange of electron between the sorbent and sorbate. The pseudo-second-order kinetic model is the best fit for adsorption since this model is generally applied to describe the chemical reactions of heterogeneous materials (Jimenez et al., 2010). This model is represented by the following equation:

$$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2 \quad \text{Eq (5)}$$

where q_t is the adsorption capacities at time t , (mg/g), q_e is the adsorption capacities at equilibrium (mg/g), t is time (min), and k_{p2} is the pseudo-second-order rate constant for the kinetic model (g/mg*min); which can be rearranged as follows:

$$\frac{dq_t}{(q_e - q_t)^2} = k_{p2}dt \quad \text{Eq (6)}$$

Integrating the preceding equation at conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, results in:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_{p2}t \quad \text{Eq (7)}$$

which can be rearranged in a linear form as follows:

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{t}{q_e} \quad \text{Eq (8)}$$

The plot of t/q_t versus t will have a linear tendency, after that the $1/q_e$ value can be obtained from the slope of the line. Thus, k_{p2} can be calculated from the linear equation of the pseudo-second-order.

Adsorption isotherm models

Adsorption process isotherm will depend on some factors are pressure or concentration of adsorbent, temperature, type of adsorbents. So the adsorption process will concern all of factors by monitoring temperature and investigate the relationship between volumes of adsorbent with pressure or concentration.

Langmuir model

The Langmuir isotherm is the most widely applied with sorption isotherms. This model suits a sorption process where the sorption energy of each molecule is the same, and independent of the surface of the material. In addition, the sorption occurs only on some sites. There are no interactions between the molecules. The model is as follows (M. Jimenez et al., 2010):

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \quad \text{Eq (9)}$$

where q_0 is the amount of dissolved organic carbon sorbed per unit weight of bone char in forming a complete monolayer on the surface (mg/g), q_e is the total amount of dissolved organic carbon sorbed per unit weight of bone char at equilibrium (mg/g),

C_e is the concentration of dissolved organic carbon in the solution at equilibrium (mg/L), and K_L is the constant related to the energy of sorption (L/mg)

The equation of Langmuir model can be rearranged into a linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0} \quad \text{Eq(10)}$$

$$\frac{1}{q_e} = \frac{1}{K_L q_0} \frac{1}{C_e} + \frac{1}{q_0} \quad \text{Eq (11)}$$

The plot of $1/q_e$ versus $1/C_e$ has a linear tendency, $1/(K_L q_0)$ is obtained from the slope and the intersection of the vertical axis is $1/q_0$.

When the Langmuir model is applied in the adsorption process, the equilibrium parameter (R_L) should be calculated. It indicates whether the characteristic of the model is consistent or inconsistent with adsorption. R_L can be calculated by the following equation: (Kowit P., 2008):

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Eq (12)}$$

C_0 is the initial concentration of dissolved organic carbon (mg/L)

Table 3 The type of isotherm based on the equilibrium parameter factor of the Langmuir model (Kowit P., 2008):

R_L value	Type of isotherm
$R_L > 1$	Unfavorable conditions for sorption
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable conditions for sorption
$R_L = 0$	Irreversible

Freundlich model

The Freundlich isotherm can be applied with non-ideal sorption on heterogeneous surfaces and multilayer sorption. The model is expressed by the following equation (M. Jimenez et al., 2010):

$$q_e = K_F C_e^{1/n} \text{ Eq (13)}$$

Where q_e is the total amount of dissolved organic carbon sorbed per unit weight of bone char at equilibrium (mg/g), C_e is the concentration of the dissolved organic carbon in the solution at equilibrium (mg/L), K_F is the Freundlich constant which can express the capacity of the adsorption process (L/g), and n is the Freundlich constant, which explains the concentration of adsorption (dimensionless).

The Freundlich equation can be rearranged into a linear form by taking the logarithm as follows:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \text{ Eq (14)}$$

The plot of $\log q_e$ versus $\log C_e$ has a linear tendency; the slope of the plot is $1/n$, which shows the strength between the bone char and concentration of absorbed, and the intersection of vertical axis is $\log K_F$. (Laura R. B., 2009).

Table 4 Characteristic of the Freundlich model based on $1/n$ value (Kowit P., 2008):

$1/n$ value	Characteristic of Freundlich model
$1/n < 1$	The adsorbent has limitation of surface area for adsorption process.
$1/n = 1$	The adsorption isotherm is linear.
$1/n > 1$	The adsorbent has high amount of surface area for adsorption process.

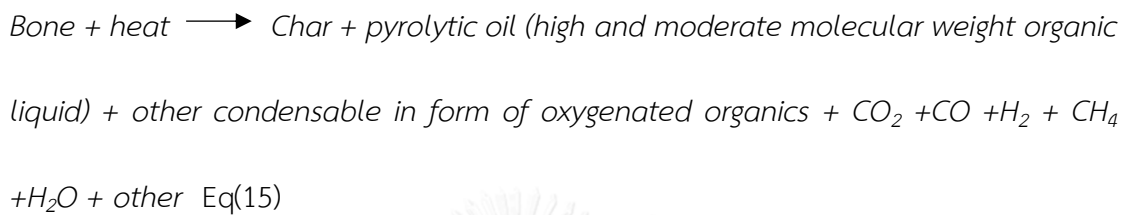
2.4. Adsorbents for removing Natural Organic Matter (NOM)

Various adsorbents can be used for removing Natural Organic Matter (NOM) in surface water. For example granular activated carbon (Capar, 2001; Velten, 2015), Poly Aluminium Chloride (PAC) (Fabris et al., 2004; Kanlayanee, 2015) and synthesis adsorbent (Lu and Su, 2007; Wang et al., 2015). It was found that various adsorbents was utilized however, a major point of concern in the adsorption process is the cost of the adsorbent.

2.4.1. Bone char and the process for generating bone char

Bone char contain 30% organic matter and 70% inorganic matter (J.C. Moreno-Piraján et al., 2011). However, Bone char can be synthesized by pyrolysis. The calcination of bones is a method that is conducted in a low-oxygen environment while the pyrolysis process is conducted in no oxygen environment. The temperature and

residual time for each process play a major role in producing bone char (C.K. Rojas-M., 2013). Pyrolysis process is a one of technology from Thermal decomposition with non-oxygen or very low oxygen (Kohoan and Barkordor, 1979) to produce char from equation (15)



Leyva-Ramos (2010) investigated at lower temperature (500-600 °C), bone char still remain of some organic matter. In addition, Sawangjang, B (2016) also remain some organic matter in bone char. So it leads to burning more than 600 °C for removing some organic of bone char as well as increasing porosity because the heating at high temperature will open the small porous which tar blocking occurs (Temyarasilp, 2008). For the reason, this study will burning at 650 and 900 °C with N₂ in 2 hours and adding-iron (III) nitrate (Fe(NO₃)₃) for separating bone char with treated water. Moreover, the doping with metal ions of adsorbent can improve their adsorption properties and performances (C.K. Rojas-Mayorga, 2015).

2.4.2. Characterization of absorbents

1. Point of zero charge (PZC)

The point of zero charge is a concept relating to the phenomenon of adsorption. It describes the condition that the electrical charge density on a surface is zero.

2. Surface charge density

Surface charge density is a measure of electric charge per unit volume of space, in one, two or three dimensions.

3. Scanning electron microscope (SEM)

Scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons.

4. Energy-dispersive X-ray spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample.

5. Brunauer–Emmett–Teller (BET)

Brunauer–Emmett–Teller (BET) is an analysis technique for the measurement of the specific surface area of a material.

2.5 Literature reviews

2.5.1. Synthesis of bone char

Bone char is the adsorbent that a useful, inexpensive, easily available, and safe way of disposing the waste of bones. For synthesis of bone char many research used pyrolysis process (C.K. Rojas-M., 2013; Juan C. Moreno-Piraján, 2011; R. Leyva-Ramos., 2010; Sangeeta Patela, 2015; Sawangjang, 2016). Juan C. Moreno-Piraján (2011) observed bovine bone char (i.e., cow bone) at 600 and 800 °C with pyrolysis process (nitrogen) and air atmosphere (oxygen). The result showed that present surface areas and pore volumes were 170 m²/g and 0.07 cm³/g for nitrogen and 130 m²/g and 0.06 cm³/g for oxygen, respectively. In addition, Sangeeta Patela (2015) studied the mesoporous bone char that obtained by pyrolysis process under 400, 450, 500 and 600 °C with two varied residence time of 1 and 2 h. the result show pyrolyzed at 400 °C with a residence time of 2 h is a very good low-cost alternative adsorbent.

However, Leyva-Ramos (2010) reported that some organic matter still remain in bone char at temperature ranged from 400 to 600 °C.

Sawangjang (2016) investigated pig bone, chicken bone and cow bone, and the result showed that pig bone char is the best adsorbent in terms of overall efficiency. Moreover, adding adding-iron (III) nitrate could separating adsorbents from treated water(Mohan, 2014).

2.5.2 The adsorption mechanism of Bone char

The pig bone char was found that it best fitted with pseudo-second order and Langmuir isotherm model (André L. Cazetta, 2016; C.K. Rojas-Mayorga, 2015; N.A. Medellin-Castillo & J.V. Flores-Cano, 2014; Sawangjang, 2016)

2.5.3 Disinfection by-products (DBPs) precursor removal

S. D. LAMBERT and N. J. D. GRAHAM (1995) observed the adsorption behavior of activated carbon, bone char, activated alumina and activated bauxite for the removal of non-specific dissolved organic matter. The result show that activated carbon (69%) provides DOC removal efficiency similar to that of bone char (61%).

Ho and Newcombe Chu (2005) investigated adsorption of PAC for removing NOM. It found that PAC has good efficiency for removing. The efficiency was about 90% especially PAC could greatly adsorb small molecule more than large molecule.

Zhang, Qu et al 2009 observed the reaction between DOM and DBPs. It found that the characteristics of DOM had important role of DBPs precursor for total trihalomethanes (TTHMs). Moreover, the pH value could affected to TTHMs. In addition, the study of FEEM shown humic acid-like substances was a good reaction with chlorine.

Hou (2012) observed DBPs on surface water and ground water from Yellow River for water supply. The study was found THMs including Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform. The concentration of

THMs were higher on surface water more than ground surface water. Similar with DBPFPs test, surface water had DBPs precursor for reaction more than ground water.

The DBPs precursor were DOC and DON.



CHAPTER 3

METHODOLOGY

3.1. Materials

3.1.1 Raw surface water

Surface water from Ping River, Chiang Mai Province, Thailand was selected as raw surface water. Amount of 60 L of raw water was collected and used for the whole experiment. The sampling point is situated 10 km upstream far from Chiang Mai municipal area as shown in Figure 2 and 3. Ping River water is currently the main water source utilized to produce water supply for Chiang Mai city. In general, turbidity of Ping River varies due to seasonal changes. However, it typically contains high concentration of suspended solid measured in term of “Turbidity value” between 50 - 220 NTU and high as 300 NTU in rainy season.



Figure 2 Sampling point in Ping River, Chiang Mai Province



Figure 3 Ping River, Chiang Mai Province

3.1.2 Bone char

Pig leg bone which defined as high percentage of surface area (Sawangjang, 2016) was selected and synthesized as pig bone char. It was collected from Chiang Mai local market.

3.2 Methods:

This research experiments were divided into four steps: synthesis bone char, characteristics bone char, adsorption experiment and DBPs precursor removal experiment.

3.2.1. Synthesis bone char

A raw pig bone was prepared before synthesis. Any fat remaining inside the bones were cleaned by boiling at 100 °C until water become which mean that colloid was released (Mayorga et al., 2014) and rinsing the bone with deionized water. Then, the clean bones were put in an incubator at 100°C for 24 hours to eliminate moisture. Next, the dry bones were crushed by a hammer into 1-2 cm and crushed again by a

mortar. Next, the crushed bone was put into a ball mill for 2 days. After that the smaller bone was obtained and filtered by sieve (250 μm). Filtered bone char was divided two portion, one portion was used directly as bone char. The remaining portion was used for synthesis magnetically bone char. The magnetically bone char was synthesized by soaking bone char with iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3$) solution for 24 hours. After that it was put in an incubator at 100°C for 24 hours to eliminate moisture. In this experiment, two types of bone char including raw pig bone char with adding iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3$) and non- adding iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3$) were obtained.

Finally, two types of bone char were pyrolyzed for 2 hours which the two temperature condition at 650 and 900 °C without oxygen to produce bone char by horizontal tube. The diagram of synthesis bone char processes are shown in Figure 4.

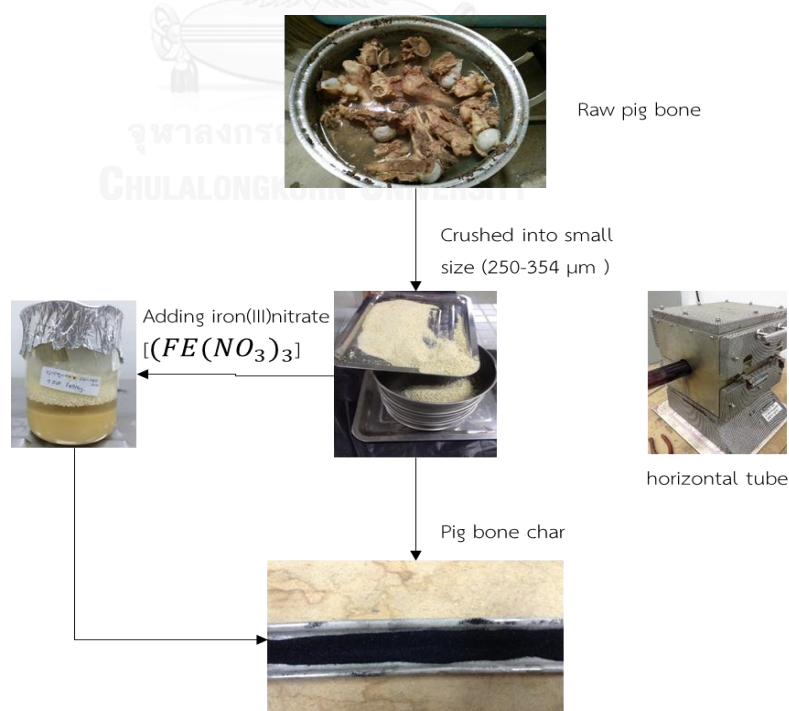


Figure 4 The diagram of synthesis bone char processes

3.3.2. Characterizations of the synthesis bone char

Characteristics of synthesis bone char were analyzed by various parameters including Point of Zero Charge (PZC), Surface Charge Density, surface area (BET), Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX).

1. Point of Zero Charge (PZC) and Surface Charge Density determination

A batch equilibrium method was applied for determining the Point of Zero Charge (PZC) and charge density of bone char by acid-base titration method (Punyapalakul and Takizawa, 2004). Bone char 0.02 g with miliQ 20 mL was added in Erlenmeyer flask (250 mL). NaOH (0.025 M) and HCl (0.025 M) were prepared in deionized water. Then, the pH of samples was varied at 0.1, 0.25, 0.50, 1.0, 2.0 and 4.0 mL. The ionic strength (IS) was fixed at 10 mM by adding 2.5 mL of NaCl solution (0.1 M). All samples were diluted with deionized water to obtain a 25 mL of final volume. The initial pH of all samples was measured. The sample was shaken at 200 rpm for 24 hours and the final pH was measured. A relationship between the initial pH and the final pH were plotted. Finally, the PZC of bone char was obtained from the common plateau of the plot (Babic' et al., 1998). The surface charge density calculated as following equation:

$$\text{Surface charge density (C m}^{-2}\text{)} = \frac{\{[HCl] - [NaOH] - [H^+] + [OH^-]\}}{M \times S_{BET}} \times 96,500 \quad (16)$$

Where [HCl]	=	Concentration of HCl to add (mol/L)
[NaOH]	=	Concentration of NaOH to add (mol/L)
[H ⁺]	=	Concentration of proton ion (mol/L)
		Calculation from $\text{pH} = -\log [\text{H}^+]$
[OH ⁻]	=	Concentration of hydroxide ion (mol/L)
		Calculation from $\text{pOH} = -\log [\text{OH}^-]$ and
pOH	=	14-pH
96500	=	Faraday's constant (C/mol)
M	=	Weight of adsorbent (g/L)
S_{BET}	=	Surface of adsorbent (m ² /g)

2. Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX)

The images of pig bone char was focused at 500, 10000, 50000 and 100000 of scanning electron microscope (SEM). The Energy-dispersive X-ray spectroscopy (EDX) was focused at 10000 for determination of element pig bone char including carbon, oxygen, phosphorus, calcium and iron.

3. Surface area

The specific surface area was measured by Brunauer–Emmett–Teller (BET).

3.3.3. Adsorption experiment

1. Adsorption kinetic study

The adsorption kinetics of dissolved organic carbon was studied in a batch condition. The bone char was varied at 30, 60, 90 and 120 mg with 150 mL of water sample. The water sample with bone char was shaken at 200 rpm and room temperature. The water sample was collected at various times including 0, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 120, 180, 360, 720 and 1440 minutes, respectively and measured for DOC concentration. After 24 hours, water sample was filtered through a nylon syringe filter with a pore size of 0.45 μm to separate the bone char from solutions. The solutions were analyzed for their remaining DOC concentration.

2. Adsorption isotherm study

The adsorption isotherm was studied by using the obtained results of the adsorption kinetic study. The bone char was put in water sample and shaken at 200 rpm at room temperature. When reach the equilibrium time of adsorption (based on the kinetic study results), the samples were filtered through a 0.45 μm nylon syringe filter for separating the bone char from solutions. The solutions were analyzed for their remaining dissolved organic carbon concentration.

3.3.4. DBPs Precursor Removal Experiment

Raw water was filtered through GF/F followed by 0.45 μm nylon and measured for DOM concentration. The amount of mass of pig bone char used in this experiment

was based on the obtained results of adsorption kinetic study. Bone char was mixed with 150 mL of water sample in Erlenmeyer flask and shaken at 200 rpm and 25°C in room temperature until equilibrium time. The water sample was collected and measured for DOM concentration. DOM concentration was determined by measured DOM surrogate parameters including DOC concentration, UV-254, FEEM and THMFP

1. DOC concentration

DOC concentration in water samples was measured in accordance with Standard Method 5310 Total Organic Carbon (TOC); aj-Analyzer multi N/C 3100; multiWin 4.09. The samples were filtered through a 0.45 micrometers. Milli-Q water (ELGA) was used on every sample for clean system and blank sample preparation. The analysis of DOC was conducted with two replications for each sample.

2. UV Absorbance at wavelength 254 nm

UV-254 of water samples was analyzed in accordance with Standard Method 5910B Ultraviolet Absorption Method. The samples were filtered through a 0.45 m filter prior to measurement. UV-254 of water samples was analyzed by using Perkin-Elmer Model Lambda 365, UV/VIS spectrophotometer: Lambda365 with matched quartz cells that provided a path length of 1 mm. The UV-254 analysis was performed with two replication for each samples.

3. Fluorescence Excitation-Emission Matrices (FEEM)

All water samples including raw water and treated water by magnetically-separable porous bone char and porous bone char was analyzed the FEEM to obtain the DOM characteristics of water samples. The excitation wavelength started from 220 nm to 600 nm by increasing frequency per 5 nm. The detail of FEEM analysis is shown in Table 5.

Table 5 the conditions of Spectrofluometer analysis

Measurement Mode	Emission
Band with excitation	5 nm
Band with emission	5 nm
Response	Fast
Sensitivity	High
Scanning speed	2000 nm/min
Excitation wavelength	Start at 220 nm, end at 600 nm
Emission wavelength	Start at 220 nm, end at 600 nm
Excitation wavelength interval	5 nm
Emission wavelength interval	1 nm

4. Trihalomethanes Formation Potential (THMFPs)

The THMFPs had 4 compounds of study including Chloroform (CHCl_3), Bromodichloromethane (CHBrCl_2), Dibromochloromethane (CHBr_2Cl) and Bromoform (CHBr_3).

The chlorine doses were followed standard method (Chen and Westerhoff, 2010) as shown in equation 16.

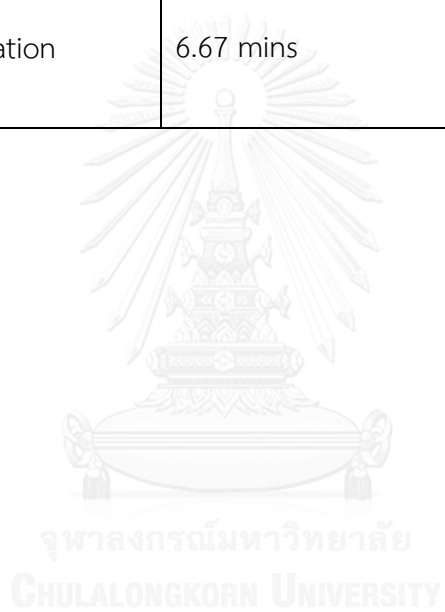
$$\text{Chlorine dose (mg/L)} = 3 \times \text{DOC} + 8 \times \text{NH}_3\text{-N} + 10 \quad \text{--- Eq(16)}$$

THMFP measurements were conducted according to APHA 5710 A-D. The phosphate solution was used as buffer solution before incubation at 25 ± 2 °C in amber bottles with PTFE liners. At the end of 24 hr reaction period, the remaining free chlorine in water samples should be between 3 to 5 mg/L. The residual chlorine was measured according to the Standard Method 4500-Cl G. The chlorine concentration was represented by the light absorbance at 515 nm using a spectrophotometer with matched quartz cells that provided a path length 10 mm. THMs were extracted with MTBE in accordance with EPA551. Agilent Gas Chromatography-6890 with an electron capture detector (ECD) was utilized for measure THMs in water samples under the operating conditions. THMFP analysis was conducted with two replication for each samples and Milli-Q water was used for dilutions, chemical preparation and final glassware cleaning. The conditions of Gas Chromatography are shown in the table 6.

Table 6 conditions of Gas Chromatography

Model	HP 6890 GC
Column	Crossbond6% cyanopropylphenyl-94% dimethyl polysiloxane Length : 30 m and Diameter : 320 μm Film thickness : 0.25 μm Model : constant flow Initial flow : 6.50 mL/min Initial pressure : 0.40 psi
Inlet condition	Model : Split Initial temp : 200 °C Pressure : 23.93 psi Split ratio 50:1 Split flow : 99.8 mL/min Gas type : Helium Total flow : 105 mL/min
Detector condition	Temperature : 250 °C Mode : constant make up flow

	Makeup flow : 45.0 mL/min Makeup gas type : nitrogen
Oven	Initial : 75 °C initial time 0.00 min Ramp 1:15 °C/min to 130 °C for 2 min
Final time	Post Run 180 °C for 1 min
duration	6.67 mins



CHAPTER 4

Result and Discussion

4.1 Physicochemical characteristics of the pig bone char adsorbents

4.1.1 The morphology of pig bone char

The morphology of all synthesis bone chars was investigated by Scanning electron microscope (SEM). The result showed that magnetically-separable porous bone char (F-PBC) had small particles (A, B) as shown in Figure 5. The small particles were iron (III) nitrate that adding into pig bone char in the synthesis process. It could approved that adding iron (III) nitrate decompose into pig bone char. On the other hand, the porous bone char (PBC) as shown in Figure 5 (C and D) had a smooth surface. So it was shown that the addition of iron (III) nitrate to pig bone char can change the

morphology of the pig bone char. While, the different temperatures in synthesis process were not affected to the morphology of pig bone chars.

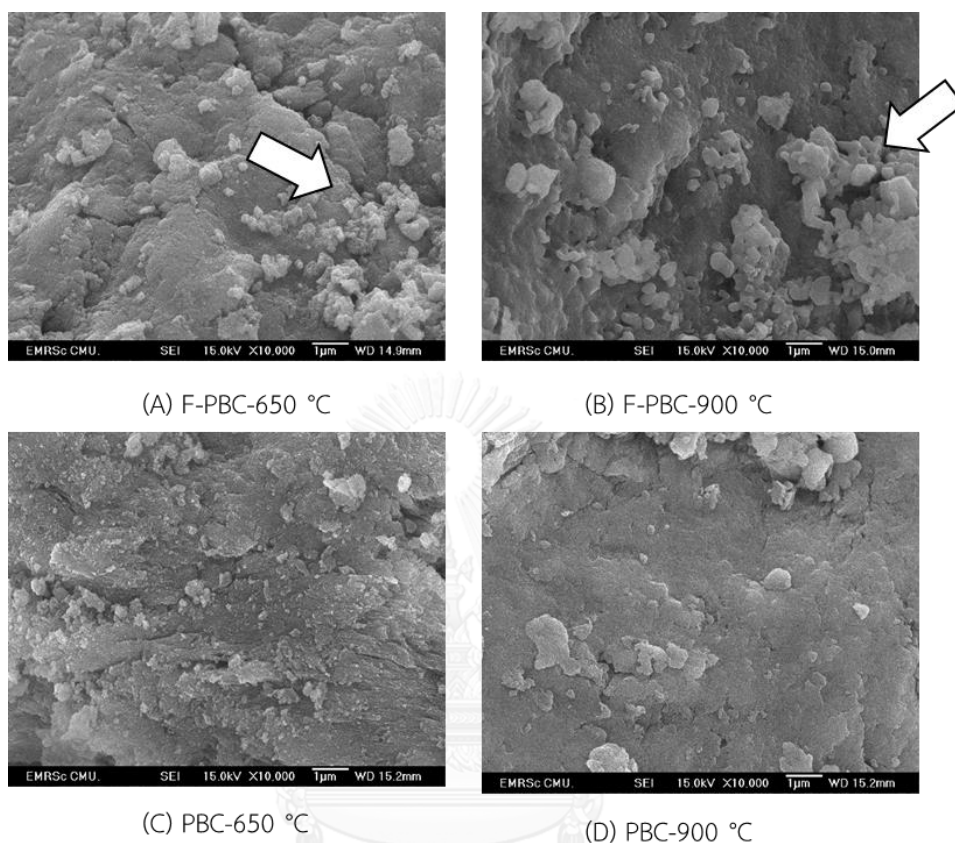


Figure 5 The morphology of pig bone char

4.1.2 The element in pig bone char

The element in all pig bone char was investigated by using Energy-dispersive X-ray spectroscopy, EDX spectrum as shown in Table 7 and 8. The element constituents of magnetically-separable porous bone char (F-PBC) and porous bone char (PBC) including carbon (C), oxygen (O), phosphorus (P), calcium (Ca), nitrogen (N) and iron (Fe).

Table 7 The results of Energy-Dispersive X-ray spectroscopy (EDX) of pig bone char at 650 °C.

F-PBC-650 °C			PBC-650 °C		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
C	13.41	21.7	C	8.67	15.35
O	47.63	57.85	O	42.15	56.06
P	12.73	7.99	P	15.82	10.87
Ca	24.39	11.83	Ca	33.37	17.72
Fe	1.83	0.64			
Totals	100		Totals	100	

Table 8 The results of Energy-Dispersive X-ray spectroscopy (EDX) of pig bone char at 900 °C.

F-PBC-900 °C			PBC-900 °C		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
C	5.46	9.49	C	8.05	13.48
O	50.4	65.8	N	2.18	3.13
P	14.07	9.49	O	48.06	60.41
Ca	27.04	14.09	P	13.9	9.03
Fe	3.02	1.13	Ca	27.81	13.95
Totals	100		Totals	100	

Table 7 and 8 summarized the result of Energy-Dispersive X-ray spectroscopy (EDX). The results shown that the F-PBC-650 °C has ferrous element (1.83 % by weight) and F-PBC-900 °C has ferrous element (3.02 % by weight) which can separate the

magnetically pig bone char from the solution by magnet. The carbon element of pig bone char at 650 °C (13.41 % and 8.67 % by weight) has higher than pig bone char at 900 °C (5.46 % and 8.05 % by weight). The carbon was the organic in the pig bone char that it remaining inside the pig bone char (R. Leyva-Ramos., 2010). It demonstrated that the pig bone char burning at high temperature (900 °C) could strongly remove organic. On the other hand, the average mass of atoms of an element used to calculating the atomic weight which using the relative abundance of isotopes in a naturally-occurring element.

The Fe mapping image in the Figure 6 showed that Fe element presented in the surface of pig bone char. There were many small particles in left side of the right picture. So the Fe element presented at left side more than right side. It can be confirmed that the Fe element decompose into pig bone char.

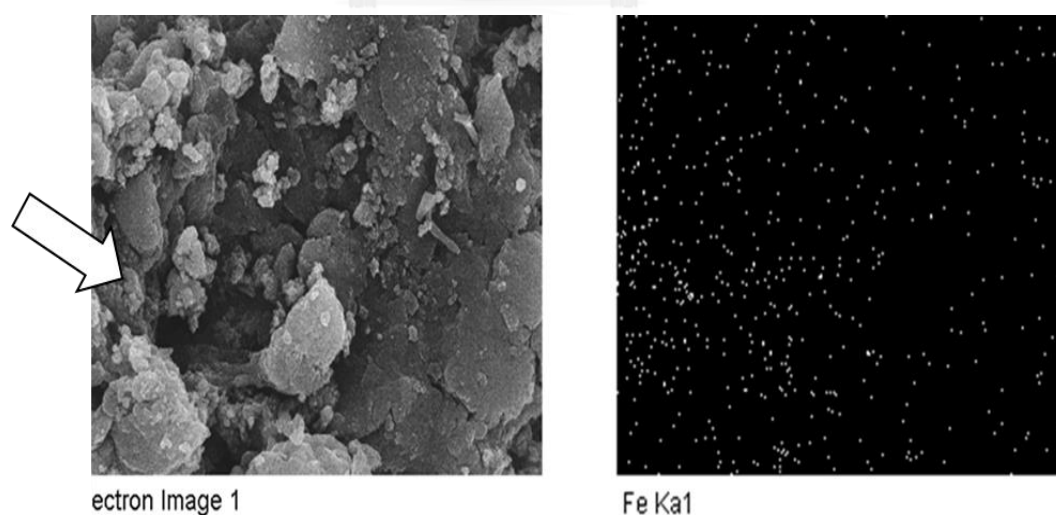


Figure 6 The Fe mapping image of F-PBC-900 °C

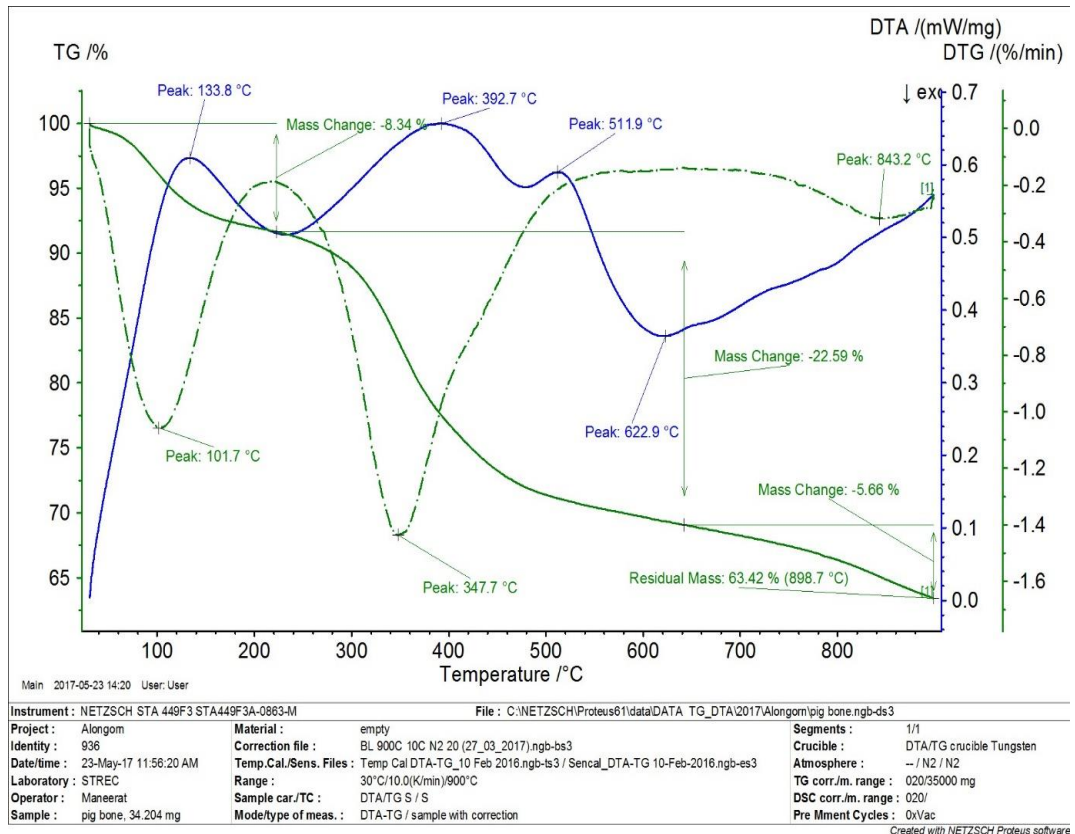


Figure 7 DTA curves and weight loss of pig bone char adsorbent

The DTA curves and weight loss of pig bone char adsorbent by using Simultaneous Thermal Analyzer as shown in the Figure 7. It presented to three-step weight loss. The first step was an endothermic change at less than 200 °C corresponded to the evaporation of ethanol and physisorbed water (-8.34%). The second step was greatly decreased weight loss at 250-650 °C. It was attributed to the thermal decomposition of surfactant molecules. The third step was observed at around 650 °C which degradation of the bridging ethylene moieties in the pig bone char (Suriyanon, Punyapalakul, & Ngamcharussrivichai, 2015). The pig bone char gave total weight loss (36.58%).

4.1.3 N₂ Adsorption-Desorption isotherms

The N₂ adsorption-desorption isotherms of F-PBC-650°C, PBC-650°C, F-PBC-900°C and PBC-900°C adsorbents presents in Figure 8, 9, 10 and 11 respectively. It was applied to the BET surface area, pore size and pore volume of each adsorbent. Brunauer-Emmett-Teller (BET) equation was used for calculating the surface area, pore volume, and average pore size of adsorbents.

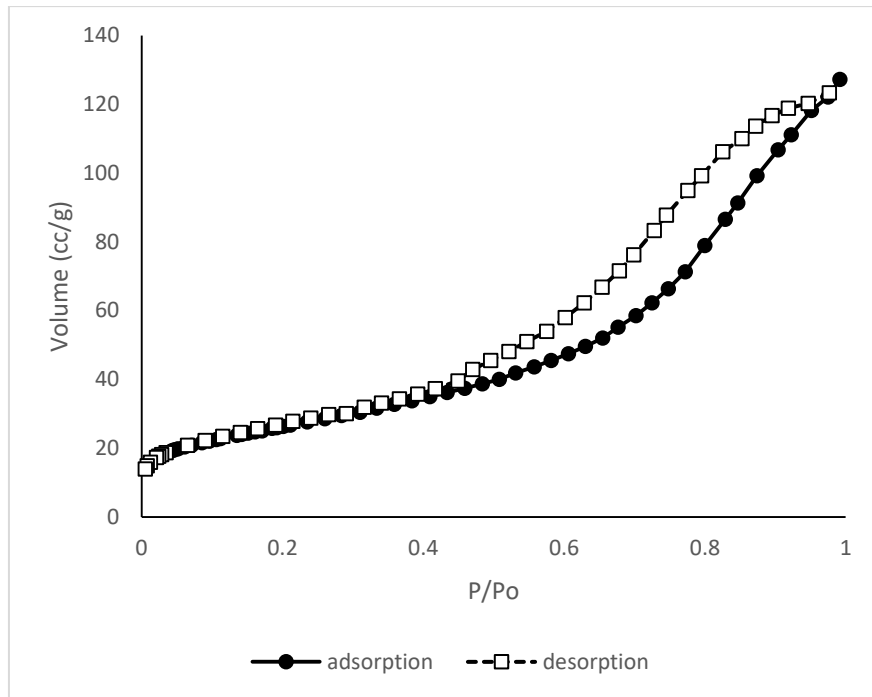


Figure 8 N₂ adsorption-desorption isotherms of F-PBC-650 °C adsorbent

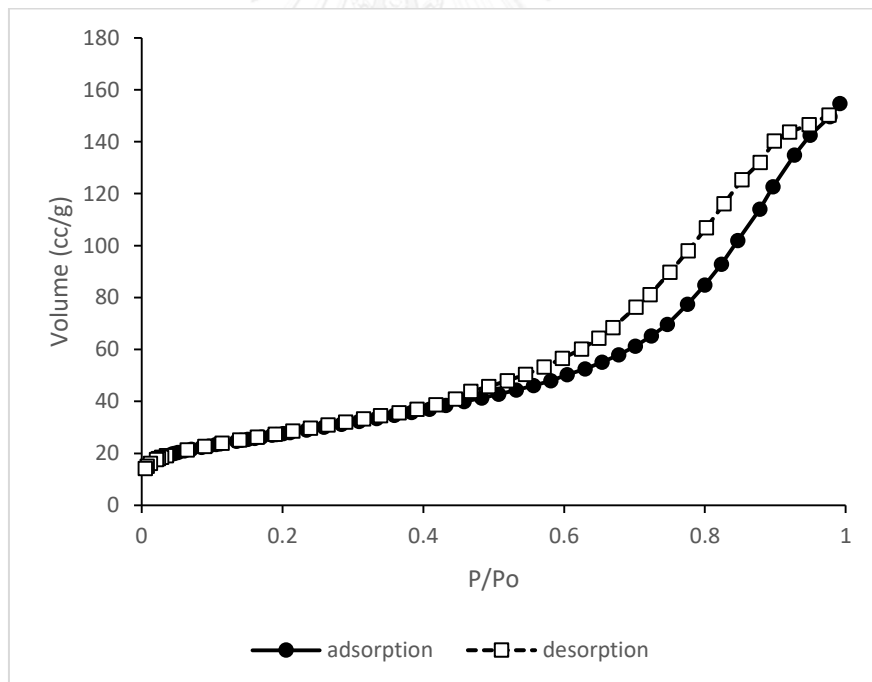


Figure 9 N₂ adsorption-desorption isotherms of PBC-650 °C adsorbent

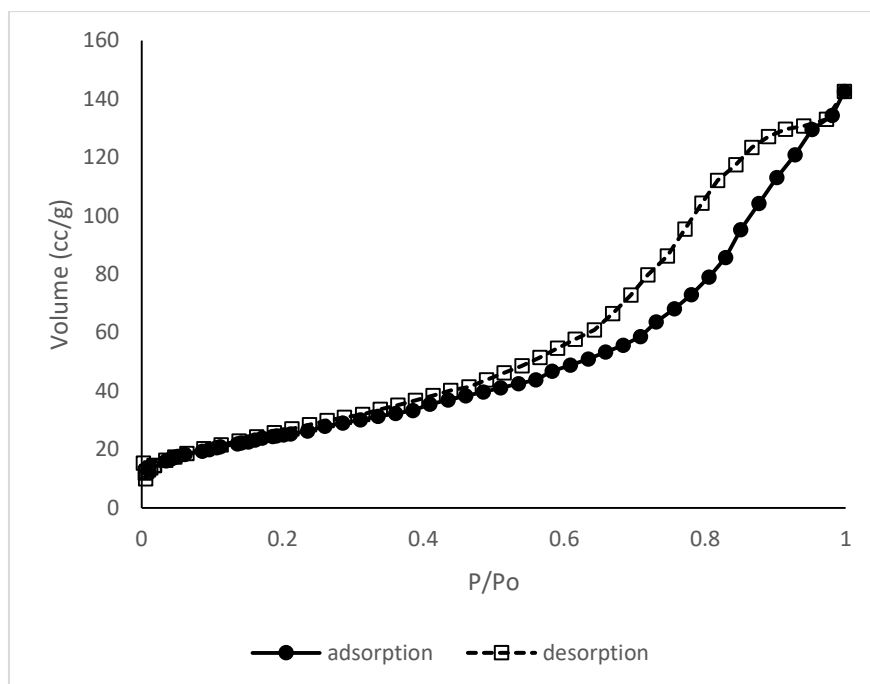


Figure 10 N₂ adsorption-desorption isotherms of F-PBC-900 °C adsorbent

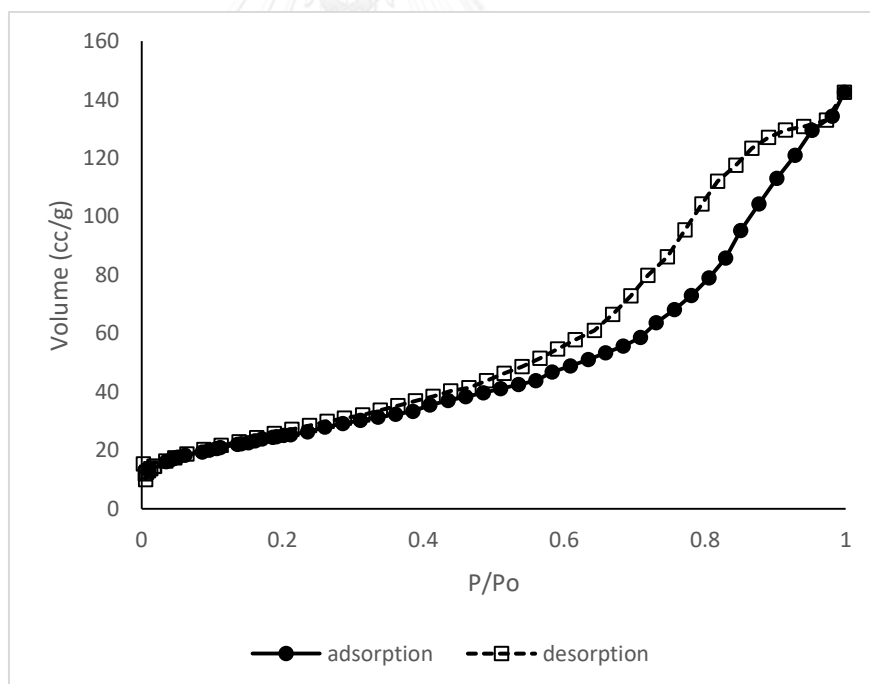


Figure 11 N₂ adsorption-desorption isotherms of PBC-900 °C adsorbent

From the result, the N_2 adsorption-desorption isotherms shown the characteristics surface area, pore size and pore volume of PBC adsorbents. They were type IV that shown the mesoporous structure (2-50 nm). The specific surface area and the volume of porosity related to the adsorption capacity (Laura R. B., 2009). According to IUPAC classification (1985), it shows in Figure 12.

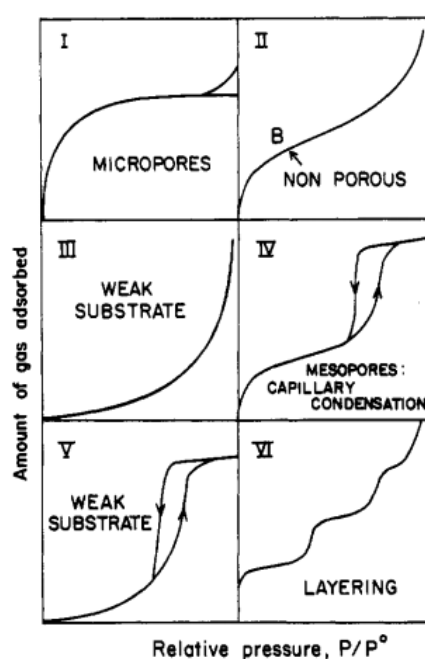


Figure 12 Types of adsorption isotherm, IUPAC classification (1985)

The specific surface area of adsorbent was analyzed by BET technique, as shown in Table 9. The mesopore volume of F-PBC-900 °C and PBC-900 °C was higher than F-PBC-650 °C and PBC-650 °C. While, the BET surface area of all PBC adsorbents followed the order: PBC-650 °C > F-PBC-650 °C > F-PBC-900 °C > PBC-900 °C > PB. According to the result of micropore volume, which the PBC-650 °C and F-PBC-650 °C higher than F-PBC-900 °C and PBC-900 °C. It indicated that micropore volume affected

the surface area of pig bone char. In addition, the F-PBC-650 °C had lower surface area than PBC-650 °C that it may be covered by iron (III) nitrate caused to decreasing of surface area.

Table 9 The Brunauer–Emmett–Teller (BET) result

Adsorbents	BET surface area (m ² /g)	Vmic_DR (cm ³ /g)	Vmeso (cm ³ /g)
Raw pig bone	3.53	-	-
F-PBC-650°C	94.92	0.04	0.19
PBC-650°C	100.63	0.04	0.24
F-PBC-900°C	81	0.0334	0.2299
PBC-900°C	78	0.0323	0.2490

As for the obtained results of bet surface area in the Table 9, the F-PBC-900 °C and PBC-900 °C had lower bet surface area than PBC-650 °C and F-PBC-650 °C. However, the F-PBC-900 °C and PBC-900 °C should be utilized as the alternative adsorbents due to the higher mesopore volume than others. The mesoporous structure was given large pore volume and high surface area which defined as the good properties adsorbents (Sangeeta Patela, 2015). Moreover, the F-PBC-900 °C could separate from treated water by magnet as shown in the Figure 13.

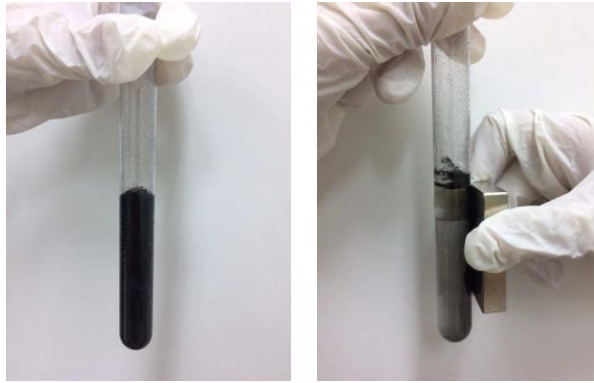


Figure 13 the F-PBC separated from solution by magnet

4.1.4 Point of zero charge (PZC) and Surface charge density

The Point of Zero Charge (PZC) was express pH value that affected to the surface charge of absorbent. The PZC of magnetically-separable porous bone char (F-PBC-900 °C) and porous bone char (PBC-900 °C) was found at approximate pH 6.5-8.5, as shown in Figure 14. If the pH of the solution was above the PZC of pig bone char (>8.5), the surface of pig bone char was negatively charged. On the other hand, if the pH of the solution was below the PZC of pig bone char (<6.5), the surface of pig bone char was positively charged.

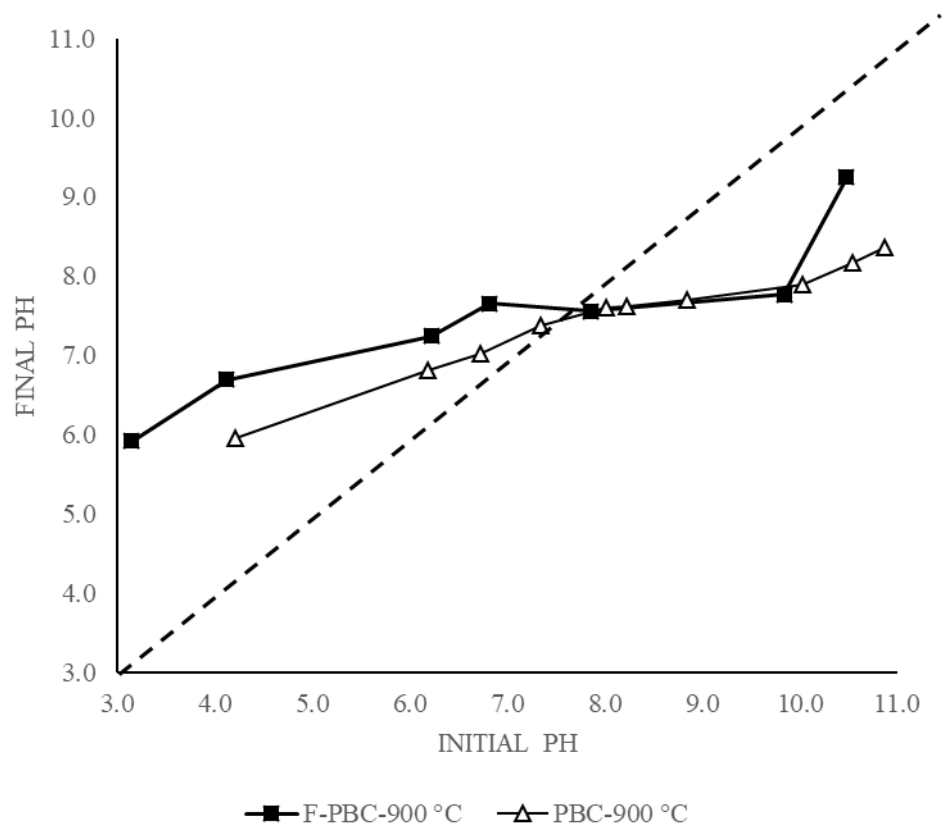


Figure 14 Point of zero charge (PZC)

Figure 14 showed the surface charge density of magnetically-separable porous bone char (F-PBC) and porous bone char (PBC). It was found that the result was in accordance with the PZC result. The result was compared with PAC (Poly Aluminum Chloride) which generally used as adsorbent in water treatment process. The pH of PZC value of PAC was 9.5 and pH value of Surface Charge Density of PAC was around 8-10 (Prarat, 2011). Therefore, magnetically-separable porous bone char and porous bone char result are approximate to the PAC result.

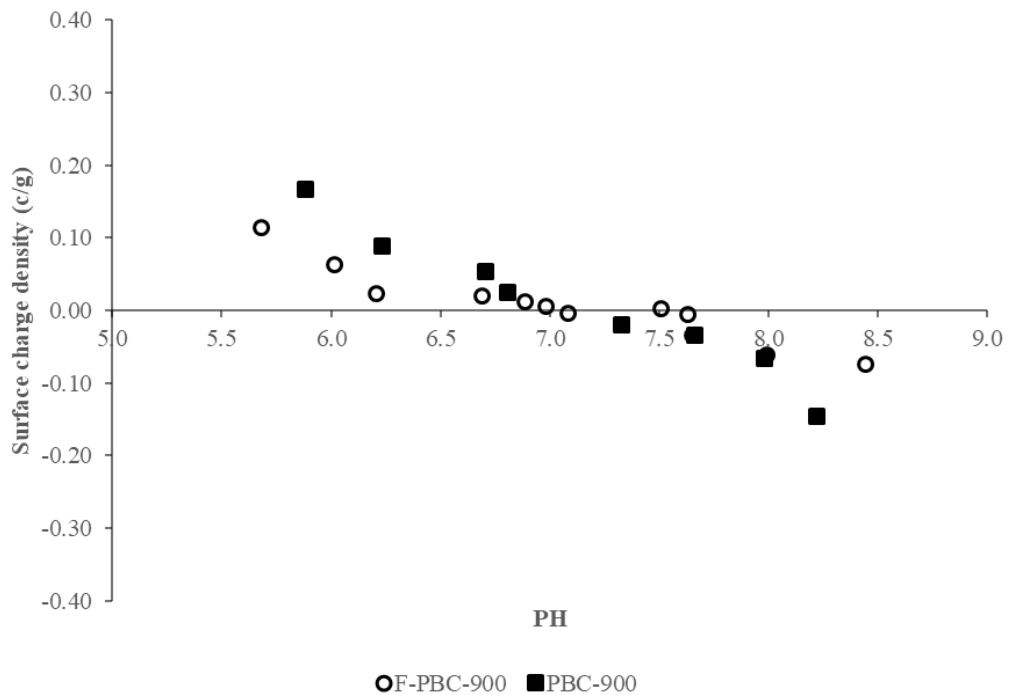


Figure 15 Surface charge density

In general, DOM normally found in hydrophobic form more than hydrophilic form. Hydrophobic was consisting of humic acids and humic-like substances (Sillanpaa et al, 2010). In addition, this substance was rich of aromatic carbon and shown anion charge (H^-) (Swietlik, Dabrowska, A., & Nawrocki, 2004). Hence, the PZC could show the range of suitable pH for DBPs precursor removal from surface water by pig bone char adsorbents.

4.2 Raw surface water characterization

Water quality and DOM surrogate parameter of raw surface water from Ping River in October, 2016 are shown in Table 10. The pH values of raw surface water were 8.0-8.8 with in the range of PZC and surface charge density results. Consequently, the surface of F- PBC-900 °C and PBC-900 °C were zero charge as following the result of PZC and Surface charge density in Figure 14 and 15. The absorption of organic matter on adsorbent was based on the pore volume. Thus, the pH adjustment of raw water not required. The turbidity of raw surface water was 51.37 NTU. The standard of turbidity of water supply was set at 5 NTU by Provincial Waterworks Authority, Thailand (PWA, 2013).

Table 10 Ping river water quality

Parameters	Raw surface water
Turbidity (NTU)	51.37
pH	8.0-8.8
DOC (mg/l)	4.492
UV-254(cm^{-1})	0.033
THMFP ($\mu\text{g/L}$)	1446.26

The values of DOC, UV-254 and THMFP of raw surface water in October, 2016 were 4.492 mg/L, 0.033 cm⁻¹, and 1446.26 µg/L, respectively. The value of DOC in water is used to indicate the aromatic and aliphatic hydrocarbons in water. The DOC concentration of raw water was found at 4.492 mg/L which is higher than DOC concentration in other water resources such as reservoir and groundwater. In addition, Hata et al (2009) found that the DOC concentration of Ping River were high at 5.7 mg/L in rainy season. The different of DOC values of Ping River was depended on the seasonal changes, collection times and also the rainfall in each year.

THMFPs investigated from the Ping River including CHCl₃, CHBrCl₂, CHBr₂Cl and CHBr₃ were 1344.09 µg/L, 57.47 µg/L and 44.69 µg/L. The value of all THMFPs was 1446.26 µg/L. While CHBr₃ was not found from the Ping River. The highest compounds of THMFPs followed the order: CHCl₃>CHBrCl₂> CHBr₂Cl. The result shown CHCl₃ was a significant compound in the THMFP which the highest value compounds. Similar with many researchers found CHCl₃ was the highest value (Krutklom, 2013; Rodriguez, 2004).

According to Rakraum (2013), the turbidity, pH, UV-254, DOC and THMFPs of Ping river water in rainy season (August,2012) were 291 NTU, 7.6, 0.076 cm⁻¹, 2.3 mg/L and 330 µg/L, respectively. When compared to the results in this study. It was found that the concentration of DOC and THMFPs of this study was higher than the results of Rakraum (2013). It can be indicated that the increasing of THMFPs was related to the higher concentration of DOC. However, the results of THMFPs not related to the

UV-254 results. It can be indicated that the formation of THMs not related to the UV-254 absorbance.

4.3 Adsorption of dissolved organic matter on pig bone char

4.3.1 Adsorption kinetic

The kinetic curves of dissolved organic carbon adsorption on F-PBC-900 °C and PBC-900 °C adsorbents with varying concentration (0.2, 0.4, 0.6 and 0.8 mg/L) were illustrated in Figure 16, 17, 18 and 19, respectively. The adsorption of organic matter by F-PBC-900 °C and PBC-900 °C was fast within a short contact time. After 1 hour, the adsorption of PBC adsorbents regularly slowed until it reached equilibrium. The highest adsorption dissolved organic carbon capacity by F-PBC-900 °C at equilibrium was 13.71, 8.330, 5.587 and 4.559 mg/g, and PBC-900 °C was 19.97, 8.505, 5.589 and 4.42 mg/g at 0.2, 0.4, 0.6 and 0.8 g/L, respectively.

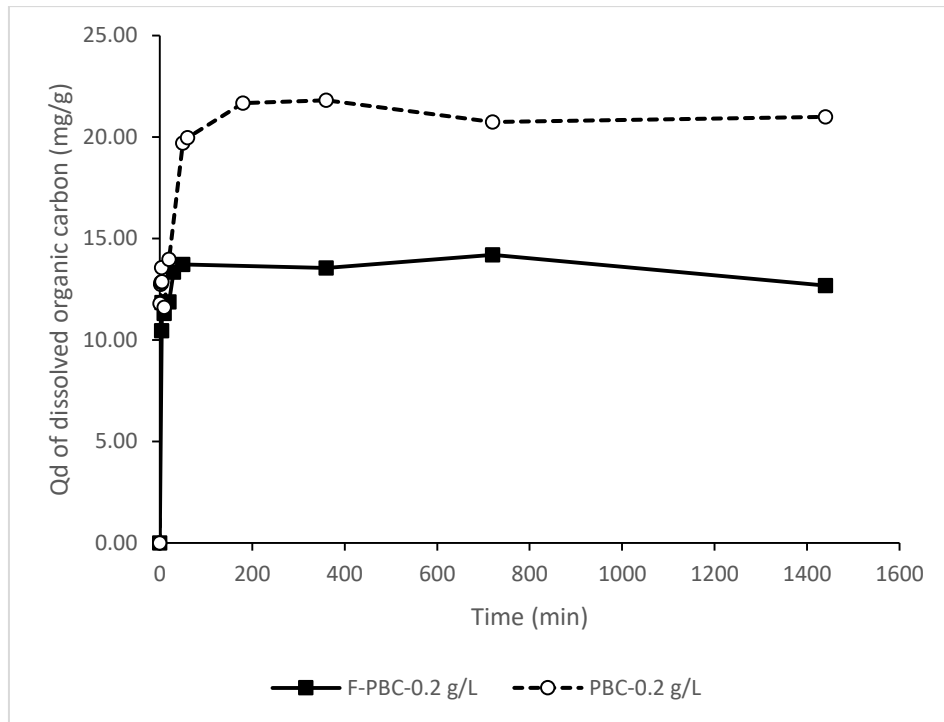


Figure 16 kinetics adsorption of dissolved organic carbon with 0.2 g/L adsorbents

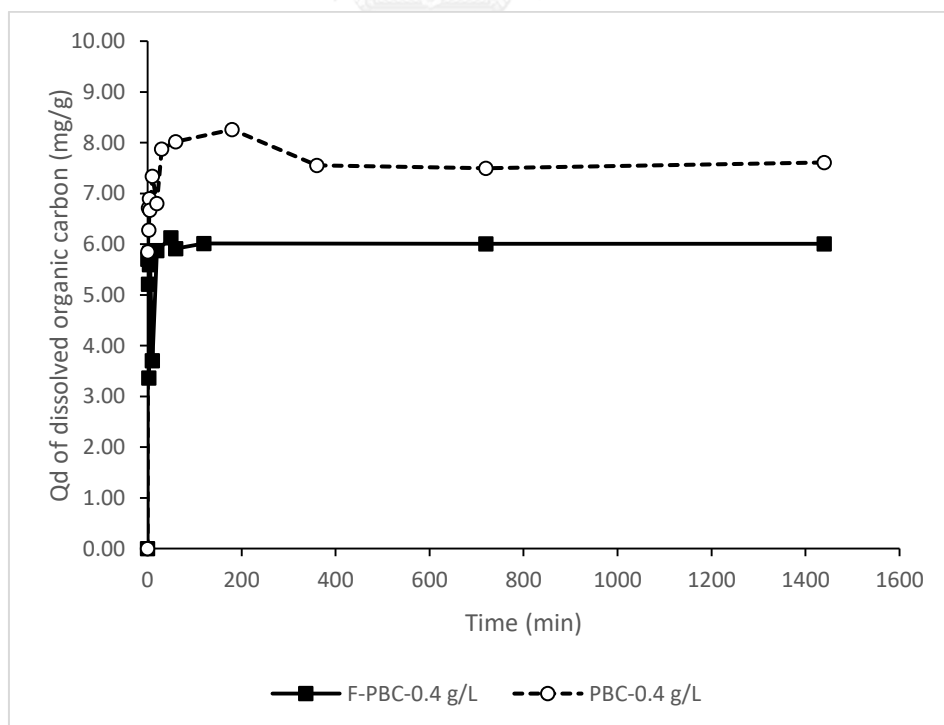


Figure 17 kinetics adsorption of dissolved organic carbon with 0.4 g/L adsorbents

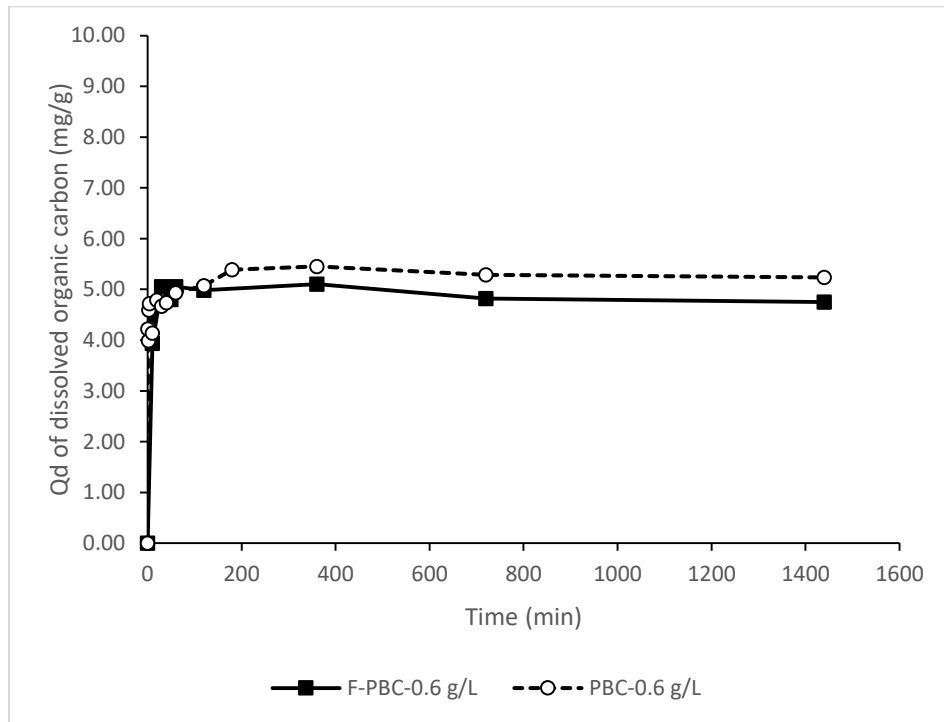


Figure 18 kinetics adsorption of dissolved organic carbon with 0.6 g/L adsorbents

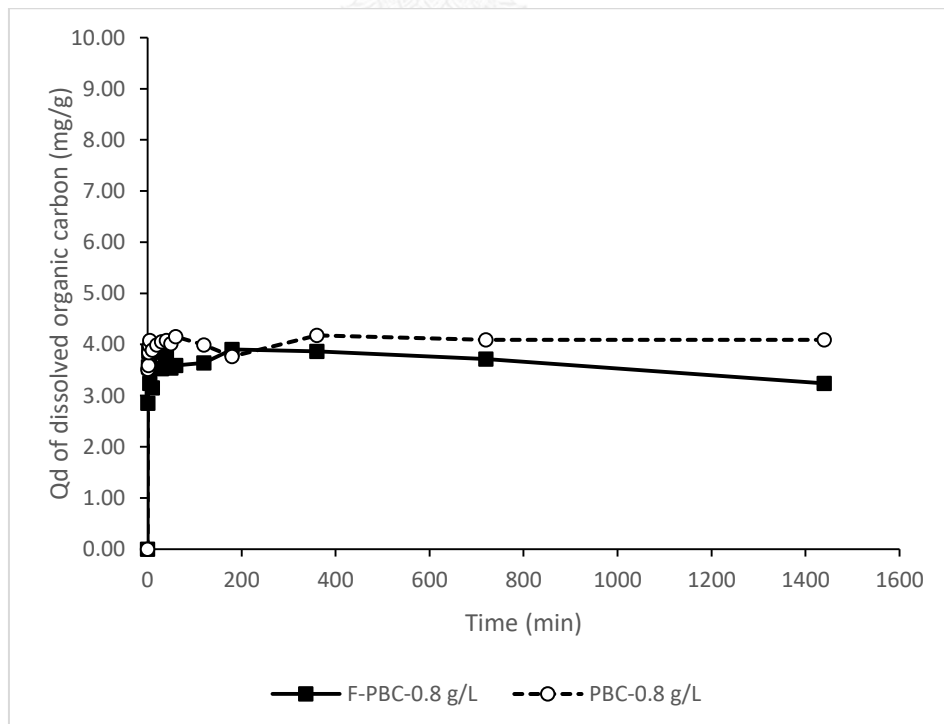


Figure 19 kinetics adsorption of dissolved organic carbon with 0.8 g/L adsorbents

The pseudo- first order and the pseudo- second order were applied for examining the adsorption kinetic of dissolved organic matter onto pig bone char adsorbents as shown in Table 11. The constant (k) values of pseudo-first order were calculated from the slope of each regression line. Besides, the square of the slope divided by the intercept of the regression line was calculated for the constant (k) of the pseudo-second order kinetic model. In this study, The R² (the correlation coefficient) value was considered for defining the kinetic model which is the best fit for adsorbents. When the R² (correlation coefficient) of each models of pig bone char was compared, The R² (the correlation coefficient) value of pseudo-second order kinetic model was higher than the R² value of pseudo-first order model for all conditions. Similar with another research that using bone char adsorbents was best fit pseudo-second order kinetic model (André L. Cazetta, 2016; C.K. Rojas-Mayorga, 2015; N.A. Medellin-Castillo & J.V. Flores-Cano, 2014; Sawangjang, 2016)

The initial adsorption rates (h) of that F-PBC-900 °C and PBC-900 °C at various concentrations were determined by using Eq 17 and the results are shown in Table 11.

$$h = k_2 q_e^2 \quad \text{Eq (17)}$$

Where k_2 pseudo-second-order rate constant (g/mg/min) and initial adsorption rate (h) (mg/g.min).

Table 11 Kinetic parameters of the dissolve organic carbon adsorption on F-PBC and PBC at 900 °C.

Adsorbents	Q _{e,exp} mg/g	Pseudo-first order			Pseudo-second order			
		Q _{e,cal} mg/g	k ₁ , min ⁻¹	R ²	Q _{e,cal} mg/g	k ₂ , min ⁻¹	R ²	h
F-PBC-0.2 g/L	13.71	1.53	-0.0002	0.0401	13.09	0.0772	0.9971	14.51
F-PBC-0.4 g/L	8.33	0.65	9*10 ⁻⁵	0.0047	5.15	0.1693	0.9944	11.75
F-PBC-0.6 g/L	5.59	0.53	-0.0002	0.0737	4.97	0.2095	0.9997	6.54
F-PBC-0.8 g/L	4.56	0.38	0.0002	0.0172	3.92	0.3008	0.9958	6.25
PBC-0.2 g/L	19.97	2.49	-0.0005	0.1227	20.05	0.0475	0.9995	18.94
PBC-0.4 g/L	8.51	4.05	-0.0003	0.1566	8.64	0.1317	0.9998	9.53
PBC-0.6 g/L	5.59	0.58	0.0002	0.095	5.31	0.1902	0.9999	5.94
PBC-0.8 g/L	4.42	0	0.0006	0.0607	4.10	0.2443	0.9999	4.77

From the R² value from Table 11, it can be concluded that F-PBC-900 °C and PBC-900 °C were pseudo-second order model. It was presented to chemisorption (Wang H, 2007) which is an electrostatic interaction between dissolved organic carbon and F-PBC-900 °C and PBC-900 °C adsorbents. The initial adsorption rate (h) of pig bone char at 900 °C followed the order: PBC-0.2 g/L > F-PBC-0.2 g/L > F-PBC-0.4 g/L > PBC-0.4 g/L > F-PBC-0.6 g/L > F-PBC-0.8 g/L > PBC-0.6 g/L > PBC-0.8 g/L. The high h values indicated the fast adsorption process. The h values of F-PBC were almost higher than PBC. Although PBC had the highest adsorption dissolved organic carbon capacity. Hence, the result indicated that the adsorption process not only occur with adsorption dissolved organic carbon capacity but also had another mechanisms

such as electrostatic interaction and interparticle diffusion (Permrunguang, 2013).

4.3.2 Adsorption isotherm

In this study, the correlation with the experimental data was investigated by using Linear, Langmuir, and Freundlich isotherm models which can be defined as following equation 18, 19 and 20 respectively.

$$q_e = k_p c_e \quad \text{Eq (18)}$$

$$\frac{1}{q_e} = \frac{1}{K_L q_0} \frac{1}{C_e} + \frac{1}{q_0} \quad \text{Eq (19)}$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad \text{Eq (20)}$$

Where q_e is the amount of dissolved organic carbon adsorbed on BC at equilibrium (mg /L), C_e is the dissolved organic carbon concentration at equilibrium, K_p is the Linear constant (L/mg), q_0 is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), K_F is the Freundlich constant (L/g), and n is the adsorption intensity.

The study of adsorption isotherm of F-PBC-900 °C and PBC-900 °C were investigated by vary concentration (0.2, 0.4, 0.6 and 0.8 g/L). The adsorption isotherm result of Linear, Langmuir and Freundlich models are shown in Figure

20, 21 and 22, respectively. Besides, the isotherm parameters of the adsorption on the F-PBC and PBC adsorbents were summarized in Table 12. When the R^2 (the correlation coefficient) value of three models of F-PBC-900 °C and PBC-900 °C adsorbents were compared, the R^2 value of Langmuir isotherm model had the highest value than the other models in F-PBC. On the other hand, the R^2 value of Freundlich isotherm model had the highest among the other model in PBC. It can be concluded that F-PBC-900 °C was best fitted to Langmuir isotherm model and PBC-900 °C was best fitted to Freundlich isotherm model. So the F-PBC-900 °C occurred on monolayer adsorption of surface while the PBC was multilayer adsorption of surface. Interestingly, the F-PBC-900 °C and PBC-900 °C were different in term of isotherm model. Because of the Langmuir and Freundlich isotherm model was depending on concentration at equilibrium time. It indicated that the Freundlich isotherm model was not best fitted with high concentration and low concentration. So the F-PBC-900 °C was lower range of concentration that was best fitted with Langmuir isotherm model similar with other resercheres (André L. Cazetta, 2016; C.K. Rojas-Mayorga, 2015; N.A. Medellin-Castillo & J.V. Flores-Cano, 2014; Sawangjang, 2016). The PBC-900 °C was medium range of concentration which best fitted with Freundlich isotherm model (Punyapalakul). In addition, the morphology and the volume of of mesopore and micropore of F-PBC and PBC were different which results in the different isotherm of these two bones char.

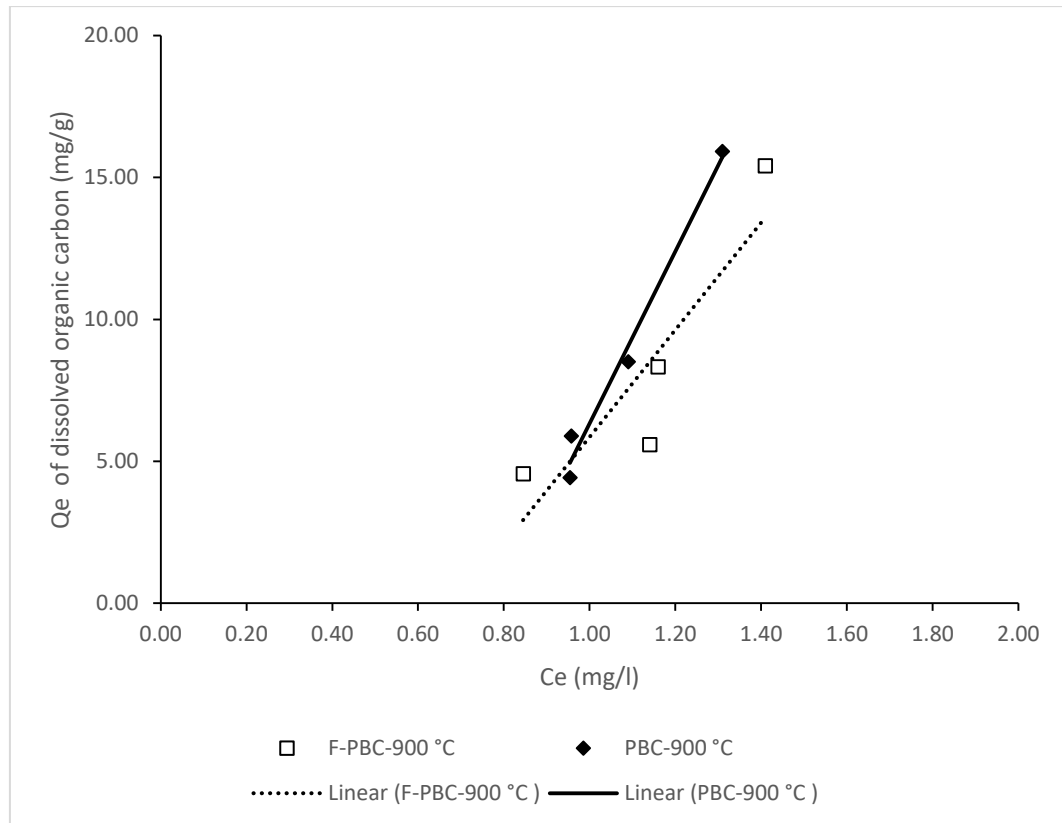


Figure 20 Comparison of linear isotherm models of F-PBC and PBC adsorbents

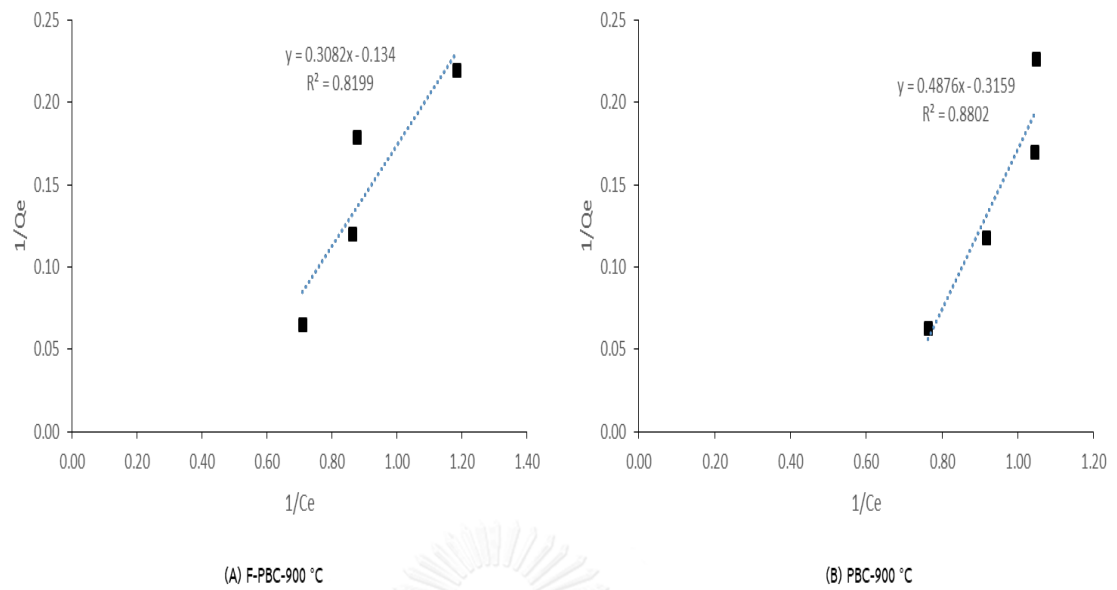


Figure 21 Langmuir isotherm models of (a) F-PBC (b) PBC adsorbents

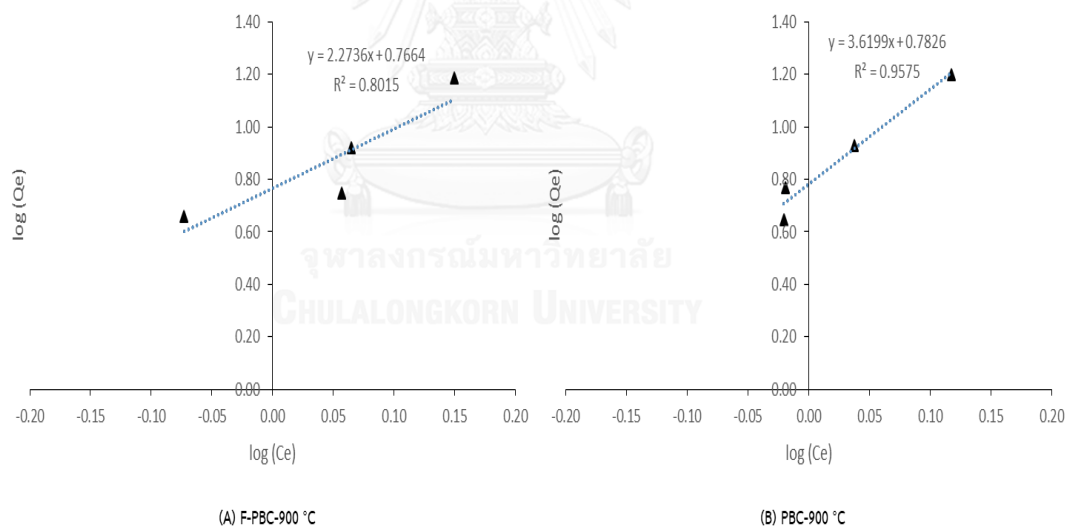


Figure 22 Freundlich isotherm models of (a) F-PBC (b) PBC adsorbents

Table 12 Isotherm parameters of the dissolved organic matter adsorption on the F-PBC and PBC

Model	parameter	F-PBC	PBC
Linear	R ²	0.7949	0.9827
	K _p , L/mg	18.868	30.25
Langmuir	R ²	0.8199	0.8802
	Q _o , mg/g	15.41	15.91
	K _L , L/mg	0.3082	0.4876
Freundlich	R ²	0.8015	0.9575
	n	3.15	2.26
	K _F , L/mg	2.2736	3.6199

4.4 Disinfection by-products (DBPs) precursor removal by pig bone char

4.4.1 Adsorption of Disinfection by-products (DBPs) precursor

The adsorption of DBPs precursor was conducted by varying the concentration of adsorbent as 0.2, 0.4, 0.6 and 0.8 g/L and continuous absorb until the equilibrium time. The treated water was collected and measured the DBPs precursor. The results of DBPs precursor removal by porous bone char absorption are illustrated in Figure 23 and 24.

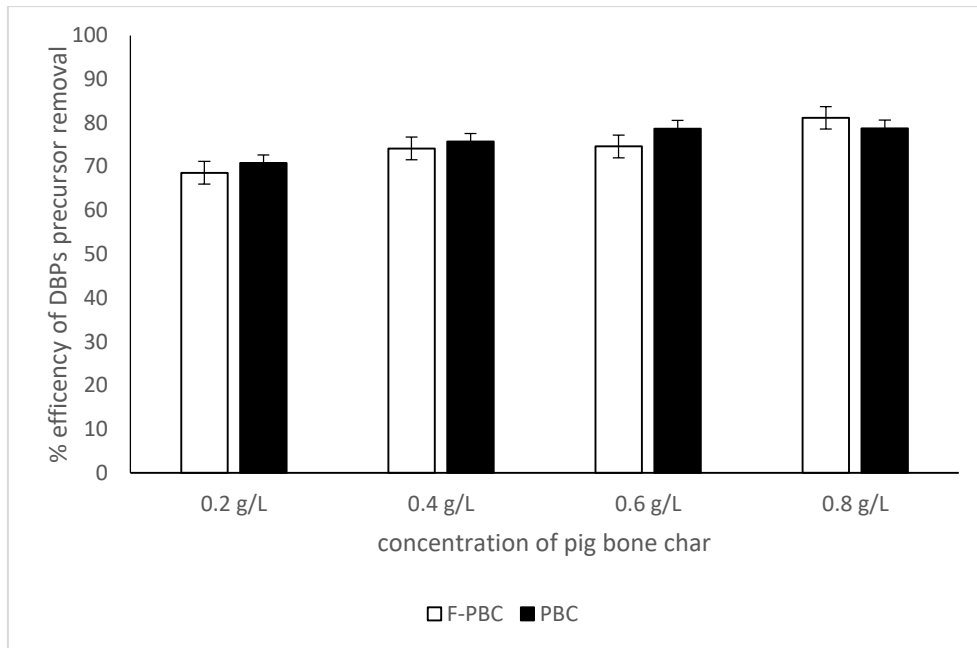


Figure 23 efficiency of Dinsinfection by-products (DBPs) precursor removal

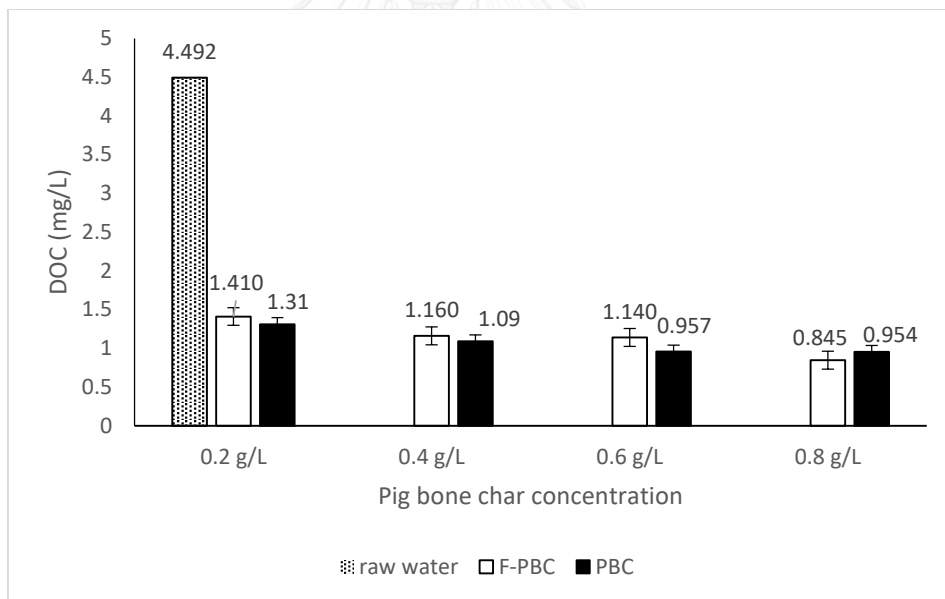


Figure 24 Dinsinfection by-products (DBPs) removal

The figure 23 presented the efficiency of DBPs precursor removal of pig bone char. The DBPs precursor removal of both of pig bone char was about 70-80 %. The Figure 24 showed the DOC concentration before and after

adsorption process. The result of DOC concentration was strongly decreased by varying the concentration of adsorbents as 0.2, 0.4, 0.6 and 0.8 g/L. The F-PBC-900 °C was 1.400, 1.160, 1.140 and 0.845 mg/L and the PBC-900 °C was 1.310, 1.090, 0.957 and 0.954 mg/L respectively. The efficiency of DBPs precursor removal related to many parameters including bet surface area, volume of mesopore and mechanisms of adsorption process. The results in Figure 23 and 24 showed that all of PBC concentration except 0.8 g/L has higher DOC removal than F-PBC. The results related with the higher volume of mesoporous of PBC. From the results, it can be indicated that the adsorb of DOM on adsorbent depend on the volume of mesoporous. The increase of mesoporous result in higher DOM removal.

4.4.2 UV-254

UV absorbance at wavelength 254 nm (UV_{254}) was the one of surrogate parameters that indicates 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 presented the hydrophobic fraction of natural organic matter (Stevenson, 1982). The HPO was greatly reactive with chlorine to forming THMs. The result of UV-254 as shown in the Table 13 and Figure 25, the UV-254 of raw surface water was 0.0328 cm^{-1} . The increasing concentration of pig bone char (0.2 g/L, 0.4 g/L, 0.6 g/L and

0.8 g/L) had significantly decrease the value of UV-254 in treated water. The UV-254 in treated water were 0.0223, 0.0177, 0.0259 and 0.0118 cm⁻¹, respectively for F-PBC. On the other hand, there were 0.0254, 0.0245, 0.0245 and 0.0084 cm⁻¹, respectively, for PBC.

Table 13 The result of UV-254 in raw water and treated water by all absorbents

Sample	UV-254 (cm ⁻¹)
Raw surface water	0.0328
F-PBC-0.2 g/L	0.0223
F-PBC-0.4 g/L	0.0177
F-PBC-0.6 g/L	0.0259
F-PBC-0.8 g/L	0.0118
PBC-0.2 g/L	0.0254
PBC-0.4 g/L	0.0245
PBC-0.6 g/L	0.0206
PBC-0.8 g/L	0.0084

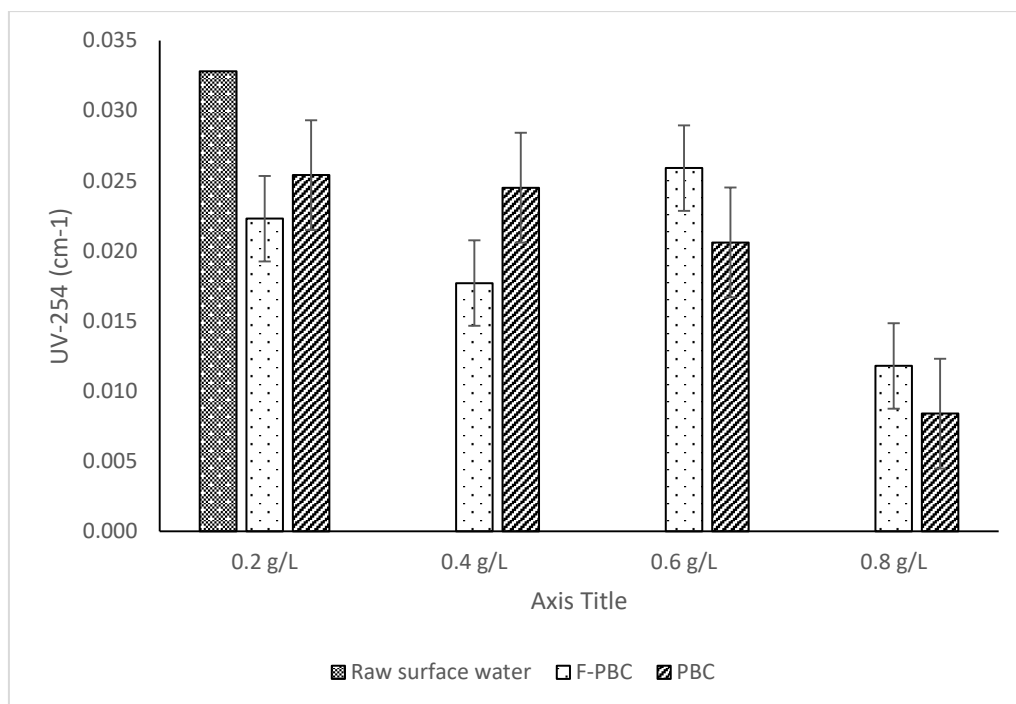


Figure 25 The result of UV-254 in raw water and treated water by all absorbents

4.4.3 Fluorescence Excitation-Emission Matrices (FEEM)

The characteristics of DOM in raw water and treated water by F-PBC-900 °C and PBC-900 °C were investigated by using FEEM technique. The result of FEEM of raw water from the Ping River is illustrated in Figure 26.

Raw surface water

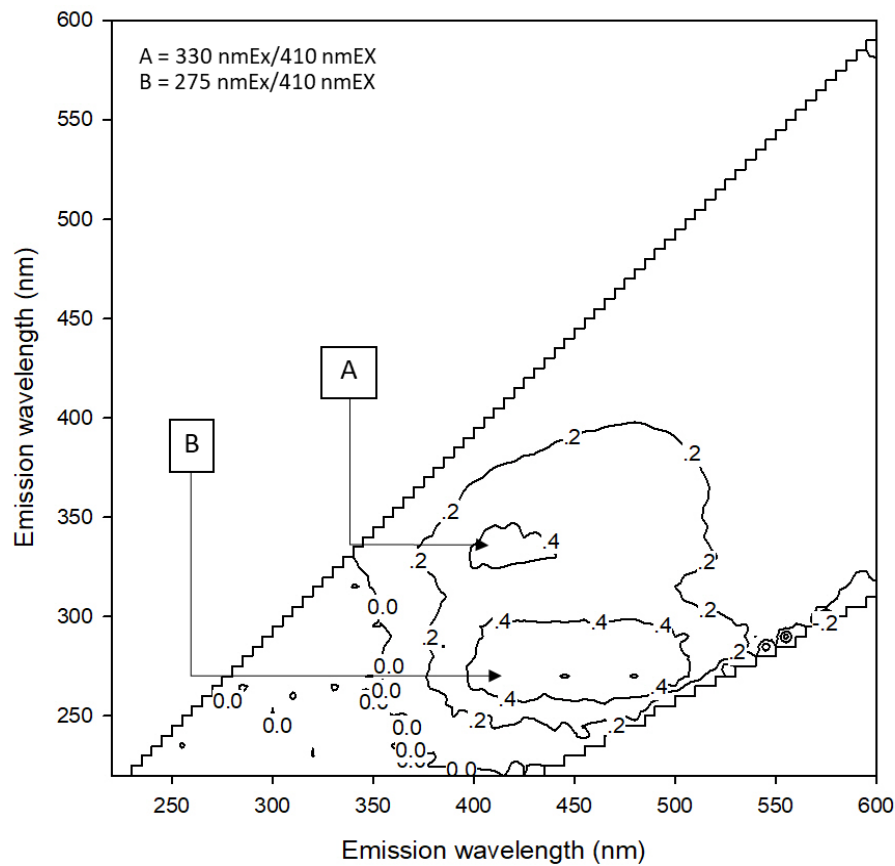


Figure 26 FEEM of rawwater from the Ping River

The obtained results showed that two peak were found in raw water sample including the fluorescent peak A and B. The peak A and B represented the Humic acids and humic-like substances of DOM (Chen, 2003; Coble, 1996; Leenheer, 2003).The major pyrolysis fragments of Humic substances were humic and fulvic acids similar with Wudthigarn, 2015. He observed adsorption of PAC on the Ping River. The result shown that the ping River represented the Humic acids and humic-like substances of DOM.

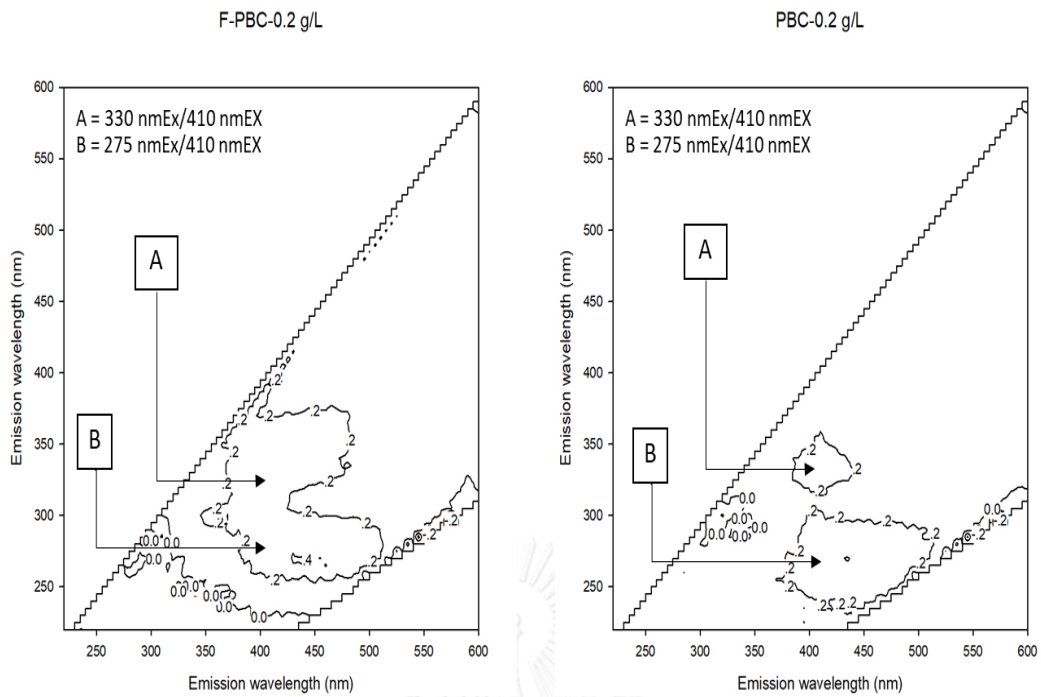


Figure 27 FEEM of 0.2 g/L pig bone char

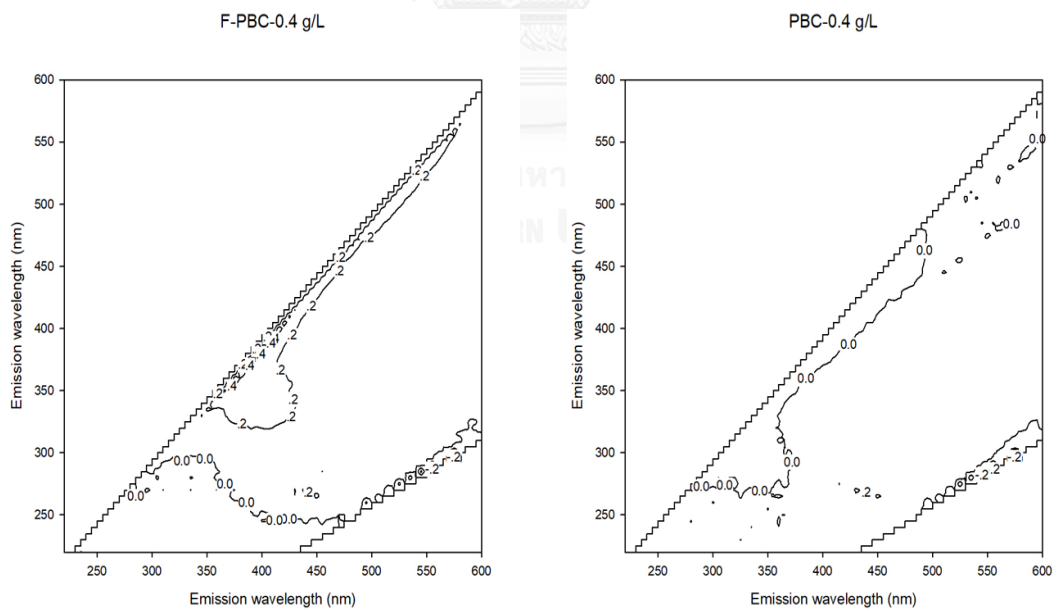


Figure 28 FEEM of 0.4 g/L pig bone char

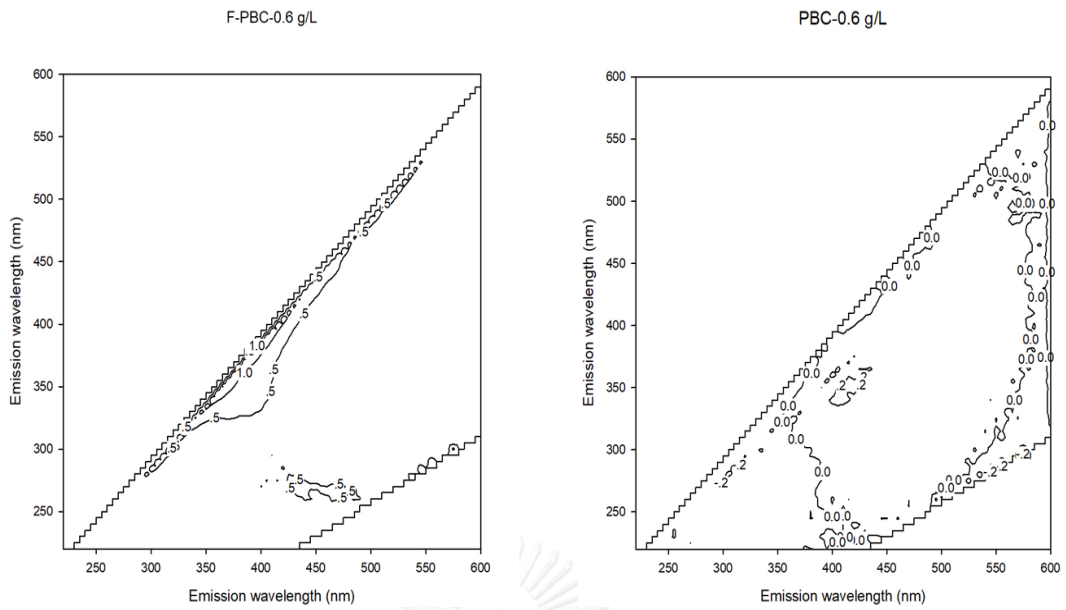


Figure 29 FEEM of 0.6 g/L pig bone char

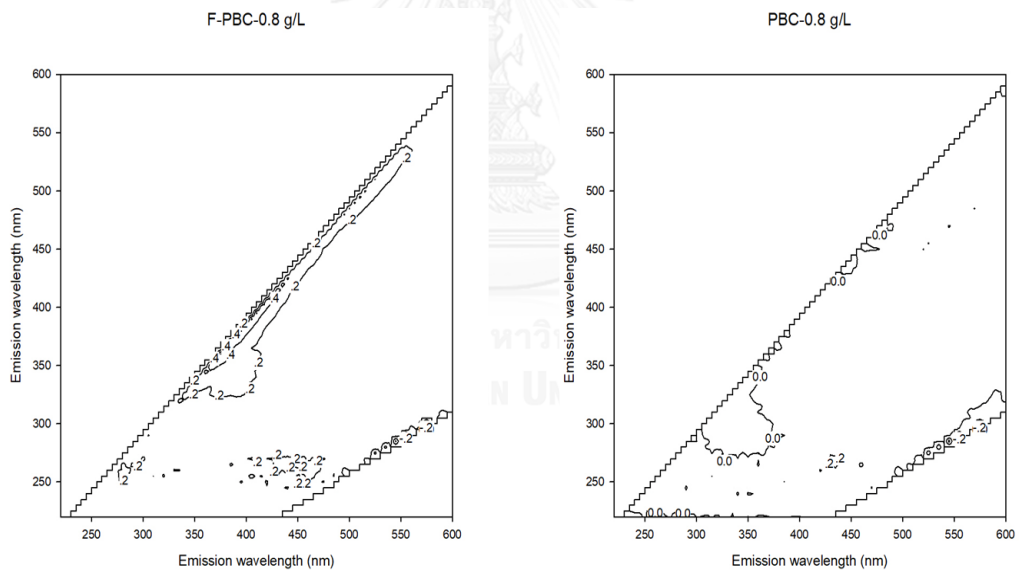


Figure 30 FEEM of 0.8 g/L pig bone char

After the adsorption process by various concentrations of pig bone char, the results of FEEM are shown in the Figure 27 to Figure 30, respectively. At pig bone char concentration 0.2 g/L, the peak of DOM shown the same peak with raw water including peak A and B. Nevertheless, the fluorescent peak were not detected in other pig bone char concentrations (0.4, 0.6 and 0.8 g/L) as shown in Figure 28, 29 and 30. Accord to the PAC adsorption, the fluorescent peak was not detected after adsorption process. (Wudthigarn, 2015).

From the results, it can be concluded that the higher concentration (> 0.2 g/L) of pig bone char can remove DOM in term of humic acids and humic-like substances.

4.4.4 Trihalomethanes formation potentials (THMFPs)

THMFPs in raw surface water after removing dissolved organic carbon by adsorption process with vary concentration of pig bone char (F-PBC-900 °C and PBC-900 °C) were shown in the Figure 31 and 32.

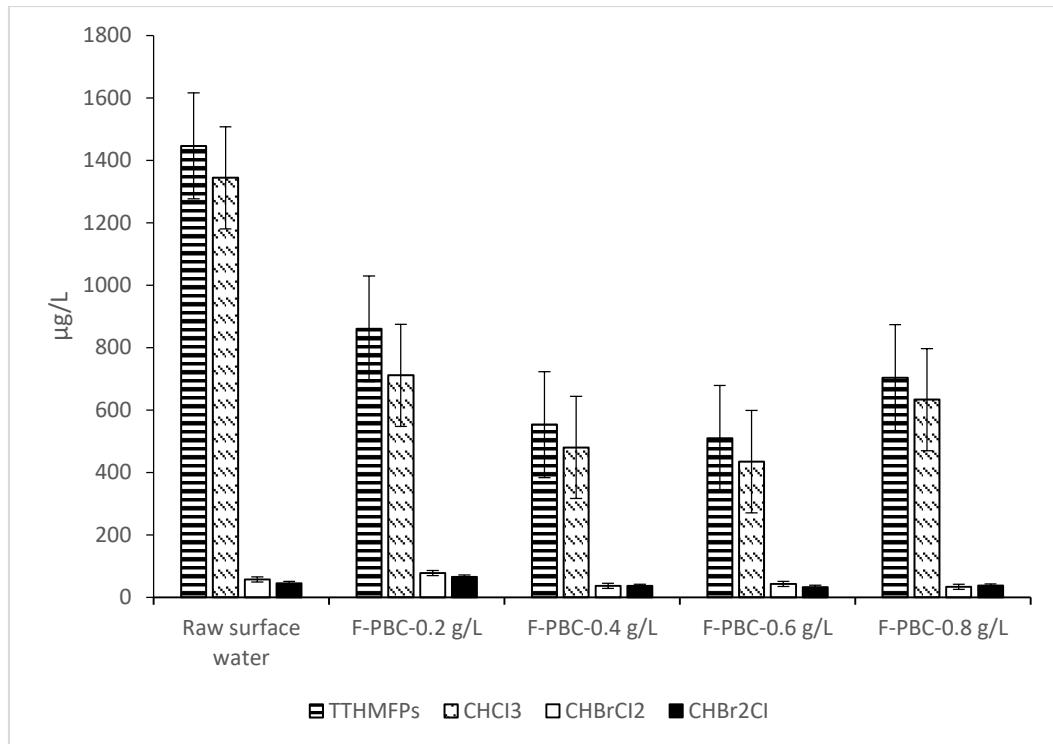


Figure 31 THMFPs after dissolved organic carbon adsorption by F- PBC-900 °C

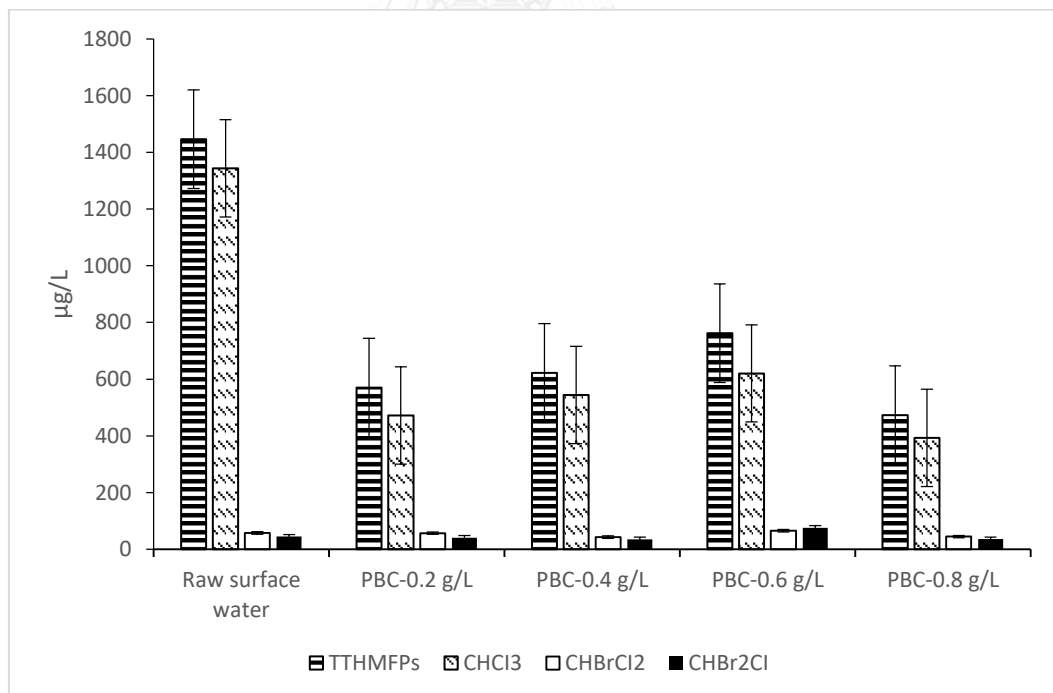


Figure 32 THMFPs after dissolved organic carbon adsorption by PBC-900 °C

From the Figure 31 and 32, the raw surface water after adsorption process by F- PBC-900 °C and PBC-900 °C found that the THMFs including Chloroform (CHCl_3), Bromodichloromethane (CHBrCl_2) and Dibromochloromethane (CHBr_2Cl) were greatly decreased. Because the decreasing of DBPs precursor was an important factor that affected to THMFs (Bond, 2009; Hua, 2007). The F-PBC-900 °C was higher removal of THMFs than PBC-900 °C except 0.2 g/L and 0.8 g/L of concentration.

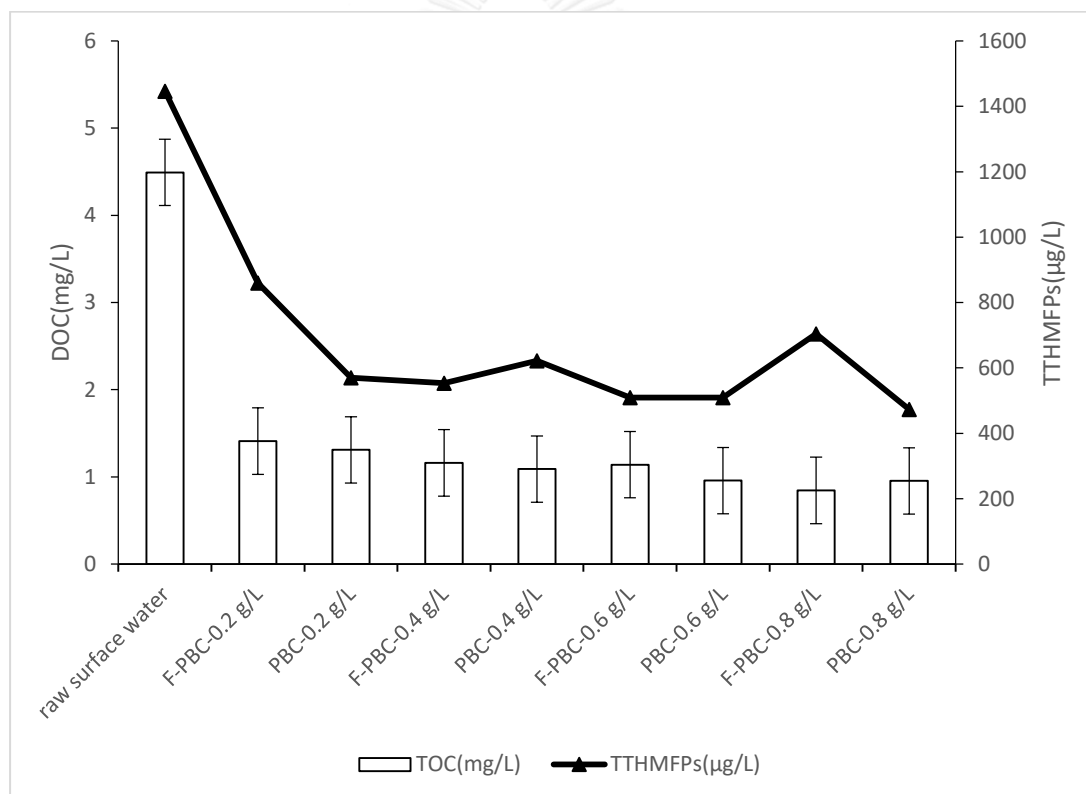


Figure 33 the relationship between DOC concentration and TTHMFs

According to DOC and UV-254 result, DOC and UV-254 were parameters of dissolved organic matter (USEPA, 1999). So the study presented DBPs precursor removal by pig bone char (F-PBC-900 °C and PBC-900 °C) had good

performance for removing dissolved organic matter in the Ping River. Furthermore, the F-PBC-900 °C and PBC-900 °C were similarly efficiency as shown in the Figure 33. The decreasing of TTHMFPs was fluctuated to DOC concentration. From the results, it can be indicated that the remove of DOC not related to the formation of THMs. The higher DOC removal results in lower THMFP removal. Thus, it can be concluded that the formation of THMs not only depend on the concentration of DOM but also the characteristics of DOM.

4.4.5 Specific Trihalomethanes formation potentials (STHMFPs)

The ratio between the THMFPs and DOC concentration was investigated for the reactivity of the organic in the formation of THMs in raw surface water after removing dissolved organic carbon (Imai, 2003) as presented in the Figure 34 and 35.

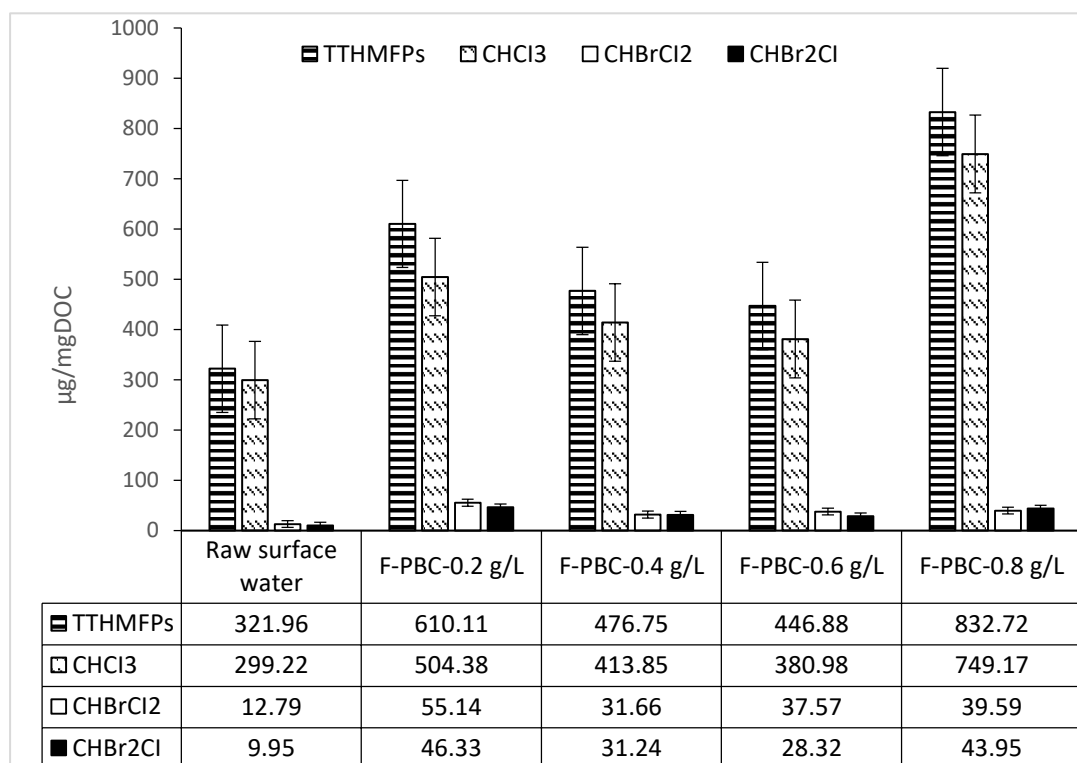


Figure 34 Specific Trihalomethanes formation potential (STHMFPs) after F-PBC-900 °C adsorption

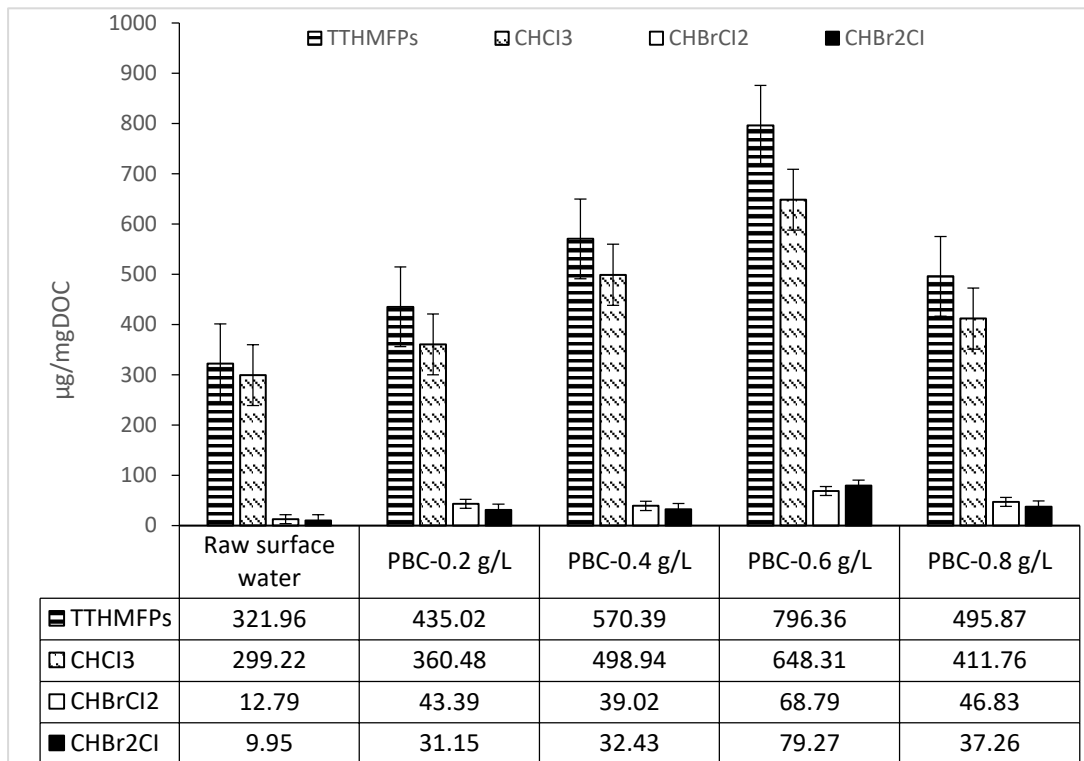


Figure 35 Specific Trihalomethanes formation potential (STHMFPs) after PBC-900 °C adsorption

From the Figure 34 and 35, the STHMFPs was increased after both of pig bone char adsorption compare with the raw surface water. This result indicated that the dissolved organic matter which remain in water samples were greatly reactive with chlorine in forming THMs. In the other hand, the DOM removed by adsorption process was slightly reactive DBPs precursor. This results can be confirmed that the formation of THMs was greatly depend on the characteristics of DOM.

The result of THMFPs was used 0.4 g/L concentration of both of pig bone char to comparing with another technologies that removal dissolved organic matter in the Ping River included commercial PAC and membranes filtration (Wudthigarn, 2015). The comparison was shown in the Figure 36.

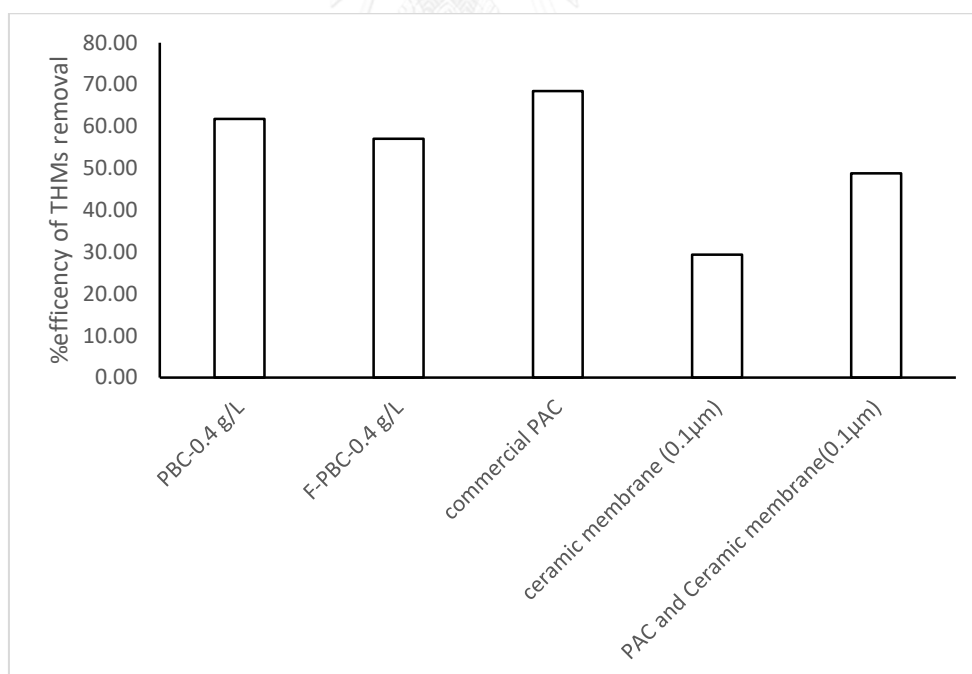


Figure 36 THMs removal

Figure 36 shown THMs removal of each technology. It indicated that commercial PAC was provided the highest value for THMs removal. While the removal efficiency of PBC-900 °C and F-PBC-900 °C at 0.4 g/L were not significantly different when compared to commercial PAC. However, PAC with ceramic membrane (0.1 µm) and ceramic membrane (0.1 µm) were lower and lowest value for THMs removal, respectively.



CHAPTER 5

Conclusion and Recommendations

5.1 Conclusion

From the pig bone char characteristics, it can be concluded that the different conditions of bone char synthesis can provided the different properties of bone char adsorbents. However, all of PBC adsorbents, the N₂ adsorption-desorption isotherms shown mesoporous structure (2-50 nm) in the Figure 8 to 11. F-PBC-900 °C and PBC-900 °C had lower the Bet surface area than F-PBC-650 °C and PBC-650 °C but the mesopore volume is still high in the Table 9. Furthermore, the pH value of PZC and Surface Charge Density was similarly to commercial PAC as shown in the Figure 14 and 15. Thus, the F-PBC-900 °C and PBC-900 °C had physical and chemical properties and can be used as adsorbents. In addition, it can easily to separate from solution by magnet.

According to the adsorption process of F-PBC-900 °C and PBC-900 °C adsorbents with 0.2, 0.4, 0.6 and 0.8 g/L, the adsorption of all conditions were reached to the equilibrium stage after 1 hour of contact time. They were best fitted with pseudo-second order and the highest adsorption capacity was found at the concentration of 0.2 g/L of pig bone char (13.09 and 20.05 mg/g). The initial adsorption rates (h) of F-PBC-900 °C were almost higher than PBC-900 °C except the concentration of PBC-900

°C at 0.2 and 0.4 g/L in the Table 11. The Langmuir isotherm model gave highest R^2 values with F-PBC-900 °C. The mechanisms were occurred on monolayer adsorption of surface. On the other hand, PBC-900 °C was fitted with Freundlich isotherm model. The PBC was occurred on multilayer adsorption of surface.

For the Disinfection by-products (DBPs) precursor removal, the efficiency of DBPs precursors removal was approximate 70-80 % with F-PBC-900 °C and PBC-900 °C as shown in the Figure 23 and 24. The UV-254 of raw surface water was decreased by increasing concentration of F-PBC-900 °C and PBC-900 °C in the Table 13 and Figure 25. The results of FEEM showed that with 0.2 g/L concentration of F-PBC-900 °C and PBC-900 °C, the humic acids and humic-like substance still presented as presented in the Figure 26 and 27. However, the increasing concentration (0.4, 0.6 and 0.8 g/L) of F-PBC-900 °C and PBC-900 °C could remove those substances in the Figure 28, 29 and 30. The THMFPs was significantly decreased by both of pig bone char adsorption in the Figure 31, 32 and 33. However, the STHMFPs was increased after adsorption compare with the raw surface water. The result shown in the Figure 34 and 35, the DOM which remain in water samples were greatly reactive with chlorine in forming THMs. It indicated DOM adsorbed by both of pig bone char was slightly reactive with chlorine in forming THMs.

From the result of DBPs precursor removal, F-PBC-900 °C and PBC-900 °C at 0.4 g/L concentration was selected to comparing another technologies include commercial PAC and membranes filtration. The efficiency of F-PBC-900 °C and PBC-

900 °C was approximate to commercial PAC which the highest value of THMs removal in the Figure 36. Hence, the pig bone char with adding iron (III) nitrate as magnetically-separable porous bone char at 0.4 g/L concentration can be utilized as low cost absorbent. Additionally, the magnetically-separable porous bone char can separate from solution by magnet.

5.2 Application for using magnetically-separable porous bone char

The adsorption process was used 0.4 g/L concentration of magnetically-separable porous bone char at 200 rpm for 1 hr. Additionally using magnet to separate pig bone char was lower cost than using filtration process.

5.3 Recommendations

1. The surface characteristics of bone char should be further investigated by using FTIR technique for both before and after adsorption.
2. The advanced method to investigate the DOM characteristics should be applied such as resin fractionation or membrane pore size distribution. The obtained results can be describing the characteristics of DOM before and after adsorption.

REFERENCES

- André L. Cazetta, A. C. M., Osvaldo Pezoti, Karen C. Bedin, Karla K. Beltrame, Tewodros Asefa, Vitor C. Almeida. (2016). Synthesis and application of N-S-doped mesoporous carbon obtained from nanocasting method using bone char as heteroatom precursor and template. *Chemical Engineering Journal*, 300, 54-63.
- Bond, T., Goslan, E. H., Jefferson, B., Roddick, F., Fan, L., & Parsons, S. A. . (2009). Chemical and biological oxidation of NOM surrogates and effect on HAA formation. *Water Res*, 43(10), 2615-2622.
- C.K. Rojas-M., e. a. (2013). Optimization of pyrolysis conditions and adsorption properties of bone char for fluoride removal from water. *Journal of Analytical and Applied Pyrolysis*, 104, 10–18.
- C.K. Rojas-Mayorga, A. B.-P., J. Silvestre-Albero, I.A. Aguayo-Villarreal, D.I. Mendoza-Castillo. (2015). Physico-chemical characterization of metal-doped bone chars and their adsorption behavior for water defluoridation. *Applied Surface Science*, 355, 748-760.
- Capar, G., Yetis, U. (2001). Removal of natural organic matter and trihalomethanes from the drinking water of Ankara City, Turk. *J. Eng. Environ. Sci*, 25, 527-535.
- Chen, W., Westerhoff, P., Leenheer, J. A., & Booksh, K. (2003). Fluorescence Excitation–Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter. *Environmental Science & Technology*, 37(24), 5701-5710.
- Coble, P. G. (1996). Characterisation of marine and terrestrial dissolved organic matter in seawater using excitation emission matrix spectroscopy. *Marine Chemistry*, 51(4), 325-346.
- Cowman, G. A., and Singer, P. C. (1994). Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of humic extracts. *Proc. Annu. Conf., American Water Works Assoc., Denver, Colo.*

- Fabris, R., Chow, C.W.K., Drikas, M., Eikebrokk, B. (2008). Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Res*, 42.
- Hua, G., & Reckhow, D. A. . (2007). Characterization of Disinfection Byproduct Precursors Based on Hydrophobicity and Molecular Size. *Environmental Science & Technology*, 41(9), 3309-3315.
- Hui Q, L. L., Bing-cai P, Qing-jian Z, Wei-ming Z, & Quan-xing Z. . (2009). Critical review in adsorption kinetic models. *J Zhejiang Univ Sci A*, 10(5), 716-724.
- Imai, A., Matsushige, K., & Nagai, T. . (2003). Trihalomethane formation potential of dissolved organic matter in a shallow eutrophic lake. *Water Research*, 37(17), 4284-4294.
- Juan C. Moreno-Piraján, L. G., Vanessa S. García-Cuello. (2011). Study of the Textural Properties of Bovine Bones Char under Different Conditions. *Journal of Water Resource and Protection*,, 3, 176-181.
- Kowit P., J. T., Piyawat P., & Chattaros K. (2008). Kinetic Adsorption of Chromium (VI) from Electroplating Factory onto Chitosan Resin. *The Journal of KMUTNB*, 18(no.1).
- Krutklom, N. (2013). *Dissolved Organic Matter Reduction Using Ceramic Membrane Combined with Alum*. (Master's Degree), Chiang Mai University, Chiang Mai.
- Laura R. B., a. D. A. S. (2009). An Evaluation of Fish Bone Char as An Appropriate Arsenic and Fluoride Removal Technology for Emerging Regions. *ENVIRONMENTAL ENGINEERING SCIENCE*, 26(no.12), 1777-1783.
- Leenheer, J. A. a. J.-P. C. (2003). Peer Reviewed: Characterizing Aquatic Dissolved Organic Matter. *Environmental Science & Technology*, 37(1), 18A-26A.
- Mohan, D., Kumar, H., Sarswat, A., Alexandre-Franco, M., Pittman Jr., C.U. (2014). Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. *Chemicals engineering*, 236, 513-528.
- N.A. Medellin-Castillo, R. L.-R., E. Padilla-Ortega, R. Ocampo Perez,, & J.V. Flores-Cano, M. S. B.-M. (2014). Adsorption capacity of bone char for removing fluoride from water solution. Role of hydroxyapatite content, adsorption mechanism and competing anions. *Journal of Industrial and Engineering Chemistry*, 20, 4014-4021.

- Permrungruang, J. (2013). *EFFECTS OF SURFACE FUNCTIONAL GROUPS AND NATURAL ORGANIC MATTER ON CLOFIBRIC ACID ADSORPTION BY MESOPOROUS SILICATE SBA-15*. (Degree of Master of Science Program in Environmental Management (Interdisciplinary Program)), Chulalongkorn University.
- Prarat, P. (2011). Adsorption characteristics of haloacetonitriles on functionalized silica-based porous materials in aqueous solution. *Journal of Hazardous Materials*, 192, 1210-1218.
- Punyapalaku, P. *Adsorption for water and Wastewater treatment*. Chulalongkorn University.
- R. Leyva-Ramos., e. a. (2010). Adsorption capacity of bone char for removing fluoride from water solution. Role of hydroxyapatite content, adsorption mechanism and competing anions. *Journal of Industrial and Engineering Chemistry*, 20(6), 4014-4021.
- Rakruam, P. (2013). *TRIHALOMETHANE FORMATION POTENTIAL OF DOM FRACTIONS IN WATER PRODUCTION BY IN-LINE COAGULATION CERAMIC MEMBRANE*. (Doctoral Degree), Chulalongkorn University.
- Rodriguez, M. J., Serodes, J. and Levallois, P. (2004). Behavior of trihalomethanes and haloacetic acids in a drinking water distribution System. *Water Research*, 38, 4367-4382.
- S. Chellam, S. W. K. (2001). Disinfection byproduct relationships and speciation in chlorinated nanofiltered waters. *Environ. Sci. Technol*, 35, 3988-3999.
- S.D.Richardson, Plewa, M. J., Wagner, E. D., Schoeny, R., & DeMarini, D. M. (2007). Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfectionby-products in drinking water:.. *a review and roadmap for research, Mutat.Res*, 636, 178-242.
- Sangeeta Patela, J. H., Wei Qiu, Wei Gao. (2015). Synthesis and characterisation of mesoporous bone char obtained by pyrolysis of animal bones, for environmental application. *Journal of Environmental Chemical Engineering.*, 3, 2368-2377.
- Sawangjang, B. (2016). *Adsorption mechanism of bone chars for defluoridation of groundwater*. (master degree), Chulalongkorn University

- Suriyanon, N., Punyapalakul, P., & Ngamcharussrivichai, C. (2015). Synthesis of periodic mesoporous organosilicas functionalized with different amine-organosiloxanes via direct co-condensation. *Materials Chemistry and Physics*, 149-150(2015), 701-712.
- Swietlik, J., Dabrowska, A., R.-S., U., & Nawrocki, J. (2004). Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Water Res*, 38, 547-558.
- Temyarasilp, P. (2008). *Preparation and Characterization of Activated Carbon from Dendrocalamus asper Backer and Dendrocalamus Latiflours*. (master degree), Kasetsart university.
- Velten, S., Knappe, D.R.U., Traber, J., Kaiser, H.-P., von Gunten, U., Boller, M., Wang, J., Tian, H., Ji, Y. (2015). Adsorption behavior and mechanism of humic acid on aminated magnetic nano-adsorbent. *Sep.Sci.Technol*, 50.
- Wang H, Z. A., Peng F, Yu H and Yang J. (2007). Mechanism study on adsorption of acidified multi-walled carbon nanotubes to Pb(II). *J. Colloid Interface Sci*, 2007(316), 277-283.
- Wudthigarn, C. (2015). *Removal of Carbonaceous and Nitrogenous Organic Matters from Surface Water by Activated Carbon Adsorption and Ceramic Membrane Filtration Processes*. (Mater of Engineering), ChiangMai University.



APPENDIX A
ADSORBENT SYNTHESIS AND CHARACTERIZATION

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1. Synthesis of F-PBC and PBC adsorbents

1.1 Preparation of pig bone



1.2 Elimination moisture by putting in oven 100 °C for 24h



1.3 Crushed into small size and sieve size (250 µm)



1.4 Adding iron (III) nitrate ($Fe(NO_3)_3$) and burning process

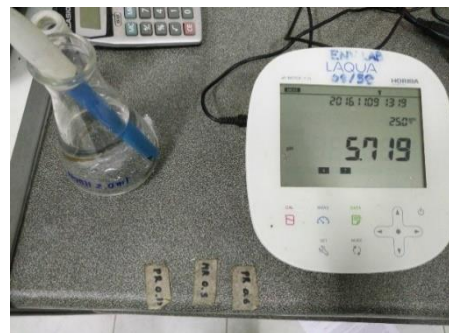


1.5 Pig bone char



2. Characterization of F-PBC and PBC adsorbents

2.1 Water sample with initial pH and final pH



2.2 Data of PZC and surface charge density

F-PBC-900 °C		PBC-900 °C	
initial pH	final pH	initial pH	final pH
3.141	5.916	4.21	5.95
4.12	6.694	6.18	6.82
6.217	7.243	6.72	7.03
6.816	7.654	7.34	7.37
7.86	7.562	8.01	7.61
9.843	7.765	8.22	7.62
10.479	9.248	8.85	7.7
		10.03	7.9
		10.54	8.17
		10.88	8.36

F-PBC-900 °C		PBC-900 °C	
pH	surface charge density	pH	surface charge density
6.984	0.005517778	6.809	0.025311345
6.886	0.011728687	6.704	0.052758622
6.689	0.020504509	6.234	0.088686869
6.205	0.023368346	5.881	0.166547768
6.017	0.062474036	7.329	-0.020634722
5.68	0.114101729	7.664	-0.034663262
7.085	-0.003610152	7.979	-0.065428191
7.507	0.002397542	8.22	-0.145148291
7.631	-0.005708123		
7.653	-0.034099838		
7.994	-0.060989169		
8.441	-0.074045556		



3. Characterization of F-PBC and PBC adsorbents

3.1 Experiment for adsorption kinetic and isotherm study in batch condition



3.2 After shaking process, the sample was filtrated



3.3 TOC analysis



3.4 Data of adsorption kinetics

3.4.1 0.2 g/L

F-PBC-900 °C		PBC-900 °C	
Time (min)	Qd(mg/g)	Time (min)	Qd(mg/g)
0	0.00	0	0.00
4	10.46	1	11.79
5	11.85	2	12.75
10	11.31	3	12.84
20	11.87	4	13.56
30	13.34	5	12.87
50	13.71	10	11.60
360	13.54	20	13.97
720	14.20	50	19.70
1440	12.68	60	19.97
		180	21.67
		360	21.81
		720	20.73
		1440	20.99

3.4.2 0.4 g/L

F-PBC-900 °C		PBC-900 °C	
Time (min)	Qd(mg/g)	Time (min)	Qd(mg/g)
0	0.00	0	0.00
1	5.71	1	5.85
2	5.21	2	6.71
3	3.37	3	6.28
4	5.60	4	6.90
5	5.83	5	6.67
10	3.70	10	7.34
20	5.88	20	6.80
50	6.13	30	7.88
60	5.91	60	8.02
120	6.01	180	8.26
720	6.01	360	7.55
1440	6.010	720	7.49
		1440	7.61

3.4.3 0.6 g/L

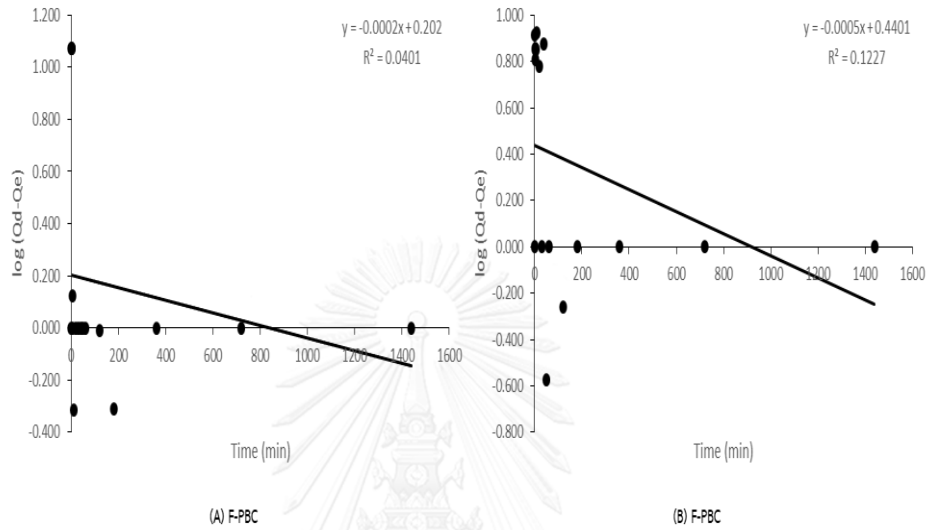
F-PBC-900 °C		PBC-900 °C	
Time (min)	Qd(mg/g)	Time (min)	Qd(mg/g)
0	0.00	0	0.00
10	3.94	1	4.22
30	5.05	2	3.99
50	4.80	3	4.59
60	5.05	4	4.72
120	4.99	10	4.14
360	5.10	20	4.79
720	4.82	30	4.67
1440	4.75	40	4.74
		60	4.94
		120	5.07
		180	5.39
		360	5.45
		720	5.29
		1440	5.236667

3.4.4 0.8 g/L

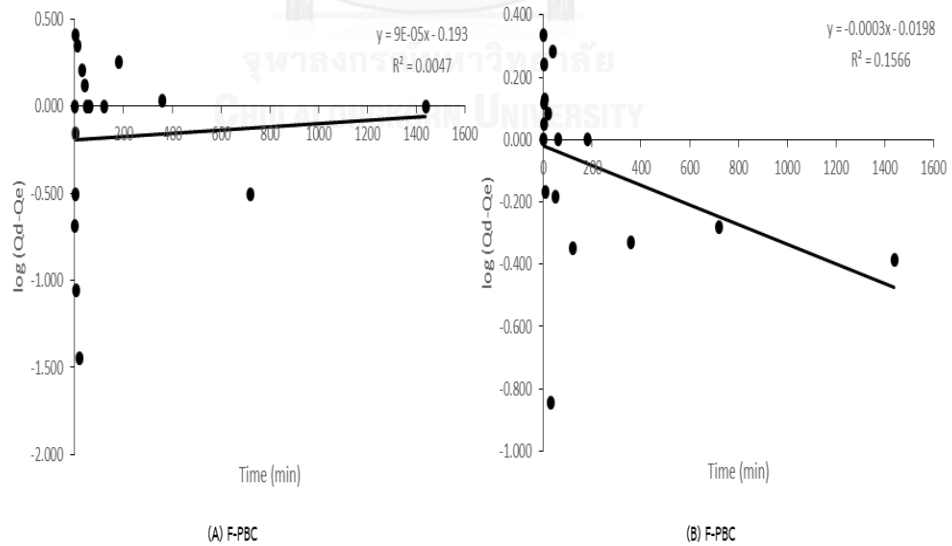
F-PBC-900 °C		PBC-900 °C	
Time (min)	Qd(mg/g)	Time (min)	Qd(mg/g)
0	0.00	0	0.00
1	2.85	1	3.52
2	3.57	2	3.59
3	3.87	3	3.84
4	3.54	4	3.98
5	3.24	5	4.08
10	3.15	10	3.89
20	3.93	20	3.99
30	3.53	30	4.05
40	3.78	40	4.08
50	3.54	50	4.02
60	3.59	60	4.15
120	3.64	120	3.99
180	3.9025	180	3.77
360	3.865	360	4.1775
720	3.715	720	4.09
1440	3.24	1440	4.09

3.5 Data of pseudo-first order model

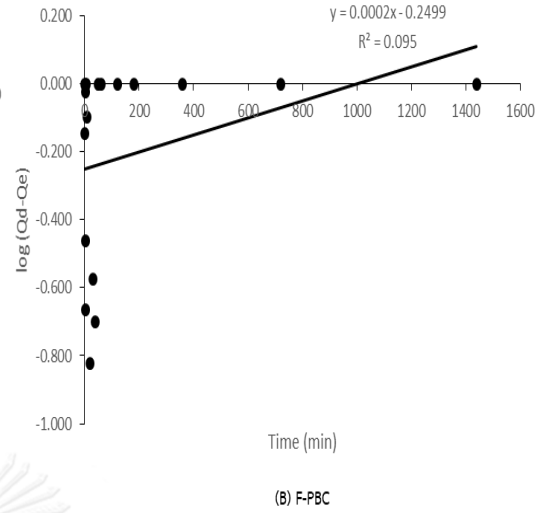
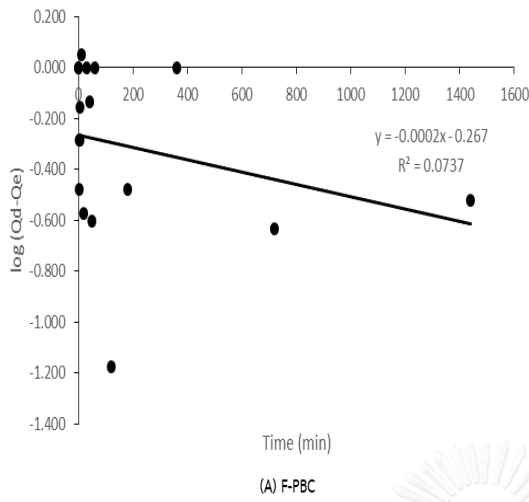
3.5.1 0.2 g/L



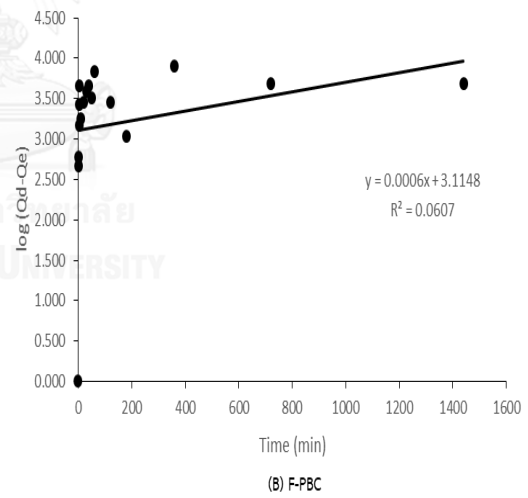
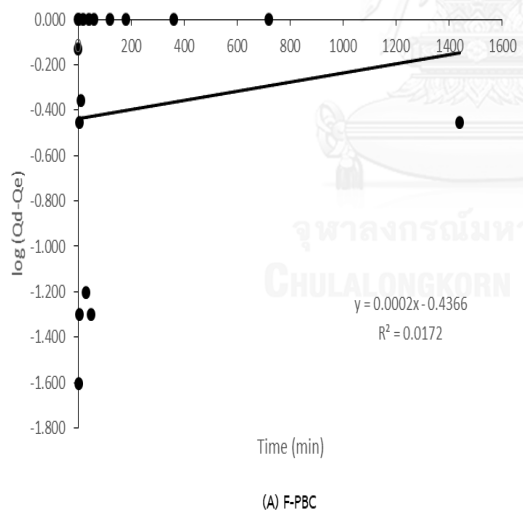
3.5.2 0.4 g/L



3.5.3 0.6 g/L

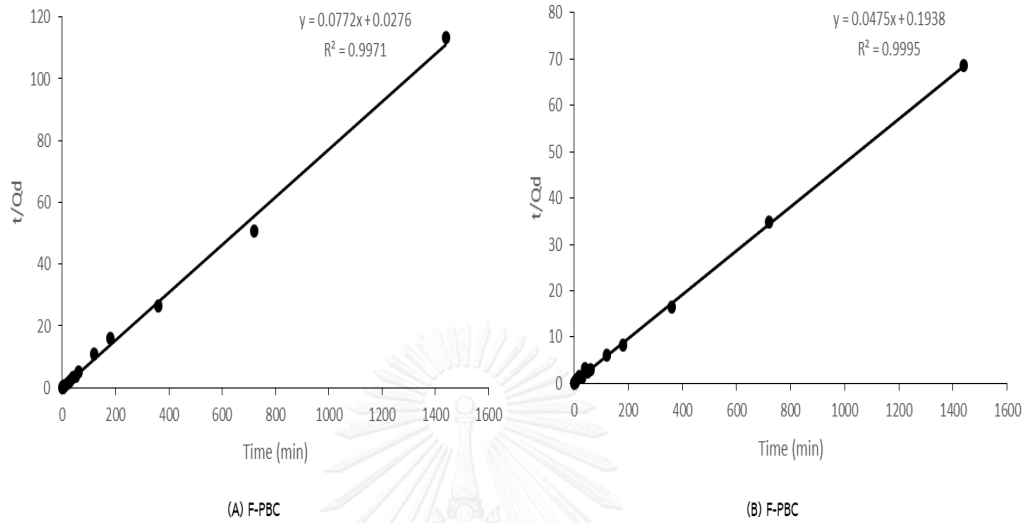


3.5.4 0.8 g/L

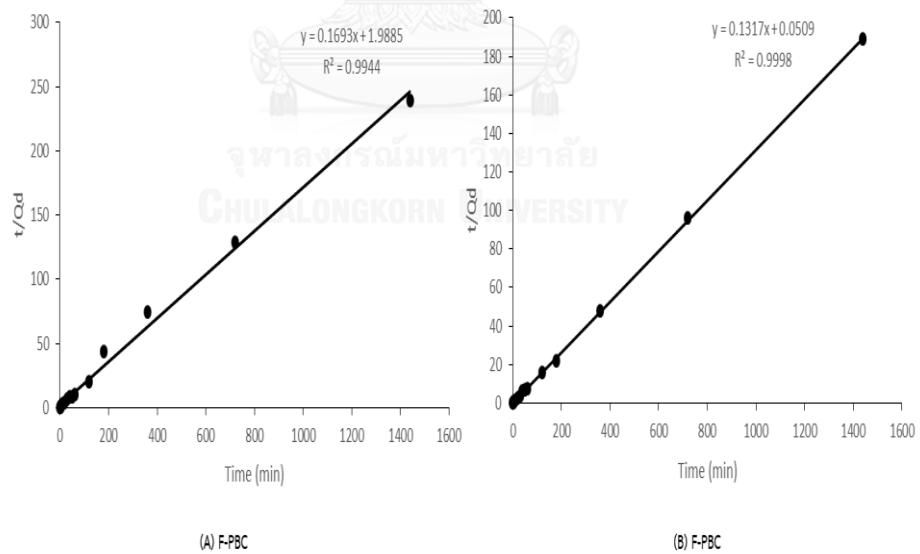


3.6 Data of pseudo-second order model

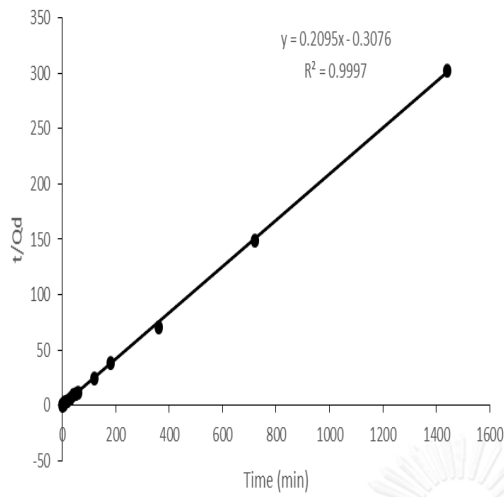
3.6.1 0.2 g/L



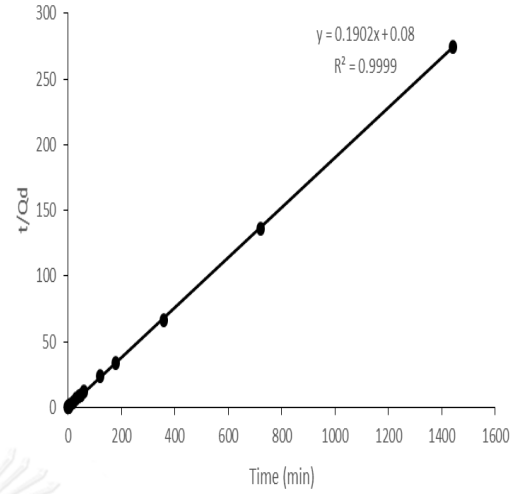
3.6.2 0.4 g/L



3.6.3 0.6 g/L

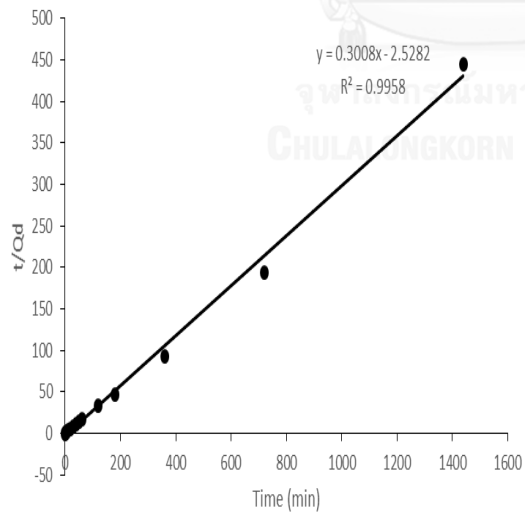


(A) F-PBC

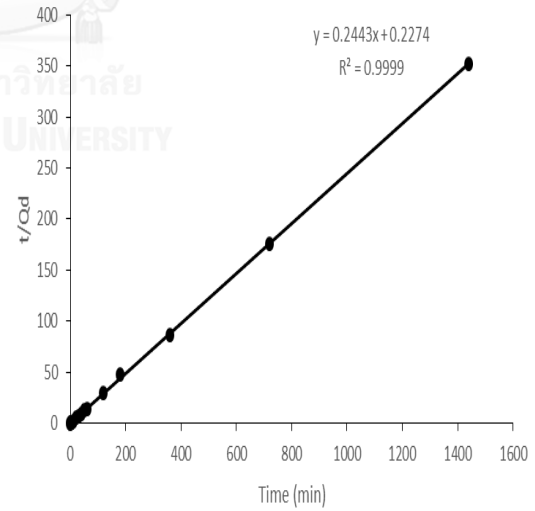


(B) F-PBC

3.6.4 0.8 g/L



(A) F-PBC



(B) F-PBC

3.7 Data of adsorption linear isotherm model

F-PBC-900 °C		PBC-900 °C	
Ce (mg/l)	Qe (mg/g)	Ce (mg/l)	Qe (mg/g)
1.410	15.410	1.31	15.91
1.160	8.330	1.09	8.505
1.140	5.587	0.957	5.891667
0.845	4.559	0.954	4.4225

3.8 Data of adsorption Langmuir and Freundlich isotherm models (F-PBC-900°C)

mass of F-PBC (mg)	Co mg/l	Ce (mg/l)	Co-Ce mg	v (L)	Qe (mg/g)	1/Ce	1/Qe	log Ce	log Qe
0.030	4.492	1.410	3.082	0.15	15.410	0.709	0.065	0.149	1.188
0.060	4.492	1.160	3.332	0.15	8.330	0.862	0.120	0.064	0.921
0.090	4.492	1.140	3.352	0.15	5.587	0.877	0.179	0.057	0.747
0.120	4.492	0.845	3.647	0.15	4.559	1.183	0.219	-0.073	0.659

3.9 Data of adsorption Langmuir and Freundlich isotherm models (PBC-900°C)

mass of PBC (mg)	Co mg/l	Ce (mg/l)	Co-Ce mg	v (L)	Qe (mg/g)	1/Ce	1/Qe	log Ce	log Qe
0.030	4.492	1.310	3.182	0.15	15.910	0.763	0.063	0.117	1.202
0.060	4.492	1.090	3.402	0.15	8.505	0.917	0.118	0.037	0.930
0.090	4.492	0.957	3.535	0.15	5.892	1.045	0.170	-0.019	0.770
0.120	4.492	0.954	3.538	0.15	4.423	1.048	0.226	-0.020	0.646



APPENDIX C

Disinfection by-products (DBPs) precursor removal experiments

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

4.1 Data of THMFPS

4.1.1 F-PBC-900 °C adsorption

THMFPS	Raw surface water	F-PBC- 0.2 g/L	F-PBC- 0.4 g/L	F-PBC- 0.6 g/L	F-PBC- 0.8 g/L
CHCl ₃	1344.09	711.17	480.07	434.32	633.05
CHBrCl ₂	57.47	77.75	36.72	42.83	33.45
CHBr ₂ Cl	44.69	65.33	36.24	32.29	37.14
TTHMFPS	1446.26	860.26	553.03	509.44	703.65

4.1.2 PBC-900 °C adsorption

THMFPS	Raw surface water	PBC-0.2 g/L	PBC-0.4 g/L	PBC-0.6 g/L	PBC-0.8 g/L
CHCl ₃	1344.09	472.23	543.84	620.43	392.82
CHBrCl ₂	57.47	56.84	42.53	65.83	44.68
CHBr ₂ Cl	44.69	40.81	35.35	75.86	35.55
TTHMFPS	1446.26	569.87	621.73	762.12	473.06

4.2 Data of STHMFP

4.2.1 F-PBC-900 °C adsorption

STHMFPs	Raw surface water	F-PBC- 0.2 g/L	F-PBC- 0.4 g/L	F-PBC- 0.6 g/L	F-PBC- 0.8 g/L
CHCl ₃	299.22	504.38	413.85	380.98	749.17
CHBrCl ₂	12.79	55.14	31.66	37.57	39.59
CHBr ₂ Cl	9.95	46.33	31.24	28.32	43.95
TTHMFPS	321.96	610.11	476.75	446.88	832.72

4.2.2 PBC-900 °C adsorption

STHMFPS	Raw surface water	PBC-0.2 g/L	PBC-0.4 g/L	PBC-0.6 g/L	PBC-0.8 g/L
CHCl ₃	299.22	360.48	498.94	648.31	411.76
CHBrCl ₂	12.79	43.39	39.02	68.79	46.83
CHBr ₂ Cl	9.95	31.15	32.43	79.27	37.26
TTHMFPS	321.96	435.02	570.39	796.36	495.87

4.3 THMs removal

raw surface water (TTHMFPS) µg/L	1446.26	583.48	% removal
PBC-0.4 g/L	553.03	-	61.76
F-PBC-0.4 g/L	621.73	-	57.01
commercial PAC	184.02		68.46
ceramic membrane (0.1µm)	412.39		29.32
PAC and Ceramic membrane(0.1µm)	299.12		48.74



aj-Analyzer multi N/C 3100; multiWin 4.09; Serial No: N3-1136/AR

CalibrationReport

Calibration: Cal_tc_pode_170529_1515
 Calibration of: 29/5/2017 15:15:36 +0700 Method: tc_pode

User: Admin
 Calibration channel: IC
 Linear regression [µg]: $c = (k1 \cdot I + k0) / V$
 $k0 = 0.28172$ $k1 = 3.775E-4$
 Residual standard deviation: 336.45AU Linearity: OK
 Method standard deviation: 1.28µg Variance homogeneity: OK
 Method variation coefficient: 4.2542% Detection limit: 0.360µg
 Quality of replicates: 0.99514 Identification limit: 0.719µg
 Correlation coefficient: 0.99757 Quantification limit: 1.16µg

Calibration with fixed concentration: 10.000mg/l

No.	Rep.	V	m-Nominal	I-Net	c-act.	c-delta
BV	Input			970.5AU/ml		
1	3-3	100.0µl	1.00µg	2,217AU	11.186mg/l	11.86%
2	3-3	200.0µl	2.00µg	4,473AU	9.852mg/l	-1.48%
3	3-3	300.0µl	3.00µg	6,813AU	9.512mg/l	-4.88%
4	3-3	400.0µl	4.00µg	9,733AU	9.890mg/l	-1.10%
5	3-3	500.0µl	5.00µg	1.277E4AU	10.203mg/l	2.03%



aj-Analyzer multi N/C 3100; multiWin 4.09; Serial No: N3-1136/AR

CalibrationReport

Calibration: Cal_tc_pode_170529_1515
 Calibration of: 29/5/2017 15:15:36 +0700

Method: tc_pode

User: Admin

Calibration channel: IC

Linear regression [μg]: $c = (k1 \cdot I + k0) / V$

k0 = 0.28172

k1 = 3.775E-4

Residual standard deviation: 336.45AU

Linearity: OK

Method standard deviation: 1.28 μg

Variance homogeneity: OK

Method variation coefficient: 4.2542%

Detection limit: 0.360 μg

Quality of replicates: 0.99514

Identification limit: 0.719 μg

Correlation coefficient: 0.99757

Quantification limit: 1.16 μg **Replicate area units**

No.	Avg.	1	2	3	4	5
		6	7	8	9	10
H2O	970.5					
1	2,217	2,198	2,206	2,246		
2	4,473	4,439	4,455	4,526		
3	6,813	6,884	6,636	6,920		
4	9,733	9,621	9,831	9,748		
5	1.277E4	1.268E4	1.271E4	1.292E4		

aj-Analyzer multi N/C 3100; multiWin 4.09; Serial No: N3-1136/AR

Calibration Report

Calibration: Cal_tc_pode_170529_1515
 Calibration of: 29/5/2017 15:15:36 +0700

Method: tc_pode

User: Admin

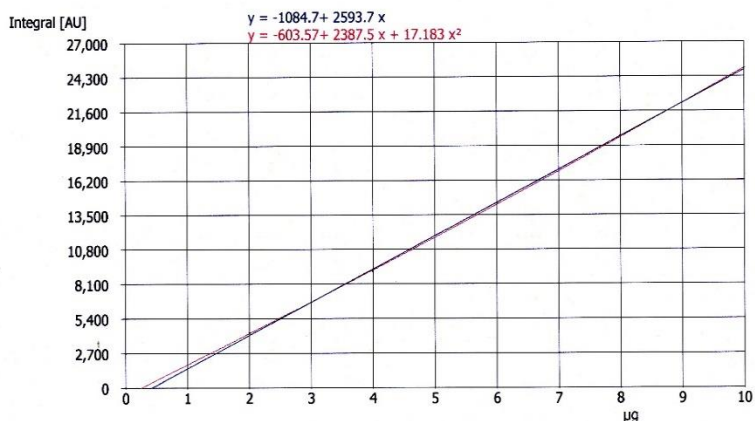
Calibration channel: TC

Linear regression [µg]: $c = (k1 \cdot I + k0) / V$
 $k0 = 0.42032$ $k1 = 3.854E-4$

Residual standard deviation:	184.46AU	Linearity:	OK
Method standard deviation:	1.42µg	Variance homogeneity:	OK
Method variation coefficient:	1.1853%	Detection limit:	0.200µg
Quality of replicates:	0.99962	Identification limit:	0.401µg
Correlation coefficient:	0.99981	Quantification limit:	0.763µg

Calibration with fixed concentration: 20.000mg/l

No.	Rep.	V	m-Nominal	I-Net	c-act.	c-delta
BV	Input			2,050AU/ml		
1	3-3	100.0µl	2.00µg	4,304AU	20.791mg/l	3.95%
2	3-3	200.0µl	4.00µg	9,074AU	19.587mg/l	-2.07%
3	3-3	300.0µl	6.00µg	1.44E4AU	19.901mg/l	-0.50%
4	3-3	400.0µl	8.00µg	1.966E4AU	19.997mg/l	-0.02%
5	3-3	500.0µl	10.00µg	2.495E4AU	20.069mg/l	0.35%



aj-Analyzer multi N/C 3100; multiWin 4.09; Serial No: N3-1136/AR

CalibrationReport

Calibration: Cal_tc_pode_170529_1515

Calibration of: 29/5/2017 15:15:36 +0700

Method: tc_pode

User: Admin

Calibration channel: TC

Linear regression [μg]: $c = (k1 \cdot I + k0) / V$

k0 = 0.42032

k1 = 3.854E-4

Residual standard deviation: 184.46AU

Linearity: OK

Method standard deviation: 1.42 μg

Variance homogeneity: OK

Method variation coefficient: 1.1853%

Detection limit: 0.200 μg

Quality of replicates: 0.99962

Identification limit: 0.401 μg

Correlation coefficient: 0.99981

Quantification limit: 0.763 μg **Replicate area units**

No.	Avg.	1		2		3		4		5	
		6	7	7	8	8	9	9	10	10	
H2O	2,050										
1	4,304	4,239	4,303		4,370						
2	9,074	9,014	9,089		9,118						
3	1.44E4	1.439E4	1.437E4		1.444E4						
4	1.966E4	1.962E4	1.963E4		1.973E4						
5	2.495E4	2.491E4	2.492E4		2.502E4						

Method C:\CHEM32\1\METHODS\PODE_ECD.M

=====
 Calibration Table
 =====

Calib. Data Modified : Wednesday, June 21, 2017 1:53:37 PM

Calculate : External Standard
 Based on : Peak Area

Rel. Reference Window : 5.000 %
 Abs. Reference Window : 0.000 min ..
 Rel. Non-ref. Window : 5.000 %
 Abs. Non-ref. Window : 0.000 min

Use Multiplier & Dilution Factor with ISTDs
 Uncalibrated Peaks : not reported
 Partial Calibration : Yes, identified peaks are recalibrated
 Correct All Ret. Times: No, only for identified peaks

Curve Type : Linear
 Origin : Included
 Weight : Equal

Recalibration Settings:
 Average Response : Average all calibrations
 Average Retention Time: Floating Average New 75%

Calibration Report Options :
 Printout of recalibrations within a sequence:
 Calibration Table after Recalibration
 Normal Report after Recalibration
 If the sequence is done with bracketing:
 Results of first cycle (ending previous bracket)

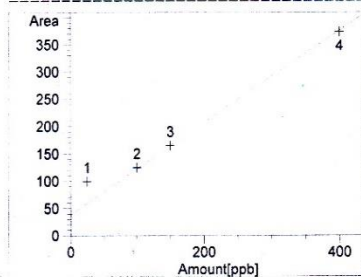
Signal 1: ECD1 A,

RetTime [min]	Lvl Sig	Amount [ppb]	Area	Amt/Area	Ref Grp Name
1.929	1 1	25.00000	98.95110	2.52650e-1	Chloroform
	2	100.00000	124.52737	8.03036e-1	
	3	150.00000	164.95622	9.09332e-1	
	4	400.00000	373.34546	1.07139	
2.695	1 1	25.00000	61.92928	4.03686e-1	Bromodichloromethane
	2	100.00000	141.71416	7.05646e-1	
	3	150.00000	182.08569	8.23788e-1	
	4	400.00000	1093.84216	3.65683e-1	
3.404	1 1	25.00000	40.81691	6.12491e-1	Dibromochloromethane
	2	100.00000	159.88170	6.25462e-1	
	3	150.00000	375.00439	3.99995e-1	
	4	400.00000	1601.47742	2.49769e-1	
4.456	1 1	25.00000	20.91681	1.19521	Bromoform
	2	100.00000	709.89758	1.40865e-1	
	3	150.00000	1501.83875	9.98776e-2	
	4	400.00000	6695.22900	5.97440e-2	

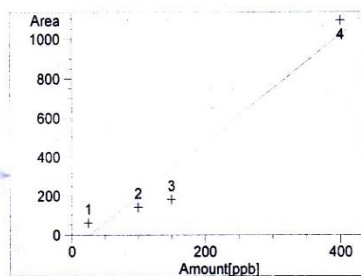
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 Peak Sum Table
 =====

Method C:\CHEM32\1\METHODS\PODE_ECD.M

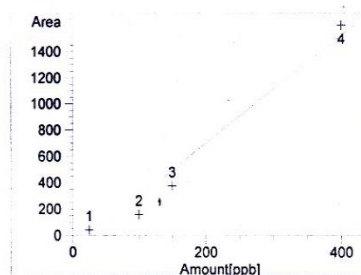
No Entries in table

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Calibration Curves
=====

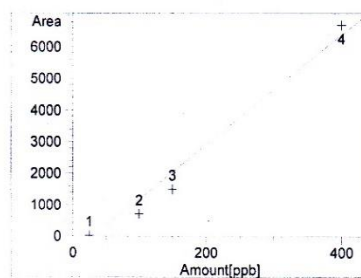
Chloroform at exp. RT: 1.929
ECD1 A,
Correlation: 0.97975
Residual Std. Dev.: 31.83770
Formula: $y = mx + b$
m: 8.44782e-1
b: 38.31040
x: Amount
y: Height



Bromodichloromethane at exp. RT: 2.695
ECD1 A,
Correlation: 0.97356
Residual Std. Dev.: 119.11044
Formula: $y = mx + b$
m: 2.75321
b: -75.76886
x: Amount
y: Height



Dibromochloromethane at exp. RT: 3.404
ECD1 A,
Correlation: 0.98426
Residual Std. Dev.: 136.28528
Formula: $y = mx + b$
m: 4.11697
b: -120.35476
x: Amount
y: Height



Bromoform at exp. RT: 4.456
ECD1 A,
Correlation: 0.98498
Residual Std. Dev.: 560.71587
Formula: $y = mx + b$
m: 17.34918
b: -556.56240
x: Amount
y: Height

VITA

Mr. Alongorn Siri was born on August 2, 1992 in Tak province. He graduated Bachelor's degree of Engineering from Department of Environmental Engineering, the Faculty of Engineering, Chiang Mai University in 2014. He continues studied Master degree in the International Program in Environmental Management, Chulalongkorn University in 2015.

