

Utilization of Rain Tree (*Samanea saman*) Residue as Modified Adsorbent to Treat Oil  
and Grease in Canteen Wastewater



A Thesis Submitted in Partial Fulfillment of the Requirements  
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การใช้ประโยชน์จากจามจู้รี (*Samanea saman*) เป็นตัวดูดซับที่ผ่านการปรับปรุงเพื่อบำบัดน้ำมัน  
และไขมันจากน้ำเสียโรงอาหาร



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
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การใช้วัสดุเหลือทิ้งเป็นตัวดูดซับกำลังได้รับความนิยมในการบำบัดน้ำมันและไขมัน (FOG) โดยเฉพาะอย่างยิ่งใน  
การบำบัดน้ำเสีย ซึ่งเศษกิ่งไม้และใบไม้เป็นของเหลือทิ้งที่มีอยู่มากมายสามารถสร้างเป็นวัสดุที่มีคุณค่าได้ งานวิจัยนี้มี  
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(carbonyls) ไฮดรอกซิล (hydroxyls) และอะลิฟาติก (aliphatic) ภาพจาก Scanning Electron Microscope (SEM)  
แสดงให้เห็นโครงสร้างของรูพรุนบนพื้นผิว การทดสอบประสิทธิภาพของตัวดูดซับที่ผ่านการปรับปรุงที่ดีที่สุดด้วยวิธี  
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สามารถใช้เป็นตัวดูดซับทางเลือกในบำบัดน้ำมันและไขมันจากน้ำเสียโรงอาหารได้

จุฬาลงกรณ์มหาวิทยาลัย  
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| สาขาวิชา   | การจัดการสารอันตรายและ<br>สิ่งแวดล้อม | ลายมือชื่อนิสิต .....            |
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# # 6288520720 : MAJOR HAZARDOUS SUBSTANCE AND ENVIRONMENTAL MANAGEMENT

KEYWORD: Rain tree (*Samanea Saman*), Chemical pretreatment, Oily wastewater

Elga Riesta Puteri : Utilization of Rain Tree (*Samanea saman*) Residue as Modified Adsorbent to Treat Oil and Grease in Canteen Wastewater. Advisor: Assoc. Prof. NUTA SUPAKATA, Ph.D. Co-advisor: Asst. Prof. Vorapot Kanokkantapong, Ph.D.

The utilization of waste materials as adsorbent precursors is gaining intention to treat fats, oils, and greases (FOG), especially in wastewater treatment. Tree residue, an abundant waste, provides a potential feedstock to be converted into valuable materials. This research aimed to develop modified adsorbent prepared from rain tree (*Samanea saman*) residue for FOG treatment. The synthesis process of modified adsorbent was conducted by chemical pretreatment using different chemical agents (i.e., NaOH, ZnCl<sub>2</sub>, and H<sub>3</sub>PO<sub>4</sub>). The pre-treated twigs and leaves (1:4 ratio) were continued by pyrolysis process at different temperatures (i.e., 350, 550, and 750°C) using a heating rate of 10°C min<sup>-1</sup> for 2 h. A batch sorption screening test was initially conducted for removing FOG from synthetic oily wastewater, and the ANOVA was employed to define the best-modified adsorbent among treatments. The result confirmed that modified adsorbent by H<sub>3</sub>PO<sub>4</sub>-treated and produced at 350°C had the highest net efficiency of FOG removal, with a yield and removal percentage of 55.87±1.40 and 79.77±1.17%, respectively. The adsorption studies of the best-modified indicated that the pseudo-second-order kinetic and Langmuir isotherm models were well-fitted to the experiment data. The maximum adsorption capacity of FOG was found to be 6.89 mg g<sup>-1</sup>. Fourier transform infrared spectroscopy (FTIR) result exhibits the present carbonyls, hydroxyls, and aliphatic groups. Scanning Electron Microscope (SEM) image showed the porous structure on the surface. The subsequent identification of the best-modified adsorbent was carried out by fixed-bed column test and performed optimum condition for canteen wastewater treatment by setting 10 cm bed height and flow rate 5 ml min<sup>-1</sup>. However, the breakthrough point could not be identified due to the column clogging (12 h). Overall, modified adsorbents produced had the ability to remove FOG, which indicated that rain tree residue could be utilized as an alternative adsorbent precursor for FOG treatment.

Field of Study: Hazardous Substance and Environmental Management Student's Signature .....

Academic Year: 2021 Advisor's Signature .....

Co-advisor's Signature .....

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Introduction

Canteens generate wastewater from the water that has been used for food preparation and cleaning activities. The effluent is usually heavily loaded with organic matters from cooking oil, oily flavorings, and food leftovers. Among many organic pollutants, one regularly found in canteen wastewaters is fat, oil, and grease (FOG). FOG is a group of organic substances with a very low affinity to water (Pintor et al., 2016). The high concentration of FOG in the wastewater tends to clog the sewer system and generates an unpleasant odor. Most importantly, it becomes a threat to aquatic organisms due to the decreasing oxygen transfer into the water (Abass, 2011). Furthermore, the direct discharge of oily wastewater to sewage will cause an extra burden to the municipal wastewater treatment. For the aforementioned impacts, FOG has become one of the significant water pollution fountainheads.

The treatment of FOG in wastewater involves a combination of different treatments. It generally consists of a primary treatment followed by secondary treatment, and tertiary treatment is commonly carried out to refine or reuse the wastewater. The primary treatment involves a gravity separation tank with a stagnant flow allowing oil to float on the surface, and the secondary treatment aims to remove the remaining oil consisted of the emulsified form. The emulsified form of

FOG removal remains a challenge in the secondary treatment since the gravity separation is ineffective (Zouboulis and Avranas, 2000). One of the promising technologies for FOG treatment is adsorption. A cost-effective and straightforward adsorption method with highly effective adsorption capacity is required to remove FOG from the wastewater (Kandanelli et al., 2018; Lam et al., 2018; Sohaimi and Ngadi, 2016). Carbonaceous materials are commonly used adsorbents in wastewater treatment. The carbon-based adsorbents have been extensively examined possessing high surface area, large porosity, and active sites for contaminant adsorption (Gusain et al., 2019; Kumar et al., 2019).

Many researchers have developed carbon-based adsorbents from inexpensive materials (González-García, 2018), and interestingly, adsorbent prepared from waste biomass has gained attention with its economic value as an available adsorbent for oily wastewater treatment (Mohan et al., 2014; Zhang et al., 2019). Several studies have utilized lignocellulosic material to produce affordable adsorbent and applied it for water pollutant removal (Hu et al., 2019; Kim et al., 2020; Sahota et al., 2018). The materials can be from various solid wastes (e.g., rice husk, cork, seedpods, corncob, fruit peels, and leaves) (Enniya et al., 2018; Liu et al., 2020; Mian and Liu, 2020).

Some studies have selected tree residue as an adsorbent precursor for organic and inorganic contaminant removal in the wastewater. The notable features of the tree residue in terms of porosities and surface functional groups for producing

adsorbent, the possibility of mass production at low cost, and the resolution of the waste disposal problem with the addition of value-added products can be justified as adsorbent precursor selection. For instance, a maple leaf-based adsorbent has been employed for tetracycline removal by providing a significant increase in hydrophobicity and surface area by pyrolysis process that facilitate the contaminant uptake (Derakhshan-Nejad and Jung, 2018).

There are numerous perennial plants in Thailand, and Chulalongkorn University is one of the homes of the prominent perennial plant named rain tree (*Samanea saman*). It has rough bark, grayish-brown with horizontal lines, and bi-pinnated leaves. The trees lose their leaves in a short time (Denia C. Delgado, 2016) and shed massive leaves, twigs, even branches in Chulalongkorn University's campus throughout the year, and their residues are considered solid waste. Approximately, one ton of rain tree residue is collected around campus area daily and currently, only some portions of rain tree residue are converted as compost, whereas the remaining amount is converted as livestock or disposed to landfills. The lignocellulosic component in the rain tree (*Samanea saman*) residue can be employed as a precursor for developing adsorbent; therefore, rain tree (*Samanea saman*) usage as available biomass could considerably become alternative way for its disposal. Accordingly, in this study, rain tree residue was selected as the raw material for the adsorbent production.

The capability of adsorbent depends on the materials' characteristics and the preparation process (Elsayed et al., 2017). Most of natural adsorbents suffer drawback in term of hydrophobicity characteristic. The FOG as the target pollutant has high hydrophobicity. Thus, the low hydrophobicity of natural adsorbent reduces the effectiveness to adsorb oil due to high water uptake (Wake, 2005). Other adsorption factors related to the surface area, pore size, molecular weight, hydrophobicity, polarity, and functional groups of the adsorbent (Azargohar and Dalai, 2008). Thus, in this study, modification of rain tree residue has been observed in order to enhance its properties for increasing oil removal efficiency. The modification processes have been carried out by chemical pretreatment and followed by pyrolysis. Some studies reported that chemical treatment before pyrolysis obtains high porosity, high yield, and less damaged surface (Maciá-Agulló et al., 2004). Chemical pretreatments of biomass have been studied, such as impregnation with acid, base, or ionic solutions. The different type of chemical treatments disrupts the complex structure of lignocellulosic component by various mechanism resulting improved surface area and pore formation (Yuan et al., 2020). These obtained modified adsorbent have been applied in the oily wastewater treatment and proved to increase the FOG removal in wastewater due to improved properties of modified adsorbent (Ngarmkam et al., 2011; Pintor et al., 2013; Santos et al., 2020). This study aimed to prepare and characterize of modified adsorbent obtained from rain tree (*Samanea saman*) residue by chemical treatment using NaOH, H<sub>3</sub>PO<sub>4</sub>, and ZnCl<sub>2</sub> followed by



pyrolysis. The prepared modified adsorbents were investigated its potential for FOG treatment in canteen wastewater.

## 1.2 Research objectives

The main objective of this study is to develop modified adsorbent prepared from rain tree (*Samanea saman*) residue for FOG treatment in canteen wastewater. Three sub-objectives are as follows.

1. To utilize rain tree (*Samanea saman*) residue as modified adsorbent precursor by chemical pretreatments using NaOH, H<sub>3</sub>PO<sub>4</sub>, and ZnCl<sub>2</sub> and pyrolysis process.
2. To investigate the potential of modified adsorbent prepared from rain tree (*Samanea saman*) residue by batch experiment for FOG in synthetic emulsified oil wastewater.
3. To subsequently investigate the potential of modified adsorbent prepared from rain tree (*Samanea saman*) residue by fixed-bed column tests for FOG removal in canteen wastewater.

## 1.3 Research hypotheses

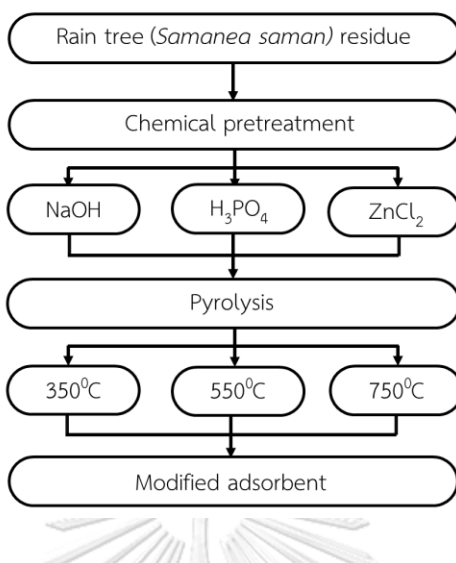
1. Chemical pretreatment (NaOH, H<sub>3</sub>PO<sub>4</sub>, and ZnCl<sub>2</sub>) followed by pyrolysis of rain tree (*Samanea saman*) residue are expected to increase modified adsorbents' sorption capability for FOG compared with natural adsorbent.

2. Modified adsorbent prepared from rain tree (*Samanea saman*) residue is an alternative adsorbent material for FOG treatment.
3. Fixed-bed column test can be used to evaluating the efficiency of the best-modified adsorbent from rain tree (*Samanea saman*) residue for FOG treatment process on the pilot scale.

#### 1.4 Scope of study

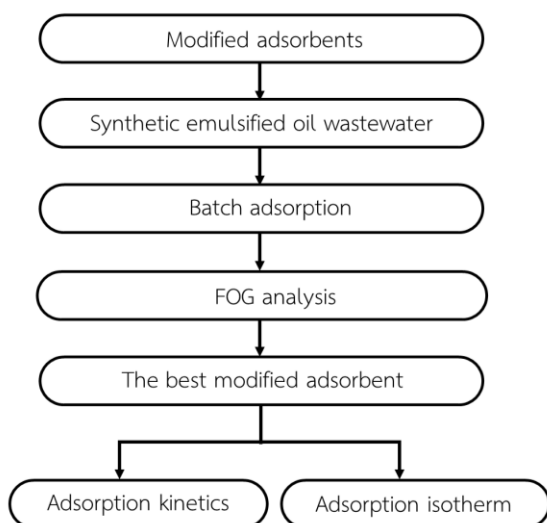
This study was divided into three main parts: modified adsorbent production, FOG treatment, and technology implementation. For the first part, modified adsorbent production from rain tree (*Samanea saman*) residue was carried out by varying chemical pretreatments (NaOH, H<sub>3</sub>PO<sub>4</sub>, and ZnCl<sub>2</sub>) and pyrolysis temperatures (350°C, 550°C, and 750°C). After the modified adsorbents were produced, all modified adsorbents were investigated its adsorption capacity for FOG in synthetic emulsified oil wastewater. Next, the modified adsorbent with the greatest adsorption performance was determined for adsorption isotherm and isotherm kinetic by batch sorption; it was also continuously examined using a fixed-bed column experiment for canteen wastewater. Finally, the best-modified adsorbent was selected for economic feasibility analysis for technology implementation (**Figure 1.1**).

## Part I : Modified adsorbent production

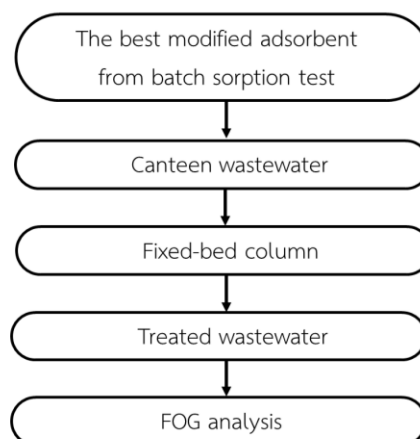


## Part II : FOG treatment

## a. Batch sorption test



## b. Fixed-bed column test



## Part III : Technology implementation

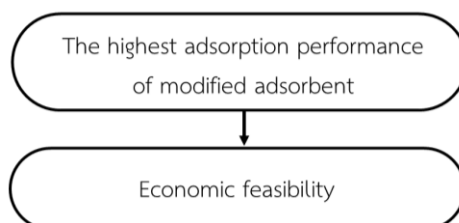


Figure 1.1 Overview of the study

## CHAPTER 2

### LITERATURE REVIEWS

#### 2.1 Canteen wastewater

There are two categories of domestic wastewater: black water and greywater. They are classified based on the source at the household scale (Boutin and Eme, 2016). Generally, black water produced from flush water or toilet ended at the septic tank system. Meanwhile, greywater contains high turbidity phosphorus, total suspended solids, oil and grease, and surfactant from food cleaning and personal care products (Chripim and Nolasco, 2017). Refers to the classification, canteen wastewater produced from food processing is categorized as greywater.

Canteen wastewater usually has a high value of fat, oil, and grease (FOG), biological oxygen demand (BOD), and chemical oxygen demand (COD) due to the existence of organic matters. FOG in the massive amount results in foul odor and sewage blockage (Brooksbank et al., 2006). FOG consists of fatty acids and glycerol that are not easily degraded and remove from the water and has a density less than water (density  $<1$ ), and thus, it floats on the water surface (Matsumiya et al., 2007). The range of value of foodservice wastewater varies from 545-1630 mg L<sup>-1</sup> of BOD, 124-1320 mg L<sup>-1</sup> of Total Suspended Solid (TSS), and 415-1970 mg L<sup>-1</sup> of FOG (Lesikar et al., 2006). Based on the building effluent standard, the maximum permitted value from the food center (size area more than 100 m<sup>2</sup>) is shown in Table 1. Therefore,

many researchers have stepped up efforts to find alternative solutions in order to treat FOG in the wastewater before directly discharging it to sewages.

**Table 2.1** Building effluent standards for food centers in Thailand (Environment, 2005)

| Parameter | Unit               | Range or Maximum Permitted Value |
|-----------|--------------------|----------------------------------|
| pH        | -                  | 5-9                              |
| BOD       | mg L <sup>-1</sup> | 50                               |
| TSS       | mg L <sup>-1</sup> | 50                               |
| FOG       | mg L <sup>-1</sup> | 20                               |

## 2.2 Treatment technologies for FOG

Treatment of oily wastewater consists of a primary treatment followed by a second step and, when needed, a tertiary stage to refine quality parameters for discharge or reuse. The primary treatment generally consists of a gravity separation tank, allowing free oil to float to the water surface, and the solid contents will settle down in the quiescence condition. The separation principle involves gravity force and difference in oil and water densities (Ahmad et al., 2005; Kamal Al-Malah, 2000). The wastewater from primary treatment goes to the secondary treatment that aims to separate the remaining oil, and mainly it occurs in the emulsified form and could not be separated under gravity separation. This type of FOG needs to be treated at the secondary treatment after gravity separation.

The breaking of oil emulsion can be carried out chemically, physically, or electrically treatments. Interestingly, the adsorption process is a favorable physicochemical method for removing FOG in wastewater systems, among other chemical and physical methods nowadays (Sohaimi and Ngadi, 2016). The economical alternative source materials of adsorbent drive the broad application of this method. There are some advantages of employing adsorption to treat oily wastewater, i.e., high removal efficiency, cheap (especially with low-cost materials), ease of operation, the possibility of regeneration (Wahi et al., 2013). Thus, a low-cost and straightforward technology using waste materials and by-products from agriculture to produce adsorbent is gaining focus among researchers to treat FOG in wastewater.

### **2.3 Utilization of tree residue as adsorbents' precursors**

Tree residue, an abundant waste, provides a potential feedstock to be converted into valuable materials. The tree residues are usually disposed of by landfilling, open burning, and composting. These tree residues generated as solid waste in large amounts can be utilized for further use than disposed of by those impractical conventional methods. Typically, biomass (plants and trees) comprises three components: cellulose, hemicellulose, and lignin. These components are firmly linked, chemically bonded by non-covalent forces, and cross-linked together,

thereby providing structure and rigidity as shown in **Figure 2.1** (Kambo and Dutta, 2015).

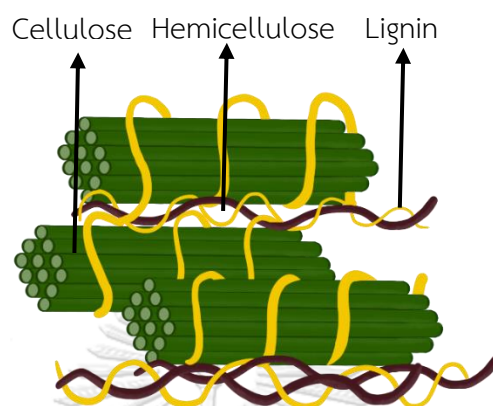


Figure 2.1 Lignocellulose

Table 2.2 Tree residue as adsorbents' precursors

| Adsorbent        | Material                                       | Pollutant        | Ref.                  |
|------------------|--|------------------|-----------------------|
| Biochar          | Ginkgo leaves                                  | Pb and Cu        | (Lee et al., 2017)    |
| Biochar          | Maple leaves ( <i>Acer palmatum Thunb.</i> )   | Tetracycline     | (Kim et al., 2020)    |
| Biochar          | Fallen leaves                                  | H <sub>2</sub> S | (Sahota et al., 2018) |
| Biochar          | <i>Magnolia grandiflora</i> Linn               | Methylene blue   | (Ji et al., 2019)     |
| Biochar          | Walnut leaves ( <i>Juglans regia</i> L.)       | Pb and Zn        | (Kabiri et al., 2019) |
| Activated carbon | Camphor leaves ( <i>Cinnamomum bodinieri</i> ) | Ciprofloxacin    | (Hu et al., 2019)     |
| Activated carbon | Coconut leaves                                 | Methylene blue   | (Rashid et al., 2016) |

The lignocellulosic composition of biomass has a strong influence on hydrophobic behavior. Among the lignocellulosic biomass compositions, hemicellulose has the most significant water adsorption capacity (Acharjee et al., 2011). Hence, removing the lignocellulosic component will improve its hydrophobicity that contribute to oil removal efficiency. Thus, carbon-based adsorbent prepared from tree residue is a promising adsorbent as it is cheap and provides some impressive properties for contaminant removal, especially FOG.

#### 2.4 Rain tree (*Samanea saman*)

*Samanea saman* or rain tree is extensively cultivated worldwide, specifically in tropical and subtropical countries. The native of rain tree is Central America and Northern South America (Magnus and Seaforth, 1965) and widespread in Thailand (Sareena Semae and Somchai Chanpongsang, 2013). The tree can reach until 25 meters high that the top of the tree forms like an umbrella with abundant foliage. Rain tree has rough and pale gray to brownish bark (Evans, 2006). During the dry periods, trees shed their leaves in a short time. Rain tree offers excellent shade, wood, and pods containing lignocellulosic components. Although this tree outstands among agroforestry species, there is a lack of information available supporting its potentialities.

The fresh leaves of rain tree contain 34% dry matter, 30% crude protein, 29% fiber, and 3.5% ash (Gohl, 1981). Meanwhile, the twigs contain 38.9% dry matter,



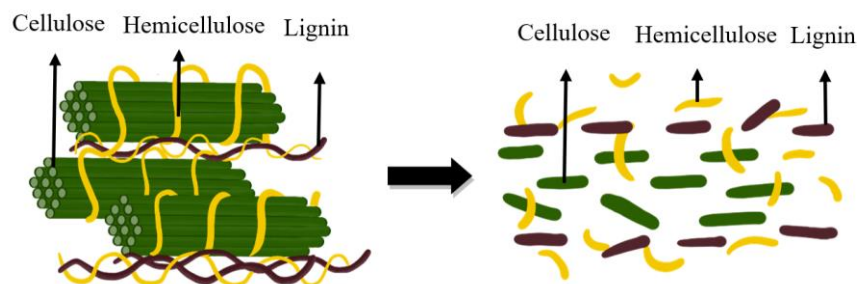
24.7% crude protein, 22.1% fiber, and 3.5% ash. A study has identified *Samanea saman* for animal feedstock and found that it contains more than 25% lignocellulosic components presented as neutral and acid detergent fiber fraction (Delgado et al., 2016). Due to the aforementioned lignocellulosic components containing, more studies related to its properties are required to explore to confirm the potential of rain tree residue as an alternative and effective adsorbent precursor.

## 2.5 Chemical pretreatment

Modified adsorbent properties depend on the characteristics of the biomass and the conditions of the production process. Modification of adsorbent can significantly increase the surface area due to the development and opening of the internal porous structure of a biomaterial (Gratuito et al., 2008). The most common methods for adsorbent treatment is chemical treatment (Lehmann and Joseph, 2012). The choice of the treatment is a crucial part for modified adsorbent.

Chemical treatment has a number of advantages, including the following: it involves low temperatures, large surface area, and fast conversion. Moreover, chemical activation offers a good pore distribution and consumes less energy (Beltrame et al., 2018; Nowicki et al., 2015; Romero-Anaya et al., 2014; Shamsuddin et al., 2016). Chemical treatment is typically performed using several pretreatments of the biomass that improve its sorption performance. It has been studied by washing the biomass with solvents, soaking in salt, acid, or base solutions (Beltrame

et al., 2018; Castro et al., 2020; Ma, 2016; Menya et al., 2018). During chemical treatment, the chemical separates the lamellae of crystallites, forming its monomers (Figure 2.2). After rinsing with water, activators are washed away, leaving behind a structure with highly improved surface area and porosity (Januszewicz et al., 2020).



**Figure 2.2** Schematic representation of the effect of pretreatment on lignocellulosic biomass structure

### *Alkaline treatment*

The various alkaline reagents commonly used for alkali pretreatment are the hydroxides of sodium, potassium, calcium, and ammonium. Among these alkaline, sodium hydroxide (NaOH) was found to be the most effective (Kim, 2018). A study reported that NaOH activation, compared with KOH activation, has advantages such as lower dosage, cheaper, more environmentally friendly, and less corrosive (Tseng, 2006). A saponification reaction occurs throughout the alkali pretreatment that causes breaking down of the intermolecular ester linkages between hemicelluloses

and lignin (Sun et al., 2016). Alkali pretreatment changes the lignocellulosic structure via cellulose swelling, leading to a reduction in crystallinity and degree of polymerization, thereby increasing internal surface area (Behera et al., 2014).

### ***Acid treatment***

Acid pretreatment of lignocellulosic material is based on the susceptibility of the glycosidic linkage between hemicellulose and cellulose to acid. Hydronium ions from the acid activator cause breakdown of the long cellulose and hemicellulose chains into sugar monomers (Lloyd and Wyman, 2005). Some acids such as  $H_2SO_4$  (Karcher et al., 2015),  $H_3PO_4$  (Hadoun et al., 2013),  $HNO_3$  (Su et al., 2019), and HCl (Zu et al., 2014) are usually employed. However,  $H_3PO_4$  is preferable chemical treatment due to its lower corrosive property compared to other acids.

### ***Ionic liquid treatment***

Chemical treatment that also usually employed for biomass pretreatment is ionic compounds. It comprises anion and cation that play an important role in solubilizing the lignocellulosic components. Impregnation with ionic activator affects carbonization, dehydration, degradation of lignocellulose. As a result, it facilitates the pyrolysis process, creates pore structure, and aromatization in carbon (Angin, 2014). Zinc chloride ( $ZnCl_2$ ) is highly effective and frequently used as chemical pretreatment. The  $Zn^{2+}$  ions distribute to the amorphous and crystalline structure of

biomass causing the fiber swelling. Thus, it simplifies the complex structure of lignocellulosic content in the biomass (Yang et al., 2011).

Many researchers have investigated various adsorbent for FOG removal in water based on the properties mentioned above by developing from different lignocellulosic materials and activation agents. Each adsorbent performs different adsorption capacities of FOG depending on many factors, i.e., adsorbent materials, treatment processes, temperature, and FOG concentration. Therefore, in this current work, chemical activation using NaOH, H<sub>3</sub>PO<sub>4</sub>, and ZnCl<sub>2</sub> will be carried out to improve physicochemical properties that are preferable for FOG adsorption.

**Table 2.3** Results of adsorption in oil-water emulsions or wastewater reported in the literature

| Adsorbent        | Treatment                           | Material                                 | Pollutant | Adsorption capacity/<br>Removal<br>percentage | Ref.                    |
|------------------|-------------------------------------|--|-----------|---|-------------------------|
| Activated carbon | NaOH                                | <i>Oleifera moringa</i> (seeds and pods) | FOG       | 79 - 87.2 %                                   | (Santos et al., 2020)   |
| Activated carbon | ZnCl <sub>2</sub> , CO <sub>2</sub> | Palm shell                               | FOG       | 90%   | (Ngarmkam et al., 2011) |

| Adsorbent | Treatment | Material    | Pollutant | Adsorption capacity/<br>Removal percentage | Ref.                      |
|-----------|-----------|-------------|-----------|--|---------------------------|
| Biochar   | -         | Rice husk   | FOG       | 2-3 g g <sup>-1</sup>                      | (Kandanelli et al., 2018) |
| Biochar   | -         | Fruit peels | FOG       | 57%  | (Lam et al., 2018)        |

## 2.6 Pyrolysis process

A few years ago, there are three terms (biochar, charcoal, and char), all of which were used in order to indicate the carbonaceous material produced by thermal degradation in oxygen-limited conditions (pyrolysis) of biomasses from plant or animal origin (Bi et al., 2019). Pyrolysis is a thermal decomposition process that involves heat in the absence of oxygen to produce bio-oil, gases, and biochar (Liew et al., 2018). Recently, applications biomass as sorbent precursors is gaining popularity. Through pyrolysis, biomass material has recently been investigated as a promising adsorbent (Derakhshan-Nejad and Jung, 2018; Hu et al., 2019; Ji et al., 2019; Kim et al., 2020). The biomass undergoes a series of chemical reactions mechanism that is highly complicated and partially understood (Tseng, 2006; Wajima, 2017). Dehydration, carboxylation, and aromatization are some of the proposed chemical reactions during the thermochemical conversion of biomass (Tseng, 2006). Dehydration is the water molecule removal from the biomass matrix under thermal

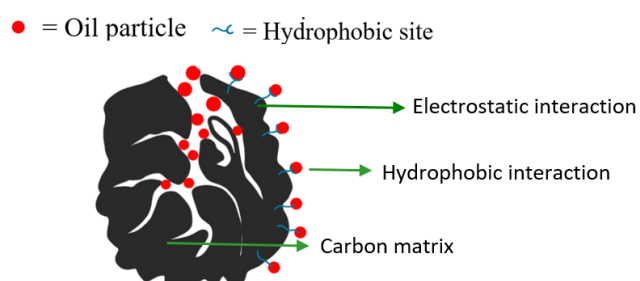
conditions. After the biomass moisture decrease, it undergoes elimination of carboxyl groups yielding  $\text{CO}_2$ . The thermal treatment also affects the formation of aromatic structures. However, it is difficult to maintain steady temperature profiles in pyrolysis reactors; therefore, the reaction mechanisms mentioned above may simultaneously occur (Wajima, 2017).

Under standard pressure conditions in pyrolysis, hemicellulose decomposition occurs between 200-300°C, followed by cellulose decomposing at higher temperatures (300-400°C). Lignin is the most thermochemically stable lignocellulose that decomposes around 600°C (Kambo and Dutta, 2015). During pyrolysis, the reaction pathway is acknowledged to be a free radical process initiated by the homolytic cleavage of bonds around 300°C (Morten Gunnar Grønli, 2002). As the reaction temperature increases (i.e., above 300°C and below 500°C), the tar components formed by the degradation of cellulose mainly consist of anhydrous sugars (anhydrous glucose) that are less reactive than the free radicals produced during bond cleavage. These anhydrous glucose intermediates (tar vapors) and inorganic compounds existing in the biomass volatilize, which later condenses, accounting for the cross-linkage crystal layered and porous char structure. The degradation of polymers (hemicellulose, cellulose, and lignin), the release of volatiles, forming intermediates compounds, and further transformations are all temperature-dependent (Kambo and Dutta, 2015). In an experiment performed on wood species under pyrolysis, the increase in reaction temperature (200-700°C)

showed a positive influence on BET surface area (10-500 m<sup>2</sup>/g); however, with further increase in reaction temperature (800°C), the surface area was significantly reduced (150 m<sup>2</sup>/g) (Schimmelpfennig and Glaser, 2012). The main reason behind the variation in the morphological properties is the volatilization of organic compounds resulting in voids within the biochar matrix. However, high reaction temperature and high heating rates can destroy the fine porous structure, resulting in pores' clogging and reducing the overall surface area (Kloss et al., 2012).

## 2.7 Interaction of FOG uptake with adsorbent

FOG is the group of organic compounds that has low affinity to water (hydrophobic). This hydrophobic substance adsorption onto adsorbent material with respect to carbonaceous adsorbent; has been demonstrated by the occurrence of  $\pi$  interaction between hydrophobic organic compound and the hydrophobic characteristic of the material (Das et al., 2014). The FOG adsorption onto an adsorbent is illustrated on the **Figure 2.3**, as follows.



**Figure 2.3** Mechanism of FOG adsorption on carbon-based adsorbent (Ahmad et al., 2014)

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Research materials

##### 3.1.1 Material

- 1) Rain tree residue

##### 3.1.2 Equipment

- 1) Soxhlet extractor (Soxtec™ 2050, Denmark)
- 2) Scanning electron microscope (Hitachi, Japan)
- 3) Surface area analyzer (Quantachrome, USA)
- 4) pH meter (Mettler Toledo, USA)
- 5) ATR-FTIR spectroscopy (Bruker, Germany)
- 6) Hot air oven (Binder, USA)
- 7) Shaker (PNP Science, Thailand)
- 8) Blender (Philips, Thailand)
- 9) Analytical balance (Mettler Toledo, USA)
- 10) Water distillers 15 M $\Omega$ -cm and 18 M $\Omega$ -cm
- 11) Muffle furnace (Nabertherm, Germany)
- 12) Sieve



- 13) Vacuum filter
- 14) Peristaltic pump (Model Master-flex, USA)
- 15) Column (diameter 3 cm, height 40 cm)

### 3.1.3 Chemicals

- 1) Sodium hydroxide (TCI, Japan)
- 2) Phosphoric acid (TCI, Japan)
- 3) Zinc chloride (TCI, Japan)
- 4) Palm oil (Sime Darby Oils Morakot Public Company Ltd.)
- 5) n-Hexane (Macron, USA)
- 6) Sulfuric acid (Orec, New Zealand)

## 3.2 Experimental procedure

### 3.2.1 Part I: Modified adsorbent production

The rain tree residues were collected from Physical Resources and Management, Chulalongkorn University, Thailand. The collected rain tree residues with 4:1 ratio of leaves and twigs were washed and dried at 105°C in an oven. Then, the biomass was crushed and sieved to get a uniform size (between 0.5 mm - 0.2 mm). The prepared biomass was stored in a sealed polypropylene plastic bag for further use.

For the chemical pretreatments, the crushed biomass was soaked for 120 min in 1M NaOH, 0.3M H<sub>3</sub>PO<sub>4</sub>, and 0.5M ZnCl<sub>2</sub> with ratio biomass: solution (1:5) (w/v). After the pretreatment step, the treated biomass was dried in the oven overnight. Eventually, the treated biomass was ready for a pyrolysis process.

The pyrolysis process was carried out by heating the treated biomass at various temperatures (350, 550, and 750°C) for 2 h after reaching the peak temperature with heating rate 10°C/min in muffle furnace. After cooling, the modified adsorbents were washed with DI water several times until pH ~7 to eliminate residues formed during the process. In the washing step, the modified adsorbents were separated using membrane filters. The modified adsorbents obtained were dried in the oven until completely dry. Thereby, modified adsorbents from rain tree (*Samanea saman*) residue were obtained, kept in tightly sealed plastic, and stored in the desiccator for further analysis. Carbon adsorbent from rain tree (*Samanea saman*) residue without pretreatment was also prepared for control treatment. The scheme of modified adsorbents production is shown in **Figure 3.1** and the yield of modified adsorbent was determined by following equation **(1)**

$$\text{Modified adsorbent yield (\%)} = \frac{W_2}{W_1} \times 100 \quad (1)$$

where, W<sub>1</sub> is dry weight of biomass and W<sub>2</sub> is weight of modified adsorbent.

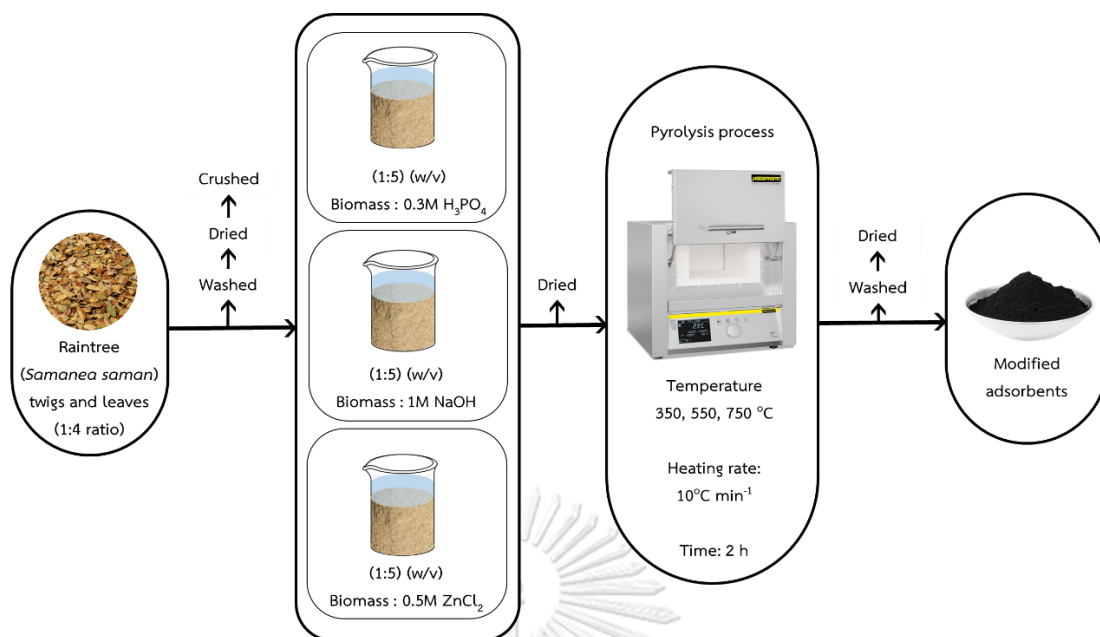


Figure 3.1 Modified adsorbents production scheme

### 3.2.2 Part II: FOG treatment

#### *Batch sorption test*

##### 1) Preliminary adsorption test

A batch sorption screening test was initially conducted to identify the performance of modified adsorbents for FOG removal. Three grams of modified adsorbents were added into 200 mL of 50 mg L<sup>-1</sup> synthetic emulsified oil wastewater. After shaking for 24 h (1440 min), the supernatant was sampled and analyzed the FOG content. The FOG content was measured by a Soxhlet extraction method (5520D), and a control treatment will be carried out in all adsorption conditions. The best-modified adsorbent was determined using ANOVA and selected for further experiment. All the experiments were run in triplicate to ascertain accuracy.

The percentage of FOG eliminated was calculated by following equation (2)

$$\text{FOG Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where  $C_o$  and  $C_e$  are initial and equilibrium FOG concentrations in  $\text{mg L}^{-1}$ , respectively.

While for the calculation of FOG adsorbed per unit modified adsorbent mass,  $q_e$  is obtained from equation (3)

$$q_e = \frac{(C_o - C_e)V}{m} \quad (3)$$

where  $q_e$  is the FOG amount adsorbed on modified adsorbent ( $\text{mg g}^{-1}$ ),  $V$  is the solution volume (L), and  $m$  is the modified adsorbent mass (g).

## 2) Adsorption kinetics

For adsorption kinetic studies, 3 g of best-modified adsorbent from the previous preliminary experiment was added to 200 mL of  $100 \text{ mg L}^{-1}$  synthetic emulsified oil wastewater. Then, the mixture was shaken for 1440 min (24 h) with 150 rpm at room temperature and sampled periodically at time intervals of 2-1440 min.

Kinetic models were applied for predicting the mechanism of FOG adsorption onto the modified adsorbent. There are two linearized kinetic adsorption models as follows:

The pseudo-first-order model in equation (4)

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q_t$  ( $\text{mg g}^{-1}$ ) are the adsorption capacities at the equilibrium time and time  $t$ , respectively,  $t$  (min) is the adsorption time; and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant for the pseudo-first-order model.

The pseudo-second-order model in equation (5)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant for pseudo-second-order model.

### 3) Adsorption isotherm

For adsorption isotherm studies, 3 g of modified adsorbent was added to 200 mL of varying synthetic emulsified oil wastewater concentrations ( $10\text{-}100 \text{ mg L}^{-1}$ ) and shaken until the equilibrium time. The adsorption data of the FOG removal was fitted to Langmuir and Freundlich isotherm models as follows:

Langmuir model is,

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad (6)$$

Freundlich model is,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

where  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum amount of the adsorbed FOG,  $C_e$  ( $\text{mg L}^{-1}$ ) is the FOG concentration in the equilibrium, and  $K_L$  ( $\text{L mg}^{-1}$ ) is the Langmuir-adsorption constant.  $K_f$  ( $\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$ ) is the Freundlich adsorption constant. The scheme of adsorption studies is shown in **Figure 3.2**.

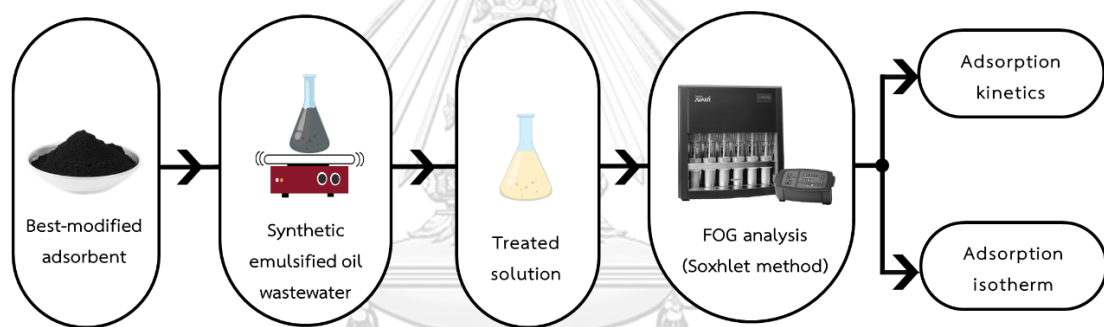


Figure 3.2 Batch sorption experiment scheme

### FOG analysis

FOG analysis was performed by a Soxhlet extraction method (5520D) (Standard Methods Committee of the American Public Health Association, 2017). The sample was acidified with  $\text{H}_2\text{SO}_4$  until pH 2 or lower. A filter paper was placed in the Buchner funnel set and connected to the vacuum pump. A 100 mL filter aid suspension was passed through filter paper and washed using DI water. The acidified

sample was filtered and applied vacuum until no more water passes through the filter. The filter paper was entirely transferred into an extraction thimble using forceps. Wiped the Buchner funnel with cotton soaked in n-hexane and placed it along in the extraction thimble. The extraction flask was weighed and added 70 mL n-hexane. The FOG was extracted in a Soxhlet apparatus. Eventually, the extraction flask was cooled before weighing and determining the initial sample volume.

Calculation FOG in a sample as follows:

$$\frac{\text{mg of FOG}}{L} = \frac{W_r}{V_s} \quad (8)$$

where  $W_r$  is the total weight of flask and residue minus tare weight of flask (mg) and  $V_s$  is initial sample volume (L).

### **Characterization of rain tree (*Samanea saman*) biomass and best-modified adsorbent**

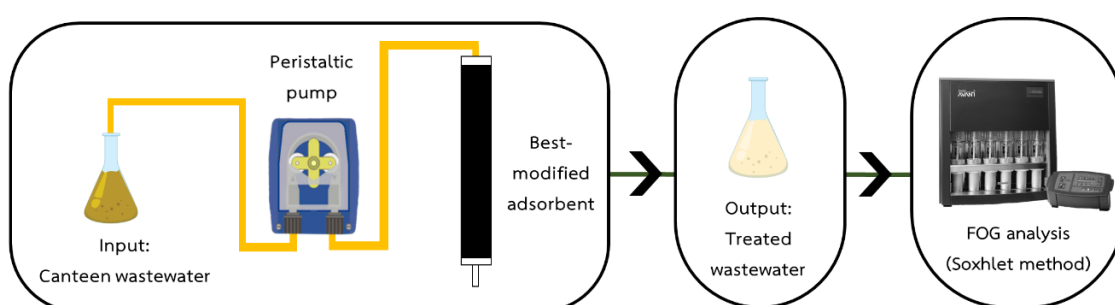
Thermogravimetric analysis of the rain tree (*Samanea saman*) biomass was performed on the Simultaneous TG-DTA Apparatus to identify the mass degradation as increasing temperature. The elemental analysis for biomass and best-modified adsorbent were performed using an element analyzer to analyze C, H, O, N, and S component. The bulk density was determined by the American Society for Testing and Materials (E873-82, 2013). The surface functional groups were characterized by

Fourier Transform Infra-Red Spectroscopy (FTIR) in the spectral range of 4000-400  $\text{cm}^{-1}$

<sup>1</sup>. Scanning electron microscopy (SEM) was applied to characterize the surface morphology of adsorbents. Iodine number and methylene blue number tests were conducted to examine microporosity (pore width > 0–20 Å) and mesoporosity (20–50 Å), respectively. Another surface properties of adsorbents were identified by the  $\text{N}_2$ -Brunauer-Emmett-Teller (BET) analysis.

### *Fixed-bed column test*

The best-modified adsorbent was continuously examined using a fixed-bed column test to identify the breakthrough times of the column, as shown in **Figure 3.3**. The experiment was conducted using a glass column of 3 cm (diameter) and 40 cm (height). The sampled canteen wastewater was allowed to pass through the bed, packed with best-modified adsorbent. The flow rate was set with a down-flow direction, and outflow was monitored. The output of the column was collected at a regular time.



**Figure 3.3** Fixed-bed column test scheme



### 3.2.3 Part III: Technology implementation

In the last part, the best-modified adsorbent among the tested modified adsorbents was selected for economic feasibility analysis. An economic feasibility analysis of the modified adsorbent production from rain tree residues was conducted using equation (9) and (10).

The break-even volume ( $N^*$ ):

$$N^* = \frac{FC}{P - V} \quad (9)$$

where  $N^*$  is the break-even volume, FC is the fixed cost (Baht), P is the price per unit (Baht/Unit), V is the variable cost (Baht).

The payback period:

$$\text{Payback Period} = \frac{N^*}{N} \quad (10)$$

where  $N^*$  is the break-even volume, N is the productivity (yield/year)

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 Part I: Modified adsorbent production

##### 4.1.1 Modified adsorbent yields and bulk densities

Three types (NaOH, ZnCl<sub>2</sub>, and H<sub>3</sub>PO<sub>4</sub>) treated rain tree biomass were produced at the different pyrolysis temperature (i.e., 350, 550, and 750°C). Carbon yield is an important indicator to evaluate the cost of modified adsorbent in large-scale production. **Table 4.1** shows the yield of modified adsorbents obtained from this study are H<sub>3</sub>PO<sub>4</sub>-treated (38.90±0.16%) – (55.87±1.40%)> ZnCl<sub>2</sub>-treated (31.99±0.88%) – (48.01±2.26%)> NaOH-treated (14.87±0.51%) – (27.50±1.27%) with decreasing pyrolysis temperature. Some researchers reported similar results, Andas and Wazil (2019) found the maximum activated carbons yield followed an order of H<sub>3</sub>PO<sub>4</sub>-treated (47.3%)> ZnCl<sub>2</sub>-treated (45.7%)> KOH-treated (8.4%), when employed mango kernel as the precursor under an production temperature of 500°C. Kiliç et al. (2012) found that the yields of *Euphorbia rigida* activated carbon varied in the range of 29.0–16.8% for H<sub>3</sub>PO<sub>4</sub>-treated, 29.5–17.8% for ZnCl<sub>2</sub>-treated, 13.3–9.7% for K<sub>2</sub>CO<sub>3</sub>-treated, and 13.4–4.1% for NaOH-treated with increasing impregnation of chemical reagent ratio. Briefly, the carbon-based adsorbent yield with an acidic treatment is higher than alkaline and ionic treatment.

Moreover, the result of this study showed that each type modified adsorbent yield decreased with the increasing of temperature. According to the study of Xu et al. (2014) reedy grass leaves showed a weight loss about 72% at 200-400°C in which carbonization process begin and mainly hemicellulose and cellulose fraction decomposition. Therefore, the mass loss is shifted to higher temperatures that contributes to the yield of the modified adsorbent. The temperature influence also depends on the treatment condition process. An excessively high production temperature may decrease the carbon yield and specific surface area. This is because high temperature may lead to excessive transformation of cross-linked substances in the solid phase to volatile matters in the gas phase (Adebisi et al., 2017; Liang et al., 2020).

In this study, the yield of modified adsorbent obtained by H<sub>3</sub>PO<sub>4</sub>-treated (38.90±0.16%) – (55.87±1.40%) is the highest among other treatments. The carbonization of lignocellulosic component (cellulose, hemicellulose, and lignin) at high temperature decomposes most of the non-carbon elements, mainly hydrogen, oxygen, and nitrogen in the form of liquid (tars) and gases, leaving behind a rigid carbon skeleton in the form of aromatic sheets and strips. The presence of phosphoric acid during process promotes depolymerization, dehydration, and redistribution of constituent biopolymers, and favoring the conversion of aliphatic to aromatic compounds; therefore, increasing the yield of modified adsorbent. Karadirek and Okay (2018) evaluated influences of H<sub>3</sub>PO<sub>4</sub> impregnation ratio, carbonization

temperature, and time on activated carbon production. The study found that activated carbon with the maximum carbon yield was obtained at 350 °C, due to the evolution of volatiles and the evaporation of water.

**Table 4.1** The yield and bulk density of modified adsorbents

| Code   | Modified adsorbent type    | Temp. (°C) | Initial weight (g) | Final weight (g) | Yield (%)  | Bulk density (g mL <sup>-1</sup> ) |
|--------|----------------------------|------------|--------------------|------------------|------------|------------------------------------|
| BAC350 | NaOH-treated               | 350        | 15.05              | 4.14             | 27.50±1.27 | 0.30                               |
| BAC550 | NaOH-treated               | 550        | 15.05              | 3.09             | 20.52±0.22 | 0.30                               |
| BAC750 | NaOH-treated               | 750        | 15.05              | 2.24             | 14.87±0.51 | 0.26                               |
| SAC350 | ZnCl <sub>2</sub> -treated | 350        | 15.05              | 7.23             | 48.01±2.26 | 0.30                               |
| SAC550 | ZnCl <sub>2</sub> -treated | 550        | 15.05              | 6.51             | 43.22±1.00 | 0.35                               |
| SAC750 | ZnCl <sub>2</sub> -treated | 750        | 15.05              | 7.94             | 31.99±0.88 | 0.35                               |
| AAC350 | ZnCl <sub>2</sub> -treated | 350        | 15.05              | 7.94             | 55.87±1.40 | 0.26                               |
| AAC550 | ZnCl <sub>2</sub> -treated | 550        | 15.05              | 6.38             | 42.38±0.59 | 0.23                               |
| AAC750 | ZnCl <sub>2</sub> -treated | 750        | 15.05              | 5.86             | 38.90±0.16 | 0.30                               |

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## 4.2 Part II: FOG treatment

### 4.2.1 Preliminary experiment on FOG treatment

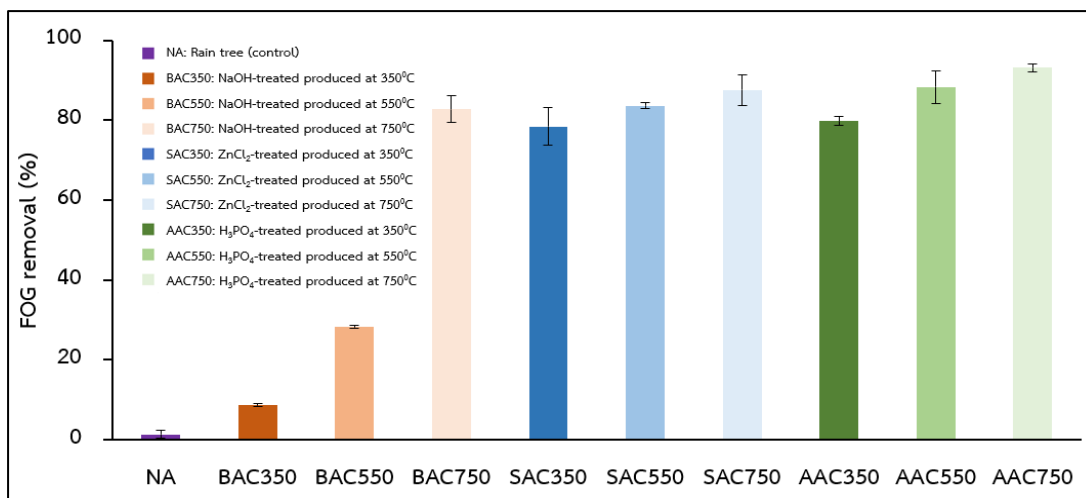
#### *Batch sorption experiment*

A batch sorption screening test was initially conducted to identify the performance of modified adsorbents for FOG and find the best-modified adsorbent among treatments for further studies. Ten experiments were run in triplicate and

ANOVA was used to assess a significant result of FOG removal compared to control treatment (natural adsorbent). Three grams of each modified adsorbents were added into 200 mL of  $50 \text{ mg L}^{-1}$  synthetic emulsified oil wastewater. The FOG removal in the synthetic emulsified oil wastewater for all treatments are shown (**Figure 4.1**) with range from  $(1.35 \pm 0.98\%)$  –  $(93.09 \pm 0.97\%)$ . However, the ANOVA result of FOG removal (**Table A-3**) indicated that most of the treatments were significantly different ( $p\text{-value} < 0.05$ ), and only one treatment (modified adsorbent by NaOH-treated produced at  $350^\circ\text{C}$ ) was not significantly different ( $p\text{-value} > 0.05$ ) from the control treatment (natural adsorbent). These results indicated that most of modified adsorbents performed higher FOG removal compared to the control treatment. In addition, AAC750, which has the highest FOG removal ( $93.09 \pm 0.97\%$ ) was not significantly different ( $p > 0.05$ ) with BAC750 ( $82.78 \pm 3.39\%$ ), SAC350 ( $78.45 \pm 4.81\%$ ), SAC550 ( $83.66 \pm 0.75\%$ ), SAC750 ( $87.62 \pm 3.84\%$ ), AAC350 ( $79.77 \pm 1.17\%$ ), and AAC550 ( $88.28 \pm 4.13\%$ ). Therefore, further identification needed to be further conducted to determine the best-modified adsorbent among treatments.

**Table 4.2** Application of different adsorbents for FOG removal

| Adsorbents   | Treatment sample         | Removal (%) | References              |
|--|--------------------------|-------------|-------------------------|
| Fruit peels biochar                                | POME                     | 57          | (Lam et al., 2018)      |
| Magnetic palm shell-based activated carbon         | POME                     | 80          | (Ngarmkam et al., 2011) |
| Cork-based activated carbon                        | Sunflower oil-in-water   | 82          | (Pintor et al., 2013)   |
| Saw dust activated carbon                          | Oil-in-water emulsion    | 98          | (Rajak et al., 2018)    |
| Palm shell activated carbon by physical activation | POME                     | 57          | (Ngarmkam et al., 2011) |
| Palm shell   | POME                     | 32          | (Ngarmkam et al., 2011) |
| Modified rice husk                                 | Crude-oil-in-water       | 49          | (Razavi et al., 2015)   |
| Rain tree residue                                  | Synthetic oil wastewater | 1.35±0.98   | This study              |
| Rain tree residue modified adsorbent               | Synthetic oil wastewater | 79.77±1.17  | This study              |



**Figure 4.1** FOG removal by different adsorbents (Adsorbent dose 3 g in 200 mL of 50 mg L<sup>-1</sup> synthetic emulsified oil wastewater, contact time 24 h)

#### *Analysis Zinc (Zn) in the treated synthetic emulsified oil wastewater*

As shown in the (Figure 4.1), the ZnCl<sub>2</sub>-treated modified adsorbents are categorized into modified adsorbents that provide high removal for FOG. Due to the involvement of heavy metal (Zn) in ZnCl<sub>2</sub> during the modified adsorbent production process, the Zn was analyzed in treated synthetic emulsified oil wastewater to identify the harmful side product after FOG treatment. The residual of Zn after FOG treatment was identified by Atomic Adsorption Spectroscopy (AAS). The result is showed in the **Table 4.3** The residual Zn in the treated synthetic emulsified oil wastewater may be caused by the excess activator agent during impregnation and incomplete washing process. Therefore, the presence of Zn after FOG treatment

became a consideration for not selecting them as best-modified adsorbent even though it provided high FOG removal with range  $(78.45 \pm 4.80\%) - (87.62 \pm 3.84\%)$ .

**Table 4.3** Atomic absorption spectroscopy (AAS) analysis of Zn after FOG treatment using SAC350

| Code   | Adsorbent type             | Concentration ( $\text{mg L}^{-1}$ ) |
|--------|----------------------------|--------------------------------------|
| SAC350 | ZnCl <sub>2</sub> -treated | $0.7 \pm 0.08$                       |

#### *Net efficiency of FOG removal*

The net efficiency of FOG removal was selected for further identification to define best-modified adsorbent by considering the modified adsorbent yields and removal percentages (**Figure 4.2**). The ANOVA result (**Table A-4**) indicated that most of the treatments were significantly different ( $p\text{-value} < 0.05$ ), and two treatments using NaOH-treated modified adsorbent were not significantly different ( $p\text{-value} > 0.05$ ) from the control treatment. However, AAC350 gave the highest net efficiency and had significant difference for FOG removal. The removal and yield percentage are  $79.77 \pm 1.40\%$  and  $55.87 \pm 1.17\%$ , respectively.

Accordingly, modified adsorbent by H<sub>3</sub>PO<sub>4</sub>-treated and produced at 350°C (AAC350) that gave the highest net efficiency of FOG removal was selected as the best-modified adsorbent for further studies.



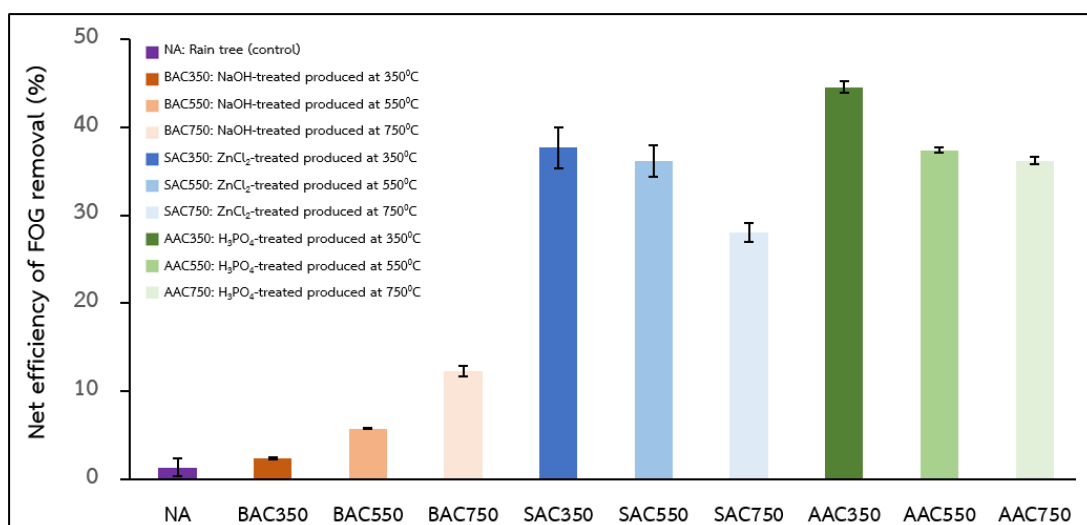


Figure 4.2 Net efficiency of FOG removal by different adsorbents

#### 4.2.2 Characterization of adsorbents

The characterization was performed for the raw material (rain tree residue) and the selected modified adsorbent from previous result (AAC350).

##### *Proximate and ultimate analyzes*

A proximate analysis and the ultimate analysis of rain tree residue (twigs and leaves with a ratio of 1:4) and AAC350 are given in **Table 4.5**. The proximate analyses of the materials are in terms of moisture content, ash content, volatile matter, and fixed carbon. The fixed carbon content of the materials was calculated by mass difference. From **Table 4.5**, the proximate composition of the raw material was 5.13 wt% moisture, 81.23 wt% volatile matter, 3.99 wt% ash, and 9.65 wt% fixed carbon. While the proximate composition of the prepared modified adsorbent was 4.74 wt% moisture, 66.12 wt% volatile matter, 7.61 wt% ash, and 21.53 wt% fixed carbon. High

volatile matter content usually reduces the solid yield in the carbonization stage while a low inorganic content be able to produce a low ash and high fixed carbon content (Macías-García et al., 2012).

The results of ultimate analysis of rain tree residue and AAC350 show that carbon and oxygen represented the major elements, whereas sulfur, nitrogen, and hydrogen were detected in low concentrations. As shown in **Table 4.4**, different raw material has different elemental component, and the rain tree residue provides comparable element values as raw material for adsorbent. In addition, the low concentration of sulfur in the raw material presents less concern on the production of undesirable sulfur-containing chemicals (e.g., H<sub>2</sub>S, SO<sub>2</sub>) in the pyrolysis process.

**Table 4.4** Elemental component (%wt) of some raw materials for adsorbent.

| Raw material      | C     | H    | O     | N    | S    | References              |
|-------------------|-------|------|-------|------|------|-------------------------|
| Saw dust          | 49.62 | 5.89 | 44.17 | 0.21 | 0.11 | (Rajak et al., 2018)    |
| Palm shell        | 50.01 | 6.85 | -     | 1.90 | -    | (Ngarmkam et al., 2011) |
| Cork              | 61.90 | 7.90 | 29.57 | 0.63 | -    | (Pintor et al., 2013)   |
| Banana peel       | 47.50 | 6.0  | 45.5  | 1.0  | 0    | (Lam et al., 2018)      |
| Orange peel       | 42.50 | 6.0  | 51.0  | 0.5  | 0    | (Lam et al., 2018)      |
| Rain tree residue | 50.64 | 6.48 | 41.06 | 1.76 | 0.06 | This study              |

An increase in carbon content from rain tree residue to AAC350 (50.64 to 57.02 wt%) has been observed. The hydrogen and oxygen content decreased from 6.48 to 3.17 wt% and 41.06 to 37.36 wt%, respectively. The increase in carbon

content from raw material to modified adsorbent due to an increasing degree of aromaticity (Angin, 2014). The value of the carbon content of the modified adsorbent shows a good agreement with the results reported by Angin (2014) and Fierro et al. (2006).

**Table 4.5** Proximate and ultimate analyzes of raw material and AAC350

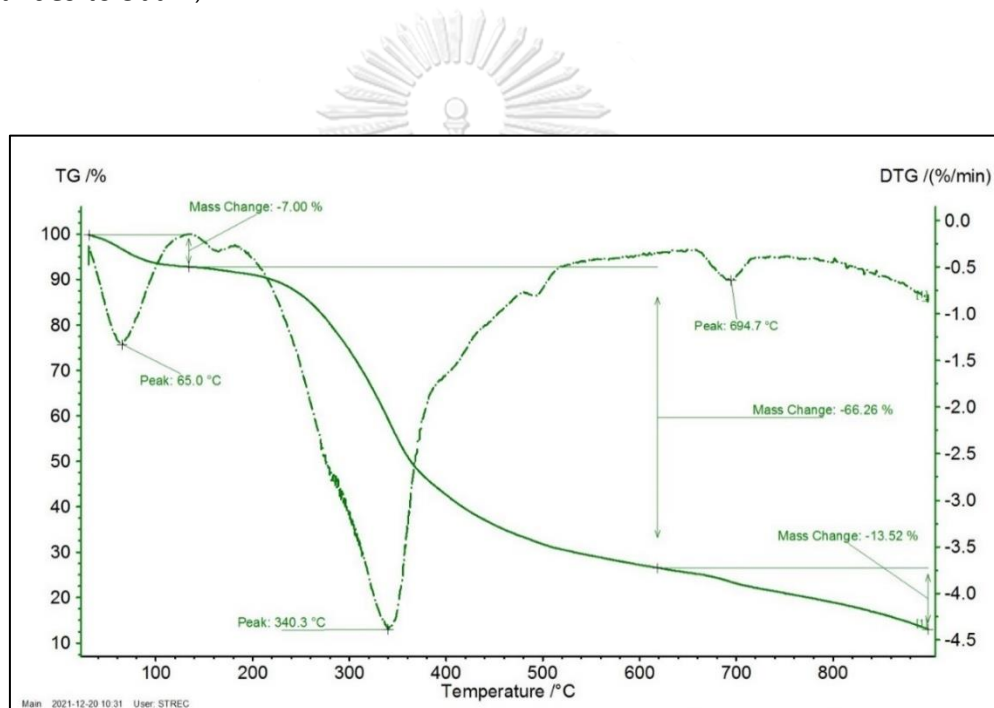
| Analysis         | Rain tree residue (%wt) | AAC350 (%wt) |
|------------------|-------------------------|--------------|
| <i>Proximate</i> |                         |              |
| Moisture         | 5.13                    | 4.74         |
| Volatile         | 81.23                   | 66.12        |
| Ash content      | 3.99                    | 7.61         |
| Fixed carbon*    | 9.65                    | 21.53        |
| <i>Ultimate</i>  |                         |              |
| Carbon           | 50.64                   | 57.02        |
| Hydrogen         | 6.48                    | 3.17         |
| Nitrogen         | 1.76                    | 2.45         |
| Sulfur           | 0.06                    | 0.00         |
| Oxygen*          | 41.06                   | 37.36        |

\*Calculated by difference.

#### *Thermogravimetry analysis of the precursor (rain tree residue)*

TG/DTG study of rain tree biomass was performed to identify the mass degradation as the increase of temperature (**Figure 4.3**). This thermal decomposition of rain tree biomass could be divided into three stages. In the first stage, the amount of moisture is removed during the temperature range of 30-150°C. Due to moisture

loss, the weight was slightly decreased during the initial drying. The second stage, decomposition of hemicellulose, protein, and carbohydrates, occurs from 150°C to approximately 350°C (Araujo et al., 2010). The last stage of the thermal degradation process that characterized the more significant part of mass loss indicated the breakdown of cellulose, lignin, and fatty acid in the sample (starts at 350°C and continues to 500°C).



**Figure 4.3** TG/DTG Rain tree residue analysis

### *Surface analysis*

The characterization was performed for the modified adsorbent with the best FOG removal in the preliminary experiment. The surface analysis of the best-modified adsorbent, which was prepared by  $H_3PO_4$  treatment and pyrolysis

temperature 350°C (AAC350), was observed by Brunauer-Emmett-Teller (BET) method. The specific surface area value is 8.93 m<sup>2</sup> g<sup>-1</sup>, which is more significant than its raw material (rain tree residue) 3.11 m<sup>2</sup> g<sup>-1</sup>. In literature, carbons with much larger surface areas than this study were examined; for example, activated carbon produced from pineapple plant and *Magnolia grandiflora* leaves have a surface area of 1031 m<sup>2</sup> g<sup>-1</sup> and 41.78 m<sup>2</sup> g<sup>-1</sup>, respectively (Beltrame et al., 2018; Ji et al., 2019).

**Table 4.6** The methylene blue and iodine number analysis result

| Adsorbent         | Iodine Number<br>(mg g <sup>-1</sup> ) | MB Number<br>(mg g <sup>-1</sup> ) |
|-------------------|--|------------------------------------|
| Rain tree residue | 198.60                                 | 2.50                               |
| AAC350            | 88.84                                  | 8.07                               |

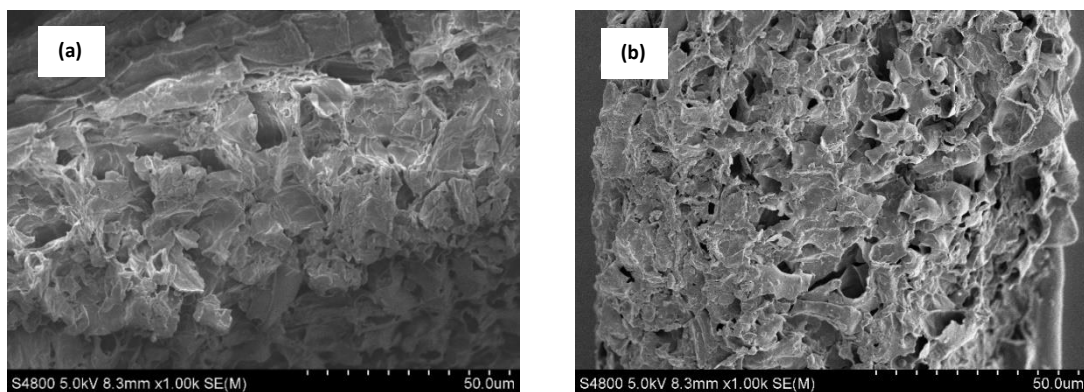
Moreover, the micropores and mesopores of the adsorbents were carried out by iodine number and methylene blue (MB) tests, respectively. The iodine and methylene blue numbers of rain tree residues adsorbent and AAC350 were shown in

**Table 4.6.** The iodine number of AAC350 with 88.84 mg g<sup>-1</sup> was lower than the rain tree residues adsorbent with 198.60 mg g<sup>-1</sup>. While the MB number of AAC350 was higher than the rain tree residues with 8.07 mg g<sup>-1</sup> and 2.50 mg g<sup>-1</sup>, respectively. The results indicated that the rain tree residues adsorbent mainly consisted of micropores and the AAC350 was consisted of mesopores. The iodine number and MB number of the AAC350 were found to be lower than the commercial activated

carbons. It can be caused by the activated carbon preparation that did not meet the optimum conditions to produce good properties of activated carbon. However, rain tree has not been previously investigated as a raw material for generating modified adsorbent. The obtained carbons, therefore, present a potential characteristic for an adsorbent.

### *Scanning electron microscopy (SEM)*

The pores of adsorbents, in turn, can be observed through **Figure 4.4**, which shows the scanning electron microscopy (SEM) results. The SEM of the rain tree biomass and AAC350 shows an uneven surface, presenting pores of different sizes all over it. The images show that the AAC350 is more porous than the rain tree biomass and reconfirmed with the surface area data. **Figure 4.4 (b)** represents that the surface of AAC350 conceives pores generated by the dehydration and activation effect. These pores allow channels for the many molecules to get into a modified adsorbent particle (Islam et al., 2017; Mistar et al., 2020)



**Figure 4.4** SEM images of (a) rain tree biomass (b) AAC350

### *Fourier transform infrared spectroscopy (FTIR)*

The FTIR spectra of rain tree residue modified adsorbent prepared by using  $\text{H}_3\text{PO}_4$  as activation agent and at temperature  $350^\circ\text{C}$  is shown in **Figure 4.5 (A)**, as well as the biomass **(B)** that gave rise to it, as a way of comparison. The result showed that the modified adsorbent spectra exhibited fewer absorption bands and intensity than the biomass, indicating that some functional groups are eliminated after the carbonization and activation processes. The FTIR spectra of the rain tree biomass showed that the broad stretching around  $3600\text{-}3200\text{ cm}^{-1}$  indicated the presence of hydroxyl (O—H groups) and water. The bands observed around  $2800\text{-}3000\text{ cm}^{-1}$  occur due to aliphatic (C—H) vibration. The peak observed at about  $1637\text{ -}1031\text{ cm}^{-1}$  indicated the vibration of the carbon double bond (C=C) and phenolic groups, respectively (Santos et al., 2020). Nevertheless, it is also characteristic of phosphorus and phospho-carbonaceous compounds in  $\text{H}_3\text{PO}_4$  modified adsorbent. The band at  $1163\text{ cm}^{-1}$  can be assigned to the vibration of hydrogen-bonded P=OOH groups from phosphates or polyphosphates to the O—C peak in the P—O—C (aromatic) linkage (Puziy et al., 2007; Xu et al., 2014).

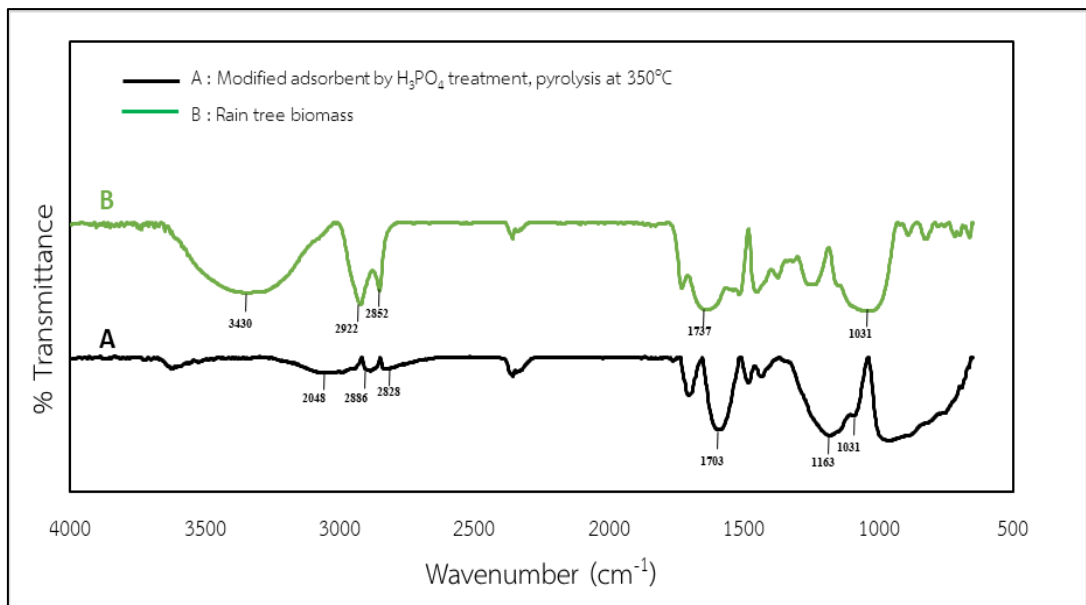


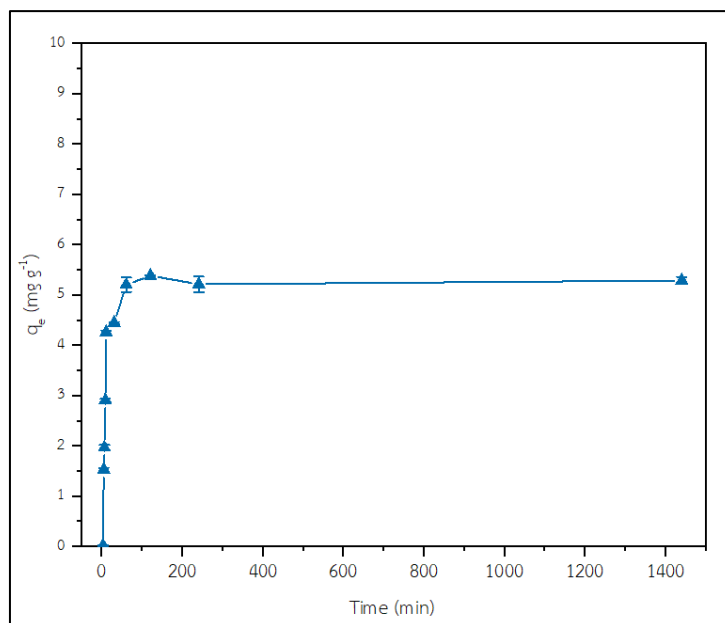
Figure 4.5 FTIR spectrum of the rain tree biomass and AAC350

#### 4.2.3 Adsorption studies of FOG removal

##### *Adsorption kinetic study*

Adsorption kinetic experiments were performed to investigate the mechanism of the adsorption. Two adsorption kinetic models were pseudo-first order and pseudo-second order model. The adsorption kinetics were considered to determine the amount of FOG separated from the solution.





**Figure 4.6** Effect of contact time on the adsorption of FOG onto AAC350

**Figure 4.6** represents the adsorption of FOG onto AAC350 consists of two phases, the rapid phase, the first 30 min, followed by a relatively slow uptake phase before reaching equilibrium. This initial high rate of FOG adsorption may be attributed to the large number of vacant surface sites being available for adsorption, and as the increasing contact time, less adsorption site on the adsorbent surfaces was available due to the FOG molecules attached to the adsorbent. At a certain point, it reached a constant value which the FOG could not be further removed from the solution. Das and Mishra (2020) observed two stages in the iron adsorption kinetics using activated carbon produced from *Limonia acidissima* shell, a plateau curve reflecting equilibrium. According to Rajak et al. (2018), most oil adsorption equilibrium on synthesized carbon occurred within 3 h. In this current study, adsorption of FOG

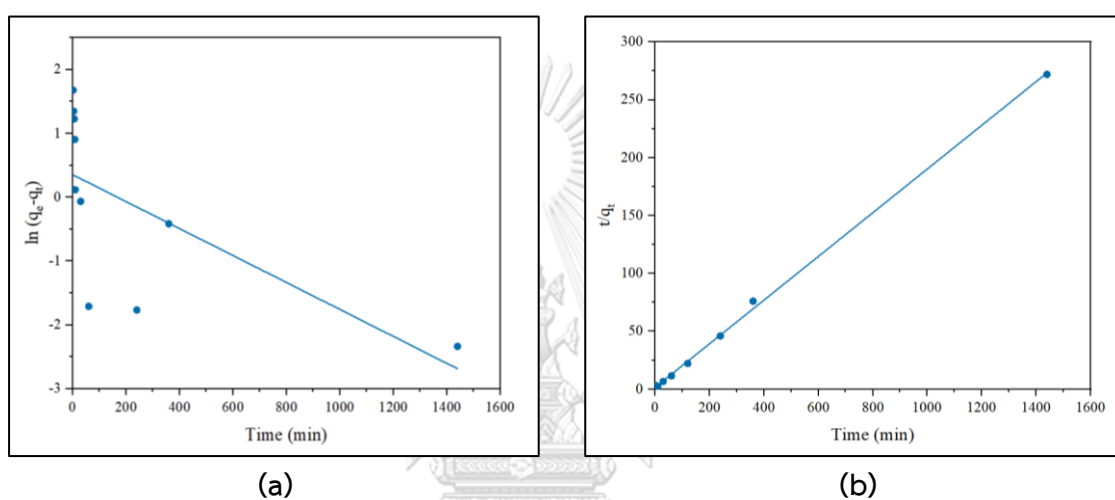
reached equilibrium in approximately 120 min (2 h), with an equilibrium adsorption capacity ( $q_e$ ) of 5.39 mg g<sup>-1</sup>.

As shown in **Table 4.7**, the adsorption process of FOG onto AAC350 was better described by the pseudo-second-order model with a high correlation coefficient ( $R^2 = 0.9991$ ) compared to the pseudo-first-order model ( $R^2=0.4324$ ). Furthermore, the calculated adsorption capacity ( $q_{e, \text{cal}}$ ) value of 5.29 mg g<sup>-1</sup> was the same as the experimental adsorption capacity ( $q_{e, \text{exp}}$ ) value of 5.29 mg g<sup>-1</sup>. It is indicated that the adsorption process was controlled by chemisorption, which involved valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate. Literature has shown that oil adsorption is closely related to functional group properties of the sorbent (Said Ael et al., 2009). Refers to the FTIR data (**Figure 4.5**), the AAC350 surface was rich in functional groups. As a result, the surfaces performed well in terms of oil adsorption. Rajak et al. (2018) investigated the adsorption of oil from oil-in-water emulsion using sawdust activated carbon obeyed the pseudo-second-order kinetic rather than pseudo-first-order kinetic model, which is similar to the present work.

According to Cai et al. (2019) and Pintor et al. (2013) research results, activated carbon prepared from crab-shell and cork for treating FOG reached 89.4 and 82 mg g<sup>-1</sup> at equilibrium, respectively, which are much higher than this study. However, rain tree residue as a modified adsorbent precursor for treating FOG has the advantage of low costs, as it can be found ubiquitously.

**Table 4.7** Adsorption kinetic models for the adsorption of FOG on AAC350

| Pseudo first order              |                            |        | Pseudo second order             |   |        |
|---------------------------------|----------------------------|--------|---------------------------------|---|--------|
| $q_{e,1}$ (mg g <sup>-1</sup> ) | $k_1$ (min <sup>-1</sup> ) | $R^2$  | $q_{e,2}$ (mg g <sup>-1</sup> ) | $k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ) | $R^2$  |
| 1.43                            | -0.00000146                | 0.4324 | 5.29                            | 0.026894189                                   | 0.9991 |

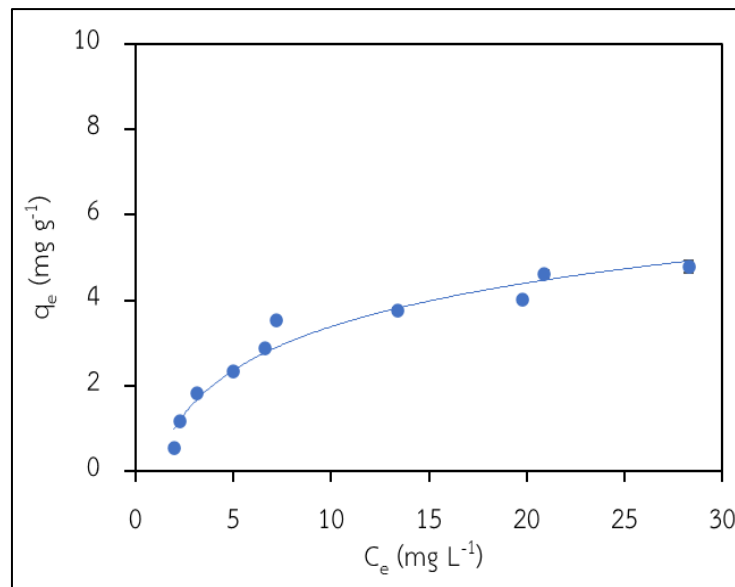


**Figure 4.7 (a)** Pseudo-first-order model **(b)** Pseudo-second-order model for adsorption of FOG on AAC350

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### *Adsorption isotherm study*

The adsorption isotherm models provide helpful information to identify the relationship between the amounts of adsorbed by a unit weight of adsorbent and help understand the adsorption mechanism of adsorbate with the adsorbent.

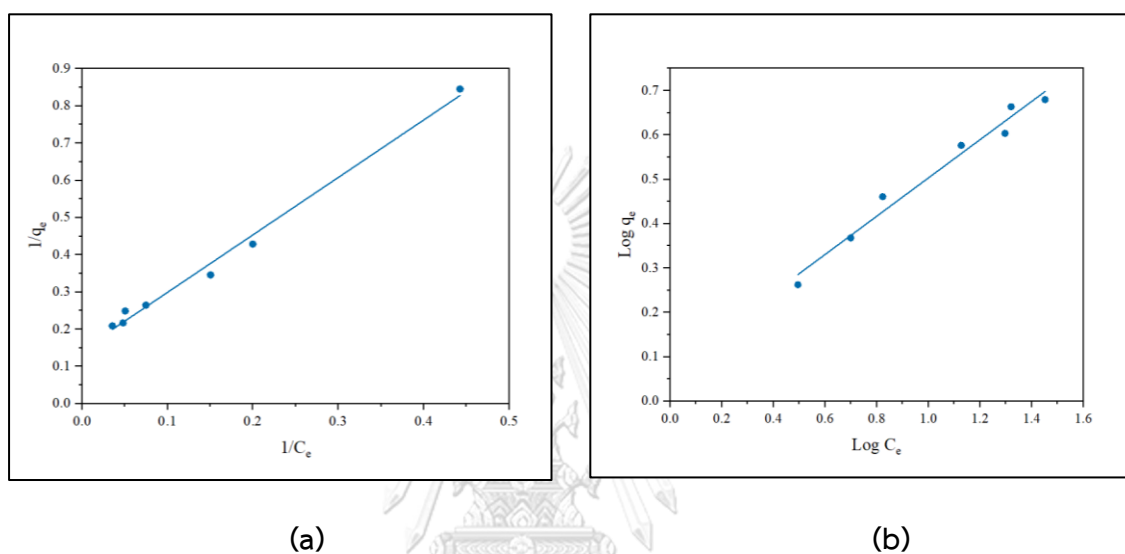


**Figure 4.8** Effect of initial concentration on the adsorption of FOG onto AAC350

In this study, Langmuir and Freundlich's isotherms were applied to examine the adsorption behavior of AAC350 for FOG uptake, as shown in **Figure 4.9** (a) and (b). The Langmuir's isotherm assumes monolayer adsorption on homogeneous surfaces. Adsorption occurs without interaction with adsorbed molecules and has similar energy on the surface (without any transmission from adsorbate). The formation of a monolayer adsorbate on the outer surface of the adsorbent obstructs further adsorption, whereas Freundlich's isotherm discusses the type of adsorption on heterogeneous surfaces with interactions between adsorbed molecules (Asep Bayu Dani Nandiyanto, 2020).

**Table 4.8** Adsorption isotherm models for the adsorption of FOG on AAC350

| Langmuir                     |                              |         |        | Freundlich |                              |        |
|------------------------------|------------------------------|---------|--------|------------|------------------------------|--------|
| $q_m$ ( $\text{mg g}^{-1}$ ) | $K_L$ ( $\text{L mg}^{-1}$ ) | $R_L$   | $R^2$  | n          | $K_f$ ( $\text{mg g}^{-1}$ ) | $R^2$  |
| 6.8918                       | 0.094                        | 0.60681 | 0.9911 | 2.3196     | 1.1809                       | 0.9755 |

**Figure 4.9** (a) Langmuir adsorption isotherm of FOG on AAC350 (b) Freundlich

adsorption isotherm of FOG on AAC350

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The results presented in **Table 4.8** confirm that Langmuir's isotherm was more suitable with the value of linear regression coefficient ( $R^2 = 0.9911$ ) than Freundlich's isotherm ( $R^2 = 0.9755$ ). Hence, the best-fitted isotherm for AAC350 is Langmuir isotherm that the adsorption process of FOG forms a monolayer without any interaction with adsorbed molecules (Wahi et al., 2013). Sohaimi et al. (2017) observed oil adsorption into synthesized biochar and fitted the experimental data into isotherm models. The model also showed that Langmuir model was the most

suitable model for describing the adsorption mechanism of oil adsorption with the highest correlation coefficient ( $R^2 = 0.9922$ ). Applying Langmuir model, the maximum adsorption capacity was  $6.89 \text{ mg g}^{-1}$ . The separation factor ( $R_L$ ) value indicates whether the isotherm was favorable ( $0 < R_L < 1$ ), unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), and irreversible ( $R_L = 0$ ). In this study,  $R_L$  of FOG adsorption on the modified adsorbent was calculated 0.6068, which indicated favorable adsorption.

#### ***Fixed-bed column experiment***

The best modified adsorbent from previous part, AAC350 was filled in a column for examining the FOG removal from canteen wastewater.

##### **1) Canteen wastewater identification**

The canteen wastewater was collected from Dormitory canteen, Chulalongkorn University, specifically the wastewater in the collecting tank before the wastewater treatment. The location of wastewater sampling was selected based on the higher activity (opened canteen) compared to other canteens during the COVID-19 situation. Characteristic of the canteen wastewater such as pH, COD, BOD and FOG were determined and compared to the Standard to Control Wastewater Discharge from Certain Types and Sizes of Buildings A.D., (2005). The wastewater parameter results are given in the **Table 4.9**. According to the report from Wastewater Management Team at Chulalongkorn University in 2018, dormitory canteen produced approximately  $5.33 \text{ m}^3$  wastewater daily. The FOG content in the

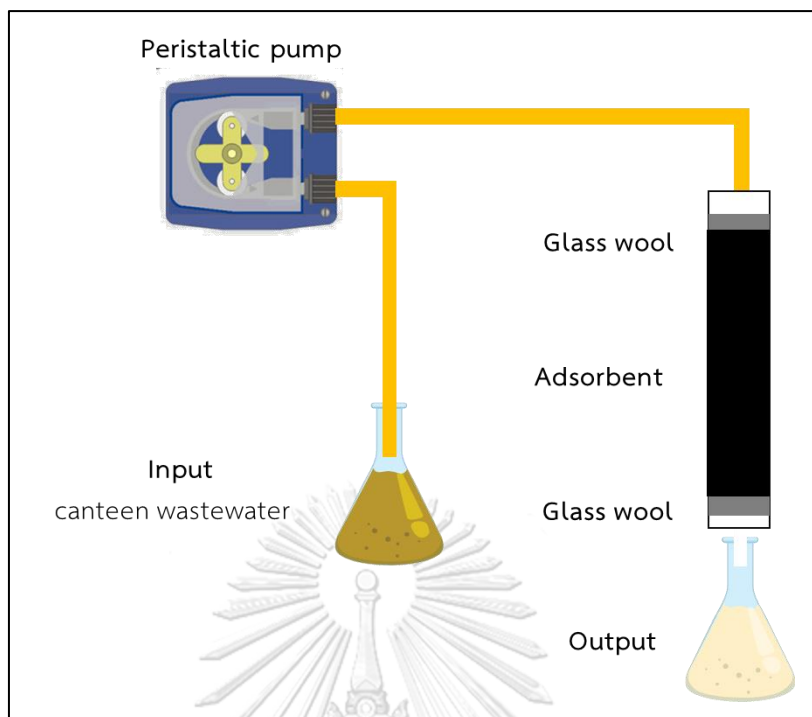
influent was detected in high concentration with  $90 \text{ mg g}^{-1}$ . While in 2022, the FOG concentration in canteen wastewater was found lower with  $50 \text{ mg g}^{-1}$ . It is because of the campus closure during COVID-19 pandemic affected the quality and quantity of wastewater produced from university's canteen. The sampled dormitory canteen wastewater was used for fixed-bed column test.

**Table 4.9** Characterization of dormitory canteen wastewater compared with Type D (area size  $100\text{-}250 \text{ m}^2$ ) building effluent standards for food centers in Thailand

| Parameters | Unit               | Range or Maximum Permitted Value | Dormitory canteen wastewater |
|------------|--------------------|----------------------------------|------------------------------|
| pH         | -                  | 5-9                              | 6.32                         |
| COD        | $\text{mg L}^{-1}$ | -                                | 2000                         |
| BOD        | $\text{mg L}^{-1}$ | 50                               | 1050                         |
| FOG        | $\text{mg L}^{-1}$ | 20                               | 50                           |

## 2) Fixed-bed column test

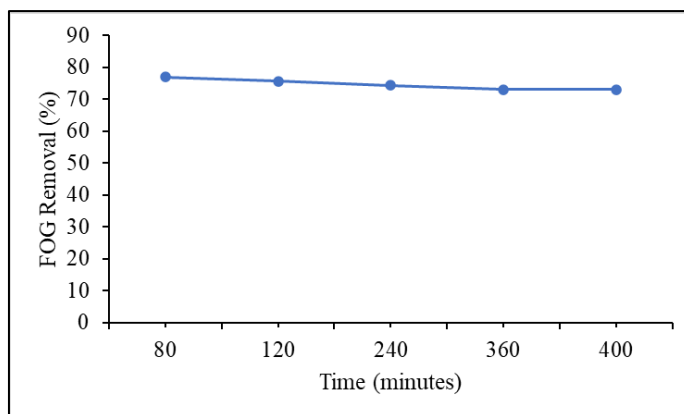
A packed bed experiment was conducted using a glass column of 3 cm diameter and 40 cm height. The bed was supported by glass wool at the top and the bottom bed to avoid bed distribution. A schematic diagram of the fixed packed column is shown in **Figure 4.10**.



**Figure 4.10** Fixed packed column experiment set

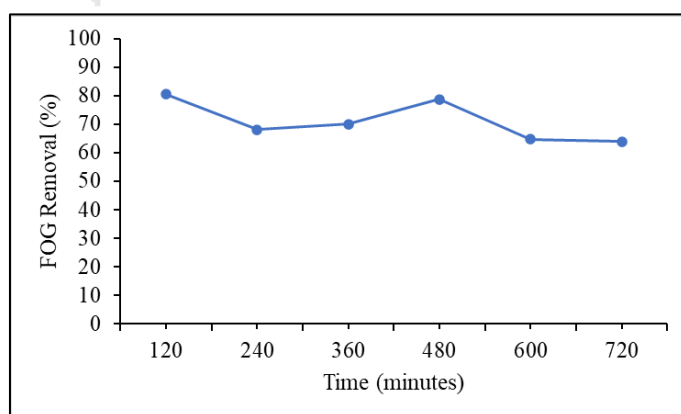
In the preliminary experiment, the identified canteen wastewater was allowed to pass through the 400 mm column, which was packed with 100 mm of AAC350, and the wastewater feed flow was set to 5 ml/min. The outlet of the column was collected at an interval time of 400 min and analyzed for the concentration of FOG. The experiment result was shown in **Figure 4.11**. The adsorption of FOG in the packed bed is still not reached a breakthrough point within 400 min with 72.94% removal.





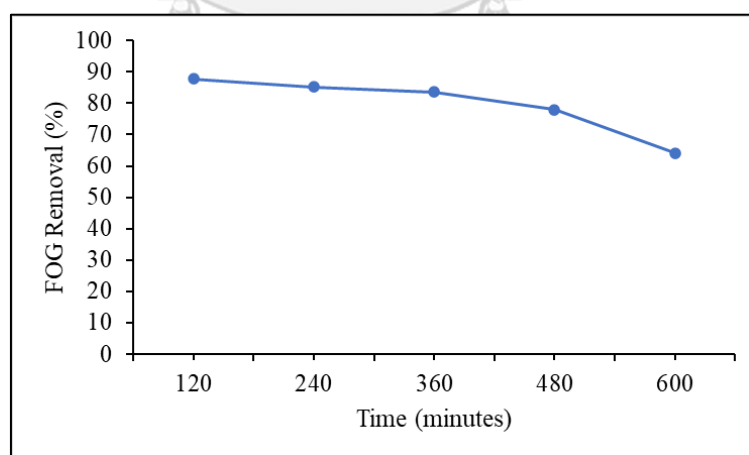
**Figure 4.11** The FOG removal in the fixed bed column (Bed height 10 cm, flow rate 5 mL/min, concentration of canteen wastewater 50 mg L<sup>-1</sup>)

According to the previous result, the sampling time was extended to identify the breakthrough point of the FOG removal in the column. The flow rate was adjusted to 10 mL/min. However, the result showed that the column had clogged (**Figure B-5**) within 12 h (720 min) without reaching the breakthrough point by 63.87% removal (shown in **Figure 4.12**).



**Figure 4.12** The FOG removal in the fixed bed column (Bed height 10 cm, flow rate 10 mL/min, concentration of canteen wastewater 50 mg L<sup>-1</sup>)

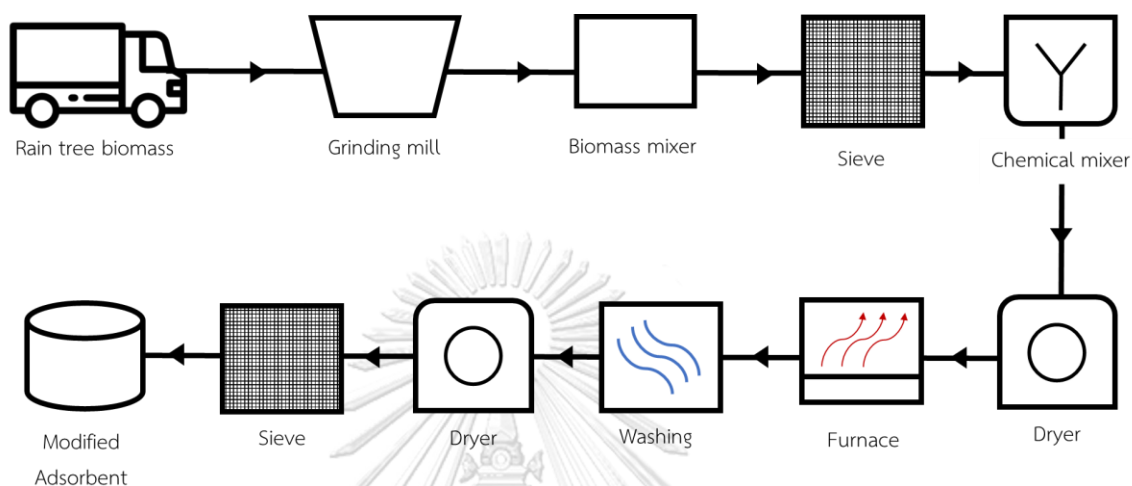
Another experiment set was further conducted by adjusting the bed height to 50 mm in order to avoid clogging before it reached breakthrough point. However, the result in **Figure 4.13** describes that the FOG removal in the packed bed reduced as the increasing of time, it is caused by the reducing of available adsorption site on the AAC350. However, the FOG removal was still not reaching a breakthrough point and clogged within 10 h (600 min) with 64.12% removal. This might be caused by the high COD value and the presence of precipitation in the canteen wastewater that might interfere the FOG adsorption in the column. Thus, the fixed bed column experiment provided longer time for FOG removal with 10 cm bed height and 10 mL/min flowrate. In addition, the fixed bed column might be more appropriate for FOG removal in the wastewater with lower COD value and less amount of precipitation.



**Figure 4.13** The FOG removal in the fixed bed column (Bed height 5 cm, flow rate 10 mL min<sup>-1</sup>, concentration of canteen wastewater 50 mg L<sup>-1</sup>)

### 4.3 Part III: Technology implementation

#### 4.3.1 Economic feasibility analysis



**Figure 4.14** Process flow diagram to produce modified adsorbent from rain tree

An economic evaluation of AC350 production cost based on the laboratory investigations and experiences were performed and a process flow diagram was established for scale-up (**Figure 4.14**). Therefore, the cost estimation was conducted based on the underestimated yield of 50% for AAC350 production to ensure feasibility, the number of working days 300 days/year of production, and the estimation of raw material (rain tree residue) loading is 500 kg/day.

**Table 4.10** Capacity of machines used for AAC350 production calculations

| Machines         | Capacity* | Cost              | Source                               |
|------------------|-----------|-------------------|--------------------------------------|
| 1. Grinding mill | 500 kg/h  | 68,300 Baht/unit  | (Eversun Machinery Co., Ltd)         |
| 2. Mixer         | 170 L     | 13,680 Baht/unit  | (S.T. Intertrade, 2022)              |
| 3. Hot air oven  | 1000 L    | 348,106 Baht/unit | (Thai Furnaces Engineering Co., Ltd) |
| 4. Furnace       | 1073 L    | 550,000 Baht/unit | (Thai Furnaces Engineering Co., Ltd) |
| 5. Storage tanks | 5000 L    | 90,000 Baht/unit  | (Gencon Engineering Co., Ltd)        |
| 6. Sieve machine | 500 kg/h  | 95,600 Baht/unit  | (Eversun Machinery Co., Ltd)         |

\* Based on of the machine specification needed.

**Table 4.11** Calculation of economic feasibility for AC350 production from rain tree residue biomass

| List                           | Cost             | Unit        |
|--------------------------------|------------------|-------------|
| <b>Fixed Cost (FC)</b>         |                  |             |
| 1. Grinding mill               | 68,300           | Baht/unit   |
| 2. Mixer                       | 13,680           | Baht/unit   |
| 3. Hot air oven                | 348,106          | Baht/unit   |
| 4. Furnace                     | 550,000          | Baht/unit   |
| 5. Acid storage tanks          | 90,000           | Baht/unit   |
| 6. Acid soak tanks             | 90,000           | Baht/unit   |
| 7. Acid wash tanks             | 90,000           | Baht/unit   |
| 8. Acid recovery tanks         | 90,000           | Baht/unit   |
| 9. Sieve machine               | 95,600           | Baht/unit   |
| <b>Total fixed cost (Baht)</b> | <b>1,435,686</b> | <b>Baht</b> |

| <b>Variable cost (V)</b>                                     |              |                |
|--|--------------|----------------|
| <b>1. Raw material (Baht/kg)</b>                             |              |                |
| 1.1 AAC350 quantity (underestimating yield by 50%)           | 250          | kg/day         |
| 1.2 Raw material demand                                      |              |                |
| 1.2.1 Rain tree residues                                     | 500          | kg/day         |
| 1.2.2 Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> ) 0.3M | 110          | L/day          |
| 1.3 Raw material cost  |              |                |
| 1.3.1 Rain tree residues                                     | 0            | Baht/kg        |
| 1.3.2 Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> ) 0.3M | 30           | Baht/L         |
| <b>Total cost raw material capital/kg</b>                    | <b>13.2</b>  | <b>Baht</b>    |
| <b>2. Transportation</b>                                     |              |                |
| <b>Total transportation capital/kg</b>                       | <b>0</b>     | <b>Baht</b>    |
| <b>3. Variable expense</b>                                   |              |                |
| 3.1 Human labor cost* (2 people)                             | 0            | Baht/day       |
| 3.2 Electricity cost**                                       | 18.64        | Baht/kg        |
| 3.3 Water cost**   | 0.2          | Baht/kg        |
| <b>Total variable expense</b>                                | <b>18.84</b> | <b>Baht/kg</b> |
| <b>Average variable cost (AVC)</b>                           | <b>32.04</b> | <b>Baht/kg</b> |
| <b>Productivity/year (N)</b>                                 |              |                |
| Working day  | 300          | days/year      |
| Productivity***  | 250          | kg/day         |
| Number (N) (Working day x Productivity)                      | 75,000       | kg/year        |
| <b>Price (P)****</b>   |              |                |
| AAC350 cost  | 36.87        | Baht/kg        |

\* Human labor cost did not cover on this study due to the labor is Chulalongkorn university staff

\*\* The detail of water and electricity cost was shown in Appendix A

\*\*\* Productivity/year was calculated from the production for 500 kilograms AAC350/day

\*\*\*\* The price was determined by increasing 15% the average variable cost (AVC)

The breakeven volume: N\* (Kg)

$$N^* = \frac{\text{Fixed Cost}}{\text{Price} - \text{Average variable cost}}$$

$$= \frac{1,435,686}{36.87 - 32.04} = \mathbf{297243.48 \text{ kg}}$$

The payback period (Years)

$$\text{Payback period} = \frac{\text{The breakeven volume}}{\text{Productivity/year}}$$

$$= \frac{297243.48}{75,000} = \mathbf{3.96 \text{ year}}$$

According to the cost calculation, average variable cost was 32.04 Baht/kg and the determined price was estimated by increasing 15% of the price (36.87 Baht/kg). The estimated cost of modified adsorbent from rain tree residue was lower than the cost of other adsorbents i.e., activated carbon prepared from iron wood with estimated cost \$1.65 per kg (60.11 Baht/kg) (Nowrouzi et al., 2017), acid-treatment adsorbent from pecan shell \$2.89 (105.35 Baht/kg) per kg (Ng et al., 2003), and activated carbon prepared from PET wastes \$1.7 per kg (61.97 Baht/kg) (Torrik et al., 2014). However, modified adsorbent from rain tree has a lower surface area. As

consequence, modified adsorbent from rain tree residue did not perform significant better quality of adsorbent compared with other commercial adsorbents. However, the laboratory result reported that the modified adsorbent from rain tree residue could be employed for FOG removal in canteen wastewater. The result of economic feasibility identification of rain tree modified adsorbent by  $H_3PO_4$  pretreatment and pyrolysis at  $350^\circ C$  shows that it must produce 297243.48 kg to meet the breakeven volume ( $N^*$ ) which is the point that total cost and total revenue meet equal value. The payback period in which the total cost invested in production can be returned in 3.96 year.



## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

In this study, modified adsorbents were produced from rain tree (*Samanea saman*) to remove FOG. The modified adsorbent by  $H_3PO_4$  pretreatment and pyrolysis at  $350^\circ C$  provided the highest net efficiency of FOG removal, with a yield and removal percentage of  $55.87 \pm 1.40$  and  $79.77 \pm 1.17\%$ , respectively. The best modified adsorbent was selected for adsorption studies. The data were fitted better to the pseudo-second-order kinetic and Langmuir model. The fixed bed column experiment provided longer time for FOG removal with 10 cm bed height and 10 mL/min flowrate. In addition, the fixed bed column might be more appropriate for FOG removal in the wastewater with lower COD value and less amount of precipitation. Future studies can be carried out to increase this adsorbent's adsorption capacity and remove other pollutants. The results showed that rain tree (*Samanea saman*) could develop adsorbent for FOG removal.

#### 5.2 Recommendations

5.2.1 The variation of raw material ratio and chemical concentration in pretreatment need to be further examined to find the optimum condition for modified adsorbent from rain tree (*Samanea saman*).



5.2.2 The management of the used modified adsorbent after treatment can be employed to produce Refuse Derived Fuel (RDF) or concrete.

5.2.3 The fixed-bed column test resulted in good FOG removal, but the column clogging cannot be denied especially for wastewater with high COD and precipitation content. Thus, this process should be combined with other processes such as grease trap before employing the fixed-bed column process.

5.2.4 The application modified adsorbent for COD and BOD treatment can be further examined to identify the other capability of adsorbent.



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## APPENDIX A

## EXPERIMENTAL DATA

**Table A-1** FOG removal by different adsorbents (Adsorbent dose 3 g in 200 mL of 50 mg L<sup>-1</sup> synthetic emulsified oil wastewater, contact time 24 h).

| Code   | Adsorbent types                         | Temperature<br>(°C) | Final<br>concentration of<br>FOG (mg L <sup>-1</sup> ) | FOG removal<br>(%) |
|--------|---|---------------------|--|--------------------|
| NA     | Rain tree (control)                     | -                   | 49.33  | 1.35±0.98          |
| BAC350 | NaOH-treated                            | 350                 | 45.65  | 8.70±0.44          |
| BAC550 | NaOH-treated                            | 550                 | 10.77  | 28.19±0.38         |
| BAC750 | NaOH-treated                            | 750                 | 10.12  | 82.78±3.39         |
| SAC350 | ZnCl <sub>2</sub> -treated              | 350                 | 35.90  | 78.45±4.81         |
| SAC550 | ZnCl <sub>2</sub> -treated              | 550                 | 8.17   | 83.66±0.75         |
| SAC750 | ZnCl <sub>2</sub> -treated              | 750                 | 5.86   | 87.62±3.84         |
| AAC350 | H <sub>3</sub> PO <sub>4</sub> -treated | 350                 | 8.61   | 79.77±1.17         |
| AAC550 | H <sub>3</sub> PO <sub>4</sub> -treated | 550                 | 6.19   | 88.28±4.13         |
| AAC750 | H <sub>3</sub> PO <sub>4</sub> -treated | 750                 | 3.46   | 93.09±0.97         |

**Table A-2** Net efficiency of FOG removal by different adsorbents

| Code   | Adsorbent types                         | Temperature (°C) | Net removal efficiency (%) |
|--------|---|------------------|----------------------------|
| NA     | Rain tree (control)                     | -                | 1.35±0.98                  |
| BAC350 | NaOH-treated                            | 350              | 2.39±0.12                  |
| BAC550 | NaOH-treated                            | 550              | 5.78±0.08                  |
| BAC750 | NaOH-treated                            | 750              | 12.31±1.09                 |
| SAC350 | ZnCl <sub>2</sub> -treated              | 350              | 37.67±2.31                 |
| SAC550 | ZnCl <sub>2</sub> -treated              | 550              | 36.16±0.32                 |
| SAC750 | ZnCl <sub>2</sub> -treated              | 750              | 28.02±0.57                 |
| AAC350 | H <sub>3</sub> PO <sub>4</sub> -treated | 350              | 44.57±0.65                 |
| AAC550 | H <sub>3</sub> PO <sub>4</sub> -treated | 550              | 37.41±1.78                 |
| AAC750 | H <sub>3</sub> PO <sub>4</sub> -treated | 750              | 36.21±0.38                 |

**Table A-3** ANNOVA analysis result of FOG removal for all treatments**Multiple Comparisons**Dependent Variable: **FOG removal**

Tukey HSD

| (I) Adsorbent_types |        | Mean<br>Difference (I-<br>J) | Std. Error | Sig. | 95% Confidence Interval |                |
|---------------------|--------|------------------------------|------------|------|-------------------------|----------------|
|                     |        |                              |            |      | Lower<br>Bound          | Upper<br>Bound |
| NA                  | BAC350 | -7.35000                     | 4.60719    | .836 | -23.6645                | 8.9645         |
|                     | BAC550 | -18.42667 <sup>*</sup>       | 4.60719    | .019 | -34.7412                | -2.1121        |
|                     | BAC750 | -81.43333 <sup>*</sup>       | 4.60719    | .000 | -97.7479                | -65.1188       |
|                     | SAC350 | -77.10667 <sup>*</sup>       | 4.60719    | .000 | -93.4212                | -60.7921       |
|                     | SAC550 | -82.31667 <sup>*</sup>       | 4.60719    | .000 | -98.6312                | -66.0021       |
|                     | SAC750 | -86.27000 <sup>*</sup>       | 4.60719    | .000 | -102.5845               | -69.9555       |
|                     | AAC350 | -78.42333 <sup>*</sup>       | 4.60719    | .000 | -94.7379                | -62.1088       |
|                     | AAC550 | -86.93000 <sup>*</sup>       | 4.60719    | .000 | -103.2445               | -70.6155       |
|                     | AAC750 | -91.74000 <sup>*</sup>       | 4.60719    | .000 | -108.0545               | -75.4255       |
| BAC350              | NA     | 7.35000                      | 4.60719    | .836 | -8.9645                 | 23.6645        |
|                     | BAC550 | -11.07667                    | 4.60719    | .373 | -27.3912                | 5.2379         |
|                     | BAC750 | -74.08333 <sup>*</sup>       | 4.60719    | .000 | -90.3979                | -57.7688       |
|                     | SAC350 | -69.75667 <sup>*</sup>       | 4.60719    | .000 | -86.0712                | -53.4421       |
|                     | SAC550 | -74.96667 <sup>*</sup>       | 4.60719    | .000 | -91.2812                | -58.6521       |
|                     | SAC750 | -78.92000 <sup>*</sup>       | 4.60719    | .000 | -95.2345                | -62.6055       |
|                     | AAC350 | -71.07333 <sup>*</sup>       | 4.60719    | .000 | -87.3879                | -54.7588       |
|                     | AAC550 | -79.58000 <sup>*</sup>       | 4.60719    | .000 | -95.8945                | -63.2655       |
|                     | AAC750 | -84.39000 <sup>*</sup>       | 4.60719    | .000 | -100.7045               | -68.0755       |
| BAC550              | NA     | 18.42667 <sup>*</sup>        | 4.60719    | .019 | 2.1121                  | 34.7412        |
|                     | BAC350 | 11.07667                     | 4.60719    | .373 | -5.2379                 | 27.3912        |
|                     | BAC750 | -63.00667 <sup>*</sup>       | 4.60719    | .000 | -79.3212                | -46.6921       |
|                     | SAC350 | -58.68000 <sup>*</sup>       | 4.60719    | .000 | -74.9945                | -42.3655       |
|                     | SAC550 | -63.89000 <sup>*</sup>       | 4.60719    | .000 | -80.2045                | -47.5755       |
|                     | SAC750 | -67.84333 <sup>*</sup>       | 4.60719    | .000 | -84.1579                | -51.5288       |
|                     | AAC350 | -59.99667 <sup>*</sup>       | 4.60719    | .000 | -76.3112                | -43.6821       |
|                     | AAC550 | -68.50333 <sup>*</sup>       | 4.60719    | .000 | -84.8179                | -52.1888       |
|                     | AAC750 | -73.31333 <sup>*</sup>       | 4.60719    | .000 | -89.6279                | -56.9988       |



Table A-3 ANNOVA analysis result of FOG removal for all treatments (cont.)

|        |        |           |         |       |          |          |
|--------|--------|-----------|---------|-------|----------|----------|
| BAC750 | NA     | 81.43333* | 4.60719 | .000  | 65.1188  | 97.7479  |
|        | BAC350 | 74.08333* | 4.60719 | .000  | 57.7688  | 90.3979  |
|        | BAC550 | 63.00667* | 4.60719 | .000  | 46.6921  | 79.3212  |
|        | SAC350 | 4.32667   | 4.60719 | .993  | -11.9879 | 20.6412  |
|        | SAC550 | -.88333   | 4.60719 | 1.000 | -17.1979 | 15.4312  |
|        | SAC750 | -4.83667  | 4.60719 | .985  | -21.1512 | 11.4779  |
|        | AAC350 | 3.01000   | 4.60719 | 1.000 | -13.3045 | 19.3245  |
|        | AAC550 | -5.49667  | 4.60719 | .965  | -21.8112 | 10.8179  |
|        | AAC750 | -10.30667 | 4.60719 | .465  | -26.6212 | 6.0079   |
| SAC350 | NA     | 77.10667* | 4.60719 | .000  | 60.7921  | 93.4212  |
|        | BAC350 | 69.75667* | 4.60719 | .000  | 53.4421  | 86.0712  |
|        | BAC550 | 58.68000* | 4.60719 | .000  | 42.3655  | 74.9945  |
|        | BAC750 | -4.32667  | 4.60719 | .993  | -20.6412 | 11.9879  |
|        | SAC550 | -5.21000  | 4.60719 | .975  | -21.5245 | 11.1045  |
|        | SAC750 | -9.16333  | 4.60719 | .615  | -25.4779 | 7.1512   |
|        | AAC350 | -1.31667  | 4.60719 | 1.000 | -17.6312 | 14.9979  |
|        | AAC550 | -9.82333  | 4.60719 | .528  | -26.1379 | 6.4912   |
|        | AAC750 | -14.63333 | 4.60719 | .102  | -30.9479 | 1.6812   |
| SAC550 | NA     | 82.31667* | 4.60719 | .000  | 66.0021  | 98.6312  |
|        | BAC350 | 74.96667* | 4.60719 | .000  | 58.6521  | 91.2812  |
|        | BAC550 | 63.89000* | 4.60719 | .000  | 47.5755  | 80.2045  |
|        | BAC750 | .88333    | 4.60719 | 1.000 | -15.4312 | 17.1979  |
|        | SAC350 | 5.21000   | 4.60719 | .975  | -11.1045 | 21.5245  |
|        | SAC750 | -3.95333  | 4.60719 | .996  | -20.2679 | 12.3612  |
|        | AAC350 | 3.89333   | 4.60719 | .997  | -12.4212 | 20.2079  |
|        | AAC550 | -4.61333  | 4.60719 | .989  | -20.9279 | 11.7012  |
|        | AAC750 | -9.42333  | 4.60719 | .581  | -25.7379 | 6.8912   |
| SAC750 | NA     | 86.27000* | 4.60719 | .000  | 69.9555  | 102.5845 |
|        | BAC350 | 78.92000* | 4.60719 | .000  | 62.6055  | 95.2345  |
|        | BAC550 | 67.84333* | 4.60719 | .000  | 51.5288  | 84.1579  |
|        | BAC750 | 4.83667   | 4.60719 | .985  | -11.4779 | 21.1512  |
|        | SAC350 | 9.16333   | 4.60719 | .615  | -7.1512  | 25.4779  |
|        | SAC550 | 3.95333   | 4.60719 | .996  | -12.3612 | 20.2679  |
|        | AAC350 | 7.84667   | 4.60719 | .782  | -8.4679  | 24.1612  |
|        | AAC550 | -.66000   | 4.60719 | 1.000 | -16.9745 | 15.6545  |
|        | AAC750 | -5.47000  | 4.60719 | .966  | -21.7845 | 10.8445  |

**Table A-3** ANNOVA analysis result of FOG removal for all treatments (cont.)

|        |        |           |         |       |          |          |
|--------|--------|-----------|---------|-------|----------|----------|
| AAC350 | NA     | 78.42333* | 4.60719 | .000  | 62.1088  | 94.7379  |
|        | BAC350 | 71.07333* | 4.60719 | .000  | 54.7588  | 87.3879  |
|        | BAC550 | 59.99667* | 4.60719 | .000  | 43.6821  | 76.3112  |
|        | BAC750 | -3.01000  | 4.60719 | 1.000 | -19.3245 | 13.3045  |
|        | SAC350 | 1.31667   | 4.60719 | 1.000 | -14.9979 | 17.6312  |
|        | SAC550 | -3.89333  | 4.60719 | .997  | -20.2079 | 12.4212  |
|        | SAC750 | -7.84667  | 4.60719 | .782  | -24.1612 | 8.4679   |
|        | AAC550 | -8.50667  | 4.60719 | .701  | -24.8212 | 7.8079   |
|        | AAC750 | -13.31667 | 4.60719 | .173  | -29.6312 | 2.9979   |
| AAC550 | NA     | 86.93000* | 4.60719 | .000  | 70.6155  | 103.2445 |
|        | BAC350 | 79.58000* | 4.60719 | .000  | 63.2655  | 95.8945  |
|        | BAC550 | 68.50333* | 4.60719 | .000  | 52.1888  | 84.8179  |
|        | BAC750 | 5.49667   | 4.60719 | .965  | -10.8179 | 21.8112  |
|        | SAC350 | 9.82333   | 4.60719 | .528  | -6.4912  | 26.1379  |
|        | SAC550 | 4.61333   | 4.60719 | .989  | -11.7012 | 20.9279  |
|        | SAC750 | .66000    | 4.60719 | 1.000 | -15.6545 | 16.9745  |
|        | AAC350 | 8.50667   | 4.60719 | .701  | -7.8079  | 24.8212  |
|        | AAC750 | -4.81000  | 4.60719 | .985  | -21.1245 | 11.5045  |
| AAC750 | NA     | 91.74000* | 4.60719 | .000  | 75.4255  | 108.0545 |
|        | BAC350 | 84.39000* | 4.60719 | .000  | 68.0755  | 100.7045 |
|        | BAC550 | 73.31333* | 4.60719 | .000  | 56.9988  | 89.6279  |
|        | BAC750 | 10.30667  | 4.60719 | .465  | -6.0079  | 26.6212  |
|        | SAC350 | 14.63333  | 4.60719 | .102  | -1.6812  | 30.9479  |
|        | SAC550 | 9.42333   | 4.60719 | .581  | -6.8912  | 25.7379  |
|        | SAC750 | 5.47000   | 4.60719 | .966  | -10.8445 | 21.7845  |
|        | AAC350 | 13.31667  | 4.60719 | .173  | -2.9979  | 29.6312  |
|        | AAC550 | 4.81000   | 4.60719 | .985  | -11.5045 | 21.1245  |

\*. The mean difference is significant at the 0.05 level.

**Table A-4** ANNOVA analysis result net efficiency of FOG removal for all treatments**Multiple Comparisons**

Dependent Variable: Net efficiency

Tukey HSD

| (I) Adsorbent_types |        | Mean<br>Difference (I-J) | Std. Error | Sig.  | 95% Confidence Interval<br>Lower Bound      Upper Bound |          |
|---------------------|--------|--------------------------|------------|-------|---|----------|
| NA                  | BAC350 | -1.04333                 | 1.32888    | 0.998 | -5.749  | 3.6624   |
|                     | BAC550 | -2.71                    | 1.32888    | 0.584 | -7.4157   | 1.9957   |
|                     | BAC750 | -10.96000*               | 1.32888    | 0     | -15.6657  | -6.2543  |
|                     | SAC350 | -36.32333*               | 1.32888    | 0     | -41.029   | -31.6176 |
|                     | SAC550 | -34.81333*               | 1.32888    | 0     | -39.519   | -30.1076 |
|                     | SAC750 | -26.68000*               | 1.32888    | 0     | -31.3857  | -21.9743 |
|                     | AAC350 | -43.22000*               | 1.32888    | 0     | -47.9257  | -38.5143 |
|                     | AAC550 | -36.07000*               | 1.32888    | 0     | -40.7757  | -31.3643 |
|                     | AAC750 | -34.86333*               | 1.32888    | 0     | -39.569   | -30.1576 |
| BAC350              | NA     | 1.04333                  | 1.32888    | 0.998 | -3.6624   | 5.749    |
|                     | BAC550 | -1.66667                 | 1.32888    | 0.953 | -6.3724   | 3.039    |
|                     | BAC750 | -9.91667*                | 1.32888    | 0     | -14.6224  | -5.211   |
|                     | SAC350 | -35.28000*               | 1.32888    | 0     | -39.9857  | -30.5743 |
|                     | SAC550 | -33.77000*               | 1.32888    | 0     | -38.4757  | -29.0643 |
|                     | SAC750 | -25.63667*               | 1.32888    | 0     | -30.3424  | -20.931  |
|                     | AAC350 | -42.17667*               | 1.32888    | 0     | -46.8824  | -37.471  |
|                     | AAC550 | -35.02667*               | 1.32888    | 0     | -39.7324  | -30.321  |
|                     | AAC750 | -33.82000*               | 1.32888    | 0     | -38.5257  | -29.1143 |
| BAC550              | NA     | 2.71                     | 1.32888    | 0.584 | -1.9957   | 7.4157   |
|                     | BAC350 | 1.66667                  | 1.32888    | 0.953 | -3.039  | 6.3724   |
|                     | BAC750 | -8.25000*                | 1.32888    | 0     | -12.9557  | -3.5443  |
|                     | SAC350 | -33.61333*               | 1.32888    | 0     | -38.319   | -28.9076 |
|                     | SAC550 | -32.10333*               | 1.32888    | 0     | -36.809   | -27.3976 |
|                     | SAC750 | -23.97000*               | 1.32888    | 0     | -28.6757  | -19.2643 |
|                     | AAC350 | -40.51000*               | 1.32888    | 0     | -45.2157  | -35.8043 |
|                     | AAC550 | -33.36000*               | 1.32888    | 0     | -38.0657  | -28.6543 |
|                     | AAC750 | -32.15333*               | 1.32888    | 0     | -36.859   | -27.4476 |

**Table A-4** ANNOVA analysis result net efficiency of FOG removal for all treatments  
(cont.)

|        |        |            |           |         |          |          |
|--------|--------|------------|-----------|---------|----------|----------|
| BAC750 | NA     | 10.96000*  | 1.32888   | 0       | 6.2543   | 15.6657  |
|        | BAC350 | 9.91667*   | 1.32888   | 0       | 5.211    | 14.6224  |
|        | BAC550 | 8.25000*   | 1.32888   | 0       | 3.5443   | 12.9557  |
|        | SAC350 | -25.36333* | 1.32888   | 0       | -30.069  | -20.6576 |
|        | SAC550 | -23.85333* | 1.32888   | 0       | -28.559  | -19.1476 |
|        | SAC750 | -15.72000* | 1.32888   | 0       | -20.4257 | -11.0143 |
|        | AAC350 | -32.26000* | 1.32888   | 0       | -36.9657 | -27.5543 |
|        | AAC550 | -25.11000* | 1.32888   | 0       | -29.8157 | -20.4043 |
|        | AAC750 | -23.90333* | 1.32888   | 0       | -28.609  | -19.1976 |
|        | SAC350 | NA         | 36.32333* | 1.32888 | 0        | 31.6176  |
| BAC350 |        | 35.28000*  | 1.32888   | 0       | 30.5743  | 39.9857  |
| BAC550 |        | 33.61333*  | 1.32888   | 0       | 28.9076  | 38.319   |
| BAC750 |        | 25.36333*  | 1.32888   | 0       | 20.6576  | 30.069   |
| SAC550 |        | 1.51       | 1.32888   | 0.974   | -3.1957  | 6.2157   |
| SAC750 |        | 9.64333*   | 1.32888   | 0       | 4.9376   | 14.349   |
| AAC350 |        | -6.89667*  | 1.32888   | 0.001   | -11.6024 | -2.191   |
| AAC550 |        | 0.25333    | 1.32888   | 1       | -4.4524  | 4.959    |
| AAC750 |        | 1.46       | 1.32888   | 0.979   | -3.2457  | 6.1657   |
| SAC550 |        | NA         | 34.81333* | 1.32888 | 0        | 30.1076  |
|        | BAC350 | 33.77000*  | 1.32888   | 0       | 29.0643  | 38.4757  |
|        | BAC550 | 32.10333*  | 1.32888   | 0       | 27.3976  | 36.809   |
|        | BAC750 | 23.85333*  | 1.32888   | 0       | 19.1476  | 28.559   |
|        | SAC350 | -1.51      | 1.32888   | 0.974   | -6.2157  | 3.1957   |
|        | SAC750 | 8.13333*   | 1.32888   | 0       | 3.4276   | 12.839   |
|        | AAC350 | -8.40667*  | 1.32888   | 0       | -13.1124 | -3.701   |
|        | AAC550 | -1.25667   | 1.32888   | 0.992   | -5.9624  | 3.449    |
|        | AAC750 | -0.05      | 1.32888   | 1       | -4.7557  | 4.6557   |
|        | SAC750 | NA         | 26.68000* | 1.32888 | 0        | 21.9743  |
| BAC350 |        | 25.63667*  | 1.32888   | 0       | 20.931   | 30.3424  |
| BAC550 |        | 23.97000*  | 1.32888   | 0       | 19.2643  | 28.6757  |
| BAC750 |        | 15.72000*  | 1.32888   | 0       | 11.0143  | 20.4257  |
| SAC350 |        | -9.64333*  | 1.32888   | 0       | -14.349  | -4.9376  |
| SAC550 |        | -8.13333*  | 1.32888   | 0       | -12.839  | -3.4276  |
| AAC350 |        | -16.54000* | 1.32888   | 0       | -21.2457 | -11.8343 |
| AAC550 |        | -9.39000*  | 1.32888   | 0       | -14.0957 | -4.6843  |
| AAC750 |        | -8.18333*  | 1.32888   | 0       | -12.889  | -3.4776  |

**Table A-4** ANNOVA analysis result net efficiency of FOG removal for all treatments

(cont.)

|        |        |           |         |       |          |         |
|--------|--------|-----------|---------|-------|----------|---------|
| AAC350 | NA     | 43.22000* | 1.32888 | 0     | 38.5143  | 47.9257 |
|        | BAC350 | 42.17667* | 1.32888 | 0     | 37.471   | 46.8824 |
|        | BAC550 | 40.51000* | 1.32888 | 0     | 35.8043  | 45.2157 |
|        | BAC750 | 32.26000* | 1.32888 | 0     | 27.5543  | 36.9657 |
|        | SAC350 | 6.89667*  | 1.32888 | 0.001 | 2.191    | 11.6024 |
|        | SAC550 | 8.40667*  | 1.32888 | 0     | 3.701    | 13.1124 |
|        | SAC750 | 16.54000* | 1.32888 | 0     | 11.8343  | 21.2457 |
|        | AAC550 | 7.15000*  | 1.32888 | 0.001 | 2.4443   | 11.8557 |
|        | AAC750 | 8.35667*  | 1.32888 | 0     | 3.651    | 13.0624 |
| AAC550 | NA     | 36.07000* | 1.32888 | 0     | 31.3643  | 40.7757 |
|        | BAC350 | 35.02667* | 1.32888 | 0     | 30.321   | 39.7324 |
|        | BAC550 | 33.36000* | 1.32888 | 0     | 28.6543  | 38.0657 |
|        | BAC750 | 25.11000* | 1.32888 | 0     | 20.4043  | 29.8157 |
|        | SAC350 | -0.25333  | 1.32888 | 1     | -4.959   | 4.4524  |
|        | SAC550 | 1.25667   | 1.32888 | 0.992 | -3.449   | 5.9624  |
|        | SAC750 | 9.39000*  | 1.32888 | 0     | 4.6843   | 14.0957 |
|        | AAC350 | -7.15000* | 1.32888 | 0.001 | -11.8557 | -2.4443 |
|        | AAC750 | 1.20667   | 1.32888 | 0.994 | -3.499   | 5.9124  |
| AAC750 | NA     | 34.86333* | 1.32888 | 0     | 30.1576  | 39.569  |
|        | BAC350 | 33.82000* | 1.32888 | 0     | 29.1143  | 38.5257 |
|        | BAC550 | 32.15333* | 1.32888 | 0     | 27.4476  | 36.859  |
|        | BAC750 | 23.90333* | 1.32888 | 0     | 19.1976  | 28.609  |
|        | SAC350 | -1.46     | 1.32888 | 0.979 | -6.1657  | 3.2457  |
|        | SAC550 | 0.05      | 1.32888 | 1     | -4.6557  | 4.7557  |
|        | SAC750 | 8.18333*  | 1.32888 | 0     | 3.4776   | 12.889  |
|        | AAC350 | -8.35667* | 1.32888 | 0     | -13.0624 | -3.651  |
|        | AAC550 | -1.20667  | 1.32888 | 0.994 | -5.9124  | 3.499   |

\*. The mean difference is significant at the 0.05 level.

**Table A-5** The FOG removal in range of time by AAC350 (Adsorbent dose 3 g in 200 mL of 100 mg L<sup>-1</sup> synthetic emulsified oil wastewater).

| Time (min) | Final concentration of FOG<br>(C <sub>o</sub> , mg L <sup>-1</sup> ) | Adsorption capacity<br>(q <sub>t</sub> , mg g <sup>-1</sup> ) |
|------------|--|---|
| 2          | 99.58  | 0.03±0.01   |
| 4          | 76.97  | 1.54±0.04   |
| 6          | 70.41  | 1.97±0.05   |
| 8          | 56.30  | 2.91±0.03   |
| 10         | 36.01  | 4.27±0.03   |
| 30         | 33.22  | 4.45±0.02   |
| 60         | 21.86  | 5.21±0.14   |
| 120        | 19.14  | 5.39±0.01   |
| 1440       | 21.71  | 5.29±0.07   |

**Table A-6** The FOG removal in the variation of initial concentration by AAC350 (Adsorbent dose 3 g in 200 mL of synthetic emulsified oil wastewater).

| Initial concentration of<br>FOG (C <sub>o</sub> , mg L <sup>-1</sup> ) | Final concentration of<br>FOG (C <sub>e</sub> , mg L <sup>-1</sup> ) | Adsorption capacity<br>(q <sub>e</sub> , mg g <sup>-1</sup> ) |
|--|--|---|
| 20   | 2.26   | 1.18±0.00   |
| 30   | 3.12   | 1.68±0.01   |
| 40   | 5.00   | 2.33±0.03   |
| 50   | 6.65   | 2.89±0.01   |
| 60   | 7.20   | 3.52±0.00   |
| 70   | 13.41  | 3.77±0.04   |
| 80   | 19.81  | 4.01±0.01   |
| 90   | 20.91  | 4.61±0.08   |
| 100  | 28.29  | 4.78±0.15   |

**Table A-7** Adsorption isotherm model fitting of FOG on AAC350.

| Initial conc.<br>( $C_o$ , mg L <sup>-1</sup> ) | Final conc.<br>( $C_e$ , mg L <sup>-1</sup> ) | Adsorption<br>capacity<br>( $q_e$ , mg L <sup>-1</sup> ) | Freundlich<br>Isotherm |          | Langmuir<br>Isotherm |           |
|---|---|--|------------------------|----------|----------------------|-----------|
|   |   |  | 1/ $C_e$               | 1/ $q_e$ | log $C_e$            | log $q_e$ |
| 10  | 0.53  | 0.53   | 0.51                   | 1.87     | 0.51                 | 1.87      |
| 20  | 2.26  | 1.18   | 0.44                   | 0.85     | 0.44                 | 0.85      |
| 30  | 3.12  | 1.83   | 0.32                   | 0.55     | 0.32                 | 0.55      |
| 40  | 5.00  | 2.33   | 0.20                   | 0.43     | 0.20                 | 0.43      |
| 50  | 6.65  | 2.89   | 0.15                   | 0.35     | 0.15                 | 0.35      |
| 60  | 7.20  | 3.52   | 0.14                   | 0.28     | 0.14                 | 0.28      |
| 70  | 13.41   | 3.77   | 0.07                   | 0.27     | 0.07                 | 0.27      |
| 80  | 19.81   | 4.01   | 0.05                   | 0.25     | 0.05                 | 0.25      |
| 90  | 20.91   | 4.61   | 0.05                   | 0.22     | 0.05                 | 0.22      |
| 100   | 28.29   | 4.78   | 0.04                   | 0.21     | 0.04                 | 0.21      |

**Table A-8** Fixed-bed column of AAC350 (Bed height 10 cm, flow rate 5 mL/min, concentration of canteen wastewater 50 mg L<sup>-1</sup>).

| Time (min) | Final concentration of FOG (mg L <sup>-1</sup> ) | FOG removal (%) |
|------------|--|-----------------|
| 40         | -  | -               |
| 80         | 11.54  | 76.92           |
| 120        | 12.23  | 75.54           |
| 160        | -  | -               |
| 200        | -  | -               |
| 240        | 12.83  | 74.33           |
| 280        | 12.23  | 75.54           |
| 320        | -  | -               |
| 360        | 13.51  | 72.97           |
| 400        | 13.51  | 72.97           |

**Table A-9** Fixed-bed column of AAC350 (Bed height 10 cm, flow rate 10 mL/min, concentration of canteen wastewater 50 mg L<sup>-1</sup>).

| Time (min) | Final concentration of FOG (mg L <sup>-1</sup> ) | FOG removal (%) |
|------------|--|-----------------|
| 120        | 9.76   | 80.47           |
| 240        | 15.95  | 68.11           |
| 360        | 15.00  | 70.00           |
| 480        | 10.67  | 78.67           |
| 600        | 17.67  | 64.67           |
| 720        | 18.06  | 63.87           |

**Table A-10** Fixed-bed column of AAC350 (Bed height 5 cm, flow rate 10 mL/min, concentration of canteen wastewater 50 mg L<sup>-1</sup>).

| Time (min) | Final concentration of FOG (mg L <sup>-1</sup> ) | FOG removal (%) |
|------------|--|-----------------|
| 120        | 6.15   | 87.70           |
| 240        | 7.44   | 85.11           |
| 360        | 8.23   | 83.54           |
| 480        | 10.99  | 78.03           |
| 600        | 17.94  | 64.12           |

**Table A-11** Methylene blue number of NA.

| Initial concentration of MB<br>(mg L <sup>-1</sup> ) | Final concentration of MB<br>(mg L <sup>-1</sup> ) | Adsorption capacity<br>(mg g <sup>-1</sup> ) |
|--|--|--|
| 5  | 0.45   | 1.14   |
| 10   | 0.58   | 2.36   |
| 20   | 0.68   | 4.83   |
| 30   | 0.90   | 7.27   |
| 40   | 1.10   | 9.73   |
| 50   | 1.38   | 12.15  |



Table A-12 Methylene blue number of AAC350.

| Initial concentration of<br>MB (mg L <sup>-1</sup> ) | Final concentration of<br>MB (mg L <sup>-1</sup> ) | Adsorption capacity (mg<br>g <sup>-1</sup> ) |
|--|--|--|
| 5  | 0.10   | 1.22   |
| 10   | 0.57   | 2.36   |
| 20   | 2.37   | 4.41   |
| 30   | 6.39   | 5.90   |
| 40   | 8.30   | 7.93   |
| 50   | 12.10  | 9.48   |

Table A-13 Iodine number of NA

| N <sub>1</sub> | N <sub>2</sub> | DF  | M     | S    | F  | C      | X/M         |
|----------------|----------------|-----|-------|------|----|--------|-------------|
| 0.1            | 0.1            | 2.2 | 2.835 | 23.9 | 50 | 0.0478 | 212.3111323 |
| 0.1            | 0.1            | 2.2 | 3.3   | 22   | 50 | 0.044  | 198.4723636 |
| 0.1            | 0.1            | 2.2 | 3.766 | 20.5 | 50 | 0.041  | 185.0360329 |

Table A-14 Iodine number of AAC350

| N <sub>1</sub> | N <sub>2</sub> | DF  | M     | S  | F  | C     | X/M         |
|----------------|----------------|-----|-------|----|----|-------|-------------|
| 0.1            | 0.1            | 2.2 | 2.835 | 36 | 50 | 0.072 | 93.12677249 |
| 0.1            | 0.1            | 2.2 | 3.3   | 35 | 50 | 0.07  | 88.46636364 |
| 0.1            | 0.1            | 2.2 | 3.766 | 34 | 50 | 0.068 | 84.93457249 |

Table A-15 Water usage

| 250 kg AAC350 production  |               |          |
|---------------------------|---------------|----------|
| List                      | Amount        | Unit     |
| Rain tree residue         | 500           | kg       |
| Soaking liquid*           |               |          |
| H3PO4 0.3M                | 110           | L        |
| Water                     | 5,000         | L        |
| Washing                   | 5,000         | L        |
| <b>Total water needed</b> | <b>10,000</b> | <b>L</b> |

\*Biomass: liquid ratio (1:5 w/v)

Table A-16 Water cost calculation

| Total water usage | Price/unit             | Total electricity cost | Water cost for 1 kg AAC350 |
|-------------------|------------------------|------------------------|----------------------------|
| 10 m <sup>3</sup> | 10 Baht/m <sup>3</sup> | 100 Baht               | 0.2 Baht                   |

Table A-17 Machine specifications

| Machines                            | Value | Unit |
|-------------------------------------|-------|------|
| <b>Grinding</b>                     |       |      |
| Capacity                            | 500   | kg/h |
| Raw material                        | 500   | kg   |
| Time usage/day                      | 1     | h    |
| Electricity (machine specification) | 11    | kW   |
| <b>Sieve</b>                        |       |      |
| Capacity                            | 500   | kg/h |
| Raw material                        | 500   | kg   |
| Time usage/day                      | 1     | h    |
| Electricity (machine specification) | 12.5  | kW   |

Table A-17 Machine specifications (cont.)

| <b>Mixer</b>                        |     |      |
|-------------------------------------|-----|------|
| Capacity                            | 170 | L    |
| Raw material                        | 500 | kg   |
| Time usage/day                      | 1   | h    |
| Electricity (machine specification) | 1.2 | kW   |
| <b>Furnace</b>                      |     |      |
| Capacity                            | 250 | kg/h |
| Raw material                        | 500 | kg   |
| Time usage/day                      | 4   | h    |
| Electricity (machine specification) | 80  | kW   |
| <b>Hot air oven</b>                 |     |      |
| Capacity                            | 250 | kg   |
| Raw material                        | 250 | kg   |
| Time usage/day                      | 24  | h    |
| Electricity (machine specification) | 18  | kW   |

Table A-18 Machine usage

| Machine      | Time usage | Unit | Power watt | Unit | Electricity usage | Unit |
|--------------|------------|------|------------|------|-------------------|------|
| Grinding     | 1          | h    | 11         | kW   | 11                | kWh  |
| Sieve        | 1          | h    | 12.5       | kW   | 12.5              | kWh  |
| Mixer        | 1          | h    | 1.2        | kW   | 1.2               | kWh  |
| Furnace      | 4          | h    | 80         | kW   | 320               | kWh  |
| Hot air oven | 24         | h    | 18         | kW   | 432               | kWh  |

Table A-19 Electricity cost calculation

| Total electricity usage | Price/unit | Total electricity cost | Electricity cost for 1 kg AAC350 |
|-------------------------|------------|------------------------|----------------------------------|
| 776.7 kWh               | 6 baht/kWh | 4660.2 Baht            | 18.64 Baht                       |



## APPENDIX B

## PHOTOGRAPHS OF EXPERIMENT

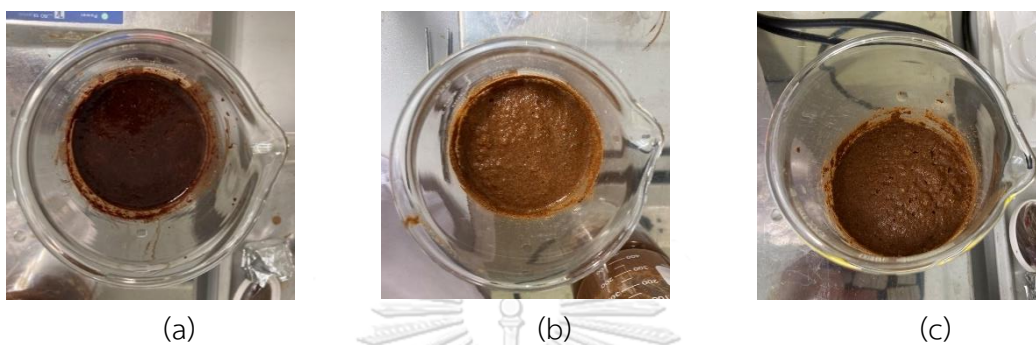


Figure B-1 Impregnation of rain tree residue in (a) NaOH, (b) ZnCl<sub>2</sub>, and (c) H<sub>3</sub>PO<sub>4</sub>



Figure B-2 Modified adsorbents from rain tree residue



Figure B-3 Batch sorption experiment of FOG Removal



Figure B-4 Fixed bed column experiment of FOG Removal



Figure B-5 Fixed bed column had clogged before reached breakthrough point

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