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SENIOR PROJECT

Title	Application of biochars derived from agriculture wastes for wastewater treatment
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Project advisor	Associate Professor Naiyanan Ariyakanon, Ph.D.
Department	Environmental Science
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Faculty of Science, Chulalongkorn University

Application of biochars derived from agriculture wastes for wastewater treatment

การนำถ่านชีวภาพที่ได้จากวัสดุเหลือใช้ทางการเกษตรมาใช้บำบัดน้ำเสีย

Worakan Soonkee

A Senior Project Submitted in Partial Fulfillment of the Requirements for
the Bachelor’s Degree of Science in
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ABSTRACT

Canteen wastewater obtains a highly organic compound which should be treated before discharge to the environment. In this study, corn cob and pineapple peel were converted to biochar by pyrolysis at 400 450 and 500°C. The yield of corn cob and biochar pineapple peel were 29.24 to 34.94% and 34.67 to 46.34%, respectively. Corn cob biochar at 400°C has a surface area 7.685 m^2/g and a high total pore volume that shows the potential of adsorption wastewater. The experiment was conducted by vary the ratio of biochar (30g, 15g and 10g) in 300 ml. of canteen wastewater for 3 day. The result showed that corn cob biochar at 400°C had high efficiency to treat canteen wastewater. The removal of total Kjeldahl nitrogen (TKN) was 85.38% of and pH was increased until the acceptable value of the domestic wastewater standard. Moreover, the result indicated that biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solid (TSS) and oil and grease of wastewater significantly decreased. Therefore, corn cob and pineapple peel can be converted to biochar for treatment canteen wastewater.

Keyword: Biochar, Pineapple peel, Corn cob, Adsorption

หัวเรื่อง การนำถ่านชีวภาพที่ได้จากวัสดุเหลือใช้ทางการเกษตรมาใช้บำบัดน้ำเสีย
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บทคัดย่อ

น้ำเสียจากโรงอาหารเป็นน้ำเสียที่มีสารอินทรีย์สูงซึ่งควรได้รับการบำบัดก่อนปล่อยออกสู่สิ่งแวดล้อม ในการศึกษาครั้งนี้ใช้ซังข้าวโพดและเปลือกสับปะรดมาเปลี่ยนรูปโดยวิธีการไพโรไลซิสที่อุณหภูมิ 400 450 และ500 °C ได้ถ่านชีวภาพจากซังข้าวโพดและเปลือกสับปะรดเป็น 29.24-34.94 เปอร์เซ็นต์ และ 34.6 7-46.34 เปอร์เซ็นต์ ตามลำดับ โดยทั้งนี้ถ่านชีวภาพจากซังข้าวโพดที่ 400°C มีพื้นที่ผิว 7.685 ตารางเมตรต่อกรัม และมีปริมาณรูพรุนมาก จึงแสดงให้เห็นถึงศักยภาพในการดูดซับสารในน้ำเสีย ซึ่งจากการทดลองเปรียบเทียบระหว่าง ถ่านชีวภาพจากซังข้าวโพดและเปลือกสับปะรดในการทดลองที่ปริมาณ ถ่านชีวภาพที่สัดส่วน 30 กรัม 15กรัม และ 10กรัม ในน้ำเสียโรงอาหาร 300 มิลลิลิตรเป็นเวลา 3 วัน พบว่า ถ่านชีวภาพจากซังข้าวโพดที่อุณหภูมิ 400 °C มีความสามารถในการบำบัดน้ำเสียจากโรงอาหารสูง สามารถบำบัดได้มากถึง 85.38 เปอร์เซ็นต์ของไนโตรเจนรวมโดยวิธีเจลดาห์ล (TKN) ได้ รวมถึงปรับค่าความเป็นกรด-เบส จนได้ค่าที่อยู่ในเกณฑ์ที่ยอมรับตามมาตรฐานน้ำทิ้งชุมชน และสามารถลดความเข้มข้นของค่า ความต้องการออกซิเจนทางชีวเคมี(BOD) ความต้องการออกซิเจนเชิงเคมี(COD) ของแข็งแขวนลอยทั้งหมด(TSS) และ น้ำมันและไขมัน(O&G) ดังนั้นจึงสามารถเปลี่ยนรูปซังข้าวโพดและเปลือกสับปะรดเป็นถ่านชีวภาพเพื่อใช้ในการใช้บำบัดเสียโรงอาหารได้

คำสำคัญ: ถ่านชีวภาพ, เปลือกสับปะรด, ซังข้าวโพด, การดูดติด

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CONTENTS

CHAPTER 1 INTRODUCTION

CHAPTER 2 THEORY AND LITERATURE REVIEW

CONTENTS (CONTINUE)

CHAPTER 3 MATERIALS AND METHODS

3.2 Biochar preparation and Application of biochar for wastewater treatment

4.1 Biochar characterization

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Abbreviation	Meaning
BOD	Biochemical Oxygen Demand
C	Corn cob biochar
COD	Chemical Oxygen Demand
H	Hour
O&G	Oil and grease
PA	Pineapple biochar
S	Second
SEM	Scanning Electron Microscope
TKN	Total Kjeldahl Nitrogen
TP	Total Phosphorus
TSS	Total Suspended Solid

CHAPTER 1

INTRODUCTION

1.1 Background and rationale

Thailand is the agriculture country which agricultural wastes was one of the most affected on environmental management (Takolpuckdee, 2014). There are Thailand exports of agricultural products more than 1,288,541,000,000 baht per year (Office of Agricultural Economics, 2018). Agriculture waste such as corn cob and pineapple peels which easily found and low cost in Thailand. The pineapple products, there are more than 2,248,000 tons per year (Office of Agricultural Economics, 2018). In 2013, Department of Alternative Energy Development and Efficiency in Thailand reported about corn cob which there was 1,215,078 tons per year. The agriculture waste normally disposed by open burning, landfilling, incinerator and composting (Pollution Control Department, 2015). Open burning, composting and landfilling released air pollution (e.g. dioxin from open burning, methane from landfilling and odor from composting) (Kimbrough and Jensen, 2012; Bu et al., 2014).

Pyrolysis is technique to convert biomass into useful product from biomass that is carried out at oxygen-free environment with low moisture (biomass material e.g. fruit wastes, rice straws) (Lam et al., 2016b, 2017a; Lin et al., 2014; Chen et al.,2018). Pyrolysis is biomass decomposition process at thermal cracking (Zheng et al., 2018). The products of pyrolysis are biochar, bio-oil and biogas (Liew al., 2017). Biochar is a carbon-rich material which made by pyrolysis depends on pyrolysis condition and source of biomass (Munera-Echeverri et al., 2018; Chan and Xu, 2009).

According to Pollution Control Department in 2015, approximately 9,590,367 m^3/day of domestic wastewater was produced that wastewater from human activities, canteen and market are the component of domestic wastewater. Canteen wastewater is the component of domestic wastewater which there is organic matter, inorganic matter, oil and grease, solids, detergent, microorganism, nutrients (e.g. nitrogen, phosphorus) and odor. The high levels of biochemical oxygen demand (BOD) and oil and grease (O&G) are detected in canteen wastewater (PCD, 2002). Oil and grease blocked the sunlight and decreased oxygen. Therefore, canteen wastewater should be treated before released to the environment.

1.2 Objective

1.2.1 To synthesize biochar from corn cob and pineapple peels.

1.2.2 To compare efficiency of corn cob biochar and pineapple peel biochar for canteen wastewater treatment.

1.3 Scope

1.3.1 Biochars from corn cob and pineapple peels were prepared at 400, 450 and 500 °C by pyrolysis.

1.3.2 Wastewater parameters before and after treatment by using corncob biochar and pineapple peels biochar were measured including pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), total phosphorus (TP), total suspended solids (TSS) and oil and grease (O&G).

1.4 Benefits

1.4.1 Biochars from corn cob and pineapple peels were alternative for wastewater treatment.

1.4.2 Biochars from the agriculture wastes were applied to treat the canteen wastewater

CHAPTER 2

LITERATURE REVIEW

2.1 Corn

Corn (*Zea mays* Linn) is the global food which there is the important serial for economic and ecology. Corn is the native plant from Maxico and Central American. Between 1900 to 1930, The harvested area of corn was about 40 million hectares in the United States. In 1970, the area of corn is increasing (NASS, 2011). Corn is a monocotyledon plant which its root is a fibrous root system so it can rapidly growth and tolerant (Sriwattanapong, 1977; Staggenborg et al., 2008). Summer season is approximately season of corn (Assefa et al., 2014). Therefore, Corn is considered as industrial (e.g. oil, glue, soap).

In Thailand, corn is widely plant since 1939 because there is highly demand of the global. Corn is an agricultural economy of Thailand which produced in the fourth of the world after America, Argentina and France respectively (Sriwattanapong, 1977). Therefore, agriculture waste from corn is a problem about waste management. Corn cob is the most component of agriculture waste from corn. There is 1,215,078.72 tons per year (2013).

2.2 Pineapple

Pineapple (*Ananas comosus*) is a perennial plant which widely in tropical whether. Pineapple is a native plant in South America. Pineapple is a monocotyledon plant which can tolerant in widely condition factor. Now, Production of pineapple, about 25 million tons, is the third of the most fruit production after bananas and citrus fruit respectively. Moreover, pineapple is economy production because its taste is unique. Therefore, it is the popular in industrial food (Seyed, 2019). Pineapple is fiber plant (e.g. leaf, peel) which thickness and tensile (Putra et al., 2018).

Pineapple in Thailand, there is a low cost and largely plants. Moreover, pineapple can easily growth and popular agriculture in Thailand so it’s very cheap. Pineapple is the first of the agricultural economy in the world (Office of Agricultural Economics, 2015).

2.3 Pyrolysis

Pyrolysis is decomposition biomass by thermochemical to benefit product. Pyrolysis can break down the large complex hydrocarbon molecule to smaller and simpler hydrocarbon molecule (Basu, 2010). Pyrolysis is a thermal technology which pyrolysis product is biochar, bio-oil and bio-gas (Chen et al., 2018). The raw material is biomass which the properties depended on pyrolysis condition and source of biomass (Munera-Echeverri et al., 2018; Chan and Xu, 2009). Biomass feedstock was pyrolysis at control temperature in an oxygen free environment and low moisture (Chen et al., 2018).

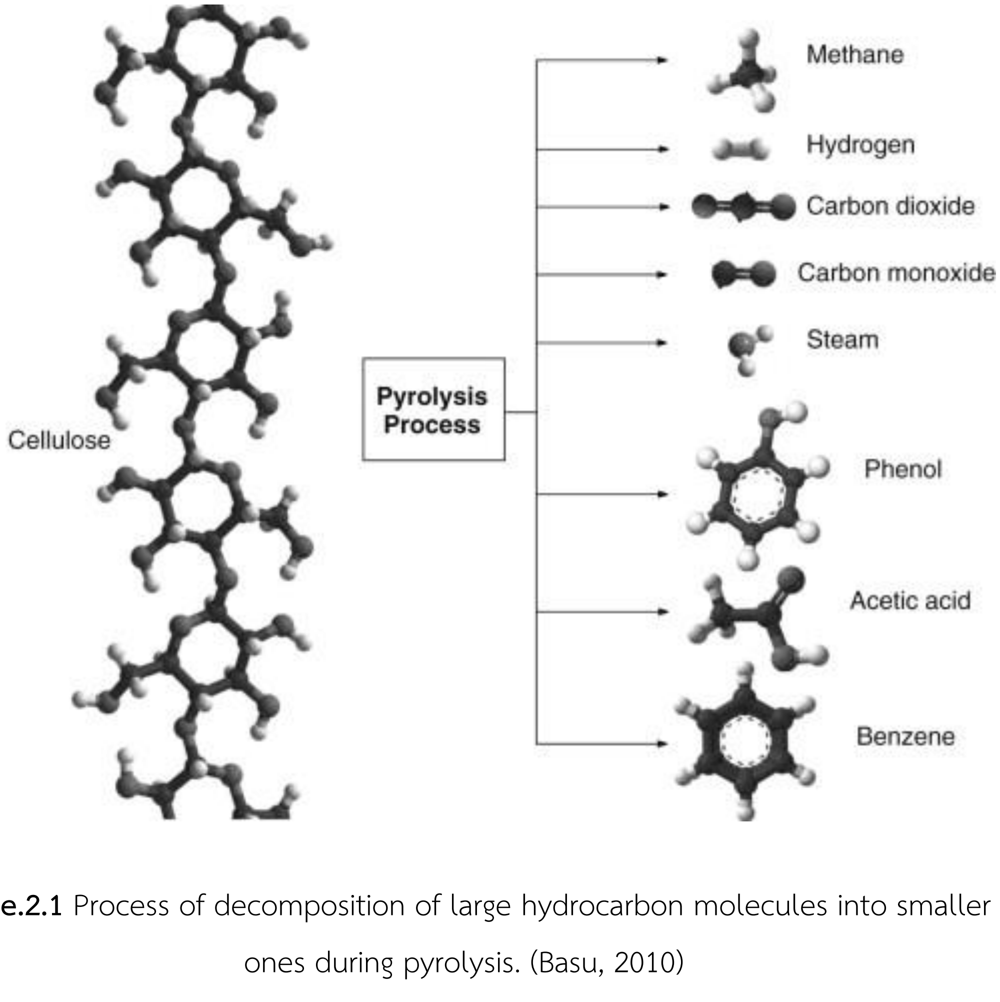


Figure.2.1 Process of decomposition of large hydrocarbon molecules into smaller ones during pyrolysis. (Basu, 2010)

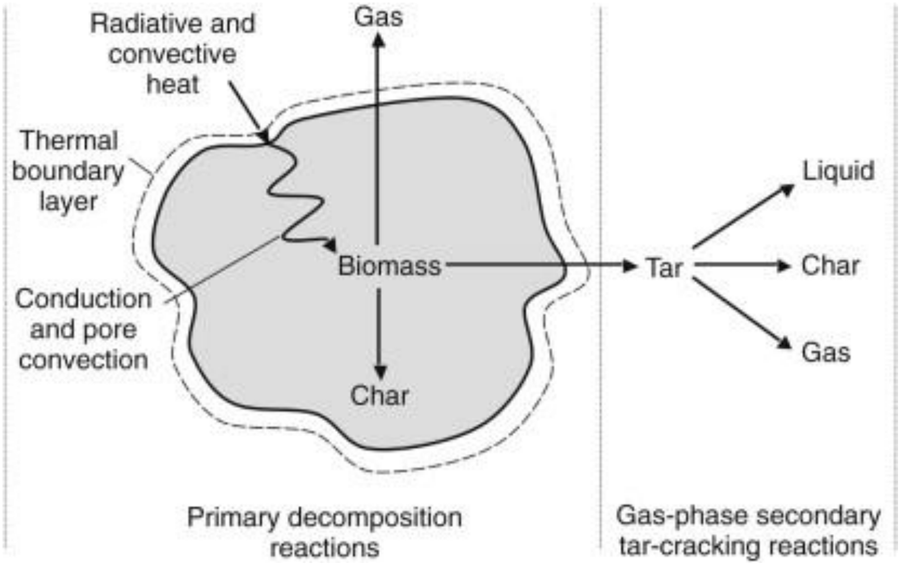


Figure.2.2 Pyrolysis in a biomass particle (Basu, 2010).

Pyrolysis process is the thermal decomposition of biomass at temperature range of 300-900^{o}C in free oxygen environment. The three state of pyrolysis process is removal moisture, biomass decomposition and formation the biochar. Increasing residue time during pyrolysis, biochar increases and tar yield from decrease (Chen et al., 2018). The pyrolysis process equation can calculate from (Basu, 2010):

$$\begin{aligned} C_nH_mO_p\ (\text{Biomass}) \xrightarrow{\text{Heat}}\ & \Sigma_{liquid}C_xH_yO_z + \Sigma_{gas}C_aH_bO_c \\ & + \mathrm{H_2O} + C\ \ (\text{char}) \end{aligned}$$

2.3.1 Types of Pyrolysis

Slow pyrolysis: the residence time about minutes or longer and the product is broken down into char. The characteristic of slow pyrolysis is carbonization and conventional (Basu, 2010).

Fast pyrolysis: the residence time about seconds or milliseconds and the product is bio-oil and gas. The main types of this pyrolysis are flash and ultra-rapid (Basu, 2010).

Table 2.1 The characteristics product of pyrolysis process

Pyrolysis Process	Residence Time	Heating Rate	Final Temperature (°C)	Products
Carbonization	Days	Very low	400	Charcoal
Conventional	5–30 min	Low	600	Char, bio-oil, gas
Fast	<2 s	Very high	~500	Bio-oil
Flash	<1 s	High	<650	Bio-oil, chemicals, gas
Ultra-rapid	<0.5 s	Very high	~1000	Chemicals, gas
Vacuum	2–30 s	Medium	400	Bio-oil
Hydropyrolysis	<10 s	High	<500	Bio-oil
Methano-pyrolysis	<10 s	High	>700	Chemicals

2.3.2 Pyrolysis Products

Pyrolysis breakdown the large complex to small molecules. Pyrolysis products are classified to three type Solid Liquid and Gas.

Solid from pyrolysis process is char which there is carbon (~85%) oxygen and hydrogen. Biomass contains very little inorganic ash and has the lower heating value about 32 MJ/kg (Diebold and Bridgwater, 1997).

Liquid from pyrolysis process (e.g. tar, bio-oil, or biocrude) is a black tarry fluid which contain water up to 20%. It contains the major of homologous phenolic compounds. Liquid yield has a lower LHV about range of 13 to 18 MJ/kg wet basis (Diebold et al., 1997). The rapid pyrolysis produces bio-oil which was depolymerized and fragmented cellulose, hemicellulose, and lignin components of biomass. Bio-oil is a microemulsion which the continuous phase is an aqueous solution of the products of cellulose and hemicellose decomposition, and small molecules from lignin decomposition (Basu, 2010) but phase which discontinuous phase is largely pyrolytic lignin macromolecules (Piskorz et al., 1988, Basu, 2010). Compounds which found in bio-oil

Gas from pyrolysis process is primary decomposition from process which there is gases (vapor) and noncondensable gases (primary gas). The product from heavier molecules are vapor which produce by condensed upon cooling. The noncondensable gas contains lower-molecular-weight gases (e.g. carbon dioxide, carbon monoxide, methane, ethane and ethylene) (Basu, 2010).

2.3.3 Pyrolysis Product Yield

The pyrolysis product depends on the design of the pyrolyzer, the physical and chemical characteristics of the biomass, and important operating parameters (e.g. heating rate, temperature and residence time (Basu, 2010).The yield of tar and other products depend on pressure, ambient gas composition and presence of mineral catalysts (Shafizadeh, 1984). Changing of final temperature and the heating rate may be relative about change of the yields solid, liquid, and gaseous products. The product of rapid pyrolysis, there is higher volatiles and more reactive char than the product of slower heating process.

2.4 Biochar

Biochar is a carbon rich product from the carbonization of biomass in pyrolysis process (e.g. wood, manure, or leaves) which is heated between 300°C and 1000°C in limiting oxygen. The product of pyrolysis process depended on pyrolysis condition (e.g. feedstock, time, temperature, pressure, time) (Komang Ralebitso-Senior and Orr, 2016).

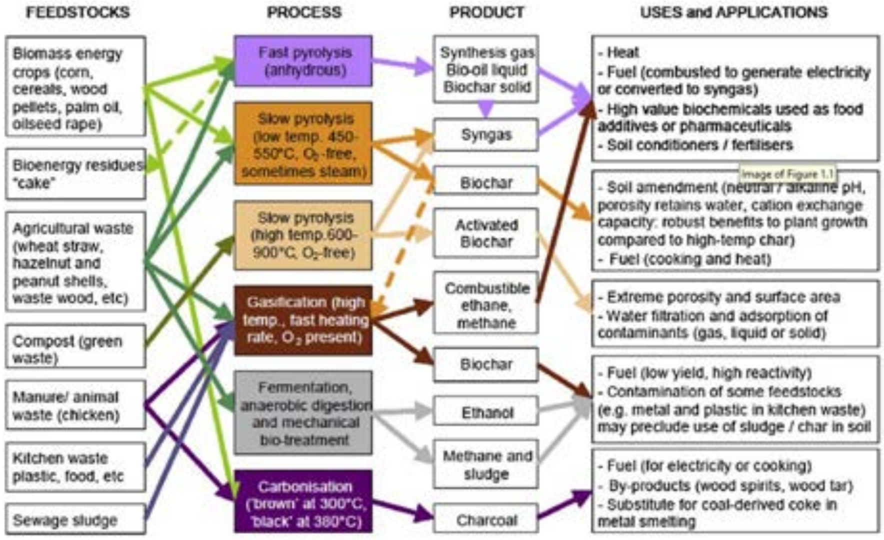


Figure.2.3 Summary of thermal conversion processes in relation to common feedstock, typical product and potential application (Sohi et al., 2010).

2.4.1 Biochar preparation

Processes to produce biochar are pylolysis, hydrothermal carbonization, gasification, and other methods (Deng et al., 2017)

Pyrolysis, the process under high temperature and limiting oxygen, which based on time, temperature and heating rate. Pyrolysis can be classified to three type: slow pyrolysis, rapid pyrolysis, and “flash” pyrolysis. The product in low temperature and slow heating rate is high yield of biochar.

Hydrothermal carbonization is the reaction of biomass underwater stagnant system at 2-6 MPa of pressure and low temperature for 5 min to 16 hours. The biochar product from this method is suitable absorption in aqueous phase. Otherwise this method is expensive reactor in high temperature and high pressure.

Gasification and other methods produce bio oil and gaseous material up to yield of solid component.

Table 2.2 comparison of different techniques to make biochar (Deng et al., 2017)

Preparation methods	**Temperature (°C)**	**Heating rate**	**Residence time**	**Yield (%)**		
				Solid	**Liquid**	**Gas**
Pyrolysis						
Slow pyrolysis	<700	Slow	H	35	30	35
Fast pyrolysis	<1000	Fast	S	10	70	20
Flash pyrolysis	775–1025	Faster	S	10–15	70–80	5–20
Hydro-carbonization	<350	Slow	min-h	50–80	–	–
Gasification	700–1500	Faster	s-min	10	5	85

2.4.2 Biochar characteristics

Biochar has carbon rich and abundant aromaticity oxygen containing functional groups. The structure of biochar up to functional groups which developed pore structure, specific surface area and performance of adsorption.

2.4.2.1 Internal surface area

Biochar has internal surface area which reach over the external surface area. Internal surface area is an important factor of an adsorbent. But internal surface area in only, there is not enough to forecast capacity of adsorption because the strength of adsorption is influence by adsorbent relate properties. The determination of surface area (standard method) is Brunauer Emmett Teller. The BET method model use for finding assumption of multilayer on nonporous adsorption.

$$q = q_{mono} \frac{C_B p}{(p_0 + (C_B - 1)p)(1 - p/p_0)}$$

Where; q is the adsorbed amount (mol/g) or (cm^3/g) or (cm^3/mol) or same V (ml.)

q_{mono} is the adsorbed amount in the first layer

p is the partial pressure of adsorbate (Pa)

p_0 is the saturation vapor pressure (Pa)

C_B is a constant

Table 2.3 typical of the specific internal surface area for different adsorbents (Worch, 2012).

Adsorbents	A_{BET} in m^2/g
Activated carbons	600-1200
Polymeric adsorbents	300-1400
Aluminum oxides	150-350
Granular ferric hydroxides	150-350
Zeolites	400-900

2.4.2.2 Pore size distribution

Classifying pore size of IUPAC are macropores mesopores and micropores. Macropores and mesopores relate with mass transfer to interior adsorption. The volume of micropores define adsorbent capacity and size of internal surface.

Table 2.4 classification of pores according to the IUPAC definition (Worch, 2012).

Pore class	Range of pore radius
Macrepores	>25nm.
Mesopores	1nm.-25nm.
Micropores	<1nm.

2.5 Sorption

Sorption is normally term of absorption and adsorption.

2.5.1 Absorption

Absorption is the process of material which retained by absorbent, the physical solution of gas, vapor, liquid or solid in liquid phase, attached gas, vapor, liquid or dissolved substance to solid surface. Wavelengths of light in spectrophotometry can identify the chemical of molecule, characteristic and concentration of substance (PAC, 1990).

2.5.2 Adsorption

2.5.2.1 Adsorption mechanism

Adsorption mechanism can classify to physical adsorption, chemisorption and electrostatic adsorption. Adsorption is the process material that gas or liquid solute can accumulate on solid or liquid surface, molecular forming, ions, atom or atomic film. The gas phase of adsorption is a multilayer and the liquid phase of adsorption is a monolayer. Adsorption is the process of material which gas or liquid substance can attach to a solid or liquid surface (Mostinsky, I.L., 2011).

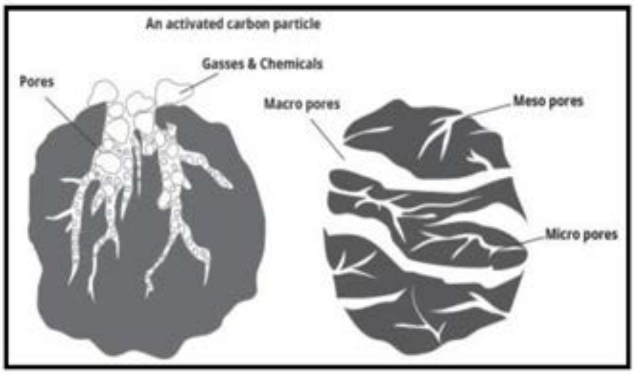


Figure.2.4 mechanism of adsorption

(Gawandde, et al., 2010).

Adsorption occurs because

- The contaminant has non polar.
- The contaminant has great affinity of carbon.
- The granular activated carbon and the powdered activated carbon are adsorbed commonly in adsorbtion process.

2.5.2.2 Adsorption isotherms

Adsorption isotherms have 5 type.

Type I isotherm is found in a few molecular layers which is limited of adsorption. In condition chemisorption, asymptotic reach to limiting of surface areas are occupied. In physical adsorption, type I isotherm is found in micro-porous particle which pore does not reach a few adsorption of particle diameter. A gas molecule is found the overlapping potential between pore wall and gas adsorption at low relative pressure.

Type II isotherm are found when adsorption occurs nonporous or micro-porous. The knee of isotherm appear near encounter of the first monolayer adsorption at increasing relative pressure. Next, higher layers are adsorbed until saturation.

Type III isotherm are found when adsorption is heated. Interaction of adsorbed layer is greater than Interaction of adsorbed surface.

Type IV isotherm is found on porous adsorbent (size pore 15-1000 angstroms). The slope increase at high pressure and porous is being filled which adsorbed. The knee of isotherm appear near encounter of the first monolayer adsorption at increasing relative pressure.

Type V isotherm has the result interaction potential same type III but found in small adsorbate - adsorbent.

Type VI isotherm is the new rare type of isotherm (Lowell and Joan, 1991).

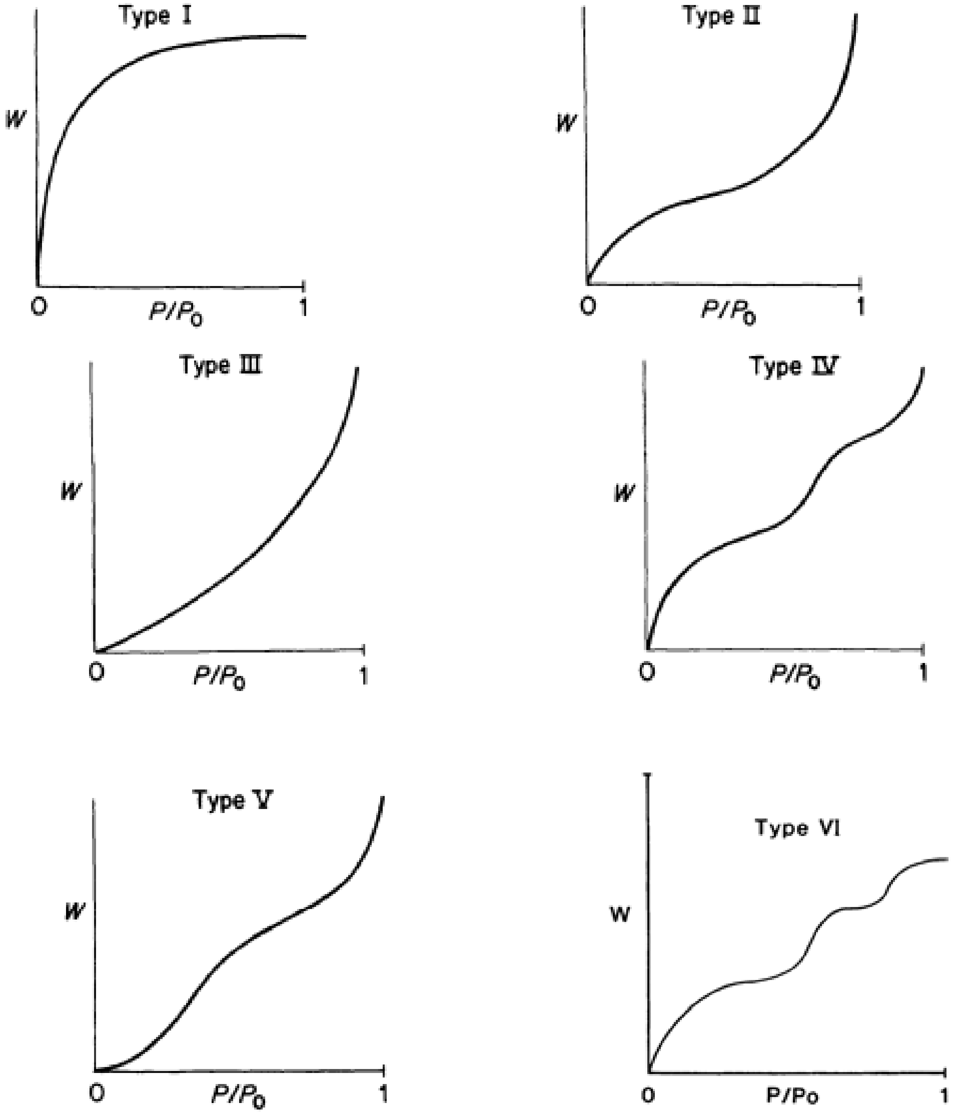


Figure.2.4 adsorption isotherm

(Lowell and Joan, 1991).

2.6 Canteen wastewater

Domestic Wastewater comes from human activity such as kitchen, toilet. Canteen wastewater is the part of domestic wastewater (PCD, 1994).

Table 2.5 order of important domestic wastewater managment (Onep, 1995).

Region	Rate of wastewater (L/person-Day)					
	1993	1997	2002	2007	2012	1017
Central	160-214	165-242	170-288	176-342	183-406	189-482
North	183	200	225	252	282	316
Northeastern	200-253	216-263	239-277	264-291	291-306	318-322
South	171	195	204	226	249	275

2.6.1 Canteen wastewater characteristic (PCD, 1994).

Organic compounds include carbohydrates, proteins and fats such as rice which can be decomposed by aerobic microorganisms. The level of dissolve oxygen is decreased by microorganism. The organic matter in water is measured by BOD which BOD increases that shows high organic matter.

Inorganic compounds include mineral which may damage organism.

Metals and toxicity may be organic or inorganic compounds which can damage organism.

Oil and grease barriers to photosynthesis and hides the diffusion of oxygen from the air into the water.

Solid sinks to the bottom so make a shallow water source.

Detergents blocks the distribution of oxygen in the water to air which harm organisms.

Microorganism include use oxygen for life which can reduce levels of dissolved oxygen. Microorganism is main cause of decreasing dissolve oxygen at night.

Nutrient include nitrogen and phosphorus nutrients. If nitrogen and phosphorus high level, algae will increase rapidly.

Odor is produced from decomposition of organic matter.

Table 2.6 parameters of kitchen wastewater and canteen wastewater (Kmutt, 1987).

Parameters	Kitchen wastewater		Canteen wastewater
	Passed filter	Non filter	
pH	7.7	7.1	7.4
COD (mg/l)	1,500	230	96
BOD (mg/l)	700	120	41
TKN (mg/l)	300	8	9.7
PO_4 (mg/l)	24	6	0.4
SS (mg/l)	560	45	158
FOG (mg/l)	540	400	527

2.6.2 Wastewater treatment (PCD, 1994).

Physical Treatment removed impurities from water, such as paper, plastic, solid large. The fragments, gravel, sand, fat and oil using equipments such as sieve.

Chemical treatment is a method by chemical process to remove impurities in the wastewater. This method treatment parameter in water. The equipment used in wastewater treatment by chemical method was stirred tank, stirred tank, slow sedimentation tank, filter tank and disinfecting tank.

Biological Treatment is a method of water treatment by using biological process which remove impurities in the water. Especially organic carbon, nitrogen and phosphorus are removed by microorganisms.

The wastewater can be divided into three steps:

Primary treatment and pretreatment are the treatment to separate sand, gravel and solid out of water by the equipment such as screen. Primary Sedimentation Tank and skimming equipment treatment can remove suspended solids were 50 – 70 percent and 25 – 40 percent of BOD.

Secondary treatment is a wastewater treatment through primary treatment process but there is residue. Secondary treatment can remove suspended solids more than 80 percent.

Advance Treatment can remove nutrients (nitrogen and phosphorus) color, suspended settling difficult. In advance treatment must improve water quality better for recycle. The process advanced treatment such as

Table 2.7 process treatment

Process Treatment	Treatment
Phosphorus removal	chemical processes and biological processes
Nitrogen removal	chemical processes and biological processes
Phosphorus and nitrogen removal by biological processes	Anaerobic and aerobic
Filtration	Physical processes
Adsorption	Adsorption on surface

2.7 Application of biochar for wastewater treatment

Product of pyrolysis hardwood at 450 °C and pyrolysis corn straw at 600 °C are biochar which there are potential of adsorption. They can remove copper and zinc from aqueous solution. The process experiment, using 0.1 g of biochar with 20 ml of 0.01 M $NaNO_3$ solution which containing either Cu (II) or Zn (II) then shaker them at 120 rpm. Until mixing well. Filtrating and then analyzed residue heavy metal. Result of this study found that the hardwood biochar that was weakly acidic, while the pH of corn straw rose to 9.54. From adsorbent data of Langmuir isotherm found the maximum of Cu (II) and Zn (II) adsorption capacities are 12.52 and 11.0 mg/g for corn straw, 6.79 and 4.54 mg/g for hardwood, respectively. Moreover, from this study biochar can adsorbed cupper more than zinc. There is potential of adsorption but the ability is an individual basis of kind agricultural waste (Chen et al., 2011).

Orange and banana are largely consumed which fruit peel wastes were abundant wastes from the fruit processing. In this study would like to generate fruit peels to biochar by pyrolysis in 300, 400 and 500 °C . This study demonstrates a alternative to divert agriculture waste to biochar to treat the palm oil mill effluent. Result of this study biochar found that had mesoporus which can reduce BOD and COD to discharge standard on 3 days. TSS was reduce in 2 day. Oil and grease was treatment by biochar in 1 day. Removal efficiency of biochar up to 57% in reducing the concentration of biochemical oxygen demand (BOD), chemical oxygen demand

(COD), total suspended solids (TSS) and oil and grease (O&G) of POME. The biochar had the increasing potential for treatment wastewater when the increasing time (Lam et al., 2018).

The application of biochar to remove trichloroethylene from water is studied by conversion of pyrolysis process residue agriculture to biochar. Soybean stove and peanut shell were pyrolysis at 300 and 700 ^{o}C. Biochar is the product of pyrolysis. In this study would like to compare potential of adsorbent of biochar (from soybean stover and peanut shells) with commercially available activated carbon. The result from batch adsorption experiments biochar from soybean stover and peanut shells can adsorbent trichloroethylene stronger affinity than activated carbon. Adsorption capacity of biochar will be increasing when pyrolysis biochar in high temperature. Moreover, biochar and activated carbon are not significantly different of percentage removal of TCE from water in the same temperature. At 700 ^{o}C of peanut shells is the best condition of pyrolysis for remove trichloroethylene from water. And pyrolysis remove oxygen from structure of biomass and carbonize biomass for increasing hydrophobicity and surface area of biochar (Ahmad et al., 2012).

CHAPTER 3

MATERIALS AND METHODS

3.1 Sampling site and study site

Canteen wastewater was collected from the tank in the canteen of Chulachakrabonse Building.

Figure.3.1 Sample site (13°44’08’’N, 100°31’52’’E)

3.2 Biochar preparation and application of biochar for wastewater treatment

3.2.1 Preparation pineapple peels and corn cobs.

3.2.1.1 Rinse the pineapple peels and corn cob with the tap water for remove particles.

3.2.1.2 Cut the pineapple peels and corn cob to 1 inch.

3.2.1.3 Remove the moisture by the sun or the oven in 65-70 °C until weight constant.

Figure.3.2 oven Binder, BD/ ED/ FD

3.2.1.4 Grinde the pineapple peels and corn cobs by grinder and then sieve pass 2-mm sieve

3.2.1.5 Store particle into bag.

3.2.2 Preparation of biochars

3.2.2.1 Get the dried particle to the reactor for pyrolysis in 400 450 and 500°C for 1 hr. under limitation of oxygen in Muffled furnace.

Figure.3.3 Muffled furnace (Carbolite ELF/11/14/201, England)

3.2.2.2 Store biochar into bag before use in pyrolysis.

3.2.3 Analysis of biochar

3.2.2.1 Calculate percent yield of biochar

3.2.2.2 Scan morphology of biochar by SEM (JEOL, JSM-IT300 from Japan)

Figure.3.4 SEM (JEOL, JSM-IT300 from Japan)

3.2.2.3 Calculating surface area by BET, BJH method

3.2.4 Application of biochar for wastewater treatment

3.2.4.1 Sampling wastewater from the canteen of Chulachakrabonse Building by use 10 L of bucket and store in 4°C to prevent biodegradation. The experiment uses 40 L of wastewater.

3.2.4.2 Analysis canteen wastewater before treatment by biochars follow by Table 3.1. and find removal efficiency

$$removal\ efficiency(\%) = \frac{influent\ concentration - effluent\ concentration}{influent\ concentration} \times 100$$

3.2.4.3 Mix biochar and the canteen wastewater then stirring 120 rpm about 10 minute (as Fig. 3.6 the experimental design). Wastewater treatment was collected for 3 day. The experiment were preform in two times.

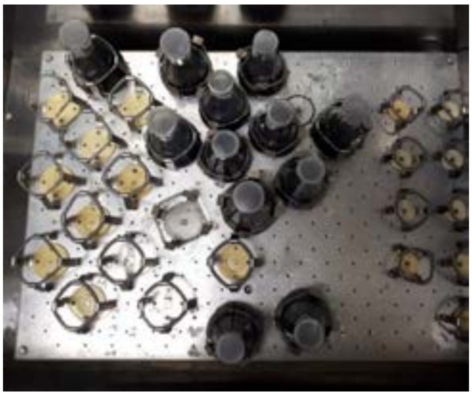


Figure.3.5 Application of biochar on shaker

3.2.4.4 Filtrate of mixing effluent by whatman No 1.

3.2.4.5 Analyze of filtration effluent (as Table).

Figure. 3.6 The ratio of pineapple peels and corn cob biochars and wastewater

Day1	PAB+WW 400°C (1/10)	PAB+WW 400°C (1/20)	PAB+WW 400°C (1/30)	PAB+WW 450°C (1/10)	PAB+WW 450°C (1/20)	PAB+WW 450°C (1/30)	PAB+WW 500°C (1/10)	PAB+WW 500°C (1/20)	PAB+WW 500°C (1/30)	C1
	CB+WW 400°C (1/10)	CB+WW 400°C (1/20)	CB+WW 400°C (1/30)	CB+WW 450°C (1/10)	CB+WW 450°C (1/20)	CB+WW 450°C (1/30)	CB+WW 500°C (1/10)	CB+WW 500°C (1/20)	CB+WW 500°C (1/30)	C2
Day2	PAB+WW 400°C (1/10)	PAB+WW 400°C (1/20)	PAB+WW 400°C (1/30)	PAB+WW 450°C (1/10)	PAB+WW 450°C (1/20)	PAB+WW 450°C (1/30)	PAB+WW 500°C (1/10)	PAB+WW 500°C (1/20)	PAB+WW 500°C (1/30)	C1
	CB+WW 400°C (1/10)	CB+WW 400°C (1/20)	CB+WW 400°C (1/30)	CB+WW 450°C (1/10)	CB+WW 450°C (1/20)	CB+WW 450°C (1/30)	CB+WW 500°C (1/10)	CB+WW 500°C (1/20)	CB+WW 500°C (1/30)	C2
Day3	PAB+WW 400°C (1/10)	PAB+WW 400°C (1/20)	PAB+WW 400°C (1/30)	PAB+WW 450°C (1/10)	PAB+WW 450°C (1/20)	PAB+WW 450°C (1/30)	PAB+WW 500°C (1/10)	PAB+WW 500°C (1/20)	PAB+WW 500°C (1/30)	C1
	CB+WW 400°C (1/10)	CB+WW 400°C (1/20)	CB+WW 400°C (1/30)	CB+WW 450°C (1/10)	CB+WW 450°C (1/20)	CB+WW 450°C (1/30)	CB+WW 500°C (1/10)	CB+WW 500°C (1/20)	CB+WW 500°C (1/30)	C2

Table 3.1 The parameters and analyzed method

Parameters	Analyzed Method	Standard*
pH	pH Meter	5.5 – 9.0
O&G	Soxhlet Extraction	≤ 5mg./l.
TSS	Glass Fibre Filter Disc	≤ 30mg./l.
COD	Close Reflux	-
BOD	Azide Modification Method	≤ 20mg./l.
TKN	Kjeldhal Method	≤ 20mg./l.
TP	Ascorbic Acid Colorimetric Method	≤ 2mg./l.

* Water Quality standards from domestic wastewater (PCD, 2010)

3.2.5 Data analysis

3.2.5.1 All of data from the experiment were analyzed using one way ANOVA (SPSS for windows 10 version 22).

3.3 Summary of experiment5

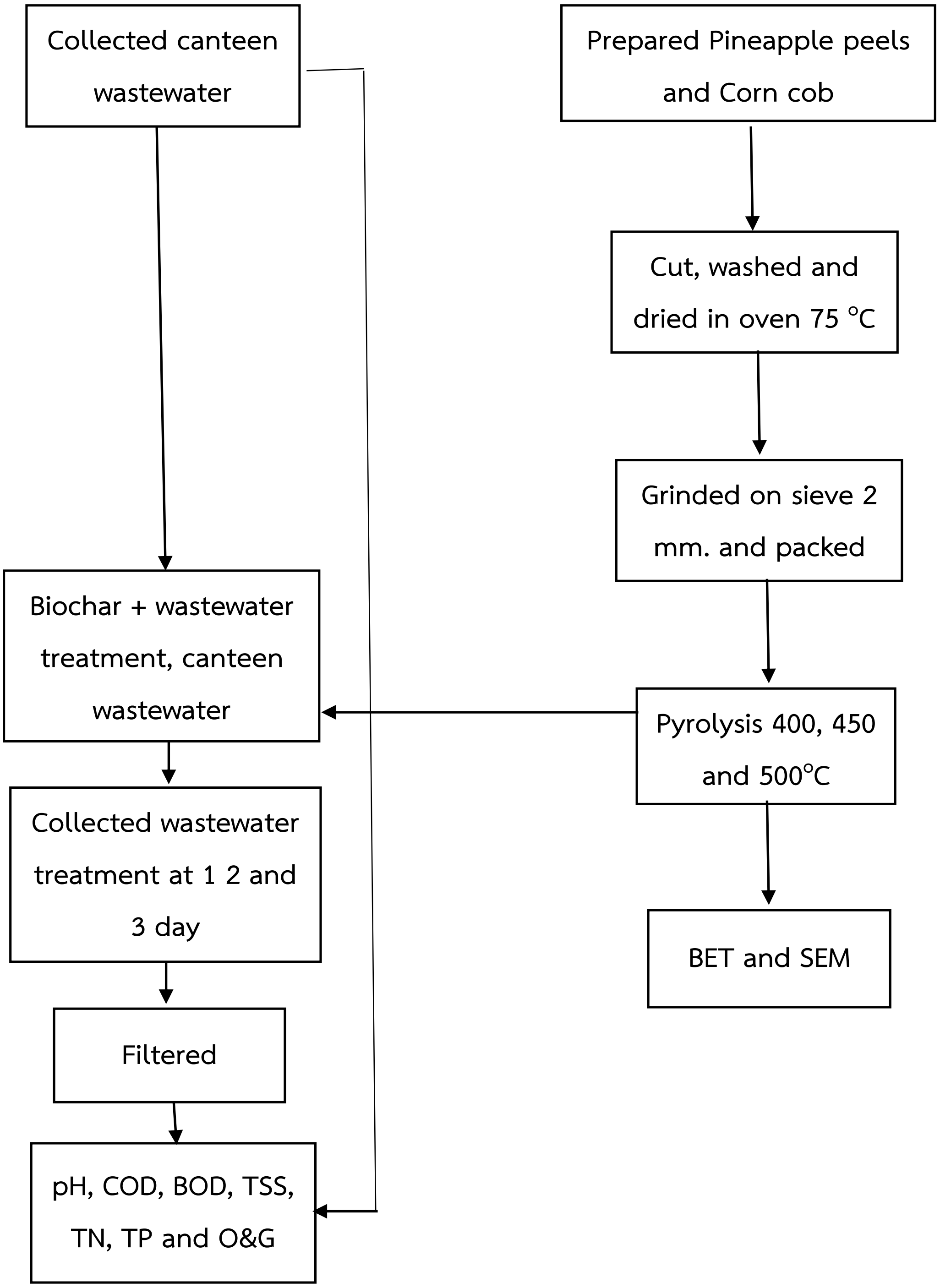


Figure.3.7 Flowchart of experiment

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Biochar characterization

4.1.1 Yield of biochar

Pyrolysis process can convert pineapple peel and corn cob to biochar (29.24-46.34%) (Table 4.1) at the different temperatures between 400-500 °C. Biochar was found the dark particle, hard texture and range size <2 mm. In low temperature (400°C) produced biochar more than high temperature. Related Lam et al., 2018 found that at high temperature the main product obtains oil and gas. In contrast, at lower temperatures produce higher biochar (Collard and Blin, 2014). From other reports the composition of raw material effect to pyrolysis volatile which high lignocellulosic component can convert to pyrolysis volatile at high temperature (400-500 °C) (Lam et al., 2018).

Table 4.1 Yield of biochar

Type of biomass	Temperature	Mean of percent yield
		Biochar
Pineapple peel	400	46.34
	450	38.21
	500	34.67
Corn cob	400	34.94
	450	30.51
	500	29.24

4.1.2 Surface and porosity

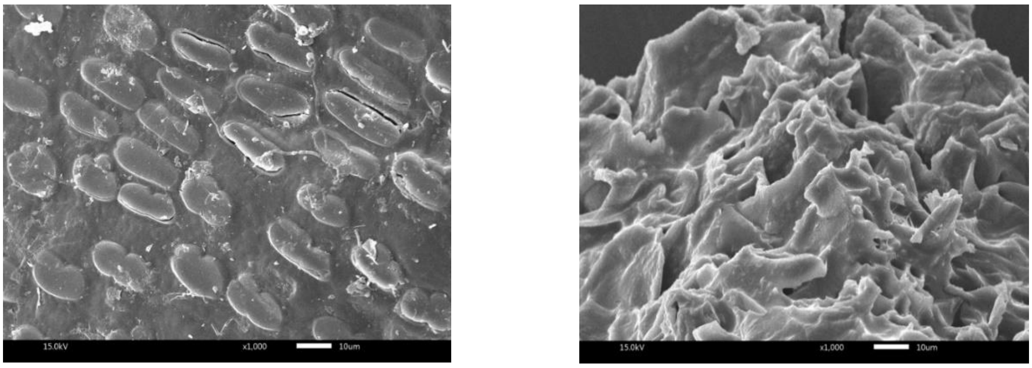
Table 4.2 shows surface area, pore volume and pore diameter from BJH method adsorption and desorption. Experiment in this study found that corn cob biochar at 400°C had a high removal efficiency. And from this report, it shows the analysis of micropore and macropore in corn cob biochar at 400°C with pore diameters above 1000 Å were macropore (Sellergren and Hall, 2001). BET methods indicated to the presence of micropore and macropore. Compared to other reports (Lam et al., 2018) found that total pore volume was 0.15 cm^3/g more than orange peel biochar at 500°C (0.04 cm^3/g). Total pore volume determined adsorption of wastewater (Cheremisinoff and Ellerbusch, 1978). The surface area of corn cob biochar at 400°C in other paper found 180.1 (m^2/g) by BET method (Yang ZHANG et al. 2014).

Table 4.2 Porous characteristics of corn cob biochar 400°C

BJH summary	
Surface Area (m^2/g)	3.901-7.685
Pore Volume (cc/g)	0.148-0.15
Pore Diameter	9.011 Å-1521.676Å

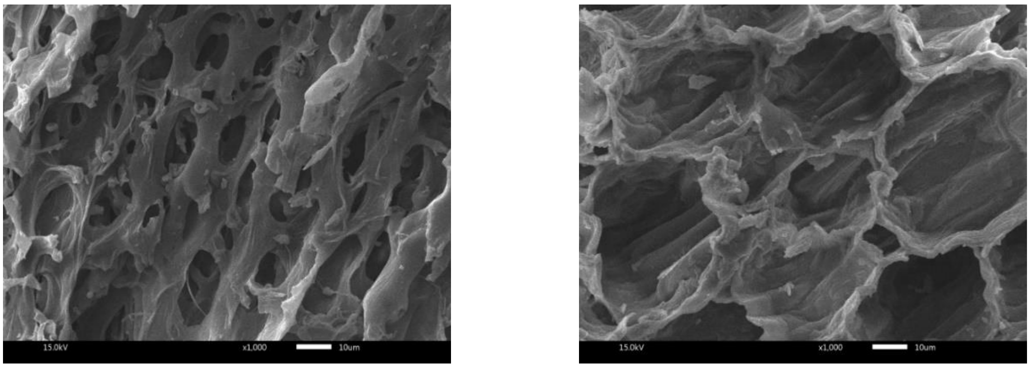
4.1.3 Surface morphology

Figure.4.2 shows corn cob, pineapple peel, corn cob biochar, and pineapple peel biochar morphology form pyrolysis process by SEM. The surface of corn cob is found smooth and scale but pineapple peel was rugged. And both of fresh kind before pyrolysis were nonporous. Otherwise, after pyrolysis process is found porous which temperature related to pore size. Higher temperature, there is the bigger pore size more than lower temperature but corn cob biochar at 450°C is as pore size as corn cob biochar at 500°C. Pyrolysis can carbonize corn cob and pineapple peel to produce biochar and release pyrolysis volatiles. Moreover from other study found that the component in corn cob and pineapple peel were cellulose about38.8% ± 2.5%, hemicellulose about 44.4% ± 5.2% and lignin about 11.9% ± 2.3% (Pointner et al., 2014) in corn cob and cellulose about 21.98±2.34 %, hemicellulose about 74.96±2.55 % and lignin about 2.68±1.54 % (Aophat et al., 2014) in pineapple peel. Related Raveedran et al., 1994 lignin was between cellulose and hemicellulose that lignin was the effective porous factor.



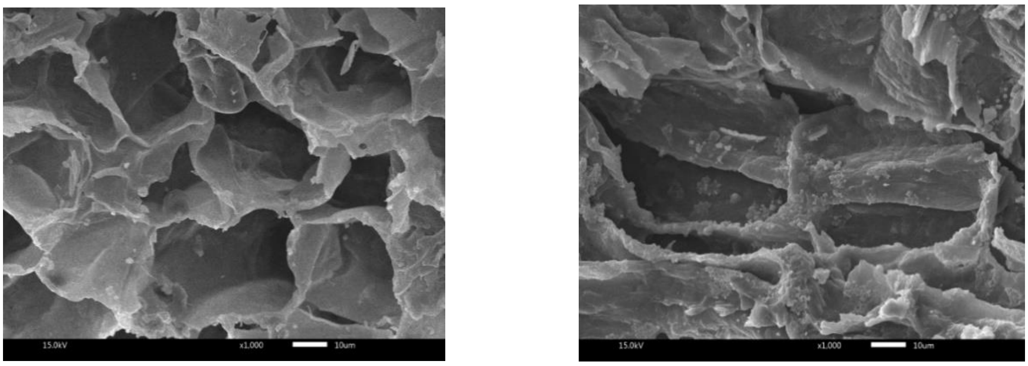
Corn cob

Pineapple peel



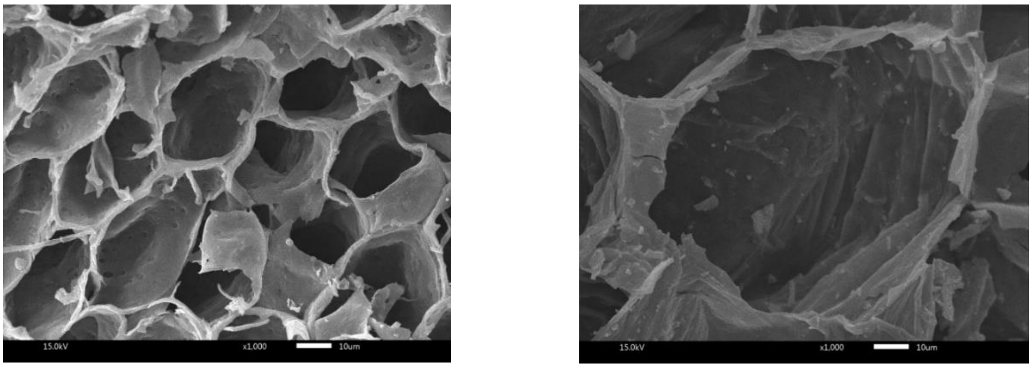
Corn cob biochar 400^{o}C

Pineapple peel biochar 400^{o}C



Corn cob biochar 450^{o}C

Pineapple peel biochar 450^{o}C



Corn cob biochar 500^{o}C

Pineapple peel biochar 500^{o}C

Figure.4.1 SEM micrograph of corn cob, pineapple peel, corn cob biochar and pineapple peel biochar at the difference condition

4.2 Canteen wastewater treatment

4.2.1 Chemical oxygen demand and biochemical oxygen demand

The result after treatment by biochar shows in figure.4.2. The horizontal axis is the time of treatment. The vertical axis is the percent removal of COD. In the right of paper is canteen wastewater which is treated by corn cob biochar. And in the left of paper is canteen wastewater which is treated by pineapple biochar. COD in canteen wastewater treatment by different biochars in 1-3 days was significant ($P \leq 0.05$). The line graph illustrates the removal efficiency of canteen wastewater treatment by biochar in day 1 to the end day 3, divided by the ratio 1 g. of biochar in 10ml. canteen wastewater, 1 g. of biochar in 20ml. canteen wastewater and 1 g. of biochar in 30ml. canteen wastewater. The removal efficiency of wastewater treatment by biochar at pineapple biochar 400° C in ratio 1/10, 1/20 and 1/30 at day 3 were -3.45, 50.0 and 70.69%, respectively. The removal efficiency of wastewater treatment by biochar at pineapple biochar 450°C in ratio 1/10, 1/20 and 1/30 at day 2 was 38.24, 53.68 and 56.76%, respectively. The removal efficiency of wastewater treatment by pineapple biochar 500°C in ratio 1/10, 1/20 and 1/30 at day 3 were 12.07, 34.49 and 75.86%, respectively. The removal efficiency of wastewater treatment by biochar at corn cob biochar 400°C, corn cob biochar 450°C and corn cob biochar 500°C at day 1- 3 fluctuated and in ratio 1/10, 1/20 and 1/30 at day 3 were 75.87, 36.21, 74.14, 48.28, 55.17, 51.72, 41.38, 41.38 and 51.73, respectively.

Before treatment, the value of COD is 6,857 mg/l. The residual of COD in treatment by corn cob biochar 400°C ratio1/10 has a trend increasing on the first day then will be constant which adsorbent went to equilibrium. Figure 4.2 showed that in 1/10 ratio of corn cob biochar 400°C was higher removal efficiency of canteen wastewater treatment by biochar more than 1/30 ratio of pineapple biochar 500°C. Both of them were the best kind of canteen wastewater treatment in this study.

The result after treatment by biochar shows in figure.4.3. The horizontal axis is the time of treatment. The vertical axis is the percent removal of BOD. In the right of paper is canteen wastewater which is treated by corn cob biochar. And in the left of paper is canteen wastewater which is treated by pineapple biochar. BOD in canteen wastewater treatment by different biochars was significant ($P \leq 0.05$). The line graph illustrates the removal efficiency of canteen wastewater treatment by biochar in day 1 to the end day 3, divided by ratio the 1 g. of biochar in 10ml. canteen wastewater, 1 g. of biochar in 20ml. canteen wastewater and 1 g. of biochar in 30ml. canteen wastewater. The removal efficiency of wastewater treatment by biochar at pineapple biochar 400° C in ratio 1/10, 1/20 and 1/30 at day 3 were increasing trend that 25.84, 50.56 and 62.92%, respectively. The removal efficiency of wastewater treatment by biochar at pineapple biochar 450°C in ratio 1/10, 1/20 and 1/30 at day 2 were 44.59, 57.44 and 39.19%, respectively. The removal efficiency of wastewater treatment by pineapple biochar 500°C in ratio 1/10, 1/20 and 1/30 at day 3 were 51.12, 55.06 and 48.31%, respectively. The removal efficiency of wastewater treatment by biochar at corn cob biochar 400°C, corn cob biochar 450°C were at day 1- 3 the same trend and in ratio 1/10, 1/20 and 1/30 at day 3 were 80.34, 79.78, 76.41, 55.62, 62.92 and59.55, respectively. But the trend of corn cob biochar 500°C was decreasing trend. The removal efficiency of wastewater treatment by biochar at corn cob biochar 500°C in ratio 1/10, 1/20 and 1/30 at day 1 were 74.8, 61.31 and 80.95%, respectively.

Before treatment, the value of BOD is 2,425 mg/l. The residual of BOD in treatment by corn cob biochar 400°C ratio1/10 hot a low of the removal efficiency on the second day, but they would rather constant. Figure 4.3 showed that in 1/10 ratio of corn cob biochar was higher removal efficiency of canteen wastewater treatment by biochar more than 1/30 ratio of pineapple biochar at 400°C. This study, both of them were the best kind of canteen wastewater treatment.

BOD was partial of COD so biochar had porous for adsorption of COD which related other reports, the porous structure of biochar provided the place for microorganism growth. Microorganism accelerated COD degradation (Zhou et al., 2017). So biochar is important for reduction COD by absorption (Kadlec and Wallace, 2008).

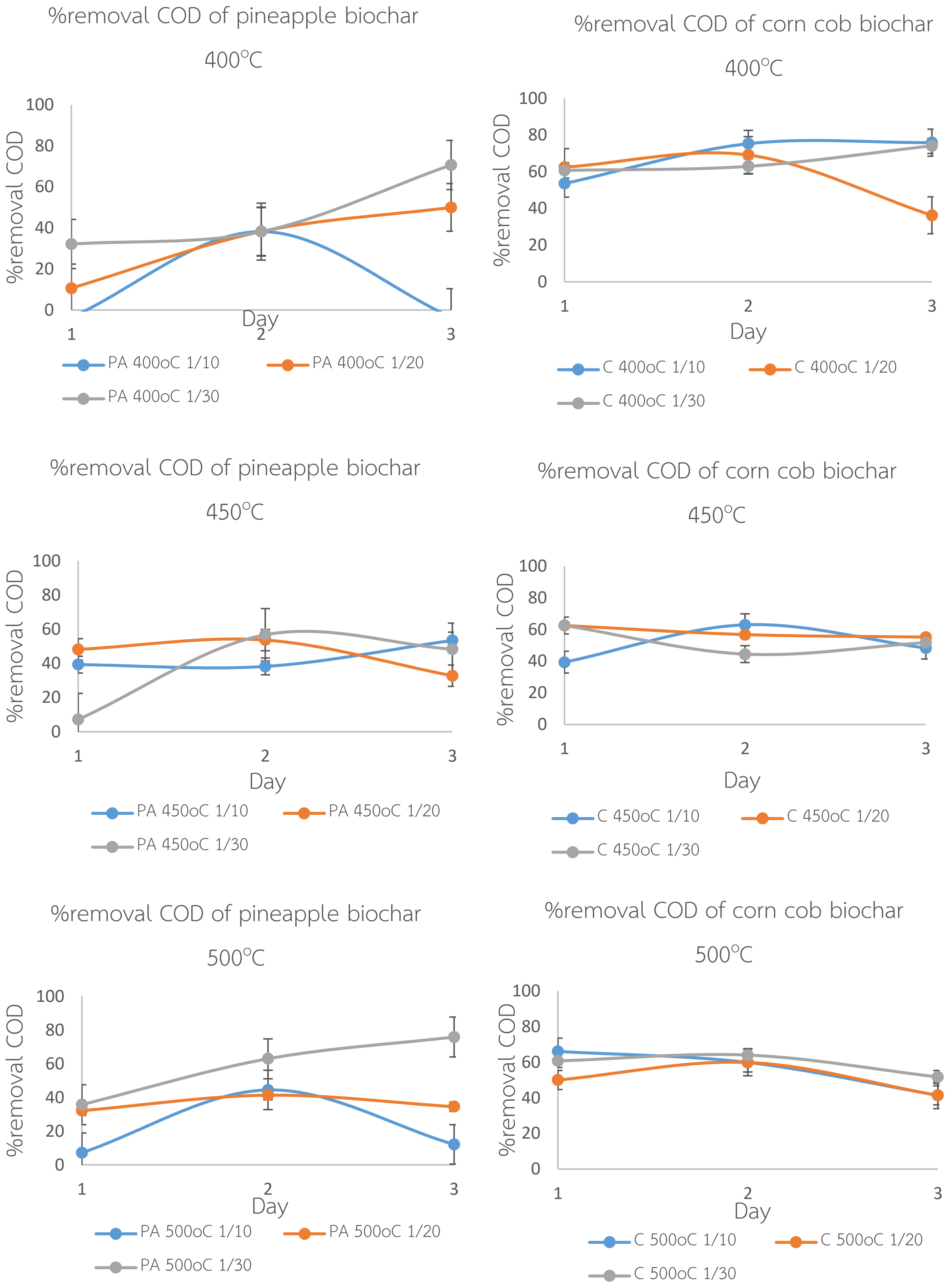


Figure.4.2 Removal efficiency of COD after treatment by biochar

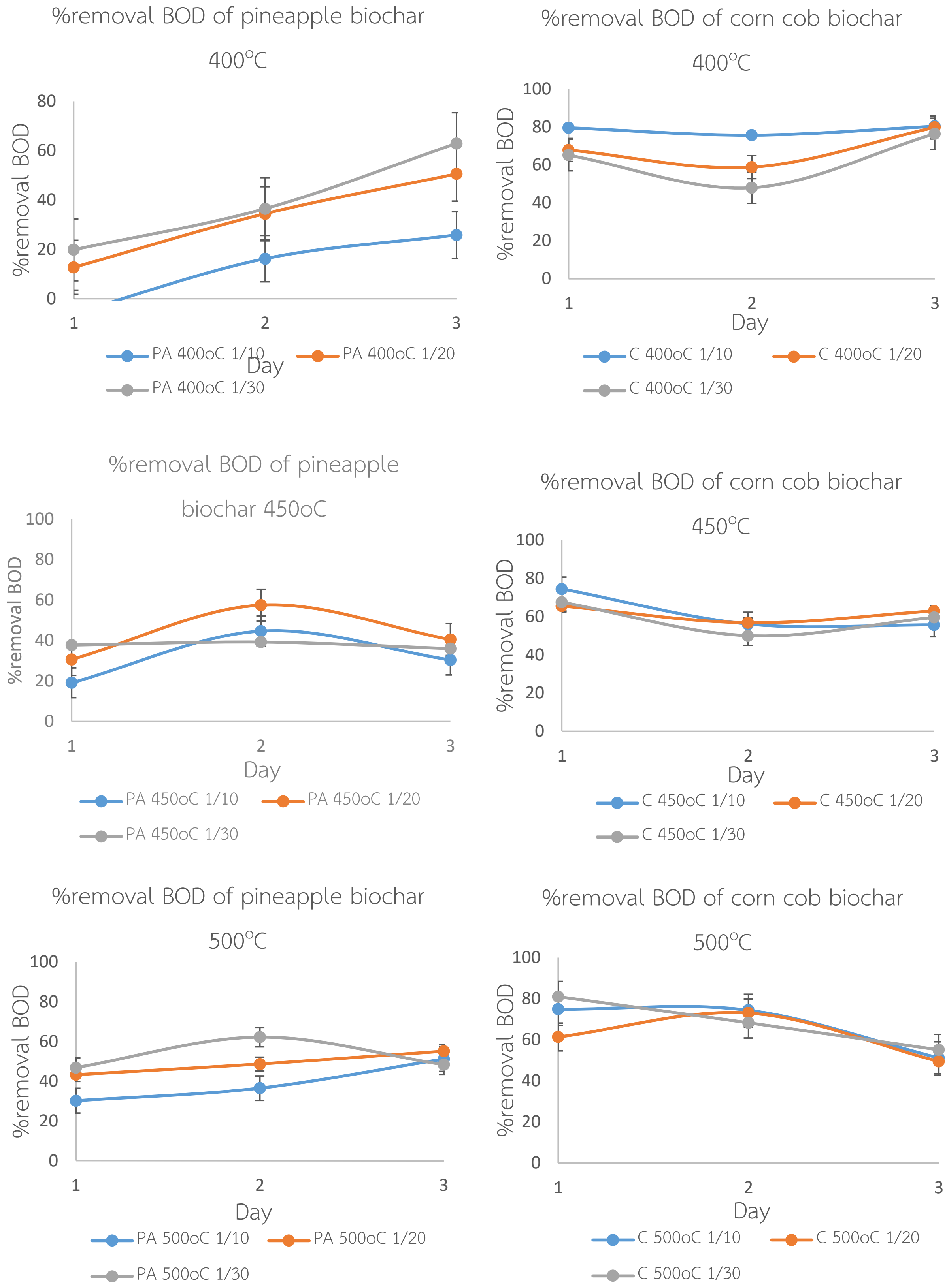


Figure.4.3 Removal efficiency of BOD after treatment by biochar

4.2.2 Total phosphorus

The result after treatment by biochar shows in figure.4.4. The horizontal axis is the time of treatment. The vertical axis is the percent increased content of TP. In the right of paper is canteen wastewater which is increased by corn cob biochar. And in the left of paper is canteen wastewater which is increased by pineapple biochar. TP content in canteen wastewater treatments by other kinds of biochar was not significant ($P>0.05$) but each day, TP content was significant ($P\leq0.05$). The line graph illustrates the total phosphorous increased content of canteen wastewater treatment by biochar in day 1 to the end day 3, divided by the ratio 1 g. of biochar in 10ml. canteen wastewater, 1 g. of biochar in 20ml. canteen wastewater and 1 g. of biochar in 30ml. canteen wastewater. The lowest increased efficiency in pineapple biochar 400^{o}C of wastewater treatment in ratio 1/10, 1/20 and 1/30 at day 2 were 1.65, 1.69 and 0.93%, respectively. The TP increased efficiency of wastewater treatment by biochar at pineapple biochar 450^{o}C and 500^{o}C in ratio 1/10, 1/20 and 1/30 were the same trends of treatment and at day 1 was 1.02, -4.08, -8.33, -4.93, 3.58 and -9.18%, respectively. Both of them the TP increased efficiency of wastewater treatment were increasing trend. Otherwise, the TP increased efficiency of wastewater treatment by biochar at corn cob biochar 400^{o}C, corn cob biochar 450^{o}C and corn cob biochar 500^{o}C at day 1-3 decreased and in ratio 1/10, 1/20 and 1/30 at day 3 were 78.31, 43.92, -32.81, 66.40, 22.75, 41.27, 66.41, 17.46 and 28.04, respectively.

Before treatment, the value of TP was 30.28 mg/l. The residual of TP in treatment by corn cob biochar 400^{o}C ratio1/30 had an increasing trend of treatment but a decreasing trend of TP increased content. Figure 4.4 showed that in 1/30 ratio of corn cob biochar 400^{o}C was lower increased efficiency of TP in canteen wastewater treatment by biochar more than 1/30 ratio of pineapple biochar 500^{o}C. Both of them were the best kind of canteen wastewater for treatment in this study.

In the initial of wastewater treatment by pineapple biochar 400^{o}C, biochar at corn cob biochar 400^{o}C, corn cob biochar 450^{o}C and corn cob biochar 500^{o}C may be spread of phosphorus by activated with stirred so biochar cannot treat canteen wastewater by experiment conditions. Otherwise, biochar at pineapple biochar 450^{o}C and 500^{o}C have decreased trend efficiency of treatment also from the other report found increasing of total phosphorus about 43% at 700^{o}C of pyrolysis and from 5.8% at 250^{o}C - 12.8% at 800oC in biochar from sewage sludge (Chan and Xu, 2009). Discussion of the full recovery phosphorus in sewage sludge biochar at 450^{o}C, total phosphorus in sewage sludge biochar depends on the wastewater treatment process (Bridle and Pritchard, 2004).

4.2.3 Total Suspended Solid

The result after treatment by biochar shows in figure.4.5. The horizontal axis is the time of treatment. The vertical axis is the percent removal of TSS. In the right of paper is canteen wastewater which is treated by corn cob biochar. And in the left of paper is canteen wastewater which is treated by pineapple biochar. TSS in canteen wastewater treatment by other kind biochars were significant ($P \leq 0.05$). The line graph illustrates the removal efficiency of canteen wastewater treatment by biochar in day 1 to the end day 3, divided by ratio the 1 g. of biochar in 10ml. canteen wastewater, 1 g. of biochar in 20ml. canteen wastewater and 1 g. of biochar in 30ml. canteen wastewater. The removal efficiency of wastewater treatment by biochar at pineapple biochar 400^{o} C and pineapple biochar 450^{o}C in ratio 1/10, 1/20 and 1/30 hit high of day 2 were 62.53, 53.39, 59.22, 73.20, 66.21 and 60.38%, respectively. The removal efficiency of wastewater treatment by biochar at pineapple biochar 500^{o}C, corn cob biochar 400^{o}C, corn cob biochar 450^{o}C, and corn cob biochar 500^{o}C was at day 1- 3 the same trend at the 1/10 were the high efficiency more than other ratios. The removal efficiency of wastewater treatment by biochar at ratio 1/10 of corn cob biochar 400^{o}C, corn cob biochar 450^{o}C, and corn cob biochar 500^{o}C were the high efficiency more than other ratios so, the weight of biochar had effected to treatment TSS. But pineapple biochar 500^{o}C had high efficiency removal TSS at 1/10, 1/30 and 1/20, respectively. The high removal efficiency of wastewater treatment by biochar at pineapple biochar 500^{o}C in ratio 1/10, 1/20 and 1/30 at day 2 were 75.53, 35.91 and 52.23, respectively. The high removal efficiency of wastewater treatment by biochar at corn cob biochar 400^{o}C and corn cob biochar 500^{o}C ratio 1/10 at day 2 were 84.86 and

84.24, respectively. But the trend of corn cob biochar 450°C was decreasing trend. The removal efficiency of wastewater treatment by biochar at corn cob biochar 500°C in ratio 1/10, 1/20 and 1/30 at day 1 were 84.36, 70.12 and 62.07%, respectively

Before treatment, the value of TSS was 420 mg/l. The residual of TSS in treatment by corn cob biochar 450°C ratio1/10 has trend hight on the first day then would be decreasing. Figure 4.5 showed that in 1/10 ratio of corn cob biochar 450°C was higher removal efficiency of canteen wastewater treatment by biochar more than 1/10 ratio of pineapple biochar 500°C. Both of them were the best kind of canteen wastewater treatment in this study.

Corn biochar pores at 400°C -500°C had value about 19.46-40.51 micrometer and pineapple biochar pores had value about 48.81- 92.30 micrometer also TSS was the particle which can't pass filter pore 2 micrometer. So biochar can adsorb and retain in porous of biochar. Otherwise, Lam et al., 2018, the sizes of suspended solid are large more than adsorption of biochar so there is low efficiency for removal TSS. The removal efficiency of orange peel biochar at 500°C was 18% (Lam et al., 2018). So this study had higher removal efficiency of pineapple peel and corn cob biochar than orange peel biochar.

4.2.4 Total Kjeldahl Nitrogen

The result after treatment by biochar shows in figure.4.6. The horizontal axis is the time of treatment. The vertical axis is the percent removal of TKN. In the right of paper is canteen wastewater which is treated by corn cob biochar. And in the left of paper is canteen wastewater which is treated by pineapple biochar. TKN in canteen wastewater treatment by other kinds of biochar in 1-3 day was significant ($P \leq 0.05$). The line graph illustrates the removal efficiency of canteen wastewater treatment by biochar in day 1 to the end day 3, divided by the ratio 1 g. of biochar in 10ml. canteen wastewater, 1 g. of biochar in 20ml. canteen wastewater and 1 g. of biochar in 30ml. canteen wastewater. Overall, the removal efficiency of wastewater treatment by biochar at pineapple biochar 400° C in ratio 1/10, 1/20 and 1/30 at day 3 were 49.97, 47.5 and 54.00%, respectively. The removal efficiency of wastewater treatment by biochar at pineapple biochar 450°C in ratio 1/10, 1/20 and 1/30 at day 3 were 57.05, 47.59 and 58.18%, respectively. The removal efficiency of wastewater treatment by pineapple biochar 500^{o}C fluctuated in ratio 1/10, 1/20 and 1/30 at high value day were 54.24, 29.94 and 42.56%, respectively. The removal efficiency of wastewater treatment by biochar at corn cob biochar 400^{o}C, corn cob biochar 450^{o}C and corn cob biochar 500^{o}C at day 2 reached a high of removal efficiency of wastewater treatment and in ratio 1/10, 1/20 and 1/30 were 83.34, 86.76, 74.91, 83.67, 100, 77.79, 83.40, 77.06 and 77.52, respectively. But in percent removal efficiency of wastewater treatment by corn cob biochar 450^{o}C in 1/20 at day 2 was not detected. So it was out liner of this analysis.

Before treatment, the value of TKN was 46.50 mg/l. The residual of TKN in treatment by corn cob biochar 400^{o}C ratio1/20 had a trend reached a high of percent removal efficiency at day 2 then decreased. Figure 4.6 showed that in 1/20 ratio of corn cob biochar 400^{o}C was higher removal efficiency of canteen wastewater treatment by biochar more than 1/30 ratio of pineapple biochar 450^{o}C. Both of them were the best kind of canteen wastewater treatment in this study.

The report about biochar from sewage sludge at a high temperature can decrease total nitrogen in biohar (Shinogi, 2004). TKN included organic nitrogen and ammonia nitrogen. From precious study which biochar can adsorb ammonia so biochar can reduce ammonia (Zhou et al., 2017, Spokas et al., 2012 and Tanghizadeh- Toosi et al., 2012). Organic nitrogen is a solid and liquid phase. Moreover, biochar can retain total nitrogen in the porous (Ding et al., 2010; Cayuela et al., 2013). Biochar can reduce cumulative of total nitrogen leached from the soil so biochar retain total nitrogen from water and biochar adsorb NO_3^-–N and NH_4^+–N from aqueous solutions (Yao et al., 2012; Wang et al., 2015). Reduce ammonia of Brazilian pepperwood and peanut hull biochar at 600^{o}C were 34.7 % and 14 % of removal efficiency by column experiment (Yao et al., 2012)

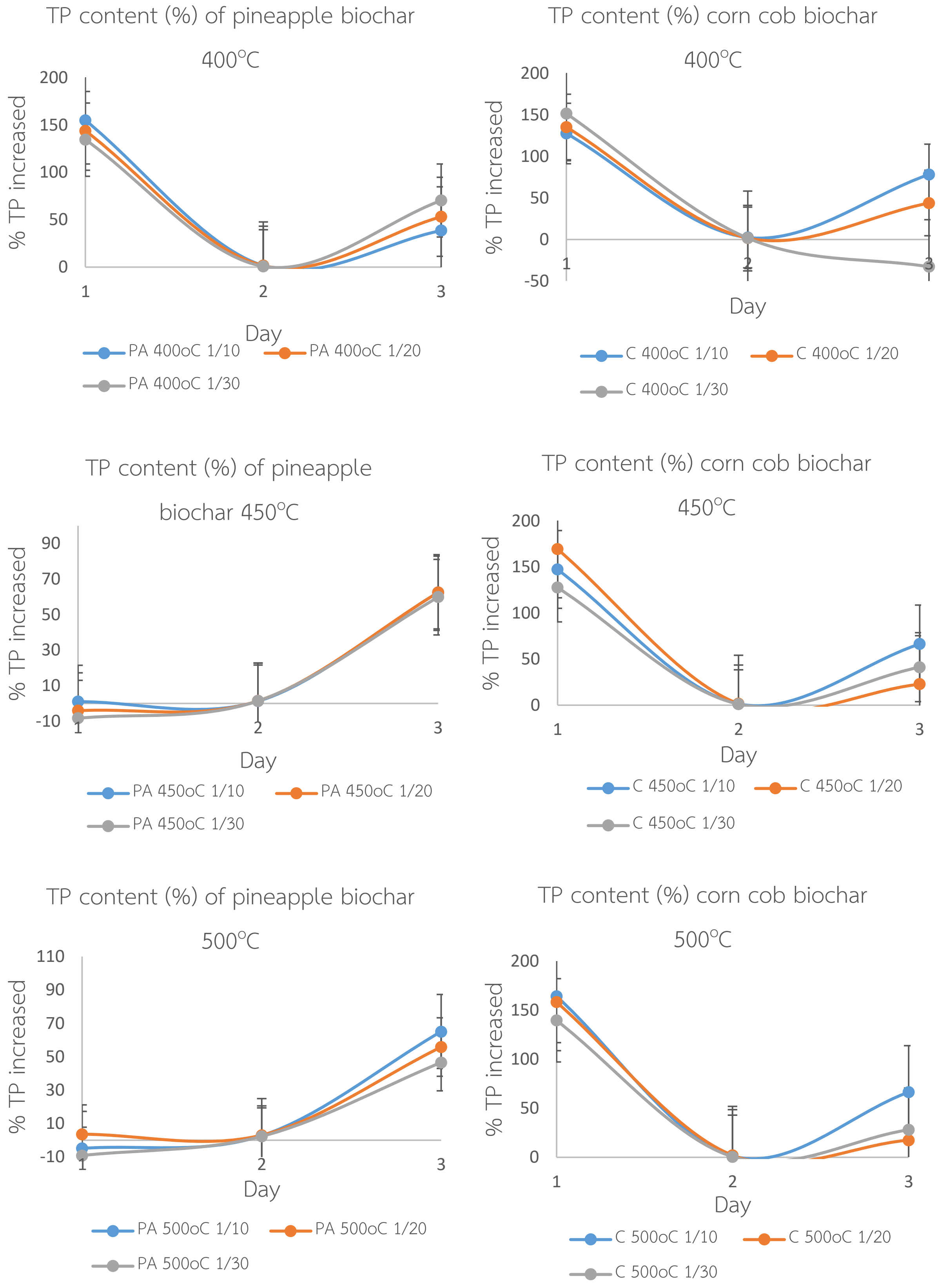


Figure.4.4 TP content after treatment by biochar

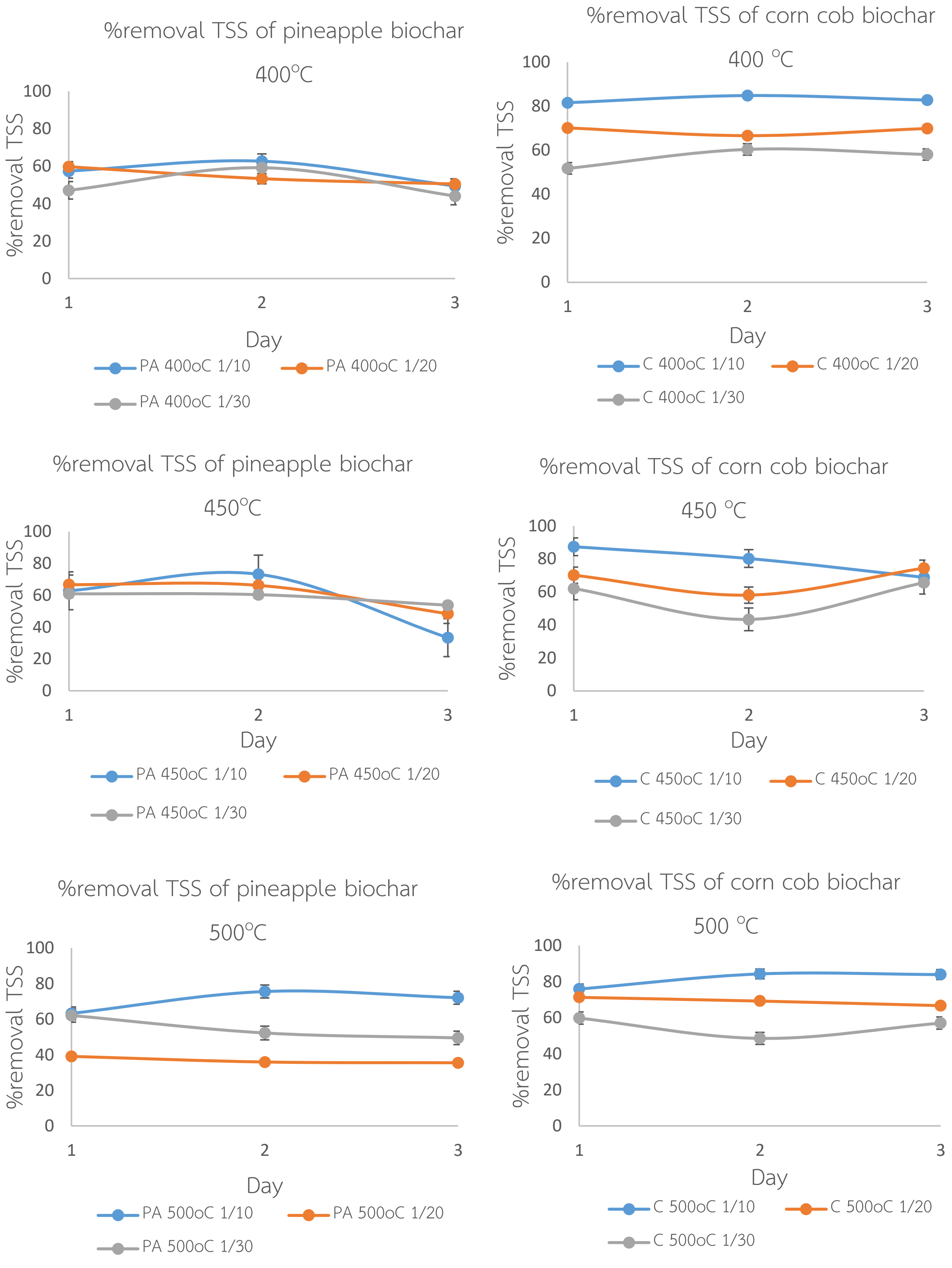


Figure.4.5 Removal efficiency of TSS after treatment by biochar

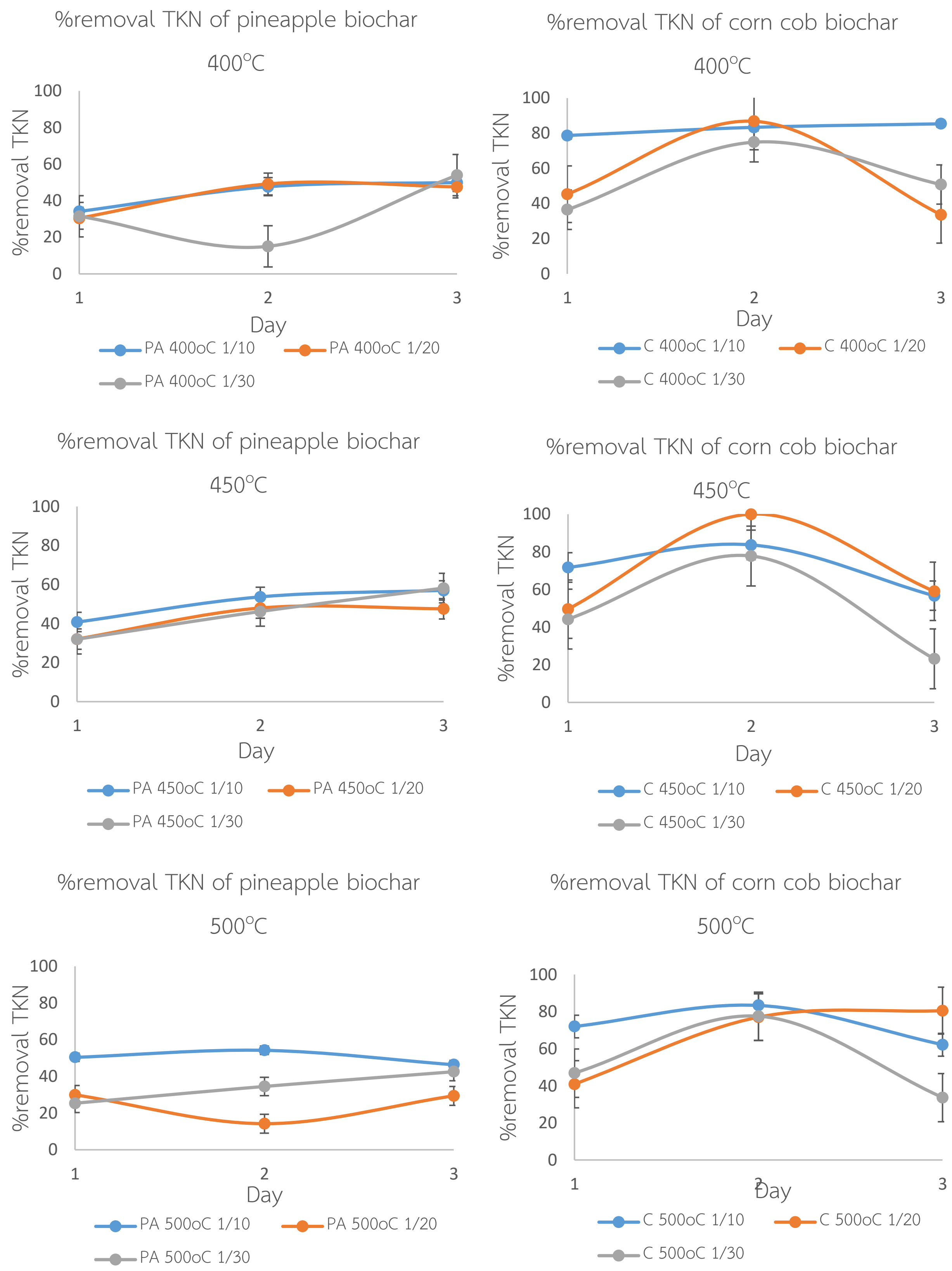


Figure.4.6 Removal efficiency of TKN after treatment by biochar

4.2.5 Oil and grease

The result after treatment by biochar shows in figure.4.7. The horizontal axis is the time of treatment. The vertical axis is the percent removal of O&G. In the right of paper is canteen wastewater which is treated by corn cob biochar. And in the left of paper is canteen wastewater which is treated by pineapple biochar. O&G in canteen wastewater treatment by biochar in 1-3 days was significant ($P \leq 0.05$). The line graph illustrates the removal efficiency of canteen wastewater treatment by biochar in day 1 to the end day 3, divided by the ratio 1 g. of biochar in 10ml. canteen wastewater, 1 g. of biochar in 20ml. canteen wastewater and 1 g. of biochar in 30ml. canteen wastewater. The removal efficiency of wastewater treatment by biochar at pineapple biochar 400° C in ratio 1/10, 1/20 and 1/30 at high value day were 45.12, 81.44 and 87.14%, respectively. The removal efficiency of wastewater treatment by biochar at pineapple biochar 450°C in ratio 1/10, 1/20 and 1/30 at day 3 were 84.29, 91.79 and 90.36%, respectively. The removal efficiency of wastewater treatments by pineapple biochar 500°C in ratio 1/10, 1/20 and 1/30 at day 2 were 72.95, 76.80 and 63.75%, respectively. The removal efficiency of wastewater treatment by biochar at corn cob biochar 400°C, corn cob biochar 450°C and corn cob biochar 500°C at day 1- 3 fluctuated and in ratio 1/10, 1/20 and 1/30 at high value of O&G removal day were 90.23, , 66.79, 71.72, 86.24, 46.34, 84.84, 81.43, 54.91 and 75.65, respectively.

Before treatment, the value of O&G is 132.5 mg/l. The residual of O&G in treatment by pineapple biochar 450°C ratio1/20 has a trend increasing hit a low of O&G removal efficiency value on the second day then increased. Figure 4.7 showed that in 1/20 ratio of pineapple biochar 450°C was higher removal efficiency of canteen wastewater treatment by biochar more than 1/10 ratio of corn cob biochar 400°C. This study, both of them were the best kind of canteen wastewater treatment.

O&G were removed by adsorption of biochar. From the other study found that oil and grease was reduced to below a standard of standard value (set by the department of environment Malaysia) by adsorption but the Palm Oil Mill effluent had a low level before treatment (Lam et al., 2018). The removal efficiency of orange peels at 500°C was 57 % (Lam et al., 2018) which removal efficiency was lower this study.

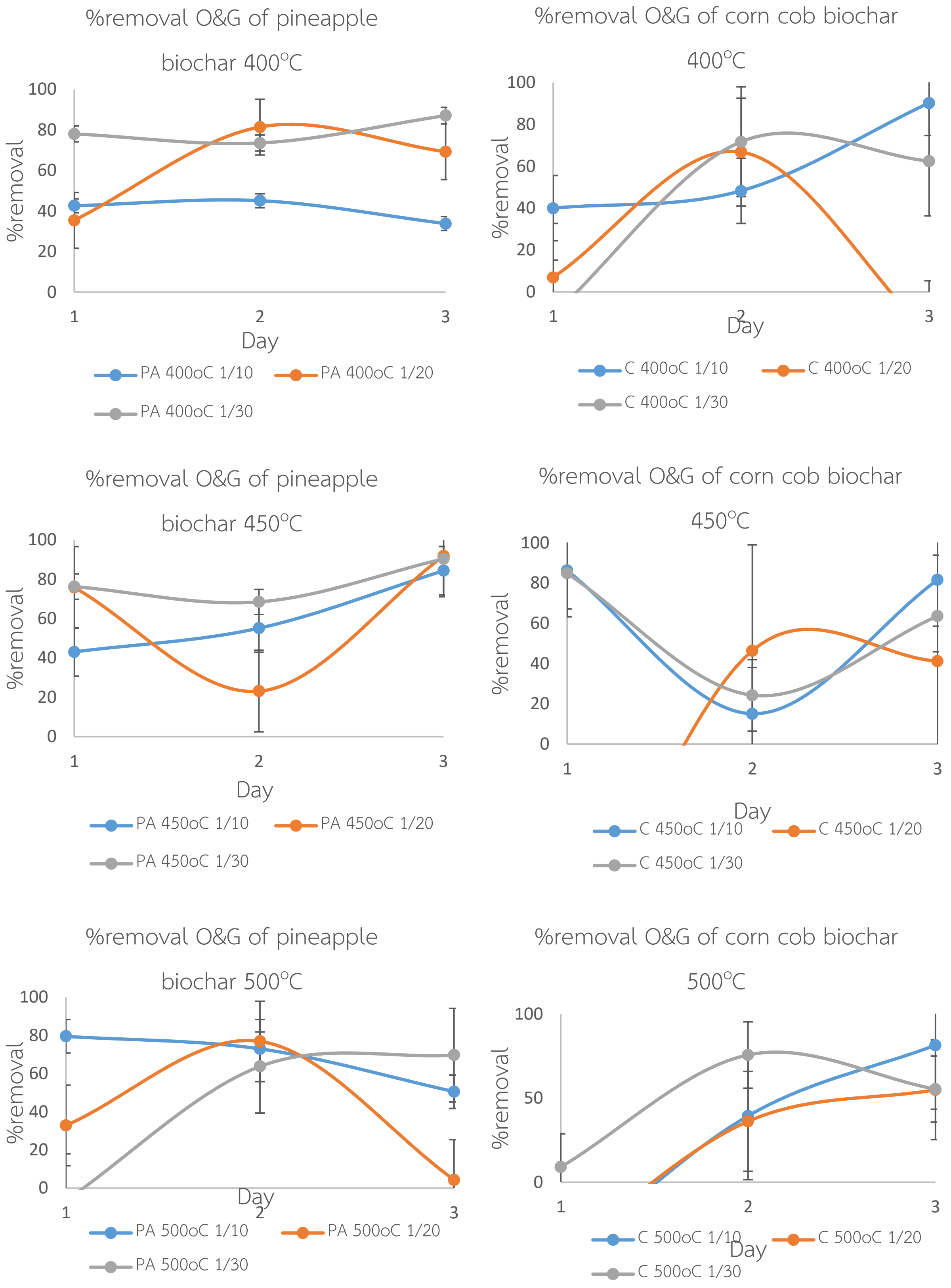


Figure.4.7 Removal efficiency of Oil and grease after treatment by biochar

Figure.4.8 Biochar after treatment canteen wastewater

Table 4.3 shows the best from the comparison between corn cob biochar and pineapple biochar results on the wastewater parameters included BOD, COD, TSS, TN, TP, pH and O&G used to compare the untreated canteen wastewater, compare discharge standard of domestics (PCD, Thailand) and wastewater treatment applied biochar. The wastewater parameters by using biochar treatment show the significantly lower concentration of BOD, COD, TSS, TN, pH, and O&G than the untreated canteen wastewater. Thus biochar had potential about reducing the concentration parameter of canteen wastewater. The values of BOD, COD, TSS, TP, and O&G still above the discharge standard of domestics after day 3 of treatment so should add the secondary treatment for treat canteen wastewater. On the other hand, the concentration of TKN was reduced by biochar treatment until the value below the standard in the first days of treatment. Moreover, the value of pH adjusts to a range of standard after one day. Because biochar has significantly about adjusted pH from 4.2 to 5.93 and from this study biochar has a pH in base phase (9.4 and 8.2) (Van Zwieten et al., 2010)

The removal efficiency of applied corncob biochar at 400°C to treatment canteen wastewater found about -78.31 to 90.23% at 3 day. The removal efficiency at 3 day for BOD, COD, TSS, TN, TP, and O&G sorted efficiency O&G> TKN> TSS> BOD> COD> TP respectively from higher to lower.

Table 4.3 Parameter of canteen wastewater before and after treatment

Waste water parameter	Standard	Canteen wastewater	Treated by corn cob biochar 400°C (1/10) at 3 day	% removal (compare with control) at 3 day
BOD (mg./L)	20	2425	437.5	80.34
COD	-	6857.1	1333.33	75.87
pH	5.5-9.0	4.93	6.77	
TKN (mg./L)	20 (TN)	46.5	3	85.38
TP (mg./L)	2	30.3	30.1	-78.31
TSS (mg./L)	30	420	80	82.80
O&G (mg./L)	5	132.5	12.63	90.23

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Biochar from corn cob and pineapple peels was produced by pyrolysis process which yield of biochar was 29.24-46.34%. Comparison of application of biochar between corn cob and pineapple peels biochar for wastewater treatment found that corn cob biochar at 400°C had high efficiency for canteen wastewater treatment. Corn cob biochar had surface area 7.685 m^2/g and total pore volume 0.15 cc/g form BJH method. The corn cob biochar at 400°C showed removal efficiency for BOD, COD, TSS, and O&G of canteen wastewater was 75.87-90.23% but the value was not acceptable level of the domestic standard. The corn cob biochar at 400°C was effective for TKN removal and increased pH to acceptable level of domestic standard. However, application of corn cob biochar at 400°C for TP removal was not effective. The optimal condition in this experiment of canteen wastewater treatment is corn cob biochar at 400°C in ratio 1:10 (biochar: wastewater) within 3 day.

5.2 Recommendations

5.2.1. Biochar can be applied for treatment of canteen wastewater but some parameters of the effluent were not meet the acceptable level of domestic standard so secondary treatment should be conducted.

5.2.2. The new kinds of agriculture wastes should be used to prepare the biochar for enhancing the wastewater treatment.

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Appendix A

Preparation of equipment

Preparation of equipment before pyrolysis

- Basin
- Bag (Polyethylene size 46 * 70 cm.)
- Cutting board
- Garbage bag
- Knife
- Muffled furnace
- Tray
- Oven (WTB BINDER FD115) Sieve 2 mm.

Preparation of equipment

- COD reactor
- Desiccator
- Filter paper: Whatman no.1, Whatman no.40
- pH meter
- Shaker
- Vaccuum pump
- Parafilm
- Hot air oven
- Muffle furnace
- Balance
- Water bath
- Evaporation dish
- Measuring cylinder
- Glassware : Beaker, Erlenmeyer flask, Buret, pipette, Volumetric flask
- GF/C filter (Diameter 4.7 cm.)
- Buchner funnel
- Dropper
- Suction flask
- Forceps

- BOD bottle
- Extraction thimble
- Cotton
- Digester
- Cuvettes
- Distillatory

Preparation of reagents

- Hydrochloric Acid (HCl)
- Sodium hydroxide (NaOH)
- Phosphate buffer solution ($MgSO_4.7H_2O$)
- Calcium chloride ($CaCl_2$)
- Ferric chloride hexahydrate ($Fecl_3.6H_2O$)
- Mercuric sulfate ($HgSO_4$)
- Pottassium dicromate ($K_2Cr_2O_7$)
- Sulfuric acid (H_2SO_4)
- Ferroin indicator
- Ammonium Ferrous Sulfate (FAS)
- Potassium hydrogen phthalate (KHP)
- n-Hexane
- Diatomaceous-silica filter aid suspension
- Digestion reagent (K_2SO_4 and $CuSO_4$)
- Sodium hydroxide-Sodium thiosulfate reagent
- Phenolphthalein indicator
- Sodium tetraborate ($Na_2B_4O_7.10H_2O$)
- Potassium antimony tartrate solution
- Ammonium molybdate solution
- Ascorbic acid
- Combined reagent
- Anhydrous potassium dihydrogen phosphate
- Manganese sulphate
- Sodium thiosulfate

COD

- Dilution of sample 1ml. sample of 25 ml. water and add 2.5 ml. to digestion of bottle
- Added 0.1 N 2.5 ml. of Pottassium dicromate ($K_2Cr_2O_7$) in digestion of bottle
- Added 3.5 ml. sulfuric acid (H_2SO_4) at slow in digestion of bottle
- Used digestion of bottle connect with reflux at 150 ^{o}C for 2 hour then close system
- Poured digesting effluent to erlenmeyer flask and Titration effluent with 0.1N ferrous ammonium sulphate (FAS) by using ferroin indicator (blue to brown)
- Used distilled water for blank comparation
- Calculated by equation

$$\mathrm{COD(mg/l)} = \frac{(A-B)\times M\times 8000}{V}$$

A = Volume of FAS for titrating blank (ml.)

B = Volume of FAS for titrating sample (ml.)

M = Concentration of FAS (Normality)

$$\mathrm{M(N)} = \frac{\mathbf{5.0\times 0.1}}{FAS(ml.)}$$

M = Concentration of FAS (Normality)

FAS = Volume of FAS for titrating (ml.)

BOD

Direct analysis BOD method

- Setting water sample to pH=7 by NaOH or HCl
- Added oxygen until saturated zone at 20oC stored in BOD bottle and closed in distilled water about 3 bottle
- Finding DO from first bottle (assumed DO_0)
- Stroed 2 bottle at 20 oC for 5 days and finding DO (assumed DO_5)
- Calculated by equation

BOD (mg/l) = DO_0-DO_5

DO_0 = DO at frist day (mg/l)

DO_5 = DO at fifth day (mg/l)

DO

- Added 1 ml. manganese sulphate and 1 ml. alkaline iodide azide while the dropper is under the sample water.
- Closed the bottle then shaked them at least 15 times.
- Waited until they precipitation
- Opened the bottle and added sulfuric acid
- Closed the bottle then shaked them at least 15 times.
- Waited until they precipitation
- Calculated volume of example for titrating
- Used volume of example for titrating into erlenmeyer flask
- Titrated with standard of 0.025 N sodium thiosulfate until solutions become yellow solution
- Added starch solution
- Titrated until colorless
- Calculated by equation

  DO (mg/l) = Volume of sodium thiosulfate for titrating (ml.)

Indirect analysis BOD method

Table Choosing volume of sample and dilution ratio for each range of BOD

volume of sample	range of BOD	dilution ratio
20,000-70,000	0.01	0.1
10,000-35,000	0.02	0.2
4,000-14,000	0.05	0.5
2,000-7,000	0.10	1
1,000-3,000	0.20	2
400-1,400	0.50	5
200-700	1.00	10
100-350	2.00	20
40-140	5.00	50
20-70	10.00	100

10-35	20.00	200
4-14	50.00	500
0-7	100.00	1,000

About BOD = 60 percent COD

- Choosing percent dilution
- Used volume of sample water up to choosing percent dilution
- Added water until solution will be 1 l.
- Used tube suction sample water to BOD bottle
- Closed the bottle in distilled water about 3 bottle
- Finding DO from first bottle (assumed DO0)
- Stroed 2 bottle at 20 oC for 5 days and finding DO (assumed DO5)
- Diluted 2 condition lower and upper choosing percent dilution
- Calculated by equation

$$\text{BOD (mg/l)} = DO_0 - DO_5$$

DO_0 = DO at frist day (mg/l)

DO_5 = DO at fifth day (mg/l)

TSS

Preparation of evaporating dish

- Baked evaporating dish at 103-105 oC for 1 hour
- Stored in desiccator

Analysis TSS

- Baked GF/C at 103-105 oC for 1 hour until weight constant and balanced evaporating dish by analytical balance (assumed A g)
- Placing GF/C on buchner funnel which connected vacuum pump
- Used distilled water rinse GF/C
- Mixed water sample about 50-100 ml and filted water sample with GF/C on buchner funnel which connected vacuum pump

- Rinsed GF/C by distilled water 3 times
- Baked GF/C which was used at 103-105 oC for 1 hour or until weight constant and stored in desiccator
- Balanced evaporating dish by analytical balance (assumed B g)
- Calculated by equation

$$TSS(mg/l) = \frac{(A-B)\times 1000}{V}$$

A = Weight of GF/C filter paper (gram)
B = Weight of GF/C filter paper and soild (gram)
V = Volume of water sample (liter)

Oil and Grease

- Used calico on filter cone and put filter paper onto buchner funnel which connected vacuum pump
- Used 100 ml. water sample for filter then rinsed by 500 ml of distilled water
- Waited until the filter dried
- Used forceps pick the filter paper and rolled into the thimble
- Used cotton which there was hexane wiped buchner funnel and put into the thimble
- Baked the thimble at 103 oC for 30 minutes
- Stored in desiccator
- Getting the thimble on extraction cup and balanced them (assumed B g)
- Used the thimble on extraction cup connected Soxhlet extractor then extracted by hexane 70 ml
- Baked the thimble on extraction cup at 103 oC for 1 hour and stored in desiccator (assumed A g)

$$Oil\ and\ Grease\ \frac{=[(A-B)-(X-Y)]\times 1000}{V}$$

A = Weight of extraction cup before experiment (gram)

B = Weight of extraction cup after experiment (gram)

V = Volume of water sample (liter)

TP

Digestion method

- Added sample water about 25-100 ml. into the kheldahl tube
- Added sulfuric acid 1 ml. and Nitric acid 5 ml.
- Digested until get clear soluton
- Added 1 drop phenolphthalein indicator and 1 molar sodium hydroxide until there was pink solution

Ascorbic Acid Method

- Pipette 50 ml. of sample water into 125 ml erlenmeyer flask
- Added 1 drop phenolphthalein indicator and 5 N sulfuric acid each drop until red removing
- Added 8 ml. combined solution then mixing them
- Waited 10 minute but don't more 30 minute
- Measured absorbance by spectrophotometer at 800 nm.
- Setting zero by blank
- Setting standard phosphorus by preparing 20 ml. standard solution which there are concentration of 0.1-2.0 mg/l. from phosphate 5.0 mg/l. (as table)
- Measured absorbance by spectrophotometer at 800 nm.

Table Standard of phosphate

End concentration	Volume of standard solution	Volume in volumetric flask
0.1	1.0	50.0
0.2	2.0	50.0
0.4	4.0	50.0
0.8	8.0	50.0
1.0	10.0	50.0
2.0	20.0	50.0

$$TP = \frac{P\times 50}{V}$$

A = Standard curve (microgram)

V = Volume of water sample (mililiter)

TKN

- Selected volume from table for optimal nitrogen
- Added 4-5 glass bead for protecting severe boil in digestion of bottle
- Added 50 ml solution for extraction in the kheldahl tube
- Boiled to remove SO2 until getting clear solution then boiled for 20-30 minutes
- Closed and waited until cooling
- Added 300ml. distilled water and phenolphthalein indicator and mixing them
- Added 50 ml. Sodium hydroxide-Sodium thiosulfate reagent per 50 ml. solution for extraction at slow rate until there is pink solution
- Distilled (the kheldahl tube connect distillator) the pink solution
- Added 200ml. distilled water and 32 percent Sodium hydroxide 80ml.
- Stored 200ml. of distilled solution in the flask containing 2 percent boric acid 50 ml.
- Titrated with 0.1 N sulfuric acid until pH 4.65

$$TKN = \frac{(A-B)\times 280}{V}$$

A = Volume of sulfuric acid for titrating sample (ml.)

B = Volume of sulfuric acid for titrating blank (ml.)

V = Volume of water sample (liter

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