PREPARATION OF BIOCHAR WITH PALM OIL MILL SLUDGE BY USING MICROWAVE FOR COPPER REMOVAL

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Environmental Engineering

Faculty of Engineering and Green Technology

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **PREPARATION OF BIOCHAR WITH PALM OIL MILL SLUDGE BY USING MICROWAVE FOR COPPER REMOVAL** was prepared by **LEE YAN BIN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Environmental Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

This study aims to prepare the bio-char from residues of palm oil mill sludge (POMS) after anaerobic digestion system through microwave pyrolysis method to remove copper. The two main parameters i.e. temperature, and holding time for the bio-char production were investigated to produce the bio-char. Results obtained were interpreted by response surface methodology. Properties of palm oil mill sludge, bio-char produced at 4, 6, 8, 10, and 12 minutes were determined in term of various functional groups. The optimum conditions for preparing bio-char from palm oil mill sludge were found to be 300 watts and 10 minutes, the maximum removal efficiency of the optimized POMS bio-char is 83%.

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LIST OF SYMBOLS / ABBREVIATIONS

C_I	Initial concentration of Copper
C_F	Final concentration of Copper
R (%)	Removal efficiency

POME	Palm oil mill effluent
POMS	Palm oil mill sludge
FFB	Fresh fruit bunch
EFB	Empty fruit bunch
DKC	Palm kernel cake
AC	Activated carbon
FC	Fixed carbon
VM	Volatile matter
RS	Raw sludge
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
FT-IR	Fourier Transform Infrared Spectroscopy

CHAPTER 1

INTRODUCTION

1.1. Palm oil production

Malaysia plays a major role in palm oil industry as world’s largest exporter of palm oil and second largest producer; while Indonesia is the world largest producer for palm oil industry in the world .The species of palm oil in Malaysia is Elaeis guineensis. Figure 1.1 shows at year 2010, Malaysia has contributed 16.99 Million tons of global oil palm production per annum; while Indonesia has produced 21.00 million tons of global oil palm production per annum. (MPOB and Oil World, 2011)

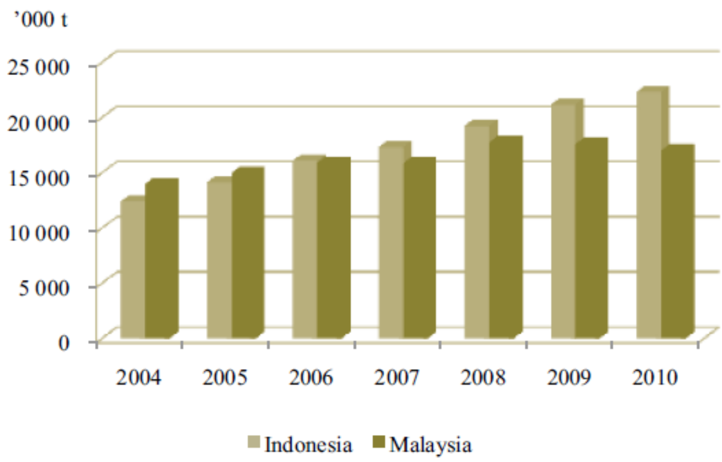

Figure 1. 1 Annual Palm Oil Production of Malaysia and Indonesia from Year 2004 to Year 2010(MPOB and Oil World, 2011)

1.2. Wastes generated from Palm oil production

Malaysia is one of the world largest palm oil producers, at the same time it also generated tons of wastes such as palm oil mill effluent (POME), empty fruit brunch, mesocarp fiber, fronds, trunk and shell. However, POME itself is considered as a major source of renewable energy, by-products from POME can be utilized by converting palm oil sludge to value added materials, for example, bio-char, bio-oil, fertilizer (Thangalazhy-Gopakumar et al., 2015). Palm oil sludge is normally disposed in palm oil plantation, which has contributed to environmental problem especially hygiene issues. (Thangalazhy-Gopakumar et al., 2015)

1.3 Bio-char

Bio-char is a by-product charcoal which produced from biomass thermochemical process, called pyrolysis. It has many applications, for example it can be used as a soil amendment for soil health improvement, store carbon in soil and improve soil properties by burying it in fields (Mohammad et al., 2014). Beside, bio-char also slacken the carbon release into atmosphere from degrading by carbon stabilization in to a form like charcoal. Furthermore, bioenergy produced from pyrolysis process is a potential substitute for fossil fuels. Palm oil mill sludge (POMS) itself is fibre rich product which is suitable for preparation of bio-char. Instead of abandon the POMS without reuse it, preparing bio-char from POMS is a better option which can save the resources and reduce the impacts from POMS to environment. Biopolymer is capable in lowering transition metal-ion concentration to part per billion (Thangalazhy-Gopakumar et al., 2015). Moreover, the solid product (bio-char) can also be used as soil amendment to improve the soil fertility. The bio-char in soil will act as sink for carbon dioxide in the atmosphere. Besides, it helps to retain nutrients in soil to prevent nutrient loss in soil. On the other hands, bio-char is a good absorbent which is excellent for metal or dyes removal (Thangalazhy-Gopakumar et al., 2015).

1.4 Heavy Metal

Increase of heavy metal disposal in Malaysia is mainly due to rapid industrialization. The increase flux of metallic materials in the aquatic environment is mainly due to the marvelous increase in the consumption of the heavy metals over the earlier few decades. The persistency of these heavy metal made them special to the environment. Human in the past few decades has dispose tons of hazardous wastes including heavy metal into water and polluted the water resource without awareness (Amuda, Giwa and Bello, 2007). Besides, human activities such as mining, smelting, electroplating and other industrial process that have residues on metal in their effluent would have high level of heavy metal content which will heavily pollute the stream (Chen and Jin, 2015). It severely threat living things .Most of the heavy metals disposed into water are considered toxic to aquatic life as well as human being, such as cadmium (Cd) and copper (Cu). If human expose to heavy metal, it will cause diseases such as malfunction of kidney or hypertension. Besides, some of the heavy metals are carcinogenic to human being. However, some of the metal is not harmful to human, such as zinc.

1.5 Problem statement

Malaysia's palm oil industry is growing rapidly, there are abundant mount of palm oil sludge waited to be processed after producing oil palm product. In order to take care of this large amount of palm oil sludge, alternate ways need to be figured out. Besides, anthropogenic activities in Malaysia also need serious attention due to these activities discharged tons of harmful materials such as toxic elements into aquatic environment. Copper, Cu is one of the toxic elements.

Preparation of bio-char was selected in my project study is because I found out the POME is a potential waste which can be convert into useful product to contribute in preserving our environment. In the other hand, palm oil sludge can be easily obtained from palm oil mill in Malaysia. Instead of using oven in traditional process of pyrolysis, microwave was used in my project study because it has shorter preparation time. Besides, it is far cheaper to produce than preparing traditional activated carbon.

1.6 Objectives

The objectives of this research study are:

a) To study the optimum parameters to prepare bio-char from palm oil sludge using microwave

b) To evaluate the adsorption performance of prepared bio-char

c) To study the characteristic of palm oil sludge bio-char.

CHAPTER 2

LITERATURE REVIEW

2.1 Palm oil mill Effluent

2.1.1 Types of Oil Palm Waste

After oil palm production process, product obtained from the process such as palm oil (Sulaiman et al., 2011) has high economic value. However other products such as empty fruit brunch, fibre and shell are no longer valuable for economic uses. These palm oil residues have contribute to biomass waste in Malaysia. In this case, several methods have been discovered to encounter this problem. For example, empty fruit bunches waste and palm kernel is used to produce bio-char (Thangalazhy-Gopakumar et al., 2015). In addition, palm fibre, palm kernel and shell are also by product from oil palm production. Palm oil mill effluent (POME) can be used for biogas production through anaerobic digestion system due to its high organic matter content (Sulaiman et al., 2011). Besides, it also can also dispose as soil amendment for oil palm plantation. Residue of POME can be pyrolysed through pyrolysis. In pyrolysis, the organic part of biomass can be converted into carbon rich product such as bio-char and bio-(Thangalazhy-Gopakumar et al., 2015). In addition, palm oil mill in Malaysia burn the palm oil fibre and shell in biomass residue to make sure the power supply to operate the production is sufficient (Sulaiman et al., 2011). Table 2.1 shows the available fresh and dry weight of fruit bunches shell, fibre and effluent in tons per hectare per year after processing 1 ha of mature palms from palm oil mill (Kosugi et al., 2010).

Table 2. 1 Products and By-product distribution in oil palm mill

	1 ha of mature palms	
	Fresh wt. (t/ha/year)	Dry wt. (t/ha/year)
FFB	20.08	10.60
EFB at 22% of FFB	4.42	1.55
Fibre 13.5% of FFB	2.71	1.63
Shell 5.5% of FFB	1.10	1.10
i) Sterilizer condensate 12% FFB ii) Clarification sludge 50% of FFB iii) Hydrocyclone washing 5% FFB	2.41 10.04 1.00	0.12 0.50 0.05
Total POME	13.45	0.67

2.1.2 Palm Oil Mill Sludge (POMS)

After treatment of the palm oil mill effluent (POME) discharge from the overall palm oil production process, the left solid phase product is as know as palm oil mill sludge (POMS). It consists of suspended solids and dissolved solids after the POME treatment.

POMS characteristics and properties must be studied and learnt in order to produce a quality bio-char. The quality of bio-char from POMS is strongly dependent on the physical and chemical properties. Table 2.1 shows physicochemical analytical result of raw POMS and empty fruit bunch for comparison. According to the Table 2.1, POMS have higher moisture content than empty fruit bunch, while empty fruit bunch has more total nitrogen than POMS.

Table 2. 2 Physicochemical Analysis of Raw POMS and EFB (Rupani, et al., 2010)

Parameters	Palm Oil Mill Sludge(POMS)	Empty fruit bunch (EFB)
Moisture content %	86	60
pH	8.4	6.7
Total Nitrogen (TN)	3.6	58.9
Phosphorus (as P_2O_5)	0.9	0.6
Potassium (as K_2O)	2.1	2.4

2.2. Bio-char

Bio-char is a type of carbon-rich dried biomass obtained from heating process, called pyrolysis. For example, wood, manure or wasted generated from industry activities. Recently, bio-char is gaining interest due to it can be widely utilize in many fields, for example soil remediation, agricultural and pollution control. It can be applied for both agricultural gains and carbon sequestration. On the other hand, bio-char is a good tool for slackening release of carbon to atmosphere. Besides, bio-char can improve soil properties and store carbon in soil by burying bio-char into the soil. Bio-char can also act as pollutant removals for aqueous solution due to its ability of absorb (Srinivasan et al., 2015).

2.2.1 Sources of feedstock for bio-char production

Bio-char is produced from many types of biomass, such as woody plant, sewage sludge, palm oil sludge and algae waste. For those woody plant such as rice straw and maple wood, after these plants contain fibre dried up, the leftover product will be lignocellulosic. Lignocellulosic is a material substance found in woody plant. It is mainly consist of cellulose, lignin and hemicelluloses and other substances which depend on biomass resources. Lignocellulosic is one of the major components of biomass product that is renewable and reusable, it is an environmental friendly product. (Wang et al., 2015); (Yuan et al., 2015)Due to the capability of conversion of lignocellulosic and its potential in bioconversion, it has been a hot topic for research now these years. On the other hand, during the production of palm oil fuel, the by-product biomass, sludge can be further processed into useful product such as bio-char to serve as adsorbent for wastewater treatment or soil amendment to enhance soil fertility. (Mohammed et al., 2011)Beside, the sewage sludge such as municipal solid waste and industrial waste can also be one of the feedstock for bio-char production.

Table 2.3 shows the types of bio-char which uses different source of feedstock. From this table, a conclusion can be made is most of the bio-char studied are using woody plant. Only one of the bio-char is made from palm oil mill sludge. Bio-char produced from palm oil mill sludge is chosen in this studied is because potential of palm oil mill sludge. According to table 2.3, recently the treatment of wastewater for heavy metal removal using bio-char is less likely to be studied. It has a high potential which can act as a replacement for activated carbon for heavy metal removal. It is much cheaper than activated carbon. This is why heavy metal removal using bio-char prepared from palm oil sludge is chosen in this study.

Table 2. 3 Source of feedstock for bio-char production.

Feedstock		**Parameter**				**References**
	Temperature or power	**Time(minutes)**	**Heating rate**	**Uses**	**Method**	
Palm oil mill sludge	800 °C	10	10,20,30,40 and 40 °C/min	Soil amendment and wastewater treatment	Pyrolysis	Thangalazhy-Gopakumar et al., 2015
Sewage sludge	300 °C	60	17 °C/ min	Adsorbents of arsenic and chromium in aqueous solution.	-	Agrafioti et al., 2013
Rice straw	500 °C	30	-	-	Pyrolysis	Xiao et al., 2015
Oak Sawdust	300 °C-600 °C	30	-	Adsorption of ammonium, nitrate and	Pyrolysis	Wang et al., 2014

				phosphate		
Cultured Algae waste	600 ^{o}C	60- 120(with sand additive) 180(without sand additive)	12 ^{o}C/ min	-	Pyrolysis	Sarkar et al., 2015
Pine wood	150 ^{o}C	720	-	Salicylic acid and ibuprofen removal	Pyrolysis	Essandoh et al., 2015
Water hyacinth	250 ^{o}C- 550 ^{o}C	60	6.5 ^{o}C/ min	Cadmium removal from aqueous solution	Pyrolysis	Zhang et al., 2015
Poultry litter	400 ^{o}C	480	-	Soil amendment	Pyrolysis	Huang et al., 2015
Kans grass straw	500 ^{o}C	120, 240	26 ^{o}C/ min	Arsenic Adsorption in	Pyrolysis	Baig et al., 2014

				aqueous solution		
Conocarpus	-	-	-	Soil amendment	-	Mohammad et al., 2014
Paper mill Sludge	200-700 ^{o}C	-	-	Bioavailability and eco-toxicity of heavy metal	Pyrolysis	Devi and Saroha, 2014
Switch grass	300 ^{o}C	30	7 ^{o}C/ min	Copper and cadmium removal in aqueous solution	Hydrothermal carbonization	Regmi et al., 2012

2.2.2. Theory of Microwave Heating and Conventional Heating

Conventional heating of bio-char is as know as normal process of pyrolysis. It is a thermal degradation of material in the absence of oxygen, and it converts raw material into reactive intermediate product. Conventional heating is a heating process applied on raw material via an external heating source. It heat up the material by applying heat through the surface of material. Different process condition yield different end product from pyrolysis. However, high pyrolysis temperature will result in thermal cracking of the material (Salema et al., 2013).

For microwave assisted pyrolysis, microwave transfer the heat energy to the biomass through the interaction of molecules within biomass. Furthermore, microwave cause dipolar molecules of biomass to attempt to rotate in phase with the alternating field of microwave during heating process of biomass. Comparing with conventional heating, microwave has the advantages which the heat is generated within the material rather than from external heating source, which resulting in rapid heating and high heating efficiency (Hoseinzadeh Hesas et al., 2013)

2.2.3. Bio-char Production

There are three methods to prepare the bio-char, which are pyrolysis, gasification and hydrothermal carbonization .These three processes are recognizing as biomass thermo-chemical processes. It not only produces bio-char but also bio-oil and tar with yield depend on the process condition. Table2.4 shows the summary of biomass conversion process. There are 3 types of pyrolysis, which are fast pyrolysis, intermediate pyrolysis and slow pyrolysis. Different process of pyrolysis has different outcome of product. For fast pyrolysis, the biomass was heated rapidly in a short while with moderate temperature (500 ℃), which still contain high percentage of liquid than solid. However, slow pyrolysis is the ideal way to generate bio-char, because it contains highest percentage of solid (Ameloot et al., 2013).

Table2.4 Summary of biomass conversion process, pyrolysis

Mode	Condition	Liquid (bio-oil)	Solid (bio-char)	Gas (Syngas)
Fast pyrolysis	Moderate temperature (~500 ^{o}C) Short vapour residence time (<2 s)	75% (25% water)	12 %	13%
Intermediate pyrolysis	Low-moderate temperature	50% (50% water)	25%	25%
Slow pyrolysis	Low-moderate temperature Long residence time	30% (70% water)	35%	35%
Gasification	High temperature (>800 ^{o}C) Long vapour residence time	5% tar (55% water)	10%	85%

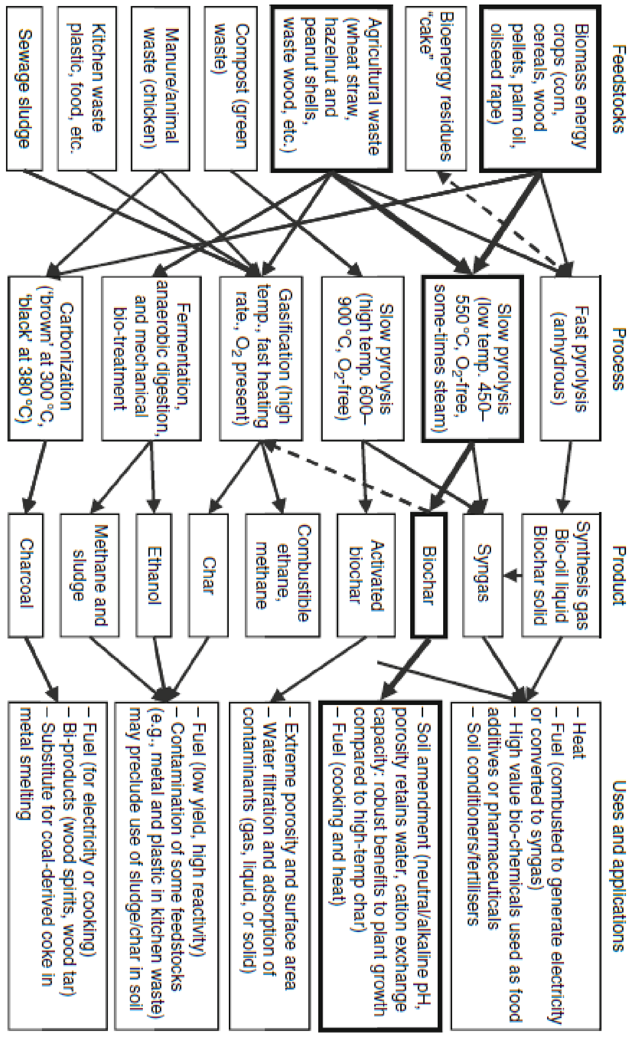

Figure2.1 Bio-char and other products of thermal conversion of biomass according to current technologies and feedstock.

In the case of preparation of bio-char, conventional pyrolysis is commonly used. According to (Dutta et al., 2015), using microwave to carry out pyrolysis is much convenient and faster than using oven. For conventional pyrolysis, the heating mechanism is from the surface towards the core of the material, it has affect the rate of cooling of bio-char, in turn also significantly affects the final structure of bio-char. It has been stated that, slow cooling of bio-char results in further pyrolysis, although heating process of biomass has stop, thus it will results in loss or carbon, which causes hardening of the normal hydrophobic bio-char and reduce the efficiency of bio-char in soil application. In the case of pyrolysis using microwave, the heat is generated by conversion of electromagnetic energy into thermal energy through volumetric method. The higher the microwave power, the higher the penetration of microwave, thus leads to higher temperature in the centre than the surface of material. Therefore, use of microwave pyrolysis is more favorable than conventional pyrolysis due to the devolatilisation reaction of biomass (Dutta et al., 2015).

2.2.4. Characteristic of sludge based Bio-char

During the preparation of bio-char, characteristic of materials must be learnt in order to achieve a better result of bio-char, such as physical and chemical properties of bio-char. Thus, both physical and chemical properties of bio-char need to be analyzed in order to ensure the precision and reliability of it.

Physical properties provide the data in term of bio-char yield, surface area, surface morphology, carbon content and physical structure, while functional group and chemical content are characterized as chemical properties which the moisture content, ash content, volatile matter, fixed carbon and function group of bio-char. Different feedstock of biomass produce different characteristic of bio-char.(Luo et al., 2014)

Increase in temperature will lead to surface area of bio-char increases, which facilitates the high adsorption of chemical such as heavy metal. For example, a bio-char made from wheat biomass at temperature of 500- 700 degree Celsius was well carbonized and its surface area is relatively high (>300m^2/g); whereas chars formed at 300 to 400 degree Celsius were partially carbonized and with small surface area (<200m^2/g) (Xiao et al., 2015).Therefore, the former will have higher absorption capability for chemicals. Figure 2.3 shows the characteristic of wastewater sludge characteristic of wastewater sludge bio-char produced is various temperature. When the temperature increase, only the ash percentage has increase, but bio-char yield, moisture content, volatile matter and fixed carbon has decreased.

Table 2.5 Bio-char Yield, Proximate and Ultimate Properties of Wastewater Sludge and Sludge Bio-char at Various Temperatures (Hossain et al., 2010)

	Unit	Wastewater sludge	Sludge bio-char			
			300 ^oC	400 ^oC	500 ^oC	600 ^oC
Bio-char yield	%		72.3	63.7	57.9	52.4
Moisture	%	7.6	4.3	4.2	3.5	3.4
Ash	%	34	52.8	63.3	68.2	72.5
FC	%	8.2	9.1	6.8	7.6	8.3
VM	%	50.2	33.8	25.7	20.7	15.8
H	%	4.47	2.55	1.28	0.88	0.51
N	%	3.27	3.32	2.40	2.13	1.20

In the aspect of chemical properties, bio-char is commonly contains of nutrient such as phosphorus and nitrogen due to it is made of sludge from plants waste. When the temperature increases from 300 to 700 degree Celsius, the amount of nitrogen in wastewater sludge decreased by 55%. Besides, it also contain of trace element and microorganism.

Table 2.6 shows that the total concentration of other nutrient element contained in wastewater sludge and sludge bio-char. Table 2.7 also shows that concentration of heavy metal increases when the pyrolysis temperature has increased.

Table 2.6 Heavy Metals Present in the Raw Sludge and Sludge Bio-char at Various Temperatures (Hossain et al., 2011)

Elements	Description	Raw Sludge	Temperature			
			300 ^{o}C	400 ^{o}C	500 ^{o}C	700 ^{o}C
As		<3	<3	<3	<3	<3
Cd	Mean	2.07	2.62	2.8	3.17	3.22
Cr		81	107.5	112.5	112.5	83
Ni		70	182.5	165	292.5	195
Pb		86.5	115	130	140	132
Se		<6.6	<6.6	<6.6	<6.6	<6.6

Table 2.7 Total Nutrients in wastewater sludge

Elements	Description	Unit	Raw Sludge	Temperature			
				300 ^{o}C	400 ^{o}C	500 ^{o}C	700 ^{o}C
Ca	Mean	%	3.02	3.47	4.17	4.62	5.35
Fe			6.17	7.8	8.85	10.15	11
Mg			0.33	0.35	0.43	0.46	0.54
S			5.17	4.47	4.72	5.9	6.17
Cu		Mg/kg	810	1150	1125	1325	1500
Zn			1350	1675	1825	2100	2175

2.2.5. Utilization of bio-char

After so many years research of bio-char, bio-char can be widely utilized in many fields. It is an important role for water treatment .It is because of the large specific surface area, porous structure, surface functional group of bio-char which had promote high removal efficiency of contaminants of bio-char. The contaminants include heavy metal, organic pollutant and other pollutants. Besides that treatment of aqueous solution, bio-char made from palm oil sludge can be used as fertilizer and soil amendment (Thangalazhy-Gopakumar et al., 2015).

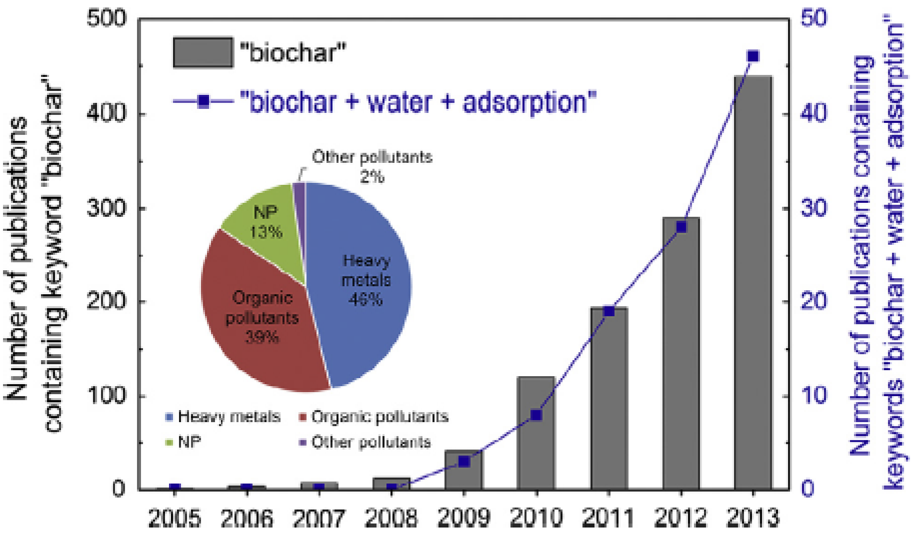

Figure 2.2 Number of journal articles concerned application of bio-char in water treatment (Tan et al., 2013)

Figure 2.1 shows the uses of bio-char in water treatment. According to the graph the, amount of application of bio-char for applied water treatment is increasing from year 2005 to year 2013. A total 46 % of bio-char was used for heavy metal removal, while there is 39%, 13% for NP, and 2% for other pollutants.

According to the Figure 2.1, heavy metal removal has been used widely which is more than 40 %, therefore, bio-char has high potential in heavy metal removal in aqueous solution. Thus, preparation of palm oil sludge bio-char for heavy metal removal is chosen in this studied.

2.3. Heavy Metal

In the past few decades until today, the rapid development of industrial and agricultural together with the population growth has threatened human health and ecological system because of the abundant harmful heavy metals can be found in water resources such as river. Heavy metal is one of the most toxicological relevance substances that can be found in the industrial and agricultural effluent (Ahmad and Shuhaimi-O, 2010). These heavy metals are non- degradable and ionic substances. Numerous tactics such as physical, chemical and biological methods including adsorption, bio-sorption, precipitation, ion-exchange, reverse osmosis, filtration and other membrane separation are used for heavy metal removal (Al-Shannag et al., 2014).

2.3.1. Copper

Copper is used widely in domestic and industrial application. It is also a vital element in mammalian nutrition as an element of metalloenzymes in which acts as an electron donor or acceptor. However, exposure to high level of copper can consequence in a number of adverse health effects. For example, high copper intake might cause genetic predisposition or disease. Besides, it also associated indirectly neurological disorders such as Alzheimer’s disease and prion diseases. Expose of human to copper frequently occurs from the consumption of food and drinks. (Stern, 2010)

Due to growing in industrial activities in Malaysia, chances of discharging contaminated effluent which contained toxic element such as copper has increased. This phenomenon has greatly affect aquaculture activities; due to discharge contaminated effluent into stream has posed risk to aquaculture food products such as fishes to be contaminated. High level of copper has been discovered in fish liver from river in Malaysia.

2.3.2. Heavy Metal Removal Methods

Numerous methods have been used for heavy metal removal in wastewater such as adsorption, chemical precipitation, chemical coagulation, ion-exchange, electrochemical methods and membrane process and ultrafilteration.

Table 2. 8 Comparison of method for heavy metal removal in wastewater

No.	Methods	Advantages	Disadvantages	References
1	Adsorption (Using Activated carbon)	• High efficiency in heavy metal removal (99%)	• Cost of activated carbon • No regeneration • Performance depends upon adsorbent.	Zhang et al. 2015
2	Adsorption (Using residue of bio-mass)	• Relatively cheap	• Still under development	DONG and LIN, 2015
3	Chemical precipitation	• Simple • Inexpensive • Can remove most of the carbon	• Large amount of sludge produced • Disposal problems	Bhatluri et al., 2015
4	Chemical coagulation	• Sludge settling • Dewatering	• High cost • Large consumption of chemicals	Guillermo et al., 2014
5	Ion-exchange	• High regeneration of materials • Metal selective	• High cost • Less number of metal ions removed	Roman et al., 2011
6	Membrane process	• Less chemical	• High initial	Zhu et al.,

	and ultrafiltration	consumption • High efficiency	running and cost • Low flow rates • Removal decreases with the presence of other metals	2015

2.3.3. Copper removal by bio-char

Copper removal is the main focus in this study. There are many types of copper removal other than bio-char. For example use activated carbon as adsorbent to remove the copper in aqueous solution. Besides, copper that exist in water can be easily removed use membrane technologies. (Bao et al., 2015) According to the (Regmi et al., 2012), bio-char prepared from switch grass via hydrothermal carbonization were used for comparison with activated carbon for copper removal in aqueous solution. This journal shows that the efficiency of copper removal using bio-char were nearly 100% close to activated carbon. (Regmi et al., 2012) Properties of switch grass are same as palm oil mill sludge as they are rich in fibre. Therefore, palm oil mill sludge based bio-char will be tested in this study.

CHAPTER 3

METHODOLOGY

3.1. Materials

Table 3.1 Materials

Material	Sources	Supplier
Copper	Copper 2 sulfate-5-hydrate	Bendosen
N_2	HiQ Nitrogen 5.0 Zero	LINDE Malaysia

3.1.1. Palm oil mill sludge(POMS)

Palm oil mill sludge that used in this experiment was obtained from Tian Siang Oil Mill (Air Kuning) Sdn Bhd in Air Kuning, Perak, Malaysia. The palm oil mill sludge obtained was from the anaerobic digestion system which is part of the wastewater treatment. It is used for bio-char preparation.

3.1.2. Heavy Metal

Copper is the heavy metal that is used in this study and it was supplied from Bendosen. It was chosen to evaluate the performance of bio-char that prepared from experiment.

3.1.3. Gases

Nitrogen gas was used for pyrolysis process using microwave to produce bio-char.

3.1.4. Material preparation process

The collected palm oil mill sludge was first dried under the sun until hard and stiff. It took about 3 days to dry under sun. After dried under the sun, it was dried in oven at temperature of 105 ^{o}C for 24 hours to further remove moisture of sludge. After all, it was crushed and sieved to 1-2mm and stored in air-tight container to avoid moisture build up and fungal infection.

3.2. Equipments

3.2.1. Microwave(pyrolyzer)

Microwave was used to prepare bio-char. Power controller on the microwave is used to adjust to dedicate power, which can achieve the desire temperatures. Besides, the convenience of microwave is it has a timer which can set the desire times. Samples were put in the crucible and then place into microwave for pyrolysis for certain time. Moreover, there is nitrogen gas flow meter which place besides the microwave to control the gas flow of nitrogen gas into microwave. Adjusted nitrogen flow was purged into microwave consistently through three control valves during pyrolysis. It is to make sure no or low oxygen in the environment of pyrolysis inside microwave. Figure 3.1 shows the microwave used for bio-char preparation.

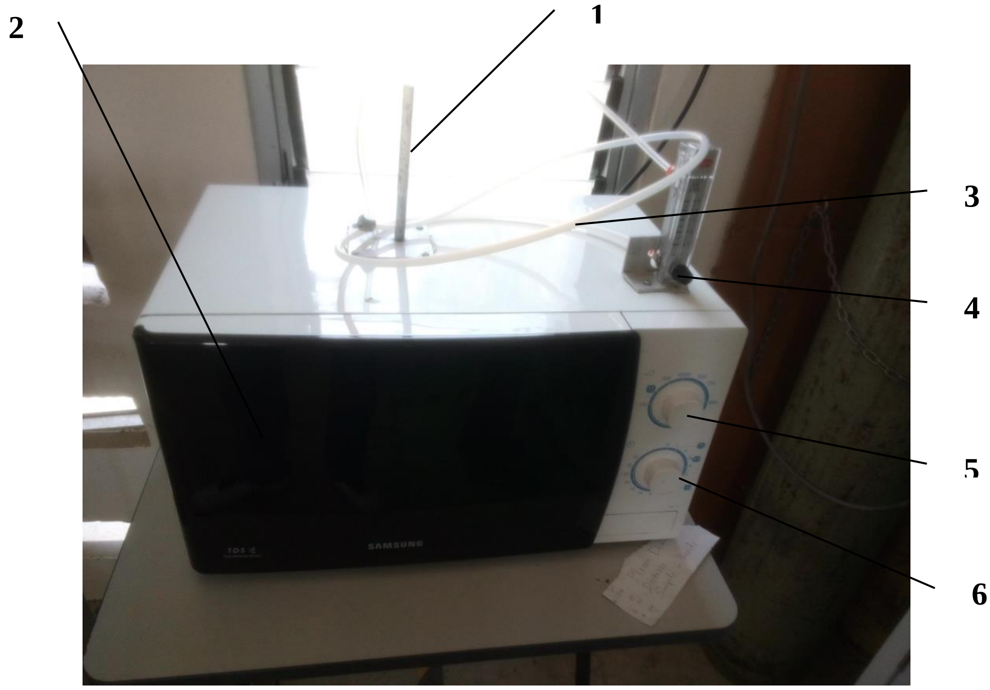

Figure 3. 1 Microwave for bio-char preparation

Table 3. 2 Label of Microwave

Number	Description
1	Nitrogen gas outlet
2	Microwave
3	Nitrogen gas flow tube
4	Nitrogen gas flow meter
5	Power control
6	Timer

3.2.2. Orbital Shaker

Electronic shaker (IKA KS 260 B S2, Germany) was used to provide and make sure well mixing of bio-char and heavy metal contained aqueous solution. It consists of timer and rotational speed adjuster.

3.2.3. Inductively coupled plasma mass spectrometer (ICP-MS)

Inductively coupled plasma mass spectrometry (PerkinElmer, NexION™300Q) (ICP-MS) was used to measure the intensity of heavy metal in aqueous solution. It is an analytical technique that performs element analysis with outstanding sensitivity to elements. ICP-MS device uses argon plasma (ICP) as ionization source and mass spectrometer (MS), together with a quadrupole mass filter, to isolate the ions produced. It measure most of the elements in periodic table including heavy metal that had been used in this study. Moreover, it also can determine the analyte concentration of elements in a sample. To determine element in solution such as wastewater, the sample is vaporized using nebulizer. Wastewater is introduced into high-energy argon plasma that contain of electrons and positively charged argon ion. The sample is then divided into individual atoms. After divides, these atoms become singly charged positive ions because of losing one electron. Figure 3.2 shows the structure and working of ICP-MS. Ions are extracted through a number of apertures to identify the element, the ions of element produced in the plasma (ICP) must b e transferred from 7000K to room temperature and atmospheric pressure from low to high vacuum. Ion of heavy metal is then enters the quadrupole mass analyser. The ions in the quadrupole are divided on the basis of their mass-to-charge ratio. Therefore, heavy metal will produce its own mass spectrum. The ions hit a special detector, after passing the quadrupole. It contains two stages which allow simultaneous measurements of high and low signals. It will detect concentration of heavy metal in single run (Falkner, 1995).

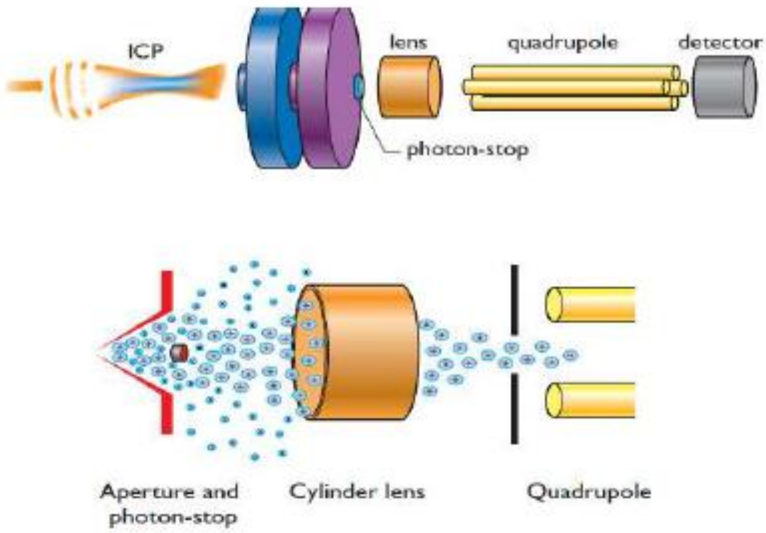

Figure 3. 2 Structure and Mechanism inside inductively coupled plasma mass spectrometry (ICP-MS)

Figure 3. 3 Inductively Couple Plasma Mass Spectrometry for measuring concentration of copper

3.3. Preparation of bio-char

5 grams of POMS was put in the conical flask (Duran) and then placed into microwave to produce bio-char. The parameters such as power of microwave and holding was studied and set to obtain the best adsorption capacity in bio-char. Total 15 bio-chars were produced based on the design of experiment. Each experiment was repeated twice to obtain accurate reading of result. Table 3.1 shows the experimental design.

Table 3. 3 Experiment Design

No.	Power (W)	Holding time (min)	Removal Efficiency (%)
1	100	4	
2	200	4	
3	300	4	
4	100	6	
5	200	6	
6	300	6	
7	100	8	
8	200	8	
9	300	8	
10	100	10	
11	200	10	
12	300	10	
13	100	12	
14	200	12	
15	300	12	

3.4. Concentration curve

Copper standard curve was prepared with different concentration of copper as follow, 0.01mg/L, 0.5mg/L and 1mg/L. Figure 3. 4 has show the calibration curve. The calibration will then move to ICP-MS to analyze the concentration of copper. 0.03 grams of prepared bio-char was added into 250 ml conical flask to remove 10mg/L of copper. Thus, the flasks were place at the orbital shaker at 250 rpm for 2 hours. The flasks are subsequently leaved on table to settle for 1 hour. 10ml of aqueous solution was taken from and filtered with syringe filter. The aqueous solution is then diluted into aqueous solution with 90ml of deionised water and into concentration of 1000 part per billion. The aqueous solution which contained copper is then digested with 1 % nitric acid to eliminate interference. The aqueous solution is then placed into ICP-MS to measure the concentration of copper. Each experiment was repeated twice. Removal efficiency of prepared bio-char can be obtained through the following formula.

$$E(\%) = \frac{C_I - C_F}{C_I} \times 100$$

Where,

C_I = Initial concentration of Copper

C_F = Final concentration of Copper

E (%) =Removal efficiency

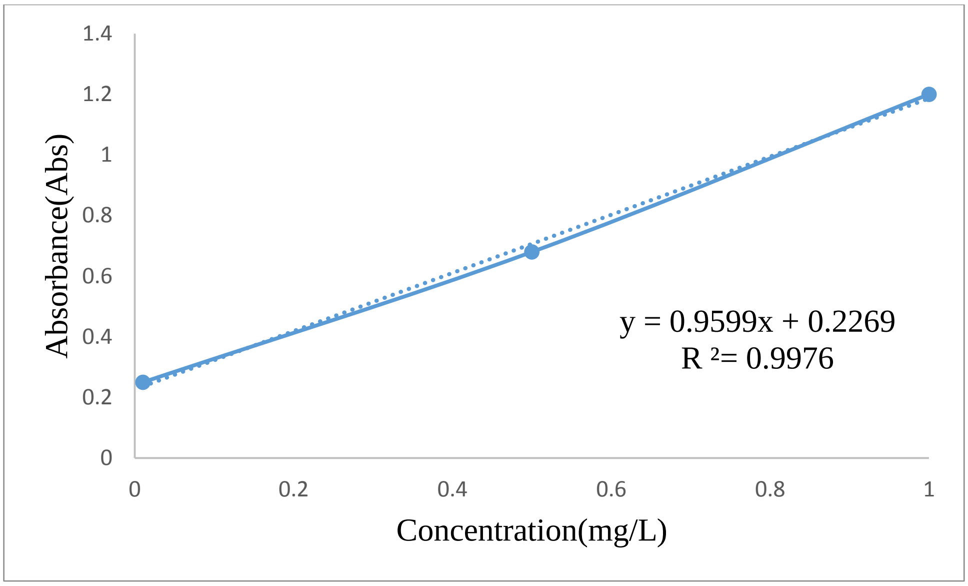

Figure 3. 4 Absorbance versus Concentration

3.5. Characterization of bio-char

There are two types of characteristic of bio-char had been measured, which are Fourier Transform Infrared Spectroscopy (FT-IR) for the study of functional group of bio-char.

3.5.1. Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared Spectroscopy method uses the emission of infrared electromagnetic wave to pass through a specimen. The infrared will be partially dispersed, transmitted and partially absorbed by the tested object. The resulting spectrum indicates the molecular adsorption and transmission. This detector would then create a resulting spectrum of the transmission and emission, like a molecular fingerprint of the sample. FTIR is use for the examination of functional groups on the surface of activated clays or carbon material (Chen and Jin, 2015).

CHAPTER 4

RESULT AND DISCUSSION

4.1. Adsorption capacity study

Experimental result of adsorption study for copper removal by different samples of microwave pyrolysed Palm Oil Mill Sludge bio-chars are as shown in the table 4.1.

Table 4. 1 Result of copper removal

No.	Power(Watts)	Holding time (min)	Removal Efficiency (%)		
			First Test	Second Test	Average
1	100	4	73.24	71.97	72.61
2	200	4	78.22	74.93	76.58
3	300	4	79.39	80.48	79.94
4	100	6	62.39	80.00	71.20
5	200	6	67.58	82.77	75.18
6	300	6	78.51	84.32	81.42
7	100	8	67.61	80.39	74.00
8	200	8	70.44	81.67	76.06
9	300	8	76.37	82.90	79.64
10	100	10	76.06	76.42	76.24
11	200	10	76.80	81.19	79.00
12	300	10	85.65	82.88	84.27
13	100	12	77.14	87.87	82.52
14	200	12	62.73	83.87	73.30
15	300	12	63.22	85.93	74.58

4.2. Performance of bio-char

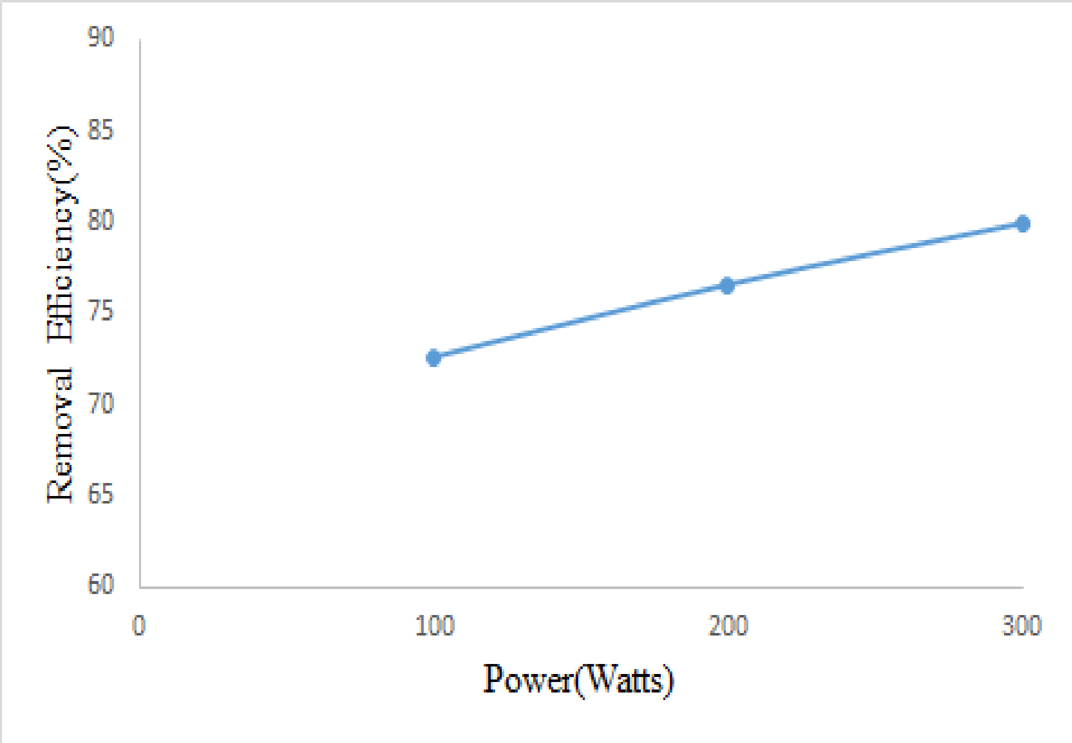

Figure 4. 1 Graph of bio-char removal efficiency against power at 4 minutes

According to Figure 4.1, at holding time of 4 minutes, linearly increasing of removal efficiency against microwave power is as shown as in the graph for both lines. At lower power of microwave, the minimum removal efficiency of this prepared bio-char is 72%; while at high microwave power, the maximum removal efficiency is 79%. According to the graph, it shows that the higher the power, the greater the removal efficiency. It has been proved by repeat this experiment twice. According to result above, the removal efficiency of bio-char is linearly increasing from lower power to higher. The greater microwave power will generate higher pyrolysis temperature, which allow the increase in pore size of bio-char itself and in turn increase the ability of adsorption(Yuan et al., 2015) ;(Zhang et al., 2014);(Zhang et al., 2015) .This had explained why the removal efficiency at higher microwave power is better than lower microwave power.

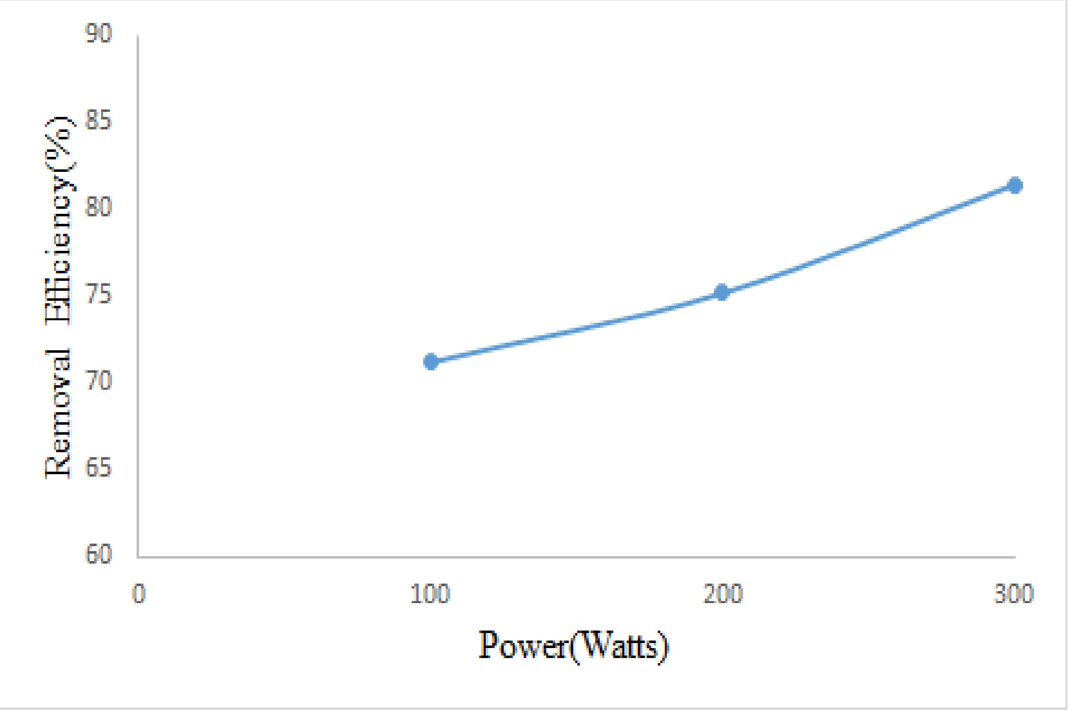

Figure 4. 2 Graph of bio-char removal efficiency against power at 6 minutes

According to Figure 4.2, at holding time of 6 minutes, linearly increasing of removal efficiency against microwave power is as shown as in the graph. Minimum removal efficiency of this prepared bio-char is 72%; while at high microwave power, the maximum removal efficiency is 81%. According to the graph, it shows that the higher the power, the greater the removal efficiency. It has been proved by repeating this experiment twice, although the minimum removal efficiency has a small gap. According to result above, the removal efficiency of bio-char is linearly increasing from lower power to higher. The greater microwave power will generate higher pyrolysis temperature, which allow the increase in pore size of bio-char itself and in turn increase the ability of adsorption(Yuan et al., 2015); (Zhang et al., 2014);(Yi et al., 2015). This had explained why the removal efficiency at higher microwave power is better than lower microwave power..The minimum difference between the result of first and the second result indicate the result of experiment is accurate. However, minor different in the removal efficiency has found comparing to holding time of 4 minutes, due the pore size of bio-char has vary due to the longer holding time, which it has result in increase of removal efficiency at 300 watts (Shabaan et.al 2014).

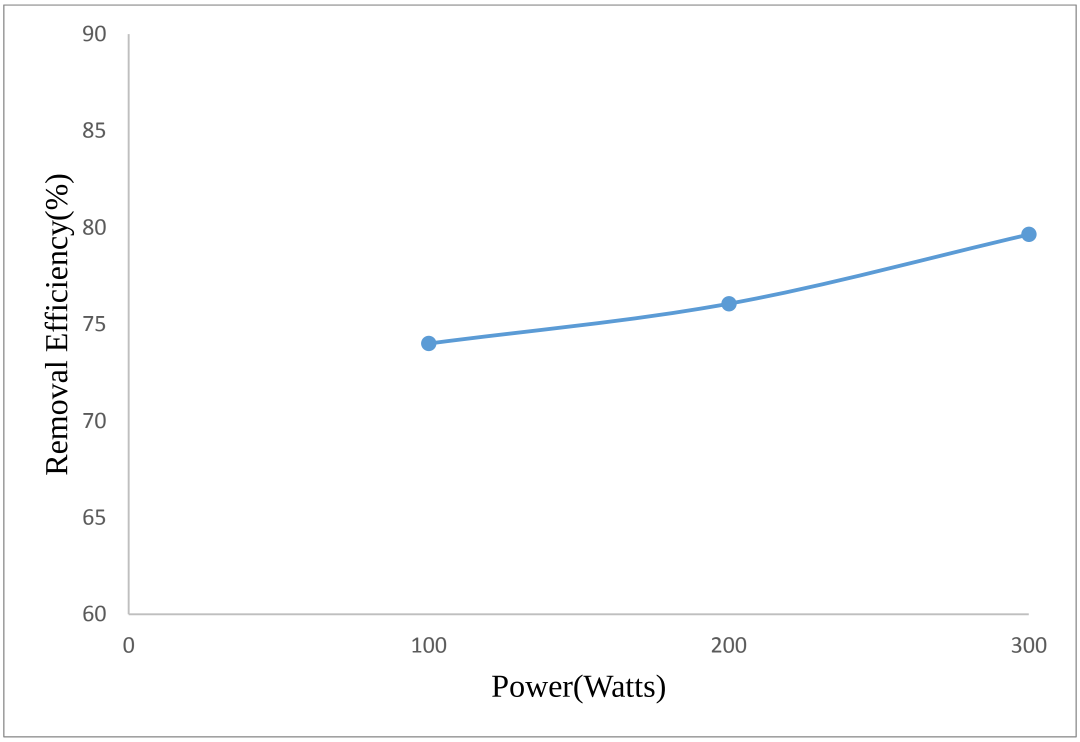

Figure 4. 3 Graph of bio-char removal efficiency against power at 8 minutes

According to Figure 4.3, at holding time of 8 minutes, linearly increasing of removal efficiency against microwave power is as shown as in the graph. Minimum removal efficiency of this prepared bio-char is 73%; while at high microwave power, the maximum removal efficiency is 79%. According to the graph, it shows that the higher the power, the greater the removal efficiency. It has been proved by repeating this experiment twice, although the minimum removal efficiency has a small gap. According to result above, the removal efficiency of bio-char is linearly increasing from lower power to higher.

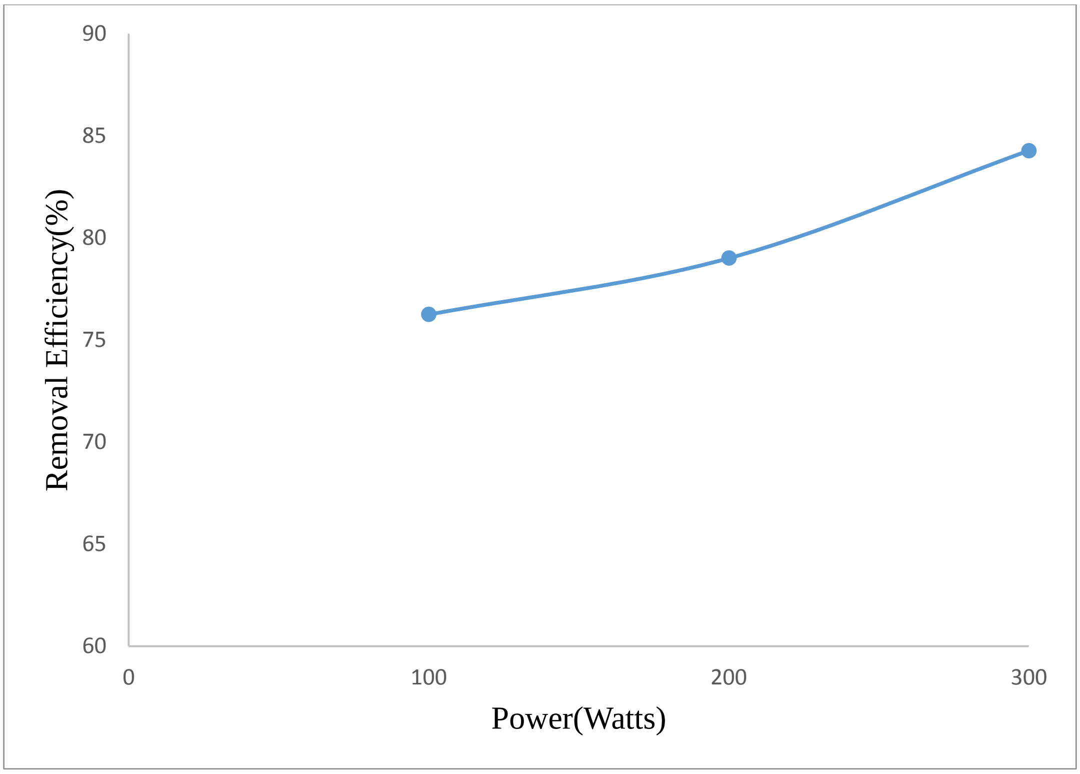

Figure 4. 4 Graph of bio-char removal efficiency against power at 10 minutes

According to Figure 4.4, at holding time of 10 minutes, linearly increasing of removal efficiency against microwave power is as shown as in the graph. Minimum removal efficiency of this prepared bio-char is 76%; while at high microwave power, the maximum removal efficiency is 84%. According to the graph, it shows that the higher the power, the greater the removal efficiency. It has been proved by repeating this experiment twice, although the minimum removal efficiency has a small gap. According to result above, the removal efficiency of bio-char is linearly increasing from lower power to higher.

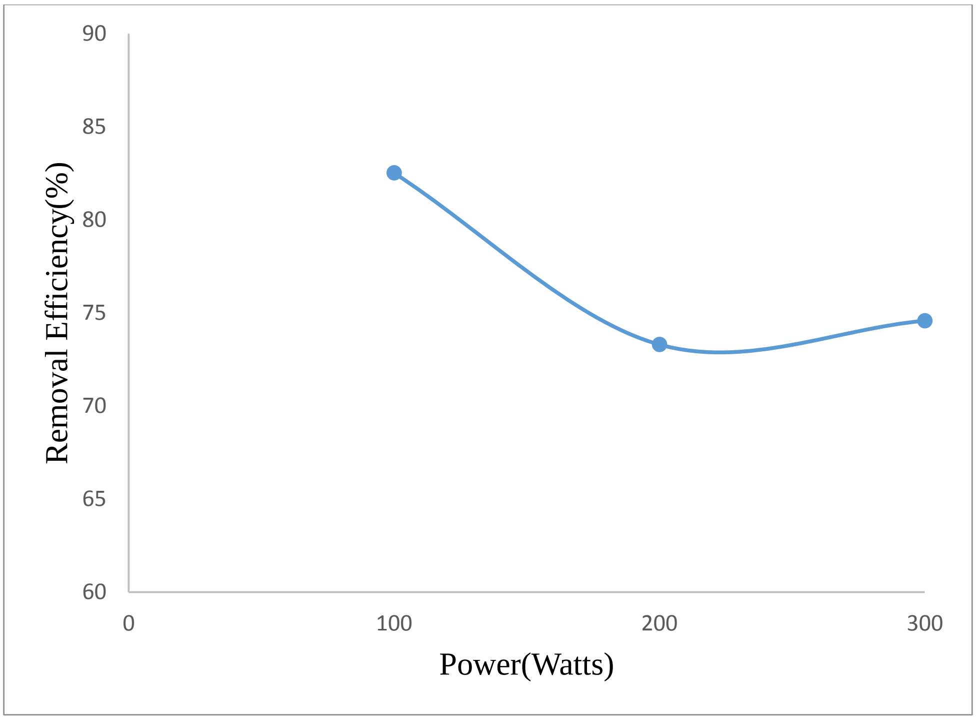

Figure 4. 5 Graph of bio-char removal efficiency against power at 12 minutes

According to Figure 4.5, at holding time of 12 minutes, linearly increasing of removal efficiency against microwave power is as shown as in the graph. Minimum removal efficiency of this prepared bio-char is 73%; while at high microwave power, the maximum removal efficiency is 83%. According to this graph, the performance of this bio-char is different with other set of bio-char. The removal efficiency is high at lower power; while at higher power, the removal efficiency has decrease. It is due to the overheating time has greatly destroyed the surface structure of bio-char, which in turn causes the decrease in removal efficiency (Shabaan et al., 2014).

4.3. Characterization of Bio-char

Characterization of palm oil mill sludge bio-char was conducted by using Fourier Transform Infrared Spectroscopy. Fourier Transform Infrared Spectroscopy is used to determine and identify the chemical compound in sample.

4.3.1. Fourier Transform Infrared Spectroscopy analysis (FT-IR)

Bio-char samples with different holding time i.e. 4 minutes, 6 minutes, 8 minutes, 10 minutes and 12 minutes in term of heavy metal removal at power of 300 watts were characterized by FT-IR analysis in order to identify the specific functional group in the bio-char. Special functional group of sample without any pyrolysis process had also been identified.

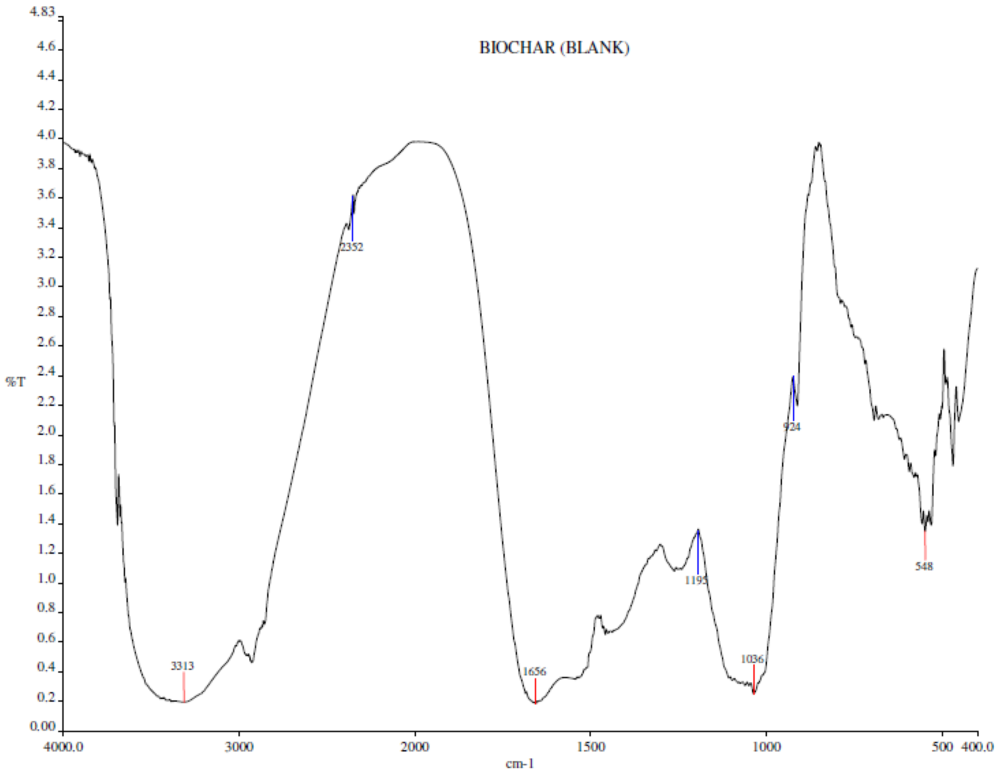

Figure 4. 6 FT-IR Spectrum of Blank sample

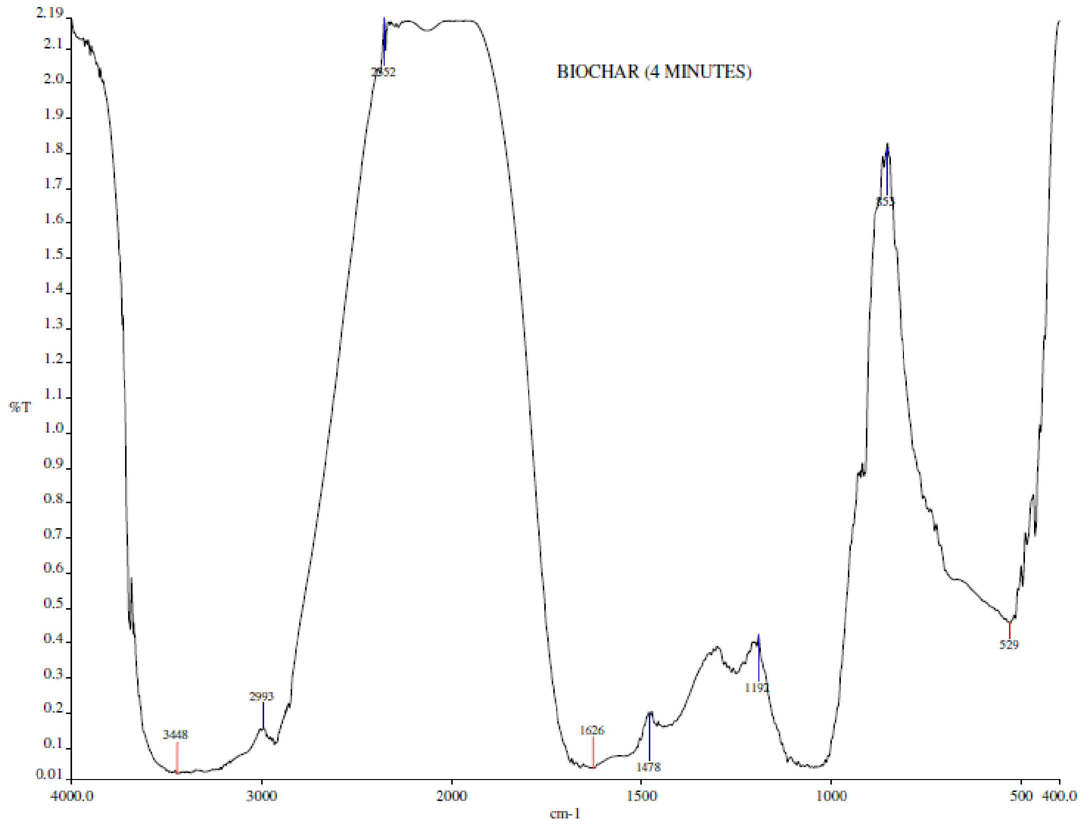

Figure 4. 7 FT-IR Spectrum of 4 minutes and 300 watts Produced Bio-char

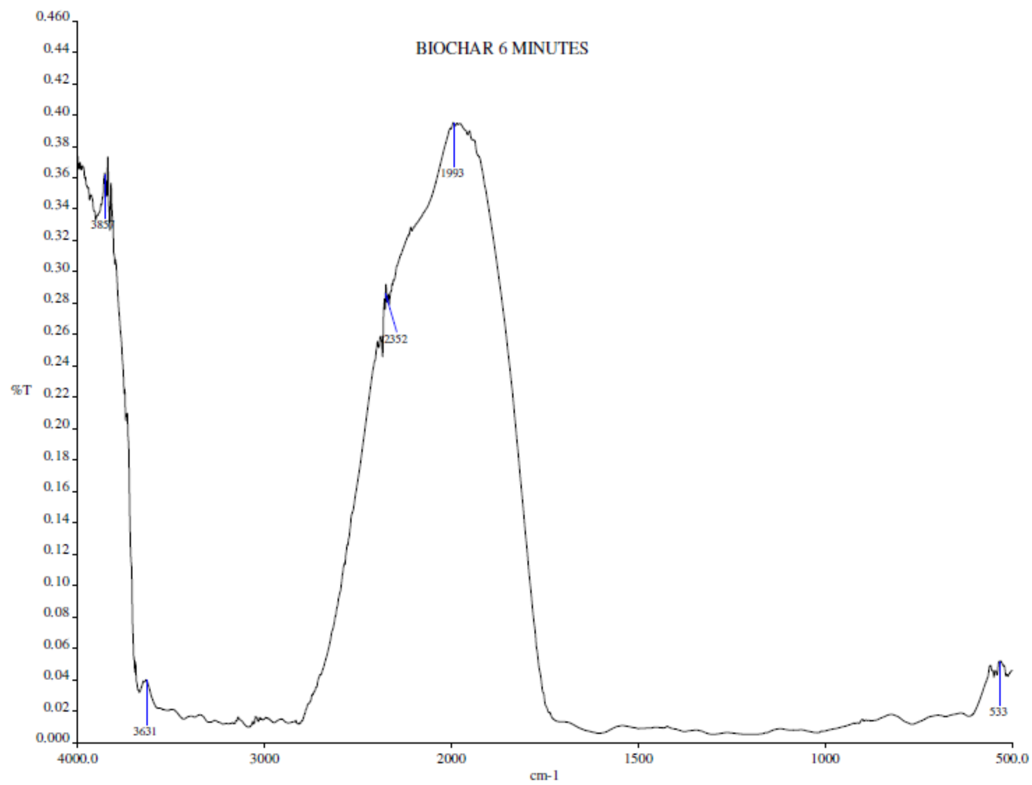

Figure 4. 8 FT-IR Spectrum of 6 minutes and 300 watts Produced Bio-char

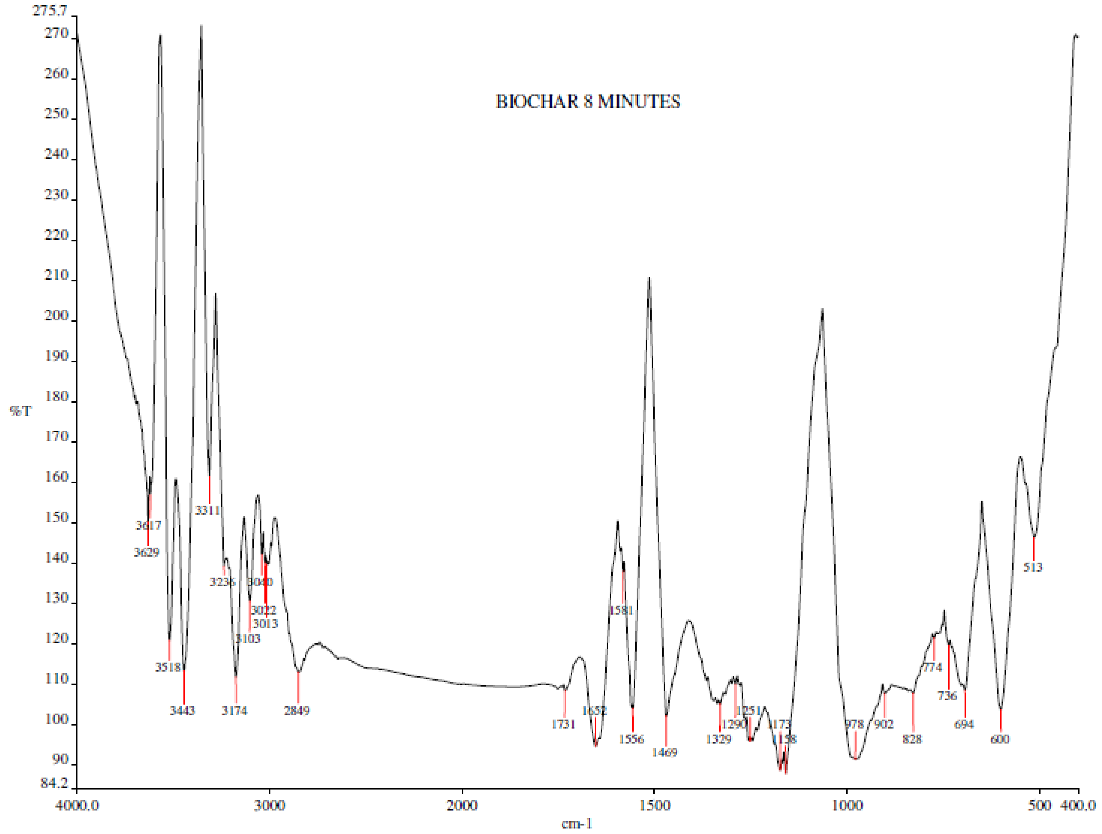

Figure 4. 9 FT-IR Spectrum of 8 minutes and 300 watts Produced Bio-char

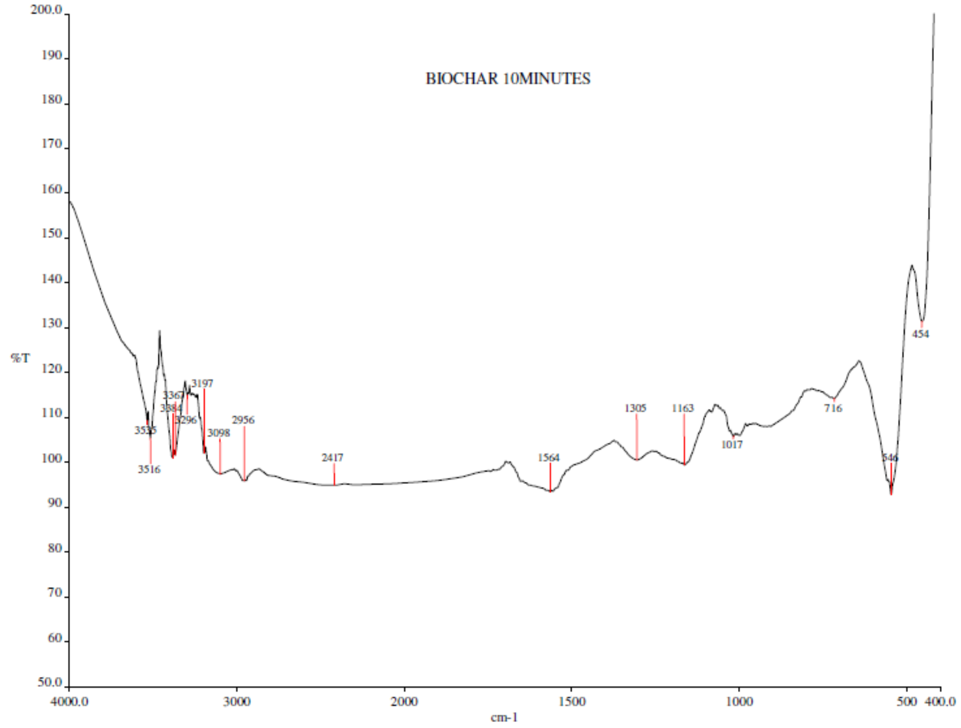

Figure 4. 10 FT-IR Spectrum of 10 minutes and 300 watts Produced Bio-char

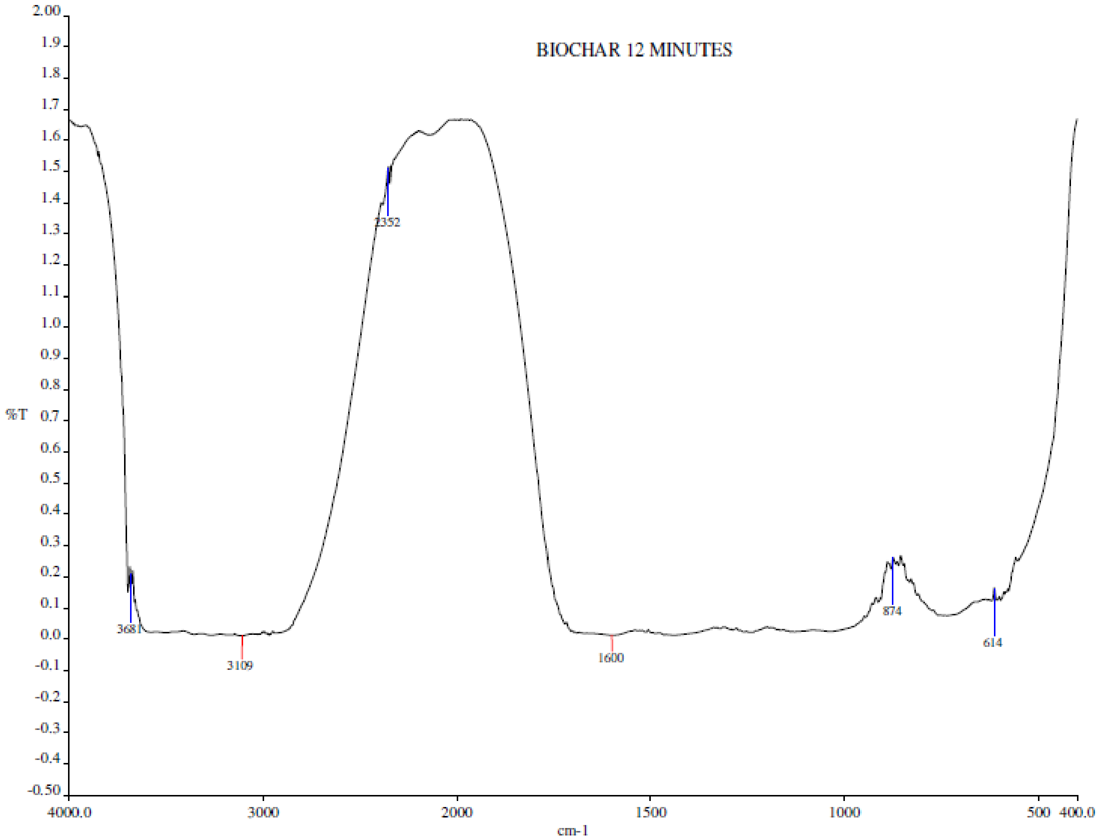

Figure 4. 11 FT-IR Spectrum of 12 minutes and 300 watts Produced Bio-char

According to analytical result of FT-IR figures, the peaks in the figures indicated the existence of functional group such as alky group (O-H), carboxyl group (C-OO-H) and ether group (C-O-C). Figure 4.6 shows spectrum of dry palm oil mill sludge without undergo any pyrolysis process had some functional groups. O-H stretching vibration bands at 3100 to 3400 cm^{-1} was the main composition of POMS, same goes to other samples such as sample shown in Figure 4.7 to Figure 4.11. According to literatures, they had reported that O-H stretching was detected in most of the bio-chars including microwave pyrolysed bio-char. (Anna et al., 2015) has reported the sludge derived bio-char was posses many hydroxyl (O-H) functional group and carboxyl (COOH) functional group. Narrow peaks such as 1036 to 3341 cm^{-1} were representing the presence of –COOH group. For example, the wide peak at 3341 cm^{-1} in Figure 4.9 representing the ether (-C-O-C) group . Figure 4.6 to Figure 4.11 also illustrated –C-O-C reading from 978 to 1731 cm^{-1}.

From the experimental result and FT-IR analysis, power is the most effective and important parameter which can affect the adsorption capacity of bio-char. This can be proved by comparing the FT-IR analysis of Figure 4.6 with Figure 4.7, 4.8, 4.9, 4.10 and 4.11. In the other hand, the wide peak of functional group C-O-C at 978 to 1731 cm^{-1} became sharper as the increase of temperature. It is due to the huge amount of fixed carbon had almost achieved. This mean the adsorption capacity of POMS bio-chars can be further improved by increasing the power of microwave (Shaaban et al., 2014).

For sample with holding time of 6 minutes in Figure 4.8, the unclear occurrence of the bands in the 3631 to 2352 cm^{-1} which representing the alky group, shows minimal reaction has occurred. With no obvious functional group in the bio-char with holding time of 6 minutes, same goes to dried palm oil mill sludge and sample with holding time of 4 minutes in Figure 4.6 and Figure 4.7. However, the number of bands whose intensity has greatly increased in Figure 4.9, the sample with holding time of 8 minutes. Ranging from 1556- 513 cm^{-1} is representing the carboxyl group; while ranging from 3443 to 3617 cm^{-1} are representing the alky group. This is due to the holding time is optimal for the bio-char (Liu, He and Uchimiya, 2014).

For Figure 4.10, the number of bands is similar to the numbers of bands of activated carbon comparing to the FT-IR analytical result in literature (Hesas et al., 2013).The numbers of bands ranging from 1564 to 454 cm^{-1} representing carboxyl group; while ranging from 3535 to 3197 cm^{-1} representing carboxyl group. A conclusion can be made is at the holding of 10 minutes, the performance of bio-char produced from palm oil mill sludge is similar to activate carbon.

For Figure 4.11, the number of peaks is even lesser than the peaks in Figure 4.7, which the numbers of bands is ranging from 874 to 614 cm^{-1} only representing carboxyl group; while ranging from 3681 cm^{-1} only representing carboxyl group. It due the long holding time has destroyed the structure of bio-char, which in turn destroyed the functional group of bio-char. (Brewer, 2012)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Based on literature reviewed to date, palm oil mill sludge that obtained from palm oil industry has never been used for producing adsorbent for copper removal for its aqueous solution. Due to Malaysia is one of the world largest oil palm exporter, palm oil mill sludge is easily available for low cost adsorbent. Therefore, assessment on copper removal potential of bio-char produced from palm oil mill sludge has been carried out using microwave pyrolysis by two different parameters such microwave power(Watts) and holding time(minutes). In addition, these two parameters are the most important parameters that would affect the result of this assessment significantly.

From the evaluation of literature review and present study, holding time and temperature, which as known as power in microwave were the main factor responsible for the performance of adsorption of bio-char. From the experimental result and analysis of Fourier Transform Infrared Spectroscopy (FT-IR), it shows the bio-char produced at holding time of 10 minutes and 300 watts had achieved high and stable performance of removal efficiency of 84%; while at holding time of 6 minutes and 100 watts, the removal efficiency of bio-char is only 72%.

5.2. Recommendation for Future Study

- Further study the adsorption capacity of bio-char produced at power above 300 watts.
- Holding time should be fixed, for example at 10 minutes.
- Grinder is needed to ensure uniform size of dry palm oil mill sludge and adsorbent.
- Design of Experiment software is needed for further improvement on finding optimum removal efficiency.
- Condition of experiment such as nitrogen flow rate can be investigates to enhance the performance of bio-char.

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