ADSORPTION OF TRIMETHYLTIN, ARSENIC (V), ZINC AND COPPER BY PALM OIL MILL SLUDGE BIOCHAR PREPARED BY MICROWAVE

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

Faculty of Engineering and Green Technology
Universiti Tunku Abdul Rahman

May 2016

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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I certify that this project report entitled **ADSORPTION OF TRIMETHYLTIN, ARSENIC (V), ZINC AND COPPER BY PALM OIL MILL SLUDGE BIOCHAR PREPARED BY MICROWAVE** was prepared by **KLINSMANN NG WENG SUM** has met the required standard for submission in partial fulfillment of the requirements for the award of Bachelor of Engineering (Hons) Environmental Engineering at Universiti Tunku Abdul Rahman.

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ACKNOWLEDGEMENT

I sincerely appreciate the support and guidance of all people that had contributed for making this project a success. I’m grateful to have Dr. Sumathi as my supervisor for all the supports, guidance and share of knowledge in completing this project, as well as patience for providing necessary advices in the project.

I would like to extend my gratitude to Leong Wai Lun for sharing his knowledge regarding this project, assisting in laboratory experimental work and valuable time spent for guidance during necessary times. Also, I would like to thanks Mr Chin Kah Seng, Mr Voon Kah Loon, Miss Noor Hazreena Binti Noor Izahar and Ms Zila Binti Mohd Tahir for assisting during laboratory work which provided a smooth and safe laboratory work.

Last but not least, I would like to place a deep sense of gratitude to my family members and friends who have been so supportive, encouraging and giving inspiration to me throughout the whole project.

ABSTRACT

The increase of palm oil production in Malaysia has led to tremendously large amount of waste generation in the form of liquid and solid annually. Palm oil mill sludge (POMS) is one of the recalcitrant wastes produced from palm oil mill that commonly being either used as palm oil plantation fertiliser or illegally disposed due to its abundance. In order to resolve this problem, reutilisation of POMS to other value added product is encouraged. In this work, POMS was turned into biochar and the product was proposed to adsorb pollutants from wastewater. POMS biochar was produced by using microwave heating. Biochar was prepared by varying the microwave power (W) and holding time (min). The ranges of parameters were as 100 W-500 W and 5 min-25 min for microwave power and holding time respectively. The biochars were tested with the following parameters i.e. trimethyltin (TMT), arsenate (As (V)), zinc (Zn) and copper (Cu). The results determined had shown that POMS biochar are able to adsorb Zn and Cu by the functional groups that are present on the biochar. However there is little or no adsorption of TMT and As (V) onto the biochar. Moreover, it was found that the removal efficiency of Zn and Cu was almost similar at different microwave power and holding time. This could be due to POMS nature. POMS could be a poor dielectric absorber which resulted in a less development of pore on the POMS biochar and alteration of functional group. This was proven by FTIR study. Hence, it can be concluded that the adsorption of Zn and Cu are adsorbed predominantly by the functional groups on POMS biochar. As for TMT and As (V), they do not show effective adsorption due to their anionic in nature which requires modified biochar for effective removal. Thus, it can be concluded that with the microwave frequency used which is 2.45GHz and under dried condition may not be suitable for pyrolysing POMS to biochar using microwave. It is suggested to determine the dielectric properties of POMS before undergo microwave pyrolysis.

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BOD	Biochemical Oxygen Demand
CERCLA	Comprehensive, Environmental, Response, Compensation and Liability Act
COD	Chemical Oxygen Demand
DNA	Deoxyribonucleic Acid
DOE	Department of Environment
FTIR	Fourier Transform Infrared Spectroscopy
IARC	International Agency for Research on Cancer
IMO	International Maritime Organization
OPEFB	Oil palm empty fruit bunch
PCB	Polychlorinated Biphenyl
POME	Palm oil mill effluent
POMS	Palm oil mill sludge
PVC	Polyvinyl Chloride
SEM	Scanning Electron
TMT	Trimethyltin
TBT	Tributyltin
TPT	Triphenyltin

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CHAPTER 1

INTRODUCTION

1.1 Background

Oil palm tree was firstly introduced into Malaysia in the 1870's where the seeds were originated from West Africa and it was planted commercially in 1917 at Tennamaran estate, Selangor (Malaysia Palm Oil Council, 2012). Knowing that palm oil is an important source of economic growth, oil palm has been planted widely in Malaysia and currently Malaysia is the largest exported and the second largest producer of palm oil worldwide (IChemE, 2015). The varieties usage of palm oil together with the latest discovery of using palm oil as a feedstock in the production of biodiesel had increased the demand of the palm oil. On top of that, demands for vegetable oil increased due to the increase in population worldwide. As refer to Figure 1.1, the consumption of vegetables oil worldwide increased tremendously from 1995/96 to 2005/06 from 15.8 million metric tons to 35.3 million metric tons. Since then, the consumption of palm oil increased gradually until 2014/15 when it reached up to 60.73 million metric tons (Statista, 2015).

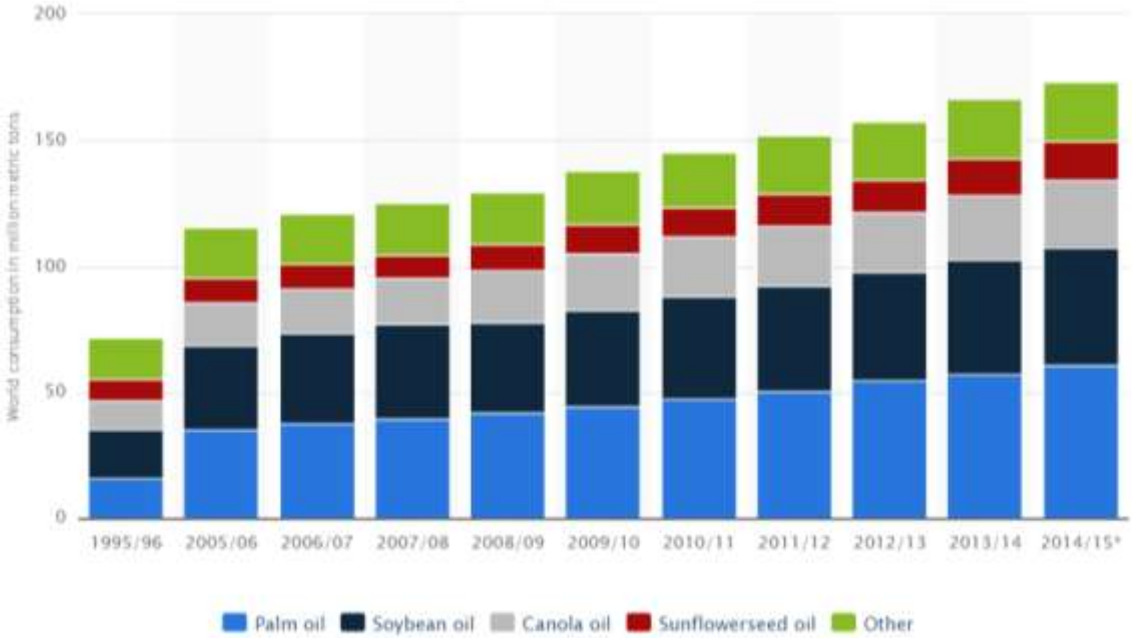


Figure 1.1: Global Consumption of Vegetable Oils from 1995/1996 to 2014/2015, by Oil Type (in million metric tons) (Statista, 2015)

The increase of consumption of oil had led to the increase of production of palm oil in order to accommodate the demands. The increase of palm oil production has led to the increase of palm oil waste production especially liquid waste which is known as Palm Oil Mill Effluent (POME). POME is generally generated from the oil extraction cleaning process and washing in the mill and generally oil and grease, contains fats, cellulose materials etc. On top of that, POME also contains suspended solids and total dissolved solids that will be turned into palm oil mill sludges (POMS) after anaerobic digestion. From the findings of Abdullah and Sulaiman (2013), POME is made up of colloidal suspension containing water up to 96 %, 0.6 % - 0.7 % of oil and 4 % – 5 % of total solids including 2 % - 4 % suspended solids. The quality of the raw materials and the palm oil production processes are the two the main influences for the characteristic of the POME. Due to the large amount of water required for the palm oil extraction, it has been estimated that 5 – 7 tons of water required to produce 1 ton of crude palm oil and worse still 50 % of it ended up to be the POME as determined by Parveen, Rajeev, Hakimi and Norizan, (2010). On top of that, it was determined that around 53 million m^3

of POME is being produced in palm oil production in 2005 itself, and with the current increased in palm oil production, POME production notably increased.

As mentioned earlier, POMS is the part of the composition of the POME where it is made up of suspended solid and total dissolve solids. Since POME production increased, clearly that POMS production would be increased. POMS contain higher nutrient content than the slurry with pH of 8.4 (Parveen, Rajeev, Hakimi and Norizan., 2010). According to Yaser, et al. (2007) and Baharaddin, et al. (2009) as cited by Parveen, Rajeev, Hakimi and Norizan (2010) that POMS contains 3.6 mg/l, 0.9 mg/l and 2.1 mg/l of total Nitrogen, Phosphorus and Potassium respectively and it is the cause of bad odours and source of surface and ground water pollution.

Since POMS is part of POME, similarly, it possesses a threat to the environment and therefore, it requires a proper designed technology to mitigate these wastes. Currently, there are two technologies as reported by Parveen, et al. (2010) that are able to manage the POMS. One of the methods is composting technology where it applies microbial technology to decompose the substrate and therefore a big portion of the biodegradable organic compounds will be broken down and the remaining of organic material is transformed into humic acid like substance. As mentioned by Yaser, et al. (2007) cited by Parveen, et al. (2010) that the ultimate of composting of the POMS exhibit some fertiliser value for plantation however needed to be adjusted to obtain an ideal substrate. Next, vermicomposting technique is another method to manage the POMS where the outcome of it is able to obtain high quality fertiliser. This technology requires earthworms to convert organic material into humus-like materials which acquires physical, biological and chemical reactions to take place. The advantage of this method is that the proteins from the earthworm biomass can be used as animal feeds. On top of that, nutrients that are vital for plants such as nitrogen, phosphorus, potassium, etc. present in the waste are transformed into more soluble and available for plants.

Technologies to manage the POMS as mentioned earlier were then the best ways to mitigate the sludge. However, recent years, there is a newly developed technology which is able to use POMS to treat another waste; in another way it can be said as using a waste to treat another waste. POMS is being proposed to act as an adsorbent to treat inorganic matters of low concentration in which it is an advanced treatment in wastewater treatment system. POMS biochar can be produced through a heating technique known as microwave pyrolysis to heat the POMS similar to activated carbon; it requires a medium to activate the pores of POME for adsorption to occur.

Metal toxicity has been a major concern to the environment and especially to human’s health. Toxic metals which also include heavy metals that possess toxicity effect in certain forms and doses that would harm the environment and human’s health. It is important to achieve an acceptable limit of metals present in water as set by local authority especially in potable water. Urbanisation and industrialisation are to be blamed for an increase of metals in sources of water especially in heavy metals. According to Shazili, et al. (2006), the major source of contribution of heavy metal pollution is from the manufacturing sector. It includes electroplating, production of metals for various industries and etching are some of the major source for high concentration of cadmium (Cd), Cu, Zn, nickel (Ni), iron (Fe), aluminium (Al), chromium (Cr) and manganese (Mn). On top of that, there are other natural sources of heavy metal pollution are from weathering and volcanic eruption (Paul, et al., 2014). Some of the common health effects of heavy metals are nausea, vomiting and diarrhoea. Some other serious health effect would be lung damage, kidney disease that cause by the long-term exposure of Cd. Similarly, long-term exposure to Cr can cause damage to kidney, liver and nerve tissue and worse of all, exposure to high levels of arsenic (As), barium (Ba) and lead (Pb) can cause death (Sabine & Wendy, 2009). Therefore, it is vital to treat the wastewater before discharging into the river and especially water to be distributed to the people for usage purposes. Hence, by resolving two of the problem which is the abundant and illegal dumping of POMS and the metal toxicity is by reutilising POMS and converting it into biochar for adsorption of the metals that involved in the metal toxicity. This way not only illegal dumping of POMS can be minimised but also the metal toxicity can be treated for acceptable discharge and possible potable water.

1.2 Problem Statements

The increased of production of palm oil without doubt had increased the palm oil mill effluent tremendously which indirectly increase the production of POMS throughout these few years due to the increased in consumption of palm oil. POME is a threat to the environment in Malaysia. In addition, it has been declared as one of the major source of environment pollution. According to Yahaya and Lau (2013a), in year 2004 itself, about 30 million tons of POME was generated from 381 oil mills in Malaysia. Despite POME is non-toxic as there is no addition of chemical being into the extraction process however the contents contain high Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), total solids and low pH. The acidic and low oxygen content of the POME will deplete a water body and cause suffocation of the aquatic life in a water body.

Organotin compounds are found to be in fungicides, insecticides and bactericides. On top of that, it acts as a heat stabilizer in Polyvinyl Chloride (PVC) and Polychlorinated Biphenyl (PCB) (Lenntech, 2015). Furthermore, plastics, food packages, paints, wood preservatives and rodent repellents are all made up of organotin compounds. Organotin can affect human's health where it can cause irritation of eyes, respiratory, gastrointestinal effects and even causing problems to neurons after a short period of exposure to high amounts of certain organotin compounds (Agency for Toxic Substances and Disease Registry, 2005). Arsenic can be found in nature such as rocks and soil or it can be anthropogenic where it being released from the industry or agricultural activities. It is often being used as a pesticide in agriculture, preservative in pressure-treated lumber, additives to Pb and Cu and in some glass manufacturing. In some countries such as Taiwan, Japan and Bangladesh, people tend to expose to arsenic through drinking water more than other source of exposures to arsenic (Agency for Toxic Substances and Disease Registry, 2009). Exposure to arsenic can cause diarrhoea, nausea, vomiting, muscle weakness and cramping and rashes for short-term exposures. Exposure to arsenic in long-term can cause irregular heartbeat, live and kidney damage and shortage of red and white blood cells (American Cancer Society, 2014). Zn can be naturally found as zinc oxide or sphalerite (ZnS) and is released into the environment through mining, smelting of Zn, lead and cadmium ores, burning of coal and waste and production of steel. Zn is usually being used as a protective coating for other metals such as iron and steel. Even though Zn is an essential trace element for humans and animals, however over consumed or exposed to Zn compound may lead to many respiratory-related health effect such as leukocytosis, acute pneumonitis and other gastrointestinal symptoms such as abdominal cramps, and diarrhoea (Agency for Toxic Substances and Disease Registry, 2015a). Cu is a reddish metal that present in nature in soil, rock, water and sediment. Cu enters into the environment mainly through the mining of copper and other metals, and also through factories where Cu are being used as part of the product compound. Despite the essential of Cu for human's good health, over dose of Cu may result in health effects such as long term exposure to Cu will result in dizzy, headache, nausea and diarrhea. High intake of Cu may result in worsen health effects such as liver and kidney damage and even worse death (Agency for Toxic Substances and Disease Registry, 2004).

Since POMS has the possibilities of being converted into biochar and currently no microwave pyrolysis has been used before for pyrolysing POMS, it is the first time to microwave pyrolyse POMS and turning it into biochar. After turning it into biochar, it is then further used to treat metal toxicity whereby compounds that made up of tin, arsenic, copper and zinc.

1.3 Research Objectives

The objectives of the thesis are shown as follows:

i. To prepare Palm Oil Mill Sludge (POMS) biochar using microwave
ii. To characterise POMS biochar using Fourier Transform Infrared Spectroscopy (FTIR)
iii. To determine the removal efficiency of trimethyltin, arsenate, zinc and copper by POMS biochar

CHAPTER 2

LITERATURE REVIEW

2.1 Metal Toxicity

Metal toxicity means any kind of metals that possesses toxicity in different forms such as organic metal and pure metal at different concentration that possesses danger to a particular target. Toxicity of metal also includes heavy metals. “Heavy Metals” can be referred to metallic elements that have high density. According to Duruibe, Ogwuegbu and Egwurugwu (2007), heavy metals with atomic density greater than 4g/cm^3 or 5 times or more or greater than water density also considered under the group of heavy metals. Heavy metals can be categorised as toxic heavy metals where it is toxic even at low concentrations. According to Klaus (2010), the toxicity of a heavy metal depends on the concentration of the heavy metal present to the cell that will bring harm to the cell. Some of the common heavy metals that are taken as the parameters when conducting water quality assessment are cadmium (Cd), copper (Cu), Zn, nickel (Ni), iron (Fe), chromium (Cr), mercury (Hg), manganese (Mn), tin (Sn) and metalloid arsenic (As). Metals exists either in nature such as rocks and soils that deposits into the water source caused by erosion or anthropogenic due to the effluent from the industrial, agricultural, pharmaceutical, geogenic, domestic and atmospheric sources (Tchounwou, et al., 2014).

It should be clear that not all heavy metals are toxic. For example iron which possesses biological role in human and it is needed by human body. However, some lighter metals such as beryllium and lithium under certain condition maybe toxic to human. Some of the groups that can be categorised as toxic are the radioactive metals, some metalloids such as arsenic and polonium (Po), Cd, Mn, lead (Pb) and Hg. According to Tchounwou, et al. (2014), even though heavy metals with certain concentration will harm human and the environment but there are some metals with certain oxidation state such as Cu, Cr (III), Fe, Zn, Mn, Ni, and magnesium (Mg) are some of the nutrients that are vital for different biochemical and physiological functions in plants and animal. Also, they are the important part of the key enzymes and play important role in different oxidation-reduction reactions. Insufficient supply of these metals will lead to diseases or syndromes. On the other hand, there are also heavy metals such as aluminium (Al), As, Hg, Sn and Cd which are not essential metals to the human body. Some of the cardiovascular diseases, cancer, kidney problems and affecting the neurology are related to the trace metals such as Cd and Cr (Rahmanian, et al., 2015). Even more, some metals such as tin are a very toxic compound when it reacts with organic compound to form a compound known as organotin which will be further described in the following section.

In the latest Environmental requirements: A Guide for Investors (11th edition) set by Department of Environment (DOE) Malaysia, the acceptable condition for discharge of industrial effluent for mixed effluent of Standards A and B for metals is as shown in Appendix A1 **(**Department of Environment, Malaysia, 2010). The difference between Standard A and B is the location of discharge where Standard A with much stricter limit are only applicable to discharge into any inland waters within catchment areas and Standard B is applicable to any other inland water or Malaysian waters (Department of Environment, Malaysia, 2010). Even with this stringent standards set by DOE of Malaysia where the lowest maximum allowable discharge of the overall standard is 0.005 mg/L for Hg, the Drinking water quality standard set by the Ministry of Health Malaysia having Hg maximum allowable limit present in drinking water is 0.001 mg/L as referred to Appendix A2.

In this study, arsenic, Zn, Cu and organotin have taken into consideration due to their toxicity and major concern by the public towards their effects and ways to treat them in order to reduce the amount present not only in the environment but also in drinking water. On top of that, arsenic had been listed as the number one substance in the Comprehensive, Environmental, Response, Compensation and Liability Act (CERCLA) Priority list of Hazardous Waste Substances (Hughes, et al., 2011) which gives more reason to ensure the presence of arsenic in sources of water is kept at its minimum.

2.1.1 Organotin

Tin (Sn) is a naturally occurring metal that is resistance to corrosion and usually being used as coating for other metals such as steel in which beverages cans and food containers are the common item where tin are being used for coating (Group, 2013). However, organotin is a different form of tin where it has a chemical compound of hydrocarbon substituent. Organotin compounds have been widely used in agricultural fungicides, rodents' repellents, molluscicides, antifouling paints and fishing nets (Nakanish, 2006). According to Jain, Singh and Kaushik (2013), organotin compounds are generally made up of tin at the centre and are tetravalent in which they can be classified as mono-, di-, tri- and tetraorganotin depending on the number of alkyl(R) group being attached onto it. Table 2.1 shows the types of organotin with different number of organic group and its applications.

Table 2.1 Types of Organotin with different Number of Organic Compound with different Applications

Types of Organotin	Number of organic attach to it	Applications	References
Tetrabutyltin Tetraoctyltin Tetraphenyltin	4	Catalyst	Department of the Environment, Australia (2014)
Tributyltin oxide	3	Fungicide and pesticide in timber treatments, antifouling paints	
Triphenyltin acetate		Insect control agent and fungicide	
Triphenyltin chloride		Biocide and an intermediate	
Triphenyltin Hydroxide		Chemical sterilise insects and fungicide	
Fenbutatin oxide		Control wide range of mites feed on plants	
Azocyclotin		Long-acting acaricide for the control of spider mites on fruits, vines, hops, cotton, vegetables and ornamentals.	
Dimethyltin Dibutyltin Diestertins	2	PVC heat stabilisers, formation of polyurethane, silicon curing and heat stabilisers for rigid food-packaging PVC	
Methyltin Butyltin Octyltin Monoestertin	1	PVC Heat stabilisers	

According to Nikolaou, et al. (2006), organotin compounds are the most common used organometallic compounds having a global amount produced to be 50, 000 tons per year. They can be detected in many places worldwide including surface water, drinking water, sediments and biota. However, one of the most notably known antifouling paint for ship hulls being used for many years has come to an alert that the tributyltin (TBT) is one of the most toxic chemicals that have been discharged into the marine environment (Cao, et al., 2007). As a result, since the late 1980's many have banned the use of antifouling paints such as in Europe and North America. To top that, prohibition on the usage of organotin compounds as biocides in antifouling paints in the year of 2008 (International Maritime Organization, 2008) was done by International Maritime Organization (IMO).

In a case study reported by Cao, et al. (2007), the usage of organotin in China was approximated to be 7500 tons/year and this huge amount of usage had caused a widespread of organotin to many of the local water source. It was reported that there is serious organotin contamination in marine and freshwater environments, especially offshore waters, port sites, and inner river dock yards in China. From the report, it was reported the present of TBT and other butyltin compounds in aquatic environments within China. It was suggested that it mainly caused by the extensive use of anti-fouling paints on ships and made up the widespread of butyltin at several major ports in China.

According to Ho and Leung (2014), human can expose to organotin mainly through three ways namely skin contact, ingestion and inhalation. Ingestion is the major pathway of human expose to organotin where fishes and shellfish such as mussels, clams and oysters. Also, it was mentioned that these compounds can be degraded through bacteria action and light which is biodegradation and irradiation respectively. Despite that, cooking couldn’t destroy these compounds and therefore organotin will be consumed by human through food. The side effect of human expose to organotin can probably affect human’s reproductive and developmental abnormalities, immunosuppression and possible carcinogenic activity. For example, the enzyme activity in ovary cells can be inhibited by as low as 2 ng mL^{-1} of TBT or triphenyltin (TPT) and promote the development of prostate cancer cells at 100 nM. Agency for Toxic Substances and Disease Registry (2005) stated that there have been reports related to exposure to certain organotin compounds that causes skin and eye irritations, gastrointestinal effects, respiratory irritation and some even having neurological problems. On top of that, there are even cases reported that the neurological problems have persisted for years after the poisoning occurred. Fatal cases have been reported after ingestion of very high amount of organotin.

In terms of environmental aspect, it has been demonstrated that TBT possesses high toxicity towards aquatic organisms which it disrupts the endocrine resulting in imposex in gastropods at very low water concentrations and thus the female proportion of aquatic organisms increase. On top of that, organotin is readily assimilated into the tissues of filter-feeding zooplankton, herbivore invertebrates and eventually to the higher level of organisms in the food chain such as fish, water birds then mammals where it accumulates. TBT can also cause chronic and acute poisoning of the aquatic organisms such as algae, molluscs and the larval of some fish. Furthermore, it was determined that organotin compound can be found in the deep sea marine organisms. It was found that the concentration of TBT in different tissues at several deep sea fish species between 1000 m and 1800 m. There were cases of where TBT affected the reproductive cycle of oysters in France (Okoro, et al., 2011).

2.1.2 Arsenic

Arsenic (As) is a type of metalloid with the common oxidation state occurring in the environment of +3 (arsenite) and +5 (arsenate) which both exhibit different level of toxicity. It is yellow or metallic grey in colour, very brittle and not soluble in water with a semi-metallic crystalline structure (Jeong, 2005). Arsenic can be differentiated into organic arsenic with links to carbon and hydrogen; inorganic arsenic combines with oxygen, chlorine, sulphur and etc (Martinez, et al., 2011). According to European Food Safety Authority (2009), that inorganic arsenic possesses higher toxicity as compared to organic arsenic and due to that reason, inorganic arsenic has been classified by the International Agency for Research on Cancer (IARC) in group 1 as carcinogens to human. There are some common sources of arsenic present naturally in the environment such as ground water, mineral ore and for some countries, geothermal processes. Moreover, arsenic is released into the air by volcanoes, through weathering of some minerals and ores that contain arsenic and of course from industrial processes (Agency for Toxic Substances & Disease Registry, 2009). According to Hughes, et al. (2011), arsenic has a long historical use as a homicidal agent but over the past 100 years, arsenic have been used as pesticide, chemotherapeutic agent and even used in some of the consumer products. Arsenic was once being used in paints and dye for clothes, paper, and wallpaper during the 19th century. Other anthropogenic source of arsenic are algaecides, desiccants used in mechanical cotton harvesting, glass manufacturing and nonferrous alloys. Currently, arsenic is widely used in electronic industries in the form of gallium arsenide and arsine gas as part of the semiconductor devices' components (Agency for Toxic Substances & Disease Registry, 2009).

The possibility of exposing to arsenic is quite high as arsenic is widely distributed throughout the environment in the air, water and land. Public can easily come in contact with the highly inorganic arsenic through drinking water, water used for preparation of food and irrigation of food crops, industrial processes, consuming contaminated food and smoking tobacco. Due to the odourless, colourless and flavourless of arsenic, it is hard for consumer to determine whether the food or water they consume contain arsenic. Exposing to arsenic can cause either acute effect or long-term effect as stated by World Health Organization (2012). Acute effect of arsenic poisoning brings immediate symptoms including vomiting, abdominal pain and diarrhoea which followed by numbness and prickling of the extremities, muscle cramps and even death. As for long-term exposure to high levels of inorganic arsenic, the long-term effect can normally be observed from the skin and pigment changes, skin lesions and hard patches on the palms and soles of the feet. There is also a possibility of skin cancer, bladder and also lungs cancer after a long-term exposure to arsenic. Some other adverse health effect after exposure to long-term of ingestion of inorganic arsenic may incur the development effects, neurotoxicity, diabetes and cardiovascular disease (World Health Organization, 2012).

In the environment, arsenic could do harms to plants where it can inhibit the root extension and proliferation of a plant. In addition, arsenic can severely impede plant growth by slowing and arresting the expansion and biomass accumulation. Other than that, arsenic can disrupt the plants' reproductive capacity through losing in fertility, yield and fruit production. When arsenic forms inorganic arsenic such as arsenate (+5) and arsenite (+3), they are easily being absorbed by plants which will result in disruption of the metabolism of the plants and if is sufficiently high concentration of arsenic, this will result in death of a plant (Finnegan and Chen, 2012).

2.1.3 Zinc

Zinc (Zn) is abundant on Earth's crust and it can be found in water, air, soil and even in food. Zn usually presents as zinc sulphate in most of the Zn ore. Zn is a glossy bluish-white metal where it present in a crystalline form under room temperature. Zn is brittle in nature but it becomes ductile and malleable when is heated between 110^{o}C and 150^{o}C. On top of that, Zn is fairy reactive metal in which it can combine with oxygen and other non-metals and also react with dilute acids to that releases hydrogen gas (Gakwisiri, et al. 2012). According to Agency for Toxic Substance and Disease Registry (2005a), powdered Zn is explosive and it is possible to burst into flames if stored in damp place.

Zn is commonly used for galvanizing which is the process to coat steel and as well as other metals such as iron to prevent corrosion and rust. In addition, Zn is used as part of the mixture to form alloy such as brass and bronze, for example is Zn and Cu alloy is used to make pennies in the United States. The applications of Zn compounds in commercial are as listed in Table 2.2.

Table 2.2 Types of Zinc Compounds with Different Applications

Type of zinc compounds	Applications	References
Zinc sulfide and Zinc oxide	Paints, ceramics and etc.	Agency for Toxic Substance and Disease Registry (2005a)
Zinc oxide	Catalyst and heat disperser in production of rubber	
Zinc Acetate, zinc chloride and zinc sulphate	Preservation of wood and manufacturing of dyes	
Zinc chloride	Smoke in smoke bombs	

Zn is an essential trace element for human health where only a certain amount of Zn is required to be consumed in order to maintain function of the body. For example, in the case of Zn deficiency for a human can cause malnutrition problem. According to Hambidge (2000), severe cases of Zn deficiency could cause many health effects, affecting epidermal, gastrointestinal, central nervous, immune, skeletal and reproductive system. The reason behind is in at least one of the many enzyme classification, Zn act as an essential part in the enzyme catalytic site which is essential for cellular and subcellular metabolism. Hundreds of Zn metalloenzymes have been found in plants and animals and therefore in the case of an increased of Zn in water, this will result in over intake of Zn by human when consuming the water. Excessive of Zn intake even for a short period of time may result stomach cramps, nausea and vomiting as mentioned by Kanawade and Gaikwad (2011) and it can damage the pancreas and disturb protein metabolism and cause arteriosclerosis (Christian, et al., 2015). Therefore, according to Department of Environment, Malaysia (2010), the maximum allowable for Zn to be present in drinking water is 3 mg/L.

Even though Zn is abundant on the Earth's crust, however due to anthropogenic activities, Zn had been overly explored and discharge into the environment uncontrollable such as in the atmosphere, surface water, groundwater and soil. Knowingly that Zn is added in huge amount into the environment through industrial activities, such as mining, coal and waste combustion and steel processing, it had damaged the aquatic ecosystem due to the toxicity of Zn. According to Cristian, et al. (2015), Zn levels in some soil samples had been determined to be 2000ppm to 180,000 ppm. Zn that accumulates in plants can result in physiological and biochemical changes.

2.1.3 Copper

Copper (Cu) has three common oxidation states such as Cu^0 (metal), Cu^+ (cuprous ion) and Cu^{2+} (cupric ion) where Cu^{2+} is the most common occurring species and easily form free hydrated ions in water (Awual, et al, 2014). Copper occurs naturally and anthropogenic where its common sources are industries such as printed circuit board production, metallurgical, fertiliser, chemical manufacturing, refining, mining drainage, paints and municipal and storm water runoff (Awual, et al, 2014). Some of the copper properties are easy to alloy, ductile, tough, catalytic, and recyclable and also it is a good electrical and thermal conductivity and corrosion resistance (Copper Development Association, 2016).

Copper is an essential trace element that is required by humans to synthesis enzyme, tissues and bones development. Nevertheless, Cu^{2+} is toxic and carcinogenic when excessively digested through ingestion. This will lead to deposition in liver and followed by vomiting, headache, nausea, respiratory problems, abdominal pain and even worse are liver and kidney failure and finally gastrointestinal bleeding (Bilal, et al., 2013). Gupta and Gogate (2016) reported that Cu can even generate reactive oxygen species in the blood stream and damage the protein, lipids and Deoxyribonucleic Acid (DNA) after overly consumed.

Copper is reported to be the most common heavy metal present in the marine ecosystem and it has found to be damaging the gills, liver, kidneys and the nervous system of fishes and even the sexual life (Gupta and Gogate, 2016). In addition, it was reported that Cu had caused detrimental effects on soil biota and damaged many plant species includes some of the Australian native plant species *Acacia holosericea and Eucalyptus crebra* (Bilal, et al., 2013).

2.2 Treatments Used to Remove Organotin, Arsenic, Zinc and Copper from Water/Wastewater

Treatment of water or wastewater are available in all kinds of technologies worldwide and some of the common ones such as coagulation and flocculation, membranes such as microfiltration, ultrafiltration nanofiltration and reverse osmosis. Furthermore, there are even adsorption using ion exchange resin and even some other processes such as advanced oxidation processes. Table 2.3, 2.4, 2.5 and 2.6 show some of the examples of treatments used to treat organotin, arsenic, Zn and Cu in the wastewater treatment world.

Table 2.3 Types of Current Treatments Used to Remove Organotin from Water/Wastewater

Pollutants	Type of Treatments	Initial Conc.	Final Conc.	Removal Efficiency (%)	Reference
Organotins					
Tributyltin	Electrochemical Treatment (Advanced Oxidation Processes)	50,000 mg/L	8.17 mg/L	99.98	Areval and Calmano (2007)
Dibutyltin		10,000 mg/L	307.15 mg/L	96.93	
Monobutyltin		5,000 mg/L	357.38 mg/L	92.85	
Tributyltin	Chemical Oxidation with Ozone	3182 ng/L	< 10 ng/L	> 99.69	Pynaert and Cautren (n.d.)
Dibutyltin		4051ng/L	82 ng/L	97.98	
Monobutyltin		1144 ng/L	206 ng/L	82.00	
Triphenyltin		1789 ng/L	< 10 ng/L	> 99.44	
Diphenyltin		91 ng/L	0	100.00	
Monophenyltin		390 ng/L	154 ng/L	60.51	
Tributyltin	Photo-Oxidation			90.00	
Dibutyltin				93.00	
Monobutyltin				60.00	
Tributyltin	Combined Photo- and Chemical Oxidation	5966 ng/L	25 ng/L	99.58	
Dibutyltin		3988 ng/L	355 ng/L	91.10	
Monobutyltin		1280 ng/L	131 ng/L	89.77	
Triphenyltin		2710 ng/L	221 ng/L	91.85	
Diphenyltin		407 ng/L	34 ng/L	91.65	

Table 2.4 Types of Current Treatments Used to Remove Arsenic from Water/Wastewater

Pollutants	Type of Treatments	Initial Conc.	Final Conc.	Removal Efficiency (%)	Reference
Arsenic					
Arsenic (V)	Combined Coagulation and Adsorption Process	100 µg/L	25 µg/L	85.90	Pio, et al. (2014)
Arsenic	Combination of Advanced Oxidation Process (AOP) with Non-Thermal Plasma	> 500 µg/L	< 0.5 µg/L	99.99	SFC Umwelttechnik (n.d.)
Arsenic	Adsorption using Zirconium Oxychloride Octahydrate + Ethanolamine	10 mg/L	< 0.011 mg/L	> 99.89	Mandal, n.d.
Arsenic (V)	Reverse Osmosis	100 µg/L	0.5 µg/L	99.50	Abejón, Garea and Irabien (2015)
Arsenic (III) Arsenic (V)	Adsorption using Polyaniline/Fe^0 composite nanofibers			> 99.30 > 99.30	Bhaumik, et al. (2015)
Arsenic (III) and (IV)	Electrocoagulation using ball electrodes	285 µg/L	1.88 µg/L	99.30	Kobya, et al. (2015)
Arsenic	Electrocoagulation using Iron rods	526 µg/L	0.4 µg/L	99.92	Wan, et al. (2011)
Arsenic (V)	*N*-methyl-D-glucamine functionalized poly(propylene) membranes	100 µg/L	6.2 µg/L	93.80	Shinde, et al. (2014)
Arsenic	Zn/Fe layered double hydroxide	710 µg/L	2.01 µg/L	99.72	Lu, et al. (2015)

Table 2.5 Types of Current Treatments Used to Remove Zinc from Water/Wastewater

Pollutants	Type of Treatments	Removal Efficiency (%)	Reference
Zinc			
Zinc	Acidophilic and autotrophic biocathode	> 99	Teng, et al. (2015)
Zinc	Biocopolymer membrane with fumed silica	96.30	Christian, et al. (2015)
Zinc	Electrocoagulation: Direct and Alternating Current with Iron electrodes and Stainless Steel electrodes.	95.50	Mansoorian, Mahvi and Jafari (2014)
Zinc	Coagulation with hydrogen peroxide	81.27	Badmus, Audu and Anyata (2006)

Table 2.6 Types of Current Treatments Used to Remove Copper from Water/Wastewater

Pollutants	Type of Treatments	Removal Efficiency (%)	Reference
Copper			
Copper	Ion-Exchange	64	Gaikwad, Sapkal and Sapkal (2010)
Copper	Liquid Emulsion Membrane	> 96	Mohamed and Ibrahim (2012)
Copper	Ion Exchange	> 90	Muzenda (2011)
Copper	Coagulation and Flocculation	79	Johnson, et al. (2008)

2.3 Adsorption

There are many types of treatment methods in the wastewater treatment world to treat inorganic matters such as heavy metals and organic matter that may present in the source of drinking water or industries’ waste. Some of the efficient methods of heavy metals removal are chemical precipitation, ion exchange, reverse osmosis, ultrafiltration, nanofiltration, coagulatiom, flocculation, flotation and etc. Methods to remove organic matter are aerobic digestion, anaerobic digestion, physicochemical treatment such as coagulation-flocculation, chemical oxidation and etc. Nevertheless, these methods have several drawbacks such as high reagent requirement, unpredictable metal ion removal, generation of toxic sludge, high cost, etc. According to Lakherwal (2014), adsorption process being very simple, economical, effective and versatile has become the most preferred methods for removal of toxic contaminants from wastewater. Adsorption is the attachment or adherence of fluid onto a surface of liquid or solid (Chromatography, 2014). Adsorption involves different forces such as electrostatic attraction, covalent bond, hydrogen bond, hydrophobic bond and salvation and desolvation of different species that are bonding the adsorbate (molecule that being adsorbed) and adsorbent together (Somasundaran, Shrotri and Huang, 1998). According to Chromatography (2014), the strength of the interaction between the adsorbent and adsorbate can be used to further differentiate adsorption into physical adsorption (physisorption) and chemical adsorption (chemisorption). Physisorption defined as the bonding between the adsorbent and adsorbate is Van der Waals force whereas chemisorption defined as the bonding involving chemical bond between adsorbent and adsorbate. As stated by Chromatography (2014) that chemisorption has a higher requirement of energy for the bonding than physisorption in which energy had become the main difference between these two processes.

There are several factors that are affecting the adsorption efficiency and capacity. First of all, the surface area of the adsorbent is one of the many factors in which the larger the surface area of contact of adsorbent, the higher the efficiency of the adsorption. This can be proven by Wang, et al. (2009) that had concluded in his experiment that the adsorptive property of activated alumina (adsorbent) for phosphorus was resulted from three factors and one of it is the surface area of the activated alumina. It was determined that the surface area of activated alumina which is the largest resulted in the highest adsorptive capacity. Secondly, according to Krishna and Swamy (2012) that the particle size of adsorbent is another factor that is affecting the adsorption. It was then concluded that when a smaller particle size reduces, the higher kinetic rate of adsorbate uptake by smaller adsorbent which was resulted by the greater accessibility to pores and greater surface area for bulk adsorption per unit weight of adsorbent. Thirdly, the contact time of the adsorbent with the adsorbate is another factor affecting adsorption where the longer the time of contact, the more complete adsorption will be. This example can be given by Dakhil (2013) presenting result on effect of contact time showing the removal of phenol using sawdust increases with increase in mixing contact time and reached equilibrium at 120 min. On top of that, it was stated by Ghauri, et al. (2012) that the adsorption of ammonia by thermally activated carbon increases with the increase of contact time and will eventually reach equilibrium.

Fourthly, the solubility of adsorbate in liquid is another factor affect the adsorption in which the adsorbate with slightly soluble in water will be more easy to be removed as compared to adsorbate with high solubility. On top of that non-polar adsorbates will be easier to be removed than polar substance as the latter has a higher affinity for water. This can be proven by Sulaymon, Kassim and Nasir (2011) in the experiment that the higher adsorption capacity of paranitrophenol on to organoclay is due to three factors and one of the factors is the lower solubility of paranitrophenol. The fifth factor affecting the adsorption is the affinity of the adsorbate for the adsorbent. The surface of the adsorbent is slightly polar and therefore non-polar adsorbate will be more easily picked up by carbon than polar ones. According to Potgieter, Bada and Petgieter-Vermaak (2009), 4-nitrophenol was found to be adsorbed more than phenol as due to the more non-polar compound, the less its affinity for solvent and therefore higher its adsorption affinity by the adsorbent. The sixth factor affecting the adsorption process is the size of the molecule with respect to size of the pores of adsorbent. This is because if the size of the adsorbate is larger than the size of the pore of the adsorbent, the adsorbate may not able to enter the pores and therefore will reduce the adsorption independently of other causes. (Al-Anber, 2011)

The seventh factor affecting the adsorption is pH where pH has a significant impact on the uptake of adsorbate where the influence of pH not only on the adsorbent surface charges but also degree of ionization and speciation of the adsorbate. At low pH, the biochar functional groups such as –COOH and –OH present on biochar are protonated and presented in positively charged form which favour adsorption of anions whereas at high pH, large number of H^+ and H_3O^+ in the aqueous solution may compete with cation for adsorption sites on biochar (Tan, et al., 2015).

2.4 Adsorbent

According to Buekens and Zyaykina (2003), there are some of the basic requirements that an adsorbent should have such as high porosity, high adsorption efficiency in a wide range of adsorbate concentration, good balance between macro pores and micro-pores in order for fast internal transport and large internal surface respectively. Also, mechanical integrity during handling and low cost for acquisition of adsorbents is some of the basic requirements of adsorbents. Currently, there are various types of adsorbent present that are used to treat different kinds of waste such as the most widely and commonly use silica gel to adsorb moisture due to its comparatively weak bonds with water as well as large pore volume and mesoporosity. According to Bhatnagar and Minocha (2005) that some of the adsorbents that are commonly used such as activated alumina and bauxite were used to remove water vapour from gases and also successfully make use of it to remove As (V), phosphate ion (PO_4^{3-}), chloride ion (Cl^-) and fluoride ion (F^-). There are also zeolites and ion exchange resins in which zeolites is commonly used to remove methylene blue dye, phenols and chlorophenols. Ion-exchange is commonly used for softening and deionizing of water. Activated carbon is the mostly used and popular adsorbent used currently in wastewater treatment throughout the world. Activated carbon purifying water has been long used to remove bad tastes and odours which it is produced from various processes from dehydration to carbonization then lastly activation. Table 2.7 shows the list of adsorbent used to treat organotin, arsenic, Zn and Cu.

Table 2.7 Types of Adsorbent Used to Treat Organotin, Arsenic, Zinc and Copper respectively

Types of Adsorbents	Pollutant(s)	References
Powdered Activated Carbon	Monobutyltin, Dibutyltin and Tributyltin	Vreysen, Maes and Wullaert (2008)
Granular Activated Carbon		
Bentonite + Flocculant		
Organically modified bentonite		
Granulated modified aluminosilicate		
Acid activated bentonite		
Sorbent based on Ca-bentonite		
Fe-Mn binary oxide impregnated chitosan bead	Arsenic (III)	Qi, Zhang and Li (2015)
Modified semi-coke	Methyltin mercaptide	Xin, et al. (2013)
Polyaniline/Fe^0 composite nanofibers	Arsenic (V) Arsenic (III) Arsenic (V)	Bhaumik, et al. (2015)
Synthesize micro/nano-structured Fe–Ni binary oxides	Arsenic (III) Arsenic (V)	Liu, et al. (2015)
3-mercaptopropyl functionalized silica entrapped polyacrylamide hydrogel	Arsenic (III)	Kumar, et al. (2015)
Cobalt ferrite nanoparticles aggregated Schwertmannite (Iron oxide hydroxide)	Arsenic (III)	Dey, Singh and Purkait (2014)
Oil palm empty fruit bunch and rice husk biochars	Arsenic	Sari, Ishak and Bakar (2014)
Biochars (rice husk, organic solid wastes and sewage sludge)	Arsenic	Agrafioti, Kalderis and Diamadopoulos (2013)
Adsorbents (peanut husk charcoal, fly ash and natural zeolite)	Zinc	Salam, Reiad and Elshafei (2011)
Biochars (lemon peel and banana peel)	Zinc	Rajoriya and Kaur (2014)

Types of Adsorbents	Pollutant(s)	References
Adsorbents (activated carbon, kaolin, bentonite, blast furnace slag and fly ash)	Zinc Chloride	Mishra and Patel (2009)
Biochars (softwood and hardwood)	Zinc	Jiang, et al. (2016)
Cork powder	Zinc	Kanawade and Gaikwad (2011)
Activated watermelon shell with ultrasound	Copper	Gupta and Gogate (2016)
Mesoporous silica based meso-adsorbent	Copper (II)	Awual, et al. (2014)
Activated carbon	Copper	Salmani, et al. (2012)
Syzygium Cumini L	Copper	Pandey, Kankal and Jadhav (2014)

2.5 Biochar

Bhatnagar and Minocha (2005) stated that due to the increasing amount of solid wastes that are produced in the agriculture sector in many countries, it has been explored and taken to test for its absorptivity. Eventually it was proven that many of the agricultural wastes are applicable to act as an adsorbent. Agricultural solid wastes can be explored as a low cost adsorbent with comparatively high fixed carbon content and porous structure. The processed agriculture waste which then turned into adsorbent can be termed as ‘Biochar’ which defined by Tan, et al. (2015) that it is a solid which is rich with carbon that formed through the process of heating with little or no oxygen which is also known as pyrolysis process. According to Tan, et al. (2015), biochar can release carbon into the atmosphere from burning or degraded by carbon stabilization into form similar to charcoal. It can then be buried into the soil to store carbon and improve soil properties. Furthermore, the bioenergy produced during the pyrolysis process gives rise to the potential to substitute fossil fuels. Some of the feedstock that had been tested to be applicable in the adsorption of contaminants is bamboo, corn straw, pine wood, sugar cane stover, cattle manure, rice husk, peanut shells and etc (Tan, et al., 2015).

Biochar stability can be measured using hydrogen to organic cabon molar ratio (H/C_{org}) and oxygen to carbon molar ratio (O:C) which reflect the physical-chemical properties of biochar which then relates it to stability. According to Budai, et al. (2013) that the higher the biochar production temperature, the lower H/C and O/C ratio. Biochar materials obtained after thermochemical process with H/C_{org} more than 0.7 is not considered as biochar as the materials would not meet the definition of biochar set by International Biochar Initiative Standard. Organic carbon was used for the ratio instead of total carbon, because biochar may contain inorganic carbonates and they do not form aromatic groups distinctive of biochar materials (International Biochar Initiative, 2014). Table 2.8 shows a list of biochars being used for many different types of applications such as treatment of dye, reduces methane emission from paddy soil, ecological restoration and etc.

Table 2.8 Application of Biochars

Types of Biochars	Application	Results	References
Sewage Sludge	Characterisation and application for dye adsorption	Adsorption mechanism appears to be associated with cation release and functional group participation	Leng, et al. (2015)
Rice Husk + Phosphorus Fertilizer	Protects rice pollen from high-temperature stress	Significantly ↓ damaging effects, resulting in ↑ pollen fertility and retention and rate of pollen germination	Fahad, et al. (2015)
Corn Stalk	Decrease methane emission from chinese paddy soils	Reduce CH_4 emission, retain more C in paddy soil, nutrients in soils are maintained and ↑ grain yield	Feng, et al. (2012)
Algal (*Oedogonium)*	Enhances the re-vegetation of stockpiled mine soils with native grass	Contribute essential trace elements (particularly K) to soil pore water. ↓ the germination time by the grass and ↑ the growth and production of plant biomass	Roberts, et al. (2015)
Orange Peel	Adsorption of 1-Naphthol	OP200(^{o}C) exhibited the optimum sorption capacity for 1-naphthol at high concentration due to its maximal partition and high-surface adsorption	Chen and Chen (2009)
Hardwood made from oak and hickory sawdust + Diary cattle solid manure	Co-application to a calcareous soil	Improved the soil water content, ↑ soil organic C content	Ippolito, et al. (2015)
Bamboo	Ecological restoration of an acidic Cd contaminated soil	Enhancements in soil pH, organic carbon and cation exchange capacity (CEC), and ↓ solubility and availability of Cd	Mohamed, et al. (2015)
Prune residues from Orchards	Application on mine tailings	↓ in bioavailability and leachability for some pollutants.	Fellet, et al. (2011)

2.5.1 Mechanism of Biochar Adsorption

Adsorption of heavy metals and organic pollutants by biochar possesses different kind of interactions between biochar and adsorbate. The interactions between heavy metals and biochar include electrostatic attraction, ion-exchange, physical adsorption, surface complextion and/or precipitation. Tan, et al. (2015) stated that different heavy metals have different mechanisms which therefore suitable properties of biochar could result in a high adsorption efficiency of heavy metals. Ample of surface functional groups of oxygen-containing such as carboxylate (-COOH) and hydroxyl (-OH) that present on biochar's surface which can produce a strong interactions with heavy metals such as electrostatic attraction, ion-exchange and surface complexation. On top of that, the mineral components in biochar played an important role in the adsorption process. The removal capability varied with different biochar feedstock sources and the mineral component such as CO_3^{2-} and PO_4^{3-}. These mineral components act as an attachment sites for the heavy metals which contributed the adsorption capacity for heavy metals.

On the other hand, organic pollutant bindings to biochar consist of different interactions as compared to heavy metals with biochars. Their interactions are controlled by hydrophobic effect, hydrogen bonds, electrostatic interaction and pore-filling. The surface property of biochar is heterogeneous due to the co-existing of carbonized and non-carbonized and of its phases generally represents different adsorption mechanisms. The adsorption of organic compound is can be partitioned into either non-carbonized organic matter and by carbonized matter. Pore-filling plays an important role as for adsorption of organic compounds onto biochars. Pore-filling is related to biochar's surface properties and its capability to adsorb is directly proportional to micropore surface area (Tan, et al., 2015). The mechanisms of bonding between adsorbent with heavy metals is shown in Figure 2.1; adsorbent with inorganic is shown in Figure 2.2.

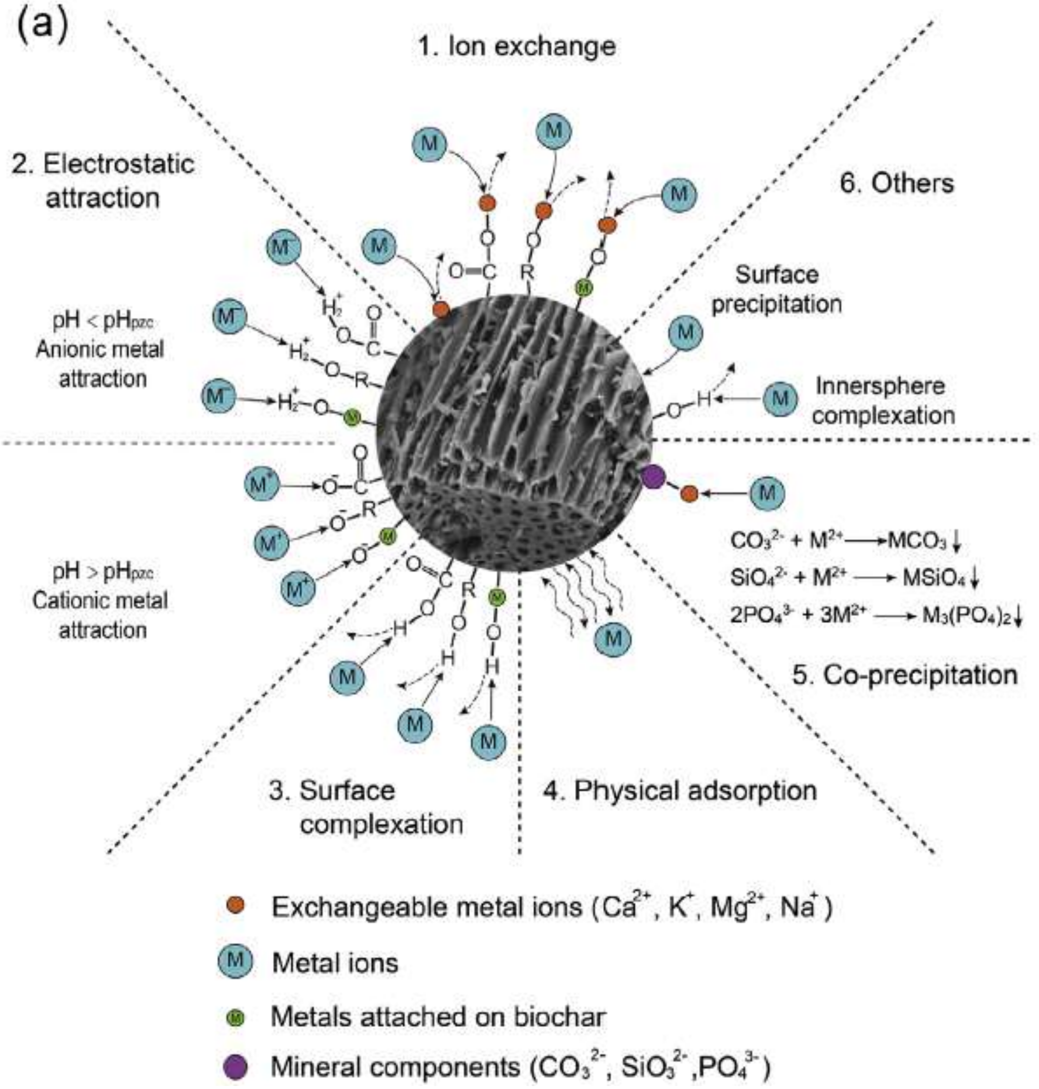


Figure 2.1 Summaries of Proposed Mechanisms for Heavy Metals and Adsorption on Biochars (Tan, et al., 2015)

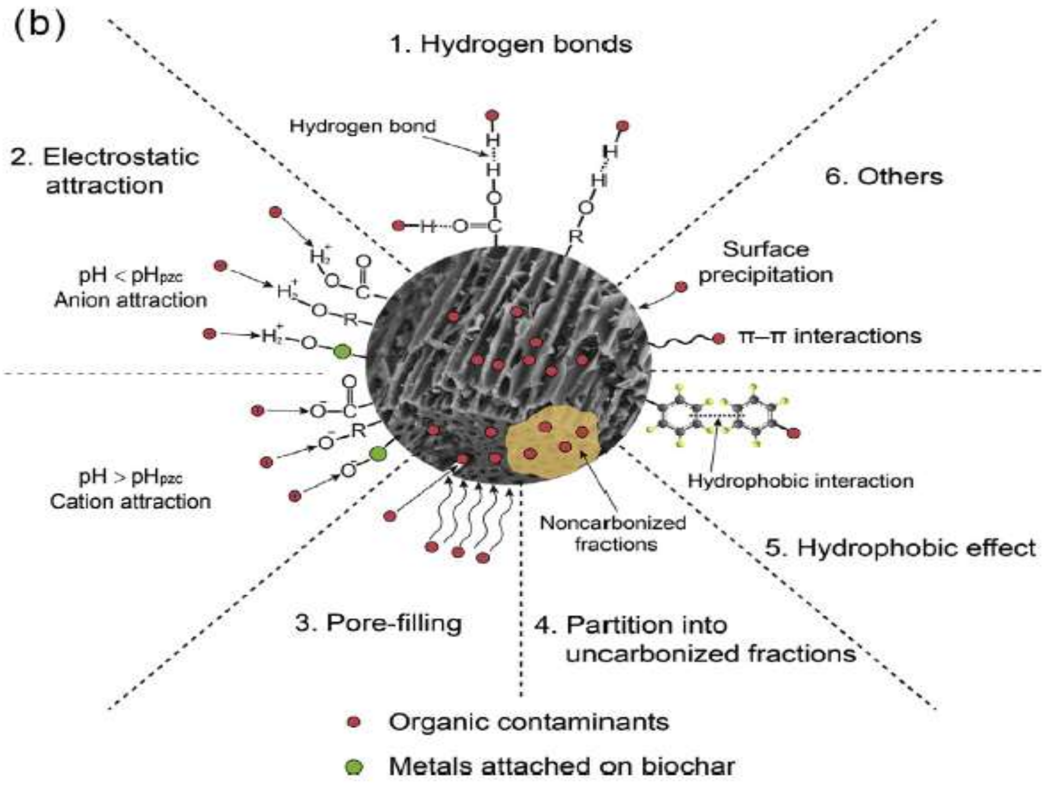


Figure 2.2 Summaries of Proposed Mechanisms for Organic Contaminants Adsorption on Biochars (Tan, et al., 2015)

2.6 Preparation of Biochar through Pyrolysis

Pyrolysis of biomass involves heat and under anaerobic or anoxic environment to decompose biomass. Ronsse (2013) reported that during the pyrolysis process, the constituents of the biomass such as lignin, cellulose, fats and starch are broken down through thermal process into three different fractions which are bio-oil, char and non-condensable gases. Different percentage of fractions obtained depends on the type of biomass feedstock, condition of pyrolysis such as the temperature applied and the heating rate. According to Libra, et al. (2011), the factors that differs the pyrolysis process from one and another is the speed of heat being transferred to fresh feedstock particles, maximum temperature that it reaches (T_{max}) and residence time of the material in the process. In this topic, two main processes will be discussed in producing biochar using conventional pyrolysis and microwaved-pyrolysis.

2.6.1 Conventional Methods in Producing Biochar

Listed in Table 2.9 are some of the conventional methods of producing biochar and the by-products – fractions which were obtained and tabulated by Ronsse (2013). The main factors which are differentiating the methods are temperature, heating rate, residence time, pressure and medium.

Table 2.9 Different Thermochemical Conversion Processes with Different Conditions and Product Yields in (%) of Char, Non-Condensable Gases and Bio-Oil (Ronsse, 2013)

	Thermochemical conversion process type			
	Fast Pyrolysis	**Slow Pyrolysis**	**Gasification**	**Torrefaction**
Temperature	~500°C	> 400°C	600 – 1800°C	< 300°C
Heating Rate	Up to 1000 °C/min	< 80 °C/min	-	-
Residence Time	Seconds	Hours ~ Days	-	< 2 hr
Pressure	Atmospheric (Vacuum)	Atmospheric (or elevated up to 1 MPa)	Atmospheric (or pressurized up to 8 MPa)	Atmospheric
Medium	Oxygen-free	Oxygen-free or Oxygen limited	Oxygen limited (air or steam/oxygen)	Oxygen-free
Bio-oil (Liquid)	75 %	30 %	5 %	5 %
Non-condensable gases	13 %	35 %	85 %	15 %
Char (Solid)	12 %	35 %	10 %	80 %

Classification of pyrolysis usually depends on the heating rate applied to the biomass in order to reach the intended pyrolysis temperature as mentioned by Ronsse (2013). Table 2.9 shows the major difference between fast and slow pyrolysis where the heating rate and residence time between these two processes made the biggest distinction. Fast pyrolysis requires faster heating rate which gives the term 'fast' pyrolysis and it requires much lesser residence time compared to slow pyrolysis. The high heating rate gives rise to higher yield of bio-oil fraction and lesser non-condensable gases and char. On the other hand, slow pyrolysis is vice versa of fast pyrolysis in terms of yield. Low heating rate resulted in maximum yields in char. After comparing the fraction of char produced by each process, the char yields are in descending order: slow pyrolysis > fast pyrolysis > gasification. According to Ronsse (2013), torrefaction method is excluded as it produces unstable biochar ($H/C_{org} > 0.7$). As such slow pyrolysis is considered the most suitable process for char production compared to other methods. Ronsse (2013) commented that the term 'slow pyrolysis' and 'carbonization' are commonly used and can be used interchangeably as both are more or less have the same process. However, slow pyrolysis is a broader term which includes carbonization as well as torrefaction.

Carbonization of biomass residuals has been proven to be environmentally sound conversion process in producing various products for environmental, catalytic, electronic and agricultural applications. Among the products, biochar is one of the promising products, not only being used to increase soil fertility but also in treating water. According to Libra, et al. (2011), carbonization is a process to increase carbon content in solid residues. Carbonization can be applied in wet or dry condition in which if carbonization is carried out in the presence of subcritical, liquid water is called as hydrothermal carbonization.

2.6.2 Microwave Pyrolysis Producing Biochar

According to Huang, et al. (2014b), microwave heating is more environmentally friendly compared to the conventional heating. On top of that, it is well-established and reduces energy consumption and reaction time. Also, microwave heating does not require direct contact with the materials when heating with higher level of safety and automation. Microwave has been utilised in many applications such as synthesis, digestion, extraction, sample pre-treatment and stabilization. The reason behind for the rapidly occurring thermochemical reactions is due to the naturally fast, volumetric and selective heating using microwave energy. Materials that have the ability to absorb microwave which is known as dielectrics and therefore microwave heating also referred to as dielectric heating. Microwaves lie between infrared radiation and radio waves in the electromagnetic spectrum. Microwaves consist of electric and magnetic field which are perpendicular to each other. In microwaves, mechanisms that contribute to the thermal energy from electromagnetic energy are dipole polarization and interfacial or also known as Maxwell-Wagner polarization. Dipole polarization mechanism works by the distortion of electron cloud surrounding non-polar molecules or atoms through the existence of external electric field. This induces temporary dipoles in the material which then exposed to the alternating electromagnetic field realign themselves approximately 2.5 billion times per second (frequency 2.45GHz) which resulted in energy dissipation as heat from internal resistance to rotation. As for Maxwell-Wagner polarization, it occurs at boundaries of two materials with different dielectric properties or dielectric solid materials. The heat is dissipated when the charged particle in the material couldn’t couple to the changes of phase of electric field. The accumulation of charge at the material interface is produced and therefore energy is dissipated as heat (Fernández, Arenillas and Menéndez, 2011).

Currently, using microwave to produce biochar has attracted many companies and researches to study and research on converting different types of biomass into biochar for different usages such as wastewater treatment, soil amendment and etc.

Listed in Table 2.10 are the examples of biochar production using microwave by other researchers.

Table 2.10 Microwave Pyrolysis of Different Type of Biomass to Biochar for Respective Purpose

Type of Biomass	Purpose	Reference
Rice Straw	Adsorption CO_2	Huang, et al. (2014a)
Sewerage sludge and rice straw	Determining the performance of co-pyrolysis of two different biomass	Huang, et al. (2014b)
Wood Biomass	CO_2 Gasification	Wu, et al. (2015)
Rice straw	Determining the effect of Alkali and alkaline earth metals towards production of biochar	Xiao, et al. (2015)
Scenedesmus almeriensis	Determining syngas production	Beneroso, et al. (2013)

2.6.3 Comparison between Conventional Pyrolysis and Microwave Pyrolysis

The main difference of conventional pyrolysis and microwave pyrolysis is the heating method. Conventional applies convection or conduction to transfer energy into a material. Convection involves the transfer of heat energy in gas or liquid by movement of currents; conduction is the transfer of heat energy from particle to particle. Two of these processes require much longer time to heat from the outer part of a material to inner part which takes longer time or more heat if time is reduced (Ronsse, 2013). On contrary, microwave pyrolysis uses dipole rotation and Maxwell-Wagner polarization uses electromagnetic energy that can heat up the material in whole and uniformly and therefore requires lesser heat and thus lesser time. Based on one of the experiment conducted by Mašek, et al. (2014), physical and functional properties of biochar produced by microwave and slow pyrolysis on straw pellets and williow chips are found to be different. It was reported that, using microwave at 200°C is better than slow pyrolysis at the same temperature for both materials. It was determined that only at 350°C of slow pyrolysis; the stability of both materials could reach stability similar to both materials produced by microwave at 200°C. Table 2.11 shows the summary of comparison between conventional pyrolysis and microwave pyrolysis.

Table 2.11 Summary of comparison between Conventional Pyrolysis and Microwave Pyrolysis

	Conventional Pyrolysis	**Microwave Pyrolysis**	**References**
Heating Pattern	Conduction or Convection	Dipole plarization and Maxwell-Wagner polarization	Fernández, Arenillas and Menéndez (2011)
Temperature/Power	350°C – 1800°C	100°C -400°C	Abbas and Ani (2014)
Residence Time	Hours to days	minutes	Ronsse (2013)
Stability of Biochar	Less stable	More stable	Mašek, et al. (2014)

Table 2.11 has display the differences between conventional pyrolysis and microwave pyrolysis. It is shown clearly that conventional pyrolysis requires much higher temperature and longer time as compared to microwave pyrolysis which is much related to its heating pattern. On top of that, microwave pyrolysis of biomass is able to produce a more stable biochar as compared to conventional pyrolysis as reported by Mašek, et al. (2014) as H/C_{org} is lesser than 0.7.

2.7 Palm Oil Mill Sludge (POMS)

Palm oil mill effluent (POME) is usually produced from the process of oil extraction of the palm oil, washing and cleaning processes in the mill. According to Yahaya and Seng (2013), an average of 30 million tonnes of POME were generated from 381 palm oil mills in Malaysia in just 2004 itself with an average of roughly 53 million m^3 of POME being produced annually in Malaysia. POME contains many solid components in the form of suspended solids and dissolved solids which will be then anaerobically treated to form palm oil mil sludge (POMS). The amount of POMS increases proportionally to POME quantity. According to Yahaya and Seng (2013), there are about 26.7 million tonnes of solid biomass produced annually in which POMS is a part of the contribution. It is vital to understand and acknowledge the characteristic of POMS before any further treatment or usage of it which it will be further discussed in details.

Characteristics of POMS are being studied by Rupani (2010) and Baharuddin (2010) as shown in Table 2.12 and Table 2.13 respectively. Both of these studies show clearly that POMS contain high amount of water for at least 85 % from Rupani (2010) study. On top of that, the pH of POMS is slightly alkaline.

Table 2.12 Characteristics of POMS

Parameters	POMS	Reference
Moisture Content %	85.0	Rupani (2010)
pH	8.4	
Organic Matter	60.0	
Total Organic Carbon (TOC)	33.0	
Total Nitrogen (TN)	3.6	
Phosphorus (as P_2O_5)	0.9	
Potassium (as K_2O)	2.1	
Moisture Content %	94.03 ± 2.3	Baharuddin (2010)
pH	7.41 ± 0.2	
Carbon, C (%)	37.51 ± 5.1	
Nitrogen, N (%)	4.68 ± 0.7	
C/N	8.0	
Oil and Grease (mg/L)	183.0 ± 10.1	
COD[a] (mg/L)	40563.0	
BOD[b] (mg/L)	15180.0	
Volatile suspended solid	21110.0	
Total suspended solid	34720.0	
Total Solid	55884.0	
Cellulose	10.45 ± 5.1	
Hemicellulose	6.01 ± 1.8	
Lignin	48.13 ± 9.2	

[a] represent Chemical Oxygen Demand

[b] represents Biochemical Oxygen Demand

2.7.1 Utilisation of POMS

There are various ways of reutilising palm oil mill sludge (POMS). Literatures have reported the main usage as fertilisers after drying. However, during rainy season, the drying process would be tough due to the slow rate drying of POMS (Yaser, Rahman and Kalil, 2007).

A proper handling of POMS is by co-composting of lignocellulose oil palm empty fruit bunch (OPEFB) with POMS. This research was done by Zainudin, et al. (2013) with an objective to speed up the composting time of OPEFB required with indigenous microbes added continuously throughout the composting period. The present of nitrogen (4.7 %), phosphorus (1.3 %) and potassium (6.5 %) possesses a potential as microbial seed for composting process. The additional of POMS throughout the composting process provides continuous nutrients and source of microbes for biodegradation of the lignocellulose OPEFB (Zainudin, et al, 2013).

In another research done by Thangalazhy-Gopakumar, et al. (2014), POMS was pyrolyzed to produce bio-oil and bio-char. Thangalazhy-Gopakumar, et al. (2014) reported 27.4 ± 1.7 wt % of bio-oil and 49.9 ± 0.3 wt % of biochar yield at the end of the experiment. On top of that, the produced biochar was tested on cadmium adsorption from synthetic wastewater.

2.8 Summary

In summary, arsenic, Zn, Cu and organotin that originate from industries or some other sources must be treated to the least amount as possible This is to ensure a safe water to be discharge into water body which may result as a source of drinking water. Also, since the palm oil anaerobic sludge is produced in mass production, it is an integrity and benefit way to palm oil mills to be able to minimize waste being dump at sites and utilizing them, turning it into biochar. Pyrolysis of POMS using microwave pyrolysis method can save on cost as the required energy to turn the sludge into biochar is minimal as compared to conventional methods due to the heating pattern of microwave is radiation which heats up the sludge quicker in whole and uniformly. Also, the residence time of heating the sludge is lesser when using microwave when compared to conventional methods. It has also been proven that using biochar produced from microwave can achieve stability at lower temperature as compared to conventional methods, where it requires higher temperature to be able to achieve biochar stability similar to biochar produced from microwave at lower temperature.

CHAPTER 3

METHODOOGY

3.1 Materials

Materials used to carry out during the experiment works are as listed below:

- Palm Oil Mill Sludge (POMS)
  The palm oil mil sludge was taken from Tian Siang Oil Mill (Air Kuning) Sdn. Bhd in Air Kuning, Perak, Malaysia. The POMS was used to produce biochar which was generated from anaerobic digestive system.

- Chemicals
  Trimethyltin (TMT) Chloride (Chem Soln, 5 g, ≥ 98 % purity, Analytical Reagent grade), Sodium Arsenate Hydrated (Fisher Scientific, 250g, 98 % purity, Analytical Reagent grade), Zinc Nitrate (QRëC, 500 g, 98 % Purity, Analytical Reagent grade), Copper Sulphate (Bendosen, 1 kg, 98 % Purity, Chemically Pure grade) and nitric acid (QRëC, 2.5 L, 98 % purity, Analytical Reagent grade)

- Gases
  Nitrogen gas (Linde) with 98 % purity was used during microwave-pyrolysis to ensure the condition in the microwave is oxygen-free.

- Ultrapure Water

  Ultrapure water was used to prepare the samples containing TMT, As (V), Zn or Cu to generate with biochar. It was also used in dilution of samples containing TMT, As (V), Zn or Cu to generate a calibration curve. Ultrapure water was produced by a machine known as PURELAB flex.

3.2 Experimental Work

The experiment involves few processes with design of experiment as an initial state followed by biochar preparation, adsorption study and last but not least is the characterization to support the experimental data.

3.2.1 Overall Experimental Flow Chart

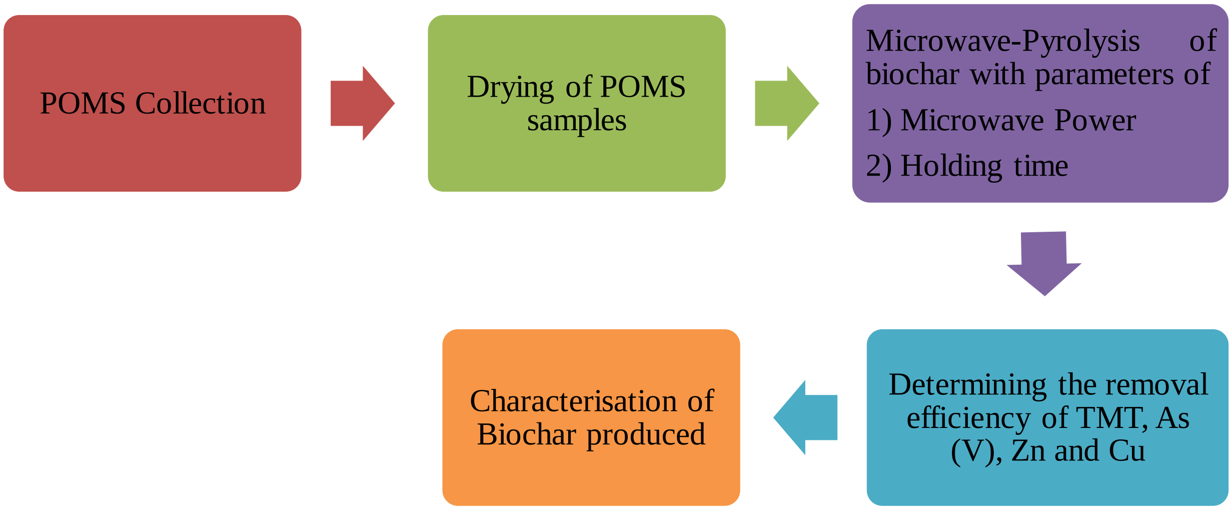


Figure 3.1 Overall Experiment Flow Chart

3.3 Design of Experiment

Two parameters were chosen to run design of experiment, i.e the heating power set to heat the biochar and holding time of biochar in the microwave. These two parameters were used to determine the optimum prepared parameters for the removal efficiency of TMT, As (V), Zn and Cu. The range for each parameter was set as shown in Table 3.1.

Table 3.1 Range of Parameters Used for the Preparation of Biochar

Coded	Parameters	Range
A	Heating power (W)	100 – 500
B	Holding time (min)	5 – 25

The parameter ranges were used as a guide to design the pyrolysis process to produce biochar from POMS by generating a list of design matrix as tabulated in Table 3.2.

Table 3.2 Experimental Design Matrix

No.	Heating Power (W)	Time of Heating (min)	Nitrogen Flow Rate (mL/min)	Removal Efficiency (%)
1	100	10	500	
2	100	15	500	
3	100	20	500	
4	100	25	500	
5	200	10	500	
6	200	15	500	
7	200	20	500	
8	200	25	500	
9	300	10	500	
10	300	15	500	
11	300	20	500	
12	300	25	500	
13	400	10	500	
14	400	15	500	
15	400	20	500	
16	400	25	500	
17	500	10	500	
18	500	15	500	
19	500	20	500	
20	500	25	500	

3.4 Biochar Preparation

The moisture in the sludge was removed by drying under the hot sun for two days consecutively to avoid the growth of fungicides or any unwanted contaminant contact. Next, it was further dried by heating the sludge in an oven (Memmert) for 24 hours at 105^{o}C. After heating, samples were left to cool and then kept in an air tight container prior to microwave pyrolysis.

First of all, a known amount of dried sludge was evenly placed into an Erlenmeyer flask to ensure an evenly heating condition. Then the flask is placed into the microwave as shown in Figure 3.2. Then, nitrogen gas (N_2) is purged into the microwave through a pipe connecting the N_2 gas tank to the Erlenmeyer flask for 10 min to ensure an inert condition inside the microwave before heating. The dried sludge was then heated with continue flowing of N_2 in the microwave according to the experimental design matrix. After heating, the biochars were left in the microwave for 20 min with constant N_2 flow to cool the biochar. After cooling, the biochars were then taken out and kept in a small air tight container.

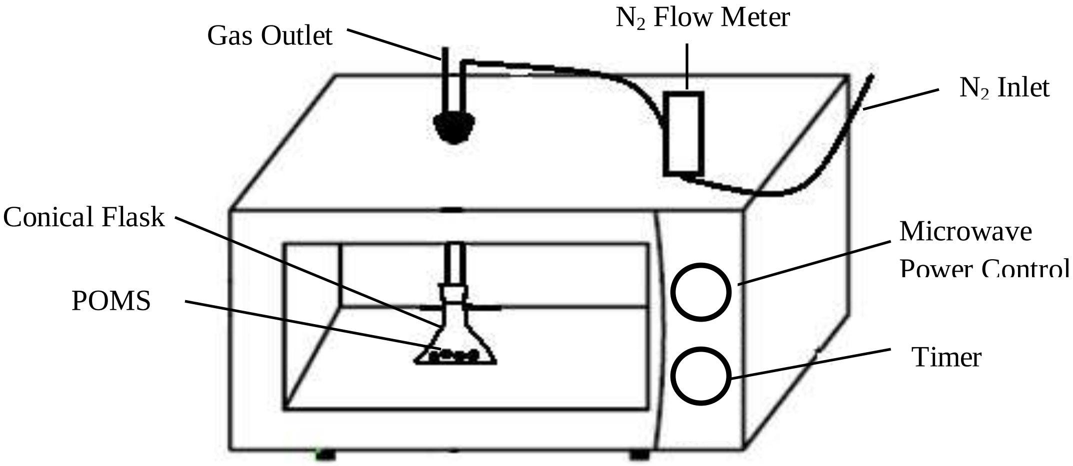


Figure 3.2 Drawing Scheme of Modified Microwave for Pyrolysing of POMS

3.5 Calibration Curve

Calibration curve for tin was prepared using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS Perkin Elmer NexION^{TM} 300Q, made in USA) (Figure 3.3) with self-prepared standard solution having concentration of 10 ppb, 500 ppb and 1000 ppb. Similar procedure was taken for arsenic, Zn and Cu. Standard solutions for the trimethyltin chloride, sodium arsenate hydroxide, zinc nitrate and copper sulphate were then measured using ICP-MS to determine its concentration and producing a standard calibration curve for TMT, As(V), Zn and Cu respectively.

Figure 3.3 ICP-MS Perkin Elmer NexION^{TM} 300Q, made in USA

3.6 Adsorption Study

0.02 g of biochar was measured using analytical balance (Shimadzu, AUX320). Then, it was poured into a 250 mL of Erlenmeyer flask. 5 g of solid trimethyltin chloride was first dissolved into a 1 L of ultrapure water in a 1 L volumetric flask. The volumetric flask was capped and shook vigorously to ensure well mixed. 2 mL of the solution was pipetted using a 10 mL pipette into a 1 L volumetric flask containing and was then diluted to 1 L using ultrapure water. After that, 100 mL of the 1 L prepared sample were transferred into the 250 mL of Erlenmeyer flask containing 0.02 g of biochar. The sample was then placed onto an orbital shaker (IKA KS 4000i) and it was set at 250 rpm for 2 hours. After 2 hours the samples was let to settle for 30min. Then dilution was done to ensure the concentration is below 1000 ppb as ICP-MS can only measure up to 1000 ppb of samples. Dilution was done by pipetting 10 ml of the sample treated with biochar into a 100mLvoluteric flask and followed by 1 % of nitric acid for acid digestion. The diluted samples were then taken to measure its concentration after treated with biochar using ICP-MS to determine its removal efficiency. Similar study was done for As (V), Zn and Cu.

3.7 Removal Efficiency

The removal efficiency was determined using the following equation:

$$\mathrm{R}(\%) = \frac{Ci - Cf}{Ci} \times 100 \qquad \text{(Eq. 3.1)}$$

Where

R(%) =Removal efficiency (%)

Ci = Initial concentration of synthetic wastewater, ppm - calculated

Cf = Final concentration of synthetic wastewater, ppm - measured

The equation to calculate the adsorption capacity of POMS biochar produced is as shown below:

$$\mathrm{Q} = \frac{(Ci - Cf)v}{w} \qquad \text{(Eq. 3.2)}$$

Where

Q = Adsorption capacity, mg/g

v = Volume of solution, L

w = weight of POMS biochar added, g

3.8 Characterisation

The characterization of POMS biochar is vital to understand the factors that are contributing to the removal efficiency. In this study, the functional groups of the prepared biochar were tested using Fourier Transform Infrared Spectroscopy (FTIR).

a) Fourier Transform Infrared Spectroscopy (FTIR)

FTIR can be used to determine the functional groups present on POMS biochar through the absorption of wavelengths of infrared light from the sample. FTIR spectroscope (Perkin Elmer Spectrum, RX1) was used in this experiment.

CHAPTER 4

RESULT AND DISCUSSIONS

4.1 Removal of Arsenic (V)

The removal efficiency of As (V) is tabulated in Appendix B1. The removal of As (V) is plotted in a graph of percentage against microwave power (W) as shown in Figure 4.1. The graph is plotted based on the removal efficiency of As (V) heated for 10 min, 15 min, 20 min and 25 min under each heating power of 100 W, 200 W, 300 W, 400 W and 500 W respectively from Appendix B1. Figure 4.2 is a graph of removal efficiency of As(V) against time of holding time under different microwave power of 100 W, 200 W , 300 W, 400 W and 500 W respectively.

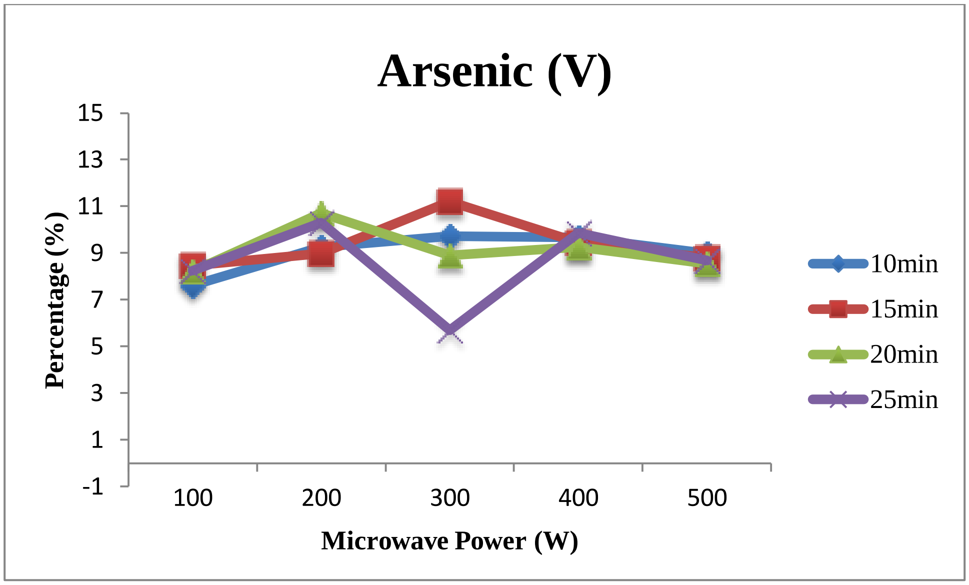


Figure 4.1 Graph of Percentage of As (V) Removal against Microwave Power (W) at 10 min, 15 min, 20 min and 25 min

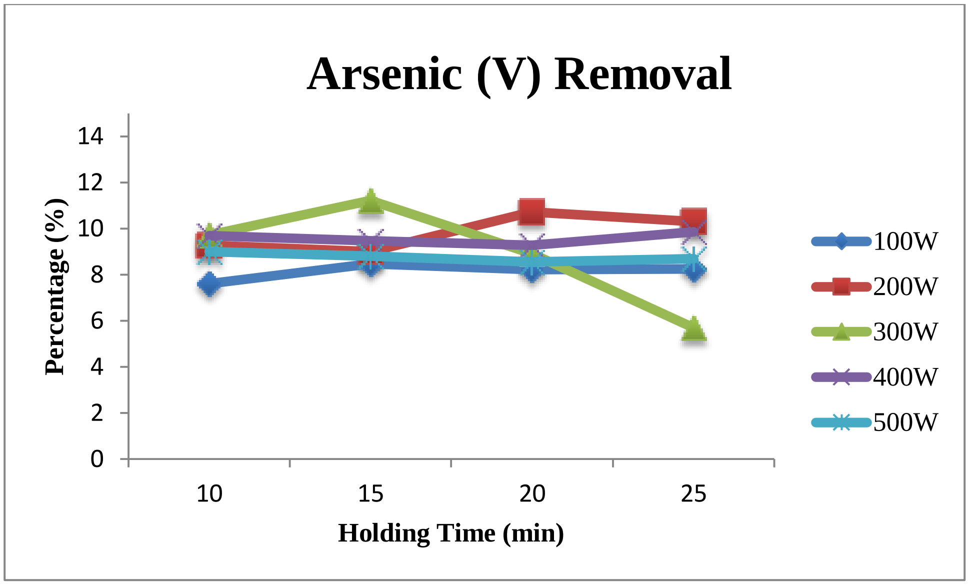


Figure 4.2 Graph of Percentage of As (V) Removal against Holding Time (min) for 100 W, 200 W, 300 W, 400 W and 500 W

The removal efficiency of As (V) using POMS biochar has highest removal efficiency of 11 %. From Figure 4.1 and Figure 4.2, the graphs show clearly that the removal efficiency for all five different microwave powers at different holding time does not have much difference among each other where it shows the highest removal efficiency of 8.4 %, 8.9 %, 11.2 %, 9.4 % and 8.8 % for 100 W, 200 W, 300 W, 400 W and 500 W at 15 min. The results show little or no adsorption of As (V) using POMS biochar which will be further discussed in detail.

4.1.1 Factors affecting the Adsorption of Arsenic (V) using Palm Oil Mill Sludge (POMS) Biochar

Adsorption of As(V) can be affected by two main factors, the pH of the synthetic water (Samsuri, Sadegh-Zadeh and She-Bardan., 2013) and the characteristics of the biochar especially the surface functional groups (Jin, et al., 2014). Arsenic (V) is categorised as anionic despite containing the common metalloid ion of arsenic. According to Samsuri, Sadegh-Zadeh and She-Bardan, (2013), two forms of As (V) may present at different pH where $H_2AsO_4^-$ at moderate acidic and neutral condition while $HAsO_4^{2-}$ at basic pH and therefore As (V) is anionic in nature.

The pH of the solution contributes to the capability of adsorption of Arsenic. The pH determined from the experiment was slightly alkaline with pH 8.2. A report by Rupani, et al. (2010) reported that the pH of the palm oil sludge is 8.4. However, the pH best for adsorption for As (V) is in acidic condition as mentioned by Samsuri, Sadegh-Zadeh and She-Bardan (2013) using empty fruit brunch biochar and rice husk biochar to treat As (V) with a maximum pH of 6 and the adsorption of As (V) decreased after pH 7. The reason of higher removal efficiency for As (V) at lower pH can very much due to the protonation of biochar where the functional groups on the biochar is protonated $pH < pH_{pzc}$ (point of zero charge) due to the increase of H^+ and H_3O^+ in the solution (Tan, et al., 2015). While at the high pH, the functional group is not protonated and since the functional group on the biochar is negatively charged, As(V) repulses and therefore no adsorption occurs as proven by (Zhou, et al., 2014) using bamboo biochar and bamboo biochar with chitosan for adsorption of As (V). In this experiment, no pH adjustment was done which therefore it can be deduced that due to the alkalinity of the solution which resulted a low adsorption capability of As (V) onto POMS biochar.

Furthermore, adsorption of As (V) also depends on the functional groups that present on the biochar. Due to the negatively charged surface functional groups such as carboxyl, carbonyl, hydroxyl group and etc. (Zhou, et al., 2014) may generate electrostatic repulsion happens and causes a little or no adsorption of As (V) on to POMS biochar. This finding is similar to the one reported by Hu, et al. (2015) using pristine hickory biochar to adsorb As (V). Some researchers have either decreases the pH solution or modify the biochar in order for the adsorption of As (V) onto negatively charged surface biochar. For example, Kalderis and Diamadopoulos (2014b) uses a Ca^{2+} and Fe^{3+} modified biochar to remove As (V) which reported to have much higher adsorption capacity of As (V) compared to non-impregnated ones. In another research, where Agrafioti, Kalderis and Diamadopoulos (2014a) turn rice husk, sewage sludge and solid waste into biochar to remove As (V). In this research, biochar solid waste possesses the highest removal efficiency due to the present of CaO ash content at alkaline condition and As (V) is removed by precipitation with CaO. Similarly for biochar sewage sludge which content CaO, Fe_2O_3 and Al_2O_3 in the ash content. However, as for biochar rice husk which contain only high ash content of SiO_2 and low content of Ca, Fe and Al oxides, it has the lowest removal efficiency of As (V). There are other supporting researchers who able to achieve high adsorption capacity of As (V) using modified biochar such as Fe^{3+} coated empty fruit brunch and rice husk biochar (Samsuri, Sadegh-Zadeh and She-Bardan, 2013) and bamboo biochar coated with chitosan and added zerovalent iron (Zhou, et al., 2014).

4.2 Removal of Trimethyltin (TMT) Chloride

The removal efficiency of TMT is tabulated in Appendix B2. The removal efficiency of TMT is plotted in a graph as shown in Figure 4.3. The graph is plotted based on the removal efficiency of trimethyltin using biochar heated for 10 min, 15 min, 20 min and 25 min under each heating power of 100 W, 200 W, 300 W, 400 W and 500 W respectively from Appendix B2. Figure 4.4 is a graph plotted with removal of TMT against holding time for 10 min, 15 min, 20 min and 25 min under 100 W, 200 W, 300 W, 400 W and 500 W respectively.

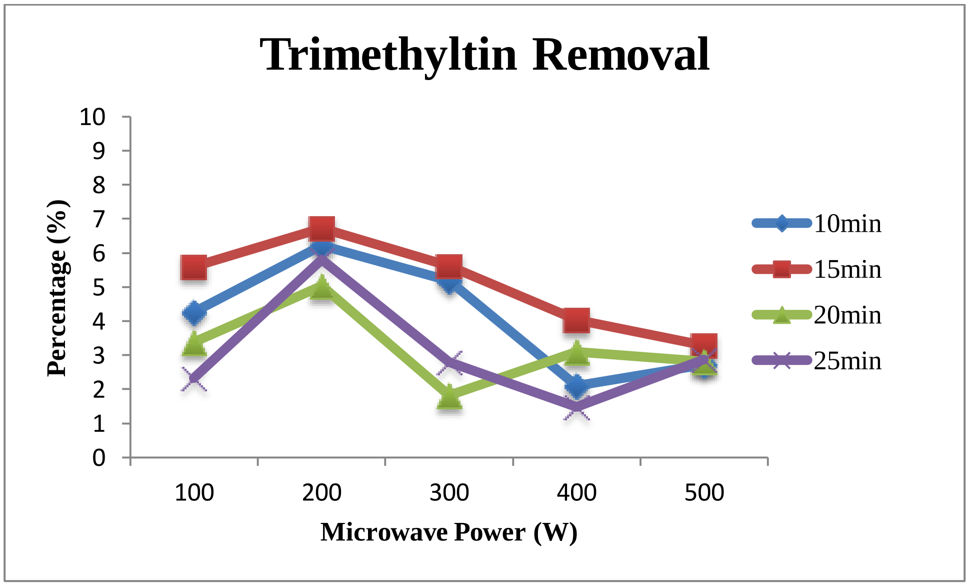


Figure 4.3 Graph of Percentage of Trimethyltin removal against Microwave Power (W) at 10 min, 15 min, 20 min and 25 min

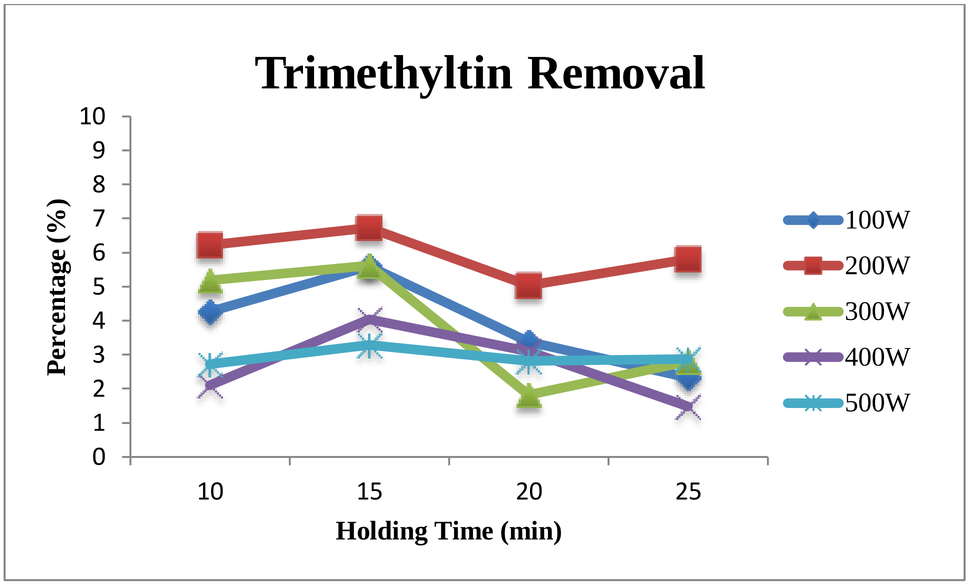


Figure 4.4 Graph of Percentage of Trimethyltin removal against Holding Time (min) at 100 W, 200 W, 300 W, 400 W and 500 W

The highest removal efficiency is 6.7% at 200 W with holding time of 15 min. The removal efficiency of TMT are 5.6 %, 6.7 %, 5.6 %, 4 % and 3.2 % for 100 W, 200 W, 300 W, 400 W and 500 W respectively with holding time of 15 min. From the graph, the results show that a little or no adsorption of TMT by POMS biochar which will be further discussed in details later.

4.2.1 Factors affecting the Adsorption of Trimethlyltin (TMT) Chloride using Palm Oil Mill Sludge (POMS) Biochar

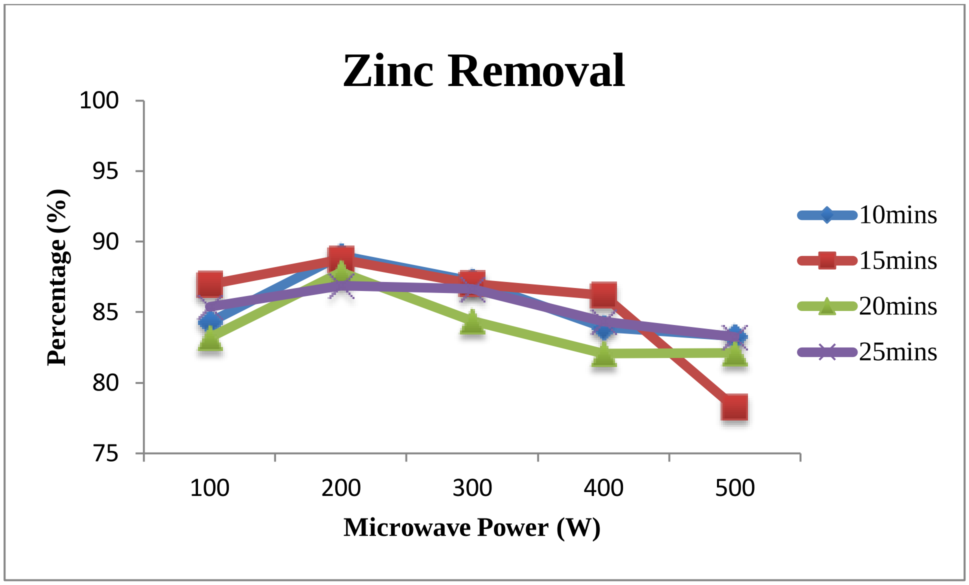
Generally, adsorption of organic onto biochar is by few mechanisms such as electrostatic interaction, hydrophobic effect, hydrogen bonds and pore-filling (Tan, et al., 2015). One of the most influencing adsorption mechanism onto the biochar is through electrostatic attraction where others such as pore filling is contributing adsorption mechanism (Tan, et al., 2015).

There is no study on adsorption of TMT chloride using biochar however a research on adsorption of TMT and TBT in landfill using iron nanoparticles was studied by Peeters, et al. (2015). It was reported that under alkaline condition, nonzerovalent nanoparticles has influence in removing tributyltin whereas there is little or almost no influence on removal of TMT for size <2.5 nm despite with acidic treatment was done after. According to Peeters, et al. (2015), iron nanoparticles can adsorb organic pollutants on to the iron nanoparticles and co-precipitate with iron corrosion products such as Fe^{2+} and H^{+}. However, there is only about 20 % of TMT was able to be adsorbed onto the surface of nonzerovalent.

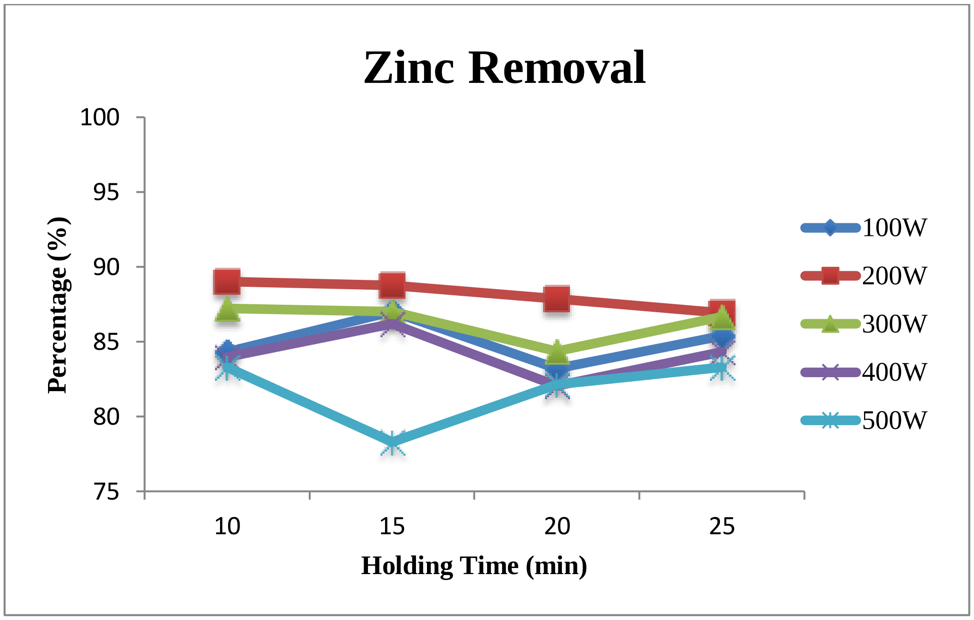
A hypothesis that can be made is that under alkaline condition, TMT requires cationic functional groups in order for the adsorption to occur. On top of that, pore filling plays an important role in adsorption of organic compound, however due to the dielectric property of the POMS biochar (will be discussed in subsection 4.6), the porous structure of POMS biochar wasn’t developed successfully as it supposed to be. This resulted in little or no adsorption of TMT onto the POMS biochar.

4.3 Removal Cations – Zinc (Zn) and Copper (Cu) using Palm Oil Mill Sludge (POMS)

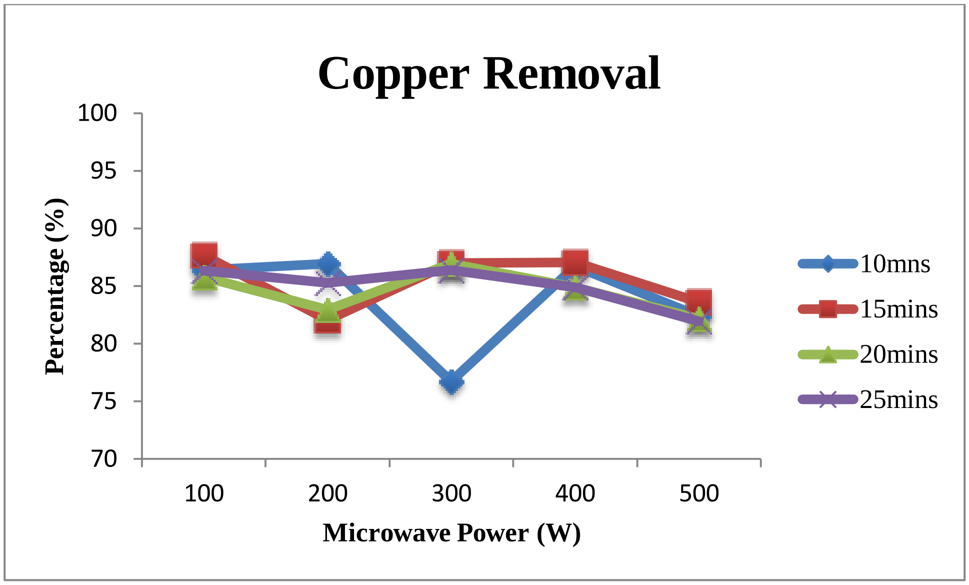
The removal efficiency of Zn and Cu is tabulated in Appendix B3 and Appendix B4 respectively. The removal efficiency of Zn and Cu are plotted in a graph as shown in Figure 4.5(a) and 4.5(b), Figure 4.5(c) and 4.5(d) respectively. The graphs of Figure 4.5(a) and Figure 4.5(c) are plotted with the removal efficiency of Zn and Cu against microwave power under holding time of 10 min, 15 min, 20 min and 25 min respectively. As for graphs of Figure 4.5(b) and 4.5(d) are plotted based on the removal efficiency of Zn and Cu using biochar heated for 10 min, 15 min, 20 min and 25 min under each heating power of 100 W, 200 W, 300 W, 400 W and 500 W respectively from Appendix B3 and Appendix B4 respectively.



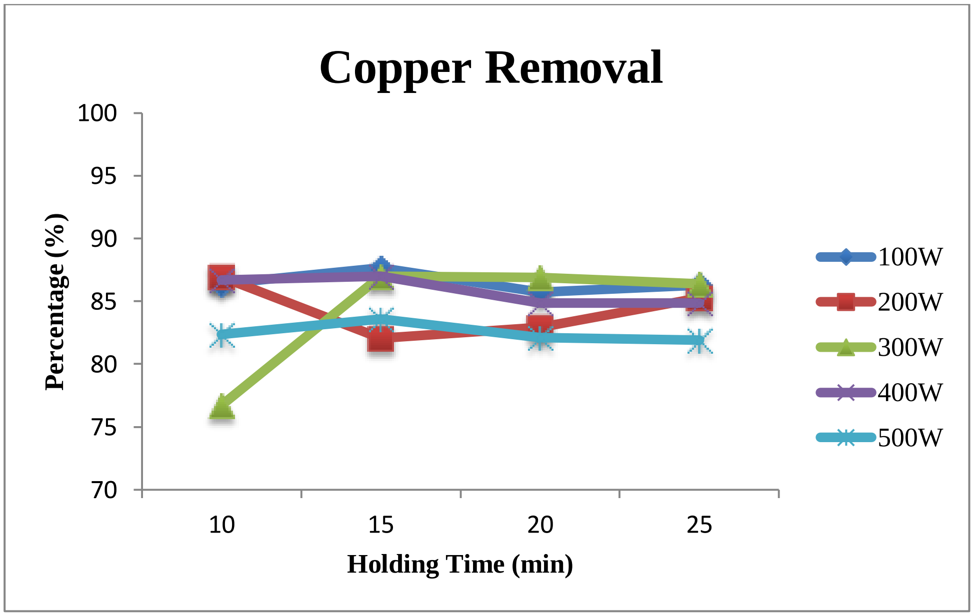
(a)



(b)



(c)



(d)

Figure 4.5 Graph of Percentage of (a) Zinc and (c) Copper removal against Microwave Power (W) under holding time of 10 min, 15 min, 20 min, 25min and Percentage of (b) Zinc and (d) Copper against holding time (min) under 100 W, 200 W, 300 W, 400 W and 500 W.

From Figure 4.5(a) and 4.5(b), the highest removal efficiency of Zn is 89 % at 200 W under holding time of 10 min and from Figure 4.5(c) and 4.5(d), highest removal is 87 % at 100 W, 300 W and 400 W for Cu under holding time of 15 min. The rest of the removal efficiency for Zn are 84 %, 87 %, 83 % and 83 % for 100 W, 300 W, 400 W and 500 W respectively under holding time of 10 min and as for Cu are 82 % and 83% for 200 W and 500 W respectively under holding time of 15 min. The results show that the removal efficiency of Zn and Cu using POMS is quite high however the differences of removal efficiency for both graphs respectively are not that high which will be discussed further.

4.3.1 Factors affecting the Adsorption of Zinc (Zn) and Copper (Cu) using Palm Oil Mill Sludge (POMS) Biochar

Generally, the adsorptions of cationic ions such as Zn and Cu by biochars are mainly due to the negatively surface charged of biochar which is influenced by solution pH and also biochar's porosity (Jiang, et al., 2016). Luo, et al. (2006) had reported that pH value has an effect on the adsorption of heavy metal ions onto the activated sludge. It is worth noting that under strong acidic solutions, H^+ competes for the adsorption sites with heavy metal ions, which then impedes the adsorption of heavy metals by activated sludge and the adsorption of heavy metal decreases with decrease in pH (Luo, et al., 2006). On the contrary, the hydrates formed with heavy metal ions in alkaline solution precipitate on the activated sludge's surface therefore result in higher adsorption of heavy metals onto the surface of activated sludge. Luo, et al. (2006) reported that the adsorption of Cu, Zn and Cd are all higher when pH varies in between pH range of 4 – 10. In this experiment, the initial pH of the solution was maintained at alkaline condition of pH 8.2 without any pH adjustment and therefore this condition allows the maximum adsorption of Zn and Cu which resulted in high removal efficiency respectively.

Function groups that present on the surface of POMS biochar is one of the major factors for the adsorption of Zn and Cu. According to Bogusz, Oleszczuk and Dobrowolski (2015), Cu has a great affinity towards carbonyl groups due to the pair of electrons present on the oxygen atoms of the biochar which was then donated to the oxygen-metal bond. Besides, Bogusz, Oleszczuk and Dobrowolski (2015) has done comparison for the functional groups hydroxyl groups and carboxyl group which are responsible for metal ions adsorption for wheat straw biochar with different preparation method. It was characterized that hydroxyl groups has lower binding energy than carboxyl groups which allows more readily binding of metal ions onto hydroxyl groups. Even so, it has proven that the present of hydroxyl group and carboxyl group present on the POMS biochar has participated in the adsorption of Zn and Cu.

In addition, the surface area (porosity) of the biochar contributes to the removal of Cu and Zn where it was reported by Jiang, et al. (2016) that activated carbon has almost twice as much micropore surface area and five times as much mesopore and macropore area as compared to pine biochar for the adsorption of Cu and Zn. Due to the large area of porosity, mainly micropores, Cu and Zn are more readily accessible into micropore through meso- and macropores which has proven that activated carbon adsorb more Cu and Zn compared to the biochars (jarrah and pine) used. In fact for the same case, jarrah biochar has a higher adsorption capacity as compared to pine biochar due to the total surface area of jarrah biochar is about 41 % higher than of the pine biochar (Jiang, et al., 2016). In this experiment, the morphology wasn’t able to perform which therefore it is unable to determine whether there are pore development and its size.

4.4 Dielectric Properties and Microwave Heating of Palm Oil Mill Sludge (POMS)

Microwave heating occurs when the microwave encounter the biomass, randomly oriented dipoles in dielectric materials align themselves, opposing to the applied external electrical field. The molecules absorb the energy and store as potential energy where applying the ionic conduction and dipole rotation, the polar molecules vibrate and produce kinetic energy (Jie, et al., 2015). It is necessary to study the dielectric properties in order to study the interaction between microwave and material and defining the characteristic of the materials (Salema, et al., 2013). Properties of dielectric that should be taken into consideration are dielectric constant (ε′), dielectric loss factor (ε″), and tangent loss (tan δ) where these properties assist in determining of the heating characteristic of material.

According to Zaini, et al. (2015), ε′ determines the behaviour of material which includes the amount of energy is reflected from material and the material's efficiency in storing energy. On top of that, ε″ can be referred to as the ability of the material to absorb and convert electromagnetic energy into heat, where it can act as the measurement of heat released from the material. Lastly, tan δ represents the ability of the material to be heated under microwave is reduced if it goes beyond right frequency (Zaini, et al., 2015).

Dielectric properties and microwave heating of oil palm fiber, oil palm shell and palm shell biochar was researched by Salema, et al., (2013) and has reported that the dielectric properties are largely dependent on the frequency where ε′ decrease with increasing frequency whereas ε″ has the vice versa effect. It was also reported that the penetration of microwave into the material is very much depends on the materials and the particle size. There was no specification of type of composition that present in the oil palm shell and fiber that limit the permittivity of microwave but based on the microwave heating profiles and dielectric properties done by Salema, et al., (2013), it was confirmed that the oil palm biomasses has low loss dielectric material which means having low ability to absorb and convert electromagnetic energy into heat. Therefore, they aren't able to reach high temperature (above 200^{o}C) when heated alone. Based on the results obtained for removal of Zn and Cu, it can be deduced that due to the low dielectric loss material of the POMS biochar, it has low ability to absorb and convert electromagnetic energy into heat which ultimately affected the development of pores on the POMS biochar surface. This is because development of pores requires certain amount of thermal decomposition of original material (Paethanom and Yoshikawa, 2012). Therefore, the removal of Zn and Cu are mainly by the functional group present on the POMS biochar surface instead of the porous structure. Hence, this can be explained for the reason of almost same removal efficiency of Zn and Cu obtained for different microwave power and resident time. It can be deduce similarly for adsorption of TMT since pore filling is a contributing adsorption mechanism of TMT and therefore low or little adsorption of TMT onto POMS biochar.

Also, Salema, et al. (2013) has reported that the only factor that contributed to the increase of temperature in the biomass was mainly due to the present of moisture in the biomass. It was further explained that due to the good microwave absorber of water, it can generate heat within the biomass. This can be deduced that due to the present of water in the POMS, the heating of water might contributed to the developed of some of the pore and enhanced the removal of TMT, Zn and Cu which resulted in some slightly higher removal efficiency as compared to the lower ones.

4.5 Characterisation of Biochar

Likewise, the less heat generated from POMS biochar due to the low ability of POMS biochar to absorb and convert electromagnetic energy into heat, the heat in the microwave is not high enough to break the bonds that present on the POMS. This had resulted the functional groups that present on POMS biochar having the same functional groups as original unpyrolyse POMS as shown in Figure 4.6. According to Dutta, et al.

(2015), the biochar formed at lower temperature has the similar characteristics to the original sample while increasing the pyrolysis temperature, the bands of the functional group will get weaker which resulted in lowered functional group activities. Figure 4.6 shows the FTIR results for original POMS and POMS microwave pyrolysed under 100 W, 200 W, 300 W, 400 W and 500 W for 15 min.

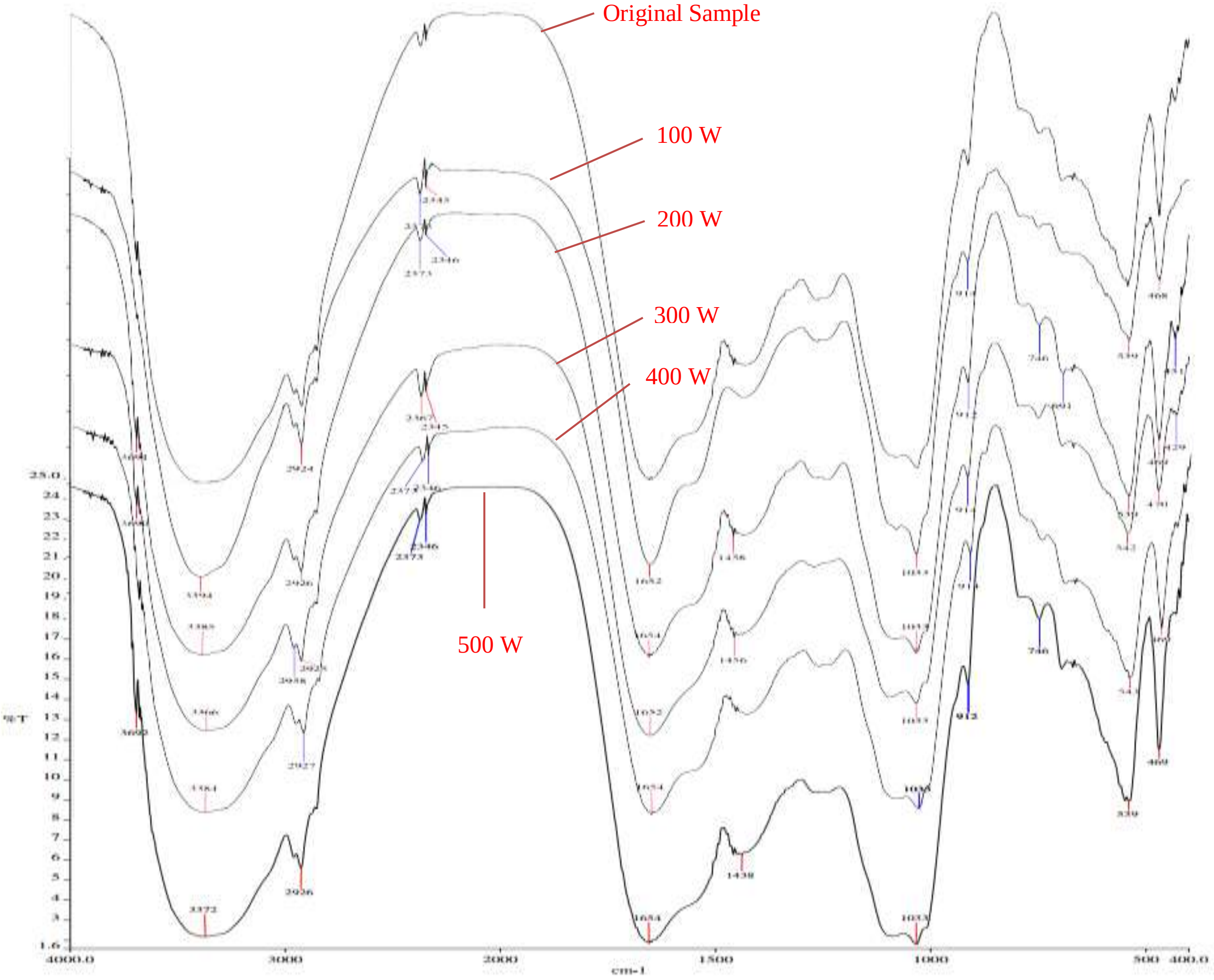


Figure 4.6 FTIR results for Microwaved POMS biochar at 100 W, 200 W, 300 W, 400 W and 500 W respectively at 15 min

Figure 4.6 shows the result of FTIR analysis of POMS biochar at different microwave power at 15 min. However, the outcome of the analysis shows that the differences between these graphs aren’t that much. However, it is essential to determine the type of functional groups that present on POMS biochar in order to understand the type of adsorption occurs with the pollutants. From Figure 4.6, the common peak lies in between region of 3700 – 3100 cm^{-1} which indicates the possible present of –OH, -NH and ≡C-H. A research done by Zaini, et al. (2013) on POME sludge, reported that the frequency that falls in the said region indicates the present of –OH functional group. Another 2 peaks in the region between 3000 – 2800 cm^{-1} indicates the possible present of aliphatic groups such as -CH, - CH_2- and -CH_3 which can supported by research done by Samsuri, Sadegh-Zadeh and She-Bardan (2013) where the wavelength was 2925.66 cm^{-1} and has reported to be a long-chain aliphatic component. There are two more peaks occurs at 2373 cm^{-1} and 2345 cm^{-1} which from Appendix B5, it indicates the present of possible components are nitriles, azides and alkynes -C≡N, -N=N+ =N- and -C≡C- respectively which falls in the region of 2000 – 2400 cm^{-1}. A peak at 1654 cm^{-1} also indicates the possible present of C=O group and amines (N-H bend) (Central Connecticut State University, 2005); 1434 cm^{-1} indicates the possible of O-H bend which is the carboxylic group –COOH similarly for 1262 cm^{-1} (Central Connecticut State University, 2005); the possible functional groups present for frequency 1032 cm^{-1} is amines and alkyl halides (Central Connecticut State University, 2005); while for 913 cm^{-1} indicates the possible present of alkenes as shown in Appendix B5 and (Central Connecticut State University, 2005); As for 745 cm^{-1}, 695 cm^{-1}, 540 cm^{-1} and 469 cm^{-1} it can be categorised under aromatics compounds and alkyl halides based on Appendix B5 and Central Connecticut State University (2005).

4.6 Adsorption Capacity of Palm Oil Mill Sludge (POMS) Biochar for each Adsorbate

Table 4.1 Adsorption Capacity of POMS Biochar for each Adsorbate

Adsorbate	Adsorption Capacity (mg/g)
Arsenic (V)	5.6
Trimethyltin Chloride	3.3
Zinc	44.5
Copper	43.5

Table 4.1 shows the different adsorption capacity of POMS biochar on different adsorbate which is As (V), TMT, zinc and copper with adsorption capacity of 5.6 mg/g, 3.3 mg/g, 44.5 mg/g and 43.5 mg/g respectively. This can be deduced that POMS biochar possesses high capability of adsorption towards cations and in this case is zinc and copper which mainly adsorb through the existence of functional groups present on POMS biochar. On the other hand, adsorption of As (V) and TMT by POMS biochar is not suitable as both requires certain functional groups which does not present on to POMS biochar which resulted in incapability of adsorption of both adsorbate. On top of that, since the activation of POMS biochar for developing of porous structure did not occur due to the low heat generated by POMS biochar, there is little or no adsorption of TMT.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, POMS was pyrolyzed using microwave to produce biochar. The produced biochar was used to remove TMT, As (V), Zn and Cu from synthetic wastewater. Result analysis was done to determine the removal efficiency of TMT, As (V), Zn and Cu. It was determined that POMS biochar is effective in removing cation pollutants with highest removal efficiency of 89 % and 87 % for Zn and Cu respectively. The adsorption capacity of Zn and Cu was reported as 44.5 mg/g and 43.5 mg/g respectively. The main mechanism for the adsorption of Zn and Cu was the presences of functional groups. On the other hand, removal of As (V) and TMT by POMS biochar was very discouraging, due to the nature of the metals which are anionic and alkaline. Furthermore, the absence of functional groups that enables the electrostatic attraction between pollutants and the functional groups hinders the adsoprtion. The highest removal efficiency for As (V) and TMT is 11 % and 6 % respectively. In addition, the dielectric properties of POMS biochar play an important role for the development of pore on the biochar surface. However, from the removal efficiency obtained for both Zn and Cu, it was determined that the results obtained were similar for the removal efficiency. This can be deduced that due to the low dielectric loss material of POMS biochar, the POMS biochar has low ability to absorb and convert electromagnetic energy into heat for the development of pore. As such, it can be concluded that, POMS biochar is effective in removing Zn and Cu but not effective in removing anion such as As (V) and organic pollutant TMT where modification on the POMS biochar is required for the treatment of anions and organic pollutants

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5.2 Recommendations

The future recommendations for this research are as shown below:

- Identify the dielectric properties of POMS in order to know whether POMS is microwavable or not
- Determine the functional groups of POMS biochar after treatment in order to determine what other functional groups that assisted in the adsorption of pollutants
- Determine the porous structure and pore sizes of POMS and POMS biochar in order to know whether is there any pore development during microwave pyrolysis process
- Identify the optimum microwave power and holding time required to produce POMS biochar by determining the range of microwave power and holding time then using Design of Expert to produce the design matrix for experimental purpose
- Chemical treatment on POMS for better adsorption of anion and organic pollutants

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APPENDICES

Appendix A1: Metals Discharge Limit for Standard A and Standard B (Department of Environment, Malaysia, 2010)

Parameter	Unit	Standard	
		A	B
Mercury	mg/L	0.005	0.05
Cadmium	mg/L	0.01	0.02
Chromium, Hexavalent	mg/L	0.05	0.05
Chromium, Trivalent	mg/L	0.20	1.00
Arsenic	mg/L	0.05	0.10
Cyanide	mg/L	0.05	0.10
Lead	mg/L	0.10	0.50
Copper	mg/L	0.20	1.00
Manganese	mg/L	0.20	1.00
Nickel	mg/L	0.20	1.00
Tin	mg/L	0.20	1.00
Zinc	mg/L	2.00	2.00
Boron	mg/L	1.00	4.00
Iron	mg/L	1.00	5.00
Silver	mg/L	0.10	1.00
Aluminium	mg/L	10.00	15.00
Selenium	mg/L	0.02	0.50
Barium	mg/L	1.00	2.00

Appendix A2: Drinking Water Quality Standards for Metals (Department of Environment, Malaysia, 2010)

Parameter	Recommended Raw Water Quality (mg/L)	Drinking Water Quality Standards (mg/L)
Mercury	0.001	0.001
Cadmium	0.003	0.003
Chromium	0.05	0.05
Arsenic	0.01	0.01
Cyanide	0.07	0.07
Lead	0.05	0.05
Copper	1.00	1.00
Manganese	0.2	0.1
Nickel	-	0.02
Tin	-	-
Zinc	3	3
Iron	1.0	0.3
Aluminium	-	0.2
Selenium	0.01	0.01

Appendix B1: Removal Efficiency of Arsenic (V) using Microwave Pyrolysed POMS Biochar

No.	Heating Power (W)	Time of Heating (min)	Nitrogen Flow Rate (mL/min)	Removal Efficiency (%)
1	100	10	500	7.61
2	100	15	500	8.47
3	100	20	500	8.21
4	100	25	500	8.25
5	200	10	500	9.26
6	200	15	500	8.98
7	200	20	500	10.72
8	200	25	500	10.29
9	300	10	500	9.72
10	300	15	500	11.20
11	300	20	500	8.91
12	300	25	500	5.69
13	400	10	500	9.68
14	400	15	500	9.45
15	400	20	500	9.26
16	400	25	500	9.86
17	500	10	500	8.98
18	500	15	500	8.79
19	500	20	500	8.54
20	500	25	500	8.69

Appendix B2: Removal Efficiency of Trimethyltin Chloride using Microwave Pyrolysed POMS Biochar

No.	Heating Power (W)	Time of Heating (min)	Nitrogen Flow Rate (mL/min)	Removal Efficiency (%)
1	100	10	500	4.27
2	100	15	500	5.60
3	100	20	500	3.38
4	100	25	500	2.32
5	200	10	500	6.21
6	200	15	500	6.72
7	200	20	500	5.03
8	200	25	500	5.81
9	300	10	500	5.18
10	300	15	500	5.62
11	300	20	500	1.81
12	300	25	500	2.80
13	400	10	500	2.10
14	400	15	500	4.04
15	400	20	500	3.10
16	400	25	500	1.49
17	500	10	500	2.73
18	500	15	500	3.28
19	500	20	500	2.81
20	500	25	500	2.87

Appendix B3: Removal Efficiency of Zinc using Microwave Pyrolysed POMS Biochar

No.	Heating Power (W)	Time of Heating (min)	Nitrogen Flow Rate (mL/min)	Removal Efficiency (%)
1	100	10	500	84.29
2	100	15	500	86.99
3	100	20	500	83.19
4	100	25	500	85.38
5	200	10	500	89.00
6	200	15	500	88.76
7	200	20	500	87.84
8	200	25	500	86.90
9	300	10	500	87.21
10	300	15	500	87.02
11	300	20	500	84.37
12	300	25	500	86.67
13	400	10	500	83.95
14	400	15	500	86.18
15	400	20	500	82.05
16	400	25	500	84.33
17	500	10	500	83.29
18	500	15	500	78.28
19	500	20	500	82.13
20	500	25	500	83.27

Appendix B4: Removal Efficiency of Copper using Microwave Pyrolysed POMS Biochar

No.	Heating Power (W)	Time of Heating (min)	Nitrogen Flow Rate (mL/min)	Removal Efficiency (%)
1	100	10	500	86.39
2	100	15	500	87.67
3	100	20	500	85.73
4	100	25	500	86.29
5	200	10	500	86.93
6	200	15	500	82.06
7	200	20	500	82.94
8	200	25	500	85.28
9	300	10	500	76.71
10	300	15	500	87.00
11	300	20	500	86.90
12	300	25	500	86.37
13	400	10	500	86.71
14	400	15	500	87.01
15	400	20	500	84.84
16	400	25	500	84.86
17	500	10	500	82.38
18	500	15	500	83.57
19	500	20	500	82.12
20	500	25	500	81.93

Appendix B5: Region of the Infrared Spectrum to determine possible present of Functional Groups (Yuen, et al., 2005)

Region (cm^{-1})	Group	Possible Compounds Present (or Absent)
3700 – 3100	-OH	Alcohol, aldehyde, carboxylic acids
	-NH	Amides, amines
	≡C-H	Alkynes
3000 - 2800	-CH, - CH_2 -, -CH_3	Aliphatic groups
2400 - 2000	-C≡N	Nitriles
	-N=N+ =N-	Azides
	-C≡C-	Alkynes
1870 – 1650	C=O	Acid halides, aldehydes, amides, amino acids, anhydrides, carboxylic acids, esters, ketones, lactams, lactones, quinines
1550 - 1300	NO_2	Nitro compound
	CH_3 and CH_2	Alkanes, alkenes, etc
1300 - 1000	C-O-C and C-OH	Ethers, alcohols, sugars
	S=O, P=O, C-F	Sulphur, phosphorus, and fluorine compounds
1100 - 800	Si-O and P-O	Organosilicon and phosphorus compounds
1000 - 650	=C-H	Alkenes and aromatic compounds
	-NH	Aliphatic amines
800 - 400	C-halogen	Halogen compounds
	Aromatic rings	Aromatic compounds