ADSORPTION OF COPPER(II) ION BY PALM OIL SLUDGE BIOCHAR PREPARED BY PYROLYSIS: EQUILIBRIUM AND KINETIC STUDIES

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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

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DECLARATION

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

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"ADSORPTION OF COPPER(II) ION BY PALM OIL SLUDGE BIOCHAR PREPARED BY PYROLYSIS: EQUILIBRIUM AND KINETIC STUDIES"** was prepared by **LEONG WAI LUN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Environmental Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : ________________________

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Date : ________________________

Specially dedicated to my beloved parents.
“Thank you for your support with my studies.
I am honoured to have you as my parents.”

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ABSTRACT

Annually, million tons of Palm Oil Sludge (POS) were produced from palm oil mill industries as side-product. Thus, it is very crucial to utilize POS for more advantageous purposes, especially in the circumstances of low-cost adsorbent development. Throughout this study, POS has been utilized for the production of bio-char through conventional pyrolysis method. Adsorption of copper(II) ion from aqueous solution was investigated using Palm Oil Sludge Bio-char (POSB). Batch adsorption studies were conducted by varying the adsorbent dosage, contact time, contact speed and initial pH of copper(II) ion solution. The optimized parameters obtained from these studies are: 0.04 g of adsorbent dosage, 240 minutes of contact time, 150 rpm of contact speed and pH of 6. In addition, it was found that adsorption equilibrium was well described by Langmuir isotherm rather than Freundlich isotherm with maximum adsorption capacity of 45.31 mg/g of copper(II) ion onto the POSB. Moreover, adsorption data was fitted into three kinetic models which are Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion models. As a result, kinetics of copper(II) ion adsorption was found to be Pseudo-second-order as the rate determining step. Experimental results clearly indicated that POSB has a homogeneous surface and it uptakes copper(II) ion by monolayer chemisorption. POSB can be an effective adsorbent for copper(II) ion removal from aqueous heavy metal solution.

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LIST OF SYMBOLS / ABBREVIATION

1/n	Adsorption Intensity
℃	Degree Celsius
μm	Micrometre
C_e	Equilibrium Concentration of Copper(II) Ion, mg/L
C_o	Initial Concentration of Copper(II) Ion, mg/L
C_t	Concentration of Copper(II) Ion at Time (*t*), mg/L
Cd^{2+}	Cadmium(II) Ion
Cu^{2+}	Copper(II) Ion
g	Gram
HCl	Hydrochloric Acid
K_1	Kinetic Constant of Pseudo-first-order Model
K_2	Kinetic Constant of Pseudo-second-order Model
K_F	Freundlich Constant, L/mg
K_i	Kinetic Constant of Intra-particle Diffusion Model
K_L	Langmuir Constant, L/mg
L	Litre
m	Mass of Dosage, g
M	Molarity, mol/L
min	Minute
mg	Milligram

NaOH	Sodium Hydroxide
ppb	Parts Per Billion
q_e	Adsorption Capacity of POSB at Equilibrium, mg/L
$q_{e.cal}$	Theoretical Equilibrium Adsorption Capacity, mg/L
$q_{e.exp}$	Experimental Equilibrium Adsorption Capacity, mg/L
q_m	Maximum Monolayer Adsorption Capacity, mg/L
q_t	Adsorption Capacity of POSB at Time (*t*), mg/L
R	Removal Percentage, %
R^2	Correlation Coefficient
R_L	Langmuir Separation Factor
rpm	Round Per Minute
t	Time, minute
V	Volume, L

BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
IUPAC	International Unit of Pure and Applied Chemistry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
MARDI	Malaysian Agriculture Research Development Institute
POME	Palm Oil Mill Effluent
POS	Palm Oil Sludge
POSB	Palm Oil Sludge Bio-char

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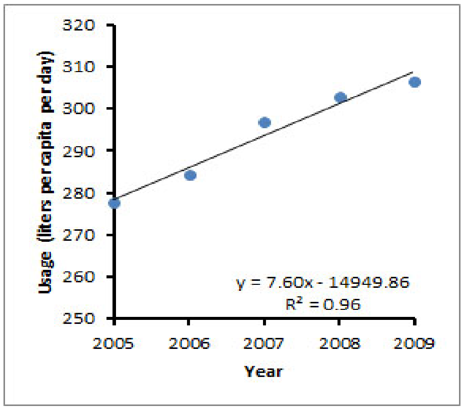
CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, water has become one of the main issues in the 21st century in worldwide. Malaysia is a country enriched with plentiful amount of rainfall and water resources. However, many areas of the country are subjecting water stress (Chan, 2009). This is mainly because of the increasing demand for water usage due to population growth in Malaysia every year. Datusahlan, Wan Ishak and Makky (2013) stated that water consumption (in litre per person per day) by Malaysians is twice as compared to Singaporeans. Consequently, consumptive water per capital per day in Malaysia is declining at a rate of 5.8 litres per year due to excessive usage of water (Datushalan, Wan Ishak and Makky, 2013). In other words, there is a great need to generate water from domestic and industrial sectors. It is estimated about 2.97 billion cubic metre of wastewater per year generated from all sectors including domestic, municipal and industrial according to Indah Water Konsortium (2011).



Malaysia's increasing water consumption
(2005-2009)

Figure 1.1: Trend in Water Consumption by Malaysian from Year 2005 to 2009 (Datushalan, Wan Ishak and Makky, 2013)

According to Syarikat Bekalan Air Selangor (Syabas), the supply of clean water in Selangor and Kuala Lumpur has gradually decreased because the production capacity of water treatment plants was unable to meet the requirement. In addition, the quality of river water has degraded in the recent years as shown in **Figure 1.2** (Japan Sanitation Consortium, 2008).

Moreover, economic growth and industrialization in Malaysia has led to environmental issues particularly heavy metals pollution in surface water and groundwater resources. It has been a worldwide concern as well because heavy metals are considered as the most significant contaminants that cause environmental issues to human and ecosystem (Chen, et al., 2015). Nonetheless, exposure to heavy metals continues and even increasing as the industrial sector develops (Tavakoly Sany, et. al, 2013).

Heavy metals such as Cadmium, Copper, Mercury, Arsenic, Zinc and Lead are regarded as highly toxic since they can lead to serious health disorders even at trace concentration (Barakat, 2011). Adverse health effects caused by heavy metals are including reduced growth, cancer, organ damage, nervous system damage, and death in extreme cases (Jarup, 2003). Heavy metals discharged from anthropogenic sources into river are able to be accumulated in marine organisms due to its high solubility in water. Through bioaccumulation, harmful metals are adequate to enter the food chain and eventually threaten the health of consumer (Faruk, Hamdan and Rezaur, 2015). For instance, Minamata disease was first discovered in Japan at 1956 which caused by released of methylmercury containing industrial wastewater from a chemical factory. Hence, the local residents had accidentally consumed the seafood that contaminated by deadly methylmercury and suffered as a result of Minamata disease. In overall, it is essential to remove these harmful metal ions from contaminated wastewater prior to discharge into the environment.

Heavy metals removal from wastewater can be accomplished by traditional wastewater treatment methods such as coagulation, reverse osmosis, chemical precipitation, ion exchange and membrane filtration process (Bakhtiari and Azizian, 2015; Chen, et al., 2015). Nevertheless, these conventional methods may have many significant drawbacks such as ineffectiveness, high energy consumption, costly and problems dealing with leftover residual sludge (Barakat, 2011). Moreover, low sewerage subsidy paid from government is unable to support such high operations and maintenance costs for advanced wastewater treatment plant (Indah Water Konsortium, 2011). Therefore, many experimentations and investigations are carried out in recent years in order to develop a cost-effective and higher efficiency of heavy metal removal technique (Barakat, 2011).

Adsorption has become one of the alternative treatment methods that being used to remove metal ions from wastewater. There are a number of publications declaring that sorption of various metal ions by adsorbent is cost cheaper and has greater removal efficiency (Bakhtiari and Azizian, 2015; Barakat, 2011; Chen, et al., 2015). Adsorbents are generally produced as tiny as nanomaterials in order to attain maximum surface area to optimize its adsorption capacity. Thus, the production cost of adsorbents can be a major constraint in adsorption technique. In order to deal with this issue, bio-char is introduced as the cheapest adsorbent with excellent removal efficiency among other nanomaterials including activated carbon, carbon nanotubes (CNTs) and metal oxides (Chen, et al, 2015).

1.2 Palm Oil Production in Malaysia

To date, Malaysia is the second largest palm oil producer in the world. Palm oil production capacity in Malaysia has increased sharply from 1.3 million tons in 1975 to approximately 18.9 million tons in 2011 as indicated in **Figure 1.2** (Malaysian Palm Oil Board, 2014). Undeniably, oil palm industry has boosted up the economic growth of this country. Meanwhile, the oil palm industry has also contributed to environmental pollution due to the production wastes resulted from crude palm oil production (Parveen, et al., 2010). The waste produced from palm oil industry generally consists of empty fruit bunches, shell, fibre and Palm Oil Mill Effluent (POME). In recent decades, increasing production of crude palm oil has led to massive generation of biomass waste. It was estimated about 3.5 cubic meter of POME would be generated for every ton of crude palm oil produced (Hassan, Kee and Hussain, 2013). Amount of solids from POME will be left over after conventional treatment process which is known as Palm Oil Sludge (POS) (Hassan, Kee and Hussain, 2013). This sludge also can poses threat to the environment if left unprocessed. Hence, cost effective and sustainable mitigation measures should be taken to tackle the waste sludge issue.

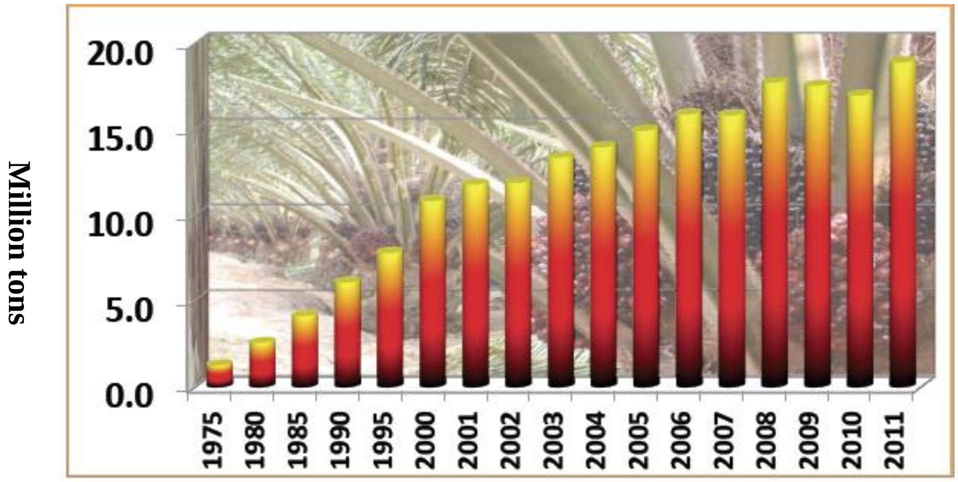


Figure 1.2: Palm Oil Production Capacity in Malaysia in Recent Decades (Malaysian Palm Oil Board, 2014)

On the other hand, according to Abnisa, et al. (2013), although combustion of POS can reduce fossil fuel consumption, but plentiful of carbon dioxide will be released which eventually contributed into greenhouse gaseous. Thus, pyrolysis has been recommended to mitigate the disposal of POS and no waste will be produced during the process (Abnisa, et al., 2013). Bio-char derived from POS is the major products in this pyrolysis process. Generally, bio-char has an adsorption property which able to adsorb dye, organic and inorganic contaminants (Batool, et al., 2014). Furthermore, studies have been carried out and proved that bio-char adsorbents are applicable in various heavy metals removal from aqueous solution and soil (Abnisa, et al., 2013; Yachigo and Sato, 2013).

1.3 Problem Statement

Over the last decades, heavy metals pollution has been a serious issue faced by our water supply and sewerage sector in Malaysia. For instance, Mamut River in Sabah is severely contaminated with heavy metals especially copper(II) ion owing to the surface runoff from mine operations (Ali, et al., 2004). Thus, supplying sufficient clean water from heavy metal contaminated surface water to the population has been a great problem (Randall, 2008).

Apart from that, biomass waste generated from palm oil mill industries has been a significant environmental issue in Malaysia (Hassan, Kee and Hussain, 2013). Excessive amount of biomass waste was being generated as unwanted products due to the extensive production of palm oil annually. Raw POME usually has a high value of Biochemical Oxygen Demand (BOD) around 25,000 mg/L which is 100 times greater than sewerage effluent (Yahaya and Lau, 2013). Hence, presence of POME in any river can cause severe oxygen depletion due to its high value of BOD (Hassan, Kee and Hussain, 2013). As a consequence, the river quality and aquatic ecosystem could be adversely affected (Yahaya and Lau, 2013). Besides, POME consists of high content of both suspended and dissolved solids. These solids are often being left over as POS after anaerobic treatment of POME effluent and this scenario has created inconvenience and disposal problem to palm oil mill industries (Hassan, Kee and Hussain, 2013). Therefore, treatment of POME and reduction of suspended solids are imperative before discharge to avoid any environmental problem in future. In this project, the POS has been re-utilized and pyrolyzed to become Palm Oil Sludge Bio-char (POMS) to achieve the purpose of waste reduction.

In fact, Malaysia is close to water emergency owing to the number of clean river is declining yearly. Action must be taken to preserve water resources if our environment is to remain clean and a safe place to live.

1.4 Research Objective(s)

- To optimize the process parameters such as adsorbent dosage, contact time, contact speed and pH of copper(II) ion removal by palm oil sludge bio-chars.
- To investigate the mechanism of copper(II) ion adsorption by palm oil sludge bio-chars using isotherm models.
- To study the kinetic behaviour of copper(II) ion adsorption by palm oil sludge bio-chars using kinetic models.

1.5 Scope of Study

In this study, Palm Oil Sludge Bio-char (POSB) was prepared by a pyrolysis method and aimed to remove copper(II) ion from synthetic wastewater solutions. Optimal removal efficiency of copper(II) ion from dilute synthetic solutions using bio-char was determined under varied parameters such as adsorbent dosage (0.01 g – 0.08 g), contact time (0 min – 270 min), contact speed (50 rpm – 250 rpm) and pH (3 – 10). Furthermore, equilibrium and kinetic studies were carried out to support the finding. Two isotherm models namely Langmuir and Freundlich were used to analyse the adsorption data of copper(II) ions using bio-char in this study. In addition, the kinetic behaviour of copper(II) ions sorption was investigated using three different kinetic models. These kinetic models were pseudo-first-order model, pseudo-second-order model and intra-particle diffusion model.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

The overall objectives of this chapter are firstly to discuss the properties of Palm Oil Sludge (POS) and sludge based bio-char. Subsequently, this chapter reviews the environmental issues of copper(II) metal ion and its current removal technique. Most importantly, elaborated information regarding the adsorption process was reviewed in this chapter. Besides that, significant parameters that influence the adsorption process were discoursed. Last but not least, equilibrium isotherm and kinetic models for adsorption process were discussed.

2.2 Palm Oil Sludge (POS)

Palm Oil Mill Effluent (POME) usually consists of dissolved solids and suspended solids which are left over after the dewatering and anaerobic treatment (Igwe and Onyegbado, 2007). These left-over solids are known as POS. Owing to huge quantity of POME generated per year in Malaysia, the amount of sludge produced increases respectively (Hassan, Kee and Hussain, 2013).

According to Igwe and Onyegado (2007), the discharged sludge from the treatment system is generally made of mainly water, oil and solids. It is reported that fresh sludge is yellowish brown in color, and results in bad odors. Nevertheless, the composition of sludge may vary widely. Unfortunately, there is no information can be found regarding the physical properties of suspended solid in POS such as melting point, density and viscosity (Reem, et al., 2013).

As stated by Parveen, et al. (2010), POS contains high amount of water, with a slightly alkaline of pH, 8.4 and abounded with variety types of nutrients. These minerals found in POS are including phosphorus, potassium, calcium, carbon and nitrogen. Furthermore, more than 15% of solid oil content can be found in POS. It is important to comprehend that chemical composition of POS may vary from sludge to sludge owing to its processing technique, source of POME as well as age and types of fruit tree. **Table 2.1** shows a sample result of physicochemical analysis of POS reported by Parveen, et al. (2010).

Table 2.1: Physicochemical Analysis of Palm Oil Sludge (Parveen, et al., 2010)

Parameters	**Palm oil sludge**
Moisture content, %	85.0
pH	8.4
Organic matter, mg/L	60.0
Total organic carbon (TOC), mg/L	33.0
Total nitrogen (TN), mg/L	3.6
Phosphorus, mg/L	0.9
Potassium, mg/L	2.1

2.2.1 Current Trend in Palm Oil Sludge Usage

Even though POS is an end product of POME treatment system, it could impose threat on environment if it is not properly dealt with. Therefore, it is necessary to mitigate these wastes and turn it into less harmful products using appropriate technology. Fortunately, there are number of ways to treat POS effectively as tabulated in **Table 2.2**.

Table 2.2: Established Methods to Treat Palm Oil Sludge

Methods to treat palm oil sludge	**End product**	**References**
Oil recovery using sludge separator	Recovered palm oil	Igwe and Onyegbado (2007)
Heavy metal removal by water spinach (Phytoremediation)	Treated sludge	Metosen (2009)
Transesterification	Biodiesel	Addeb, et al. (2010)
Composting technique	Compost containing organic residues	Parveen, et al. (2010)
Dietary substitution for livestock	-	Yahaya and Lau (2013)
Pyrolysis	Bio-char and bio-oil	Suchithra, et al. (2014)

It was reported by Igwe and Onyegbado (2007) that POS contained 15% or more useful oil which can be recovered from the sludge. Useful oil can be extracted from the sludge through the separator and recycled back to collection stream. Thereafter, volume of sludge was greatly reduced and more tolerable for disposal.

POS is a left-over product generated from the anaerobic treatment of POME which contains unacceptable level of contaminants such as heavy metals. In this way, it is essential to reduce the concentration of these contaminants. Phytoremediation using water spinach which studied by Metosen (2009) is an alternative way to solve this problem.

In view of research conducted by Adeeb, et al. (2010), POS has been utilized to produce biodiesel through transesterification with acidic catalyst. Due to its high abundant availability and low cost, POS has become a potential renewable source for biodiesel production. Besides that, Yahaya and Lau (2013) declared that dried POS can be used as dietary substitute for livestock and aquaculture organisms. The Malaysian

Agricultural Research Development Institute (MARDI) proved that dried POS can be safely feed to the sheep and cut the cost of animal feed (Yahaya and Lau, 2013).

In agreement with Parveen, et al. (2010), POS can be employed as a fertilizer under composting technology. Composting is a microbial technology used to degrade organic substances biologically. Due to the degraded organic matters still contain considerable amount of nutrients, it is advisable to be applied as fertilizer for agricultural purpose. Likewise, according to Yahaya and Lau (2013), the employment of POS as fertilizer was able to increase the soil productivity as well as the yield of crops by improving the soil structure.

Last but not least, POS can be turned into bio-char and bio-oil through pyrolysis at extreme high temperature with limiting amount of oxygen (Suchithra, et al., 2015). Detailed information about bio-char was studied and reviewed in the next section of this chapter.

2.3 Bio-char

Lehmann and Joseph (2015) have defined bio-char as a solid material obtained from biomass heating under an extremely high temperature condition with the presence of limited amount of oxygen. This production process can be known as pyrolysis or charring. Unlike charcoal is produced as energy carrier, presence of bio-char can mitigate on variant of agricultural and environmental issues. In general, materials used for bio-char production are animal or plant based biomass including rice-husk, corncob, animal manure and most agricultural residues as reported in **Table 2.3**.

Table 2.3: Bio-Char Produced from Various Types of Biomass over the Recent Years (2010-2016)

Bio-char	**References**
Sugarcane bagasse	Inyang, et al. (2010)
Rice-husk and corncob	Liu, et al. (2011)
Pig and cow manure	Kolodynska, et al. (2012)
Oil palm tree residue	Abnisa, et al. (2013)
Brewers draff	Trakal, et al. (2014)
Lignocellulosic biomass	Leng, et al. (2015)
Sewage sludge	Yuan, et al. (2016)

2.3.1 Sludge Based Bio-char and Its Preparation Methods

Abnisa, et al. (2013) showed that thermal degradation was a possible method to utilize waste sludge. Through this process waste sludge can be converted to bio-char. Leng, et al. (2015) reported that many researchers are focusing on the conversion of sludge into bio-char adsorbents owing to its high carbon content, copiousness and low cost.

Table 2.4 shows preparation of sludge based bio-char using various types of sludge originated from sewage, paper mill and palm oil. Sewage sludge apparently was selected by numbers of researchers to be prepared as sludge based bio-char. Preparation methods for sludge based bio-char include conventional pyrolysis, microwave pyrolysis and liquefaction.

Table 2.4: Tabulated Data of Preparation Methods for Different Types of Sludge Based Bio-Chars under Conditions

Types of sludge	Preparation methods	Heating temperature (℃) / Power (Watts)	Heating time (minute)	Heating rate (℃/minute)	References
Sewage sludge	Pyrolysis	450	30	5	Liu, Liu and Zhang (2014)
Paper mill sludge	Pyrolysis	500	-	-	Reckamp, Garrido and Satrio (2014)
Palm oil sludge	Pyrolysis	300-350	-	-	Suchithra, et al. (2015)
Anaerobic granular sludge	Pyrolysis	650	120	15	Shi, et al. (2014)
Sewage sludge	Pyrolysis	400-550	-	-	Song, et al. (2014)
Sewage sludge	Microwave pyrolysis	200-250	-	-	Huang, et al. (2015)
Sewage sludge	Liquefaction	280-380	-	-	Leng, et al. (2015)

Song, et al. (2014) reported that sludge based bio-char can be prepared by a pyrolysis process and need to be dried under the sun for at least 1 day prior to pyrolysis. This is done to remove moisture content and pathogen completely. The sample is encouraged to be dried again in an oven at 105℃ for 24 hours. Pyrolysis of sewage sludge sample can be performed at temperature range of 400 ℃ to 550 ℃. This temperature range is recommended by Song, et al. (2014) as the author noted that the formation of bio-char occurs within this range. In addition, this temperature range was verified and followed by other researchers such as Liu, Liu and Zhang (2014), and Reckamp, Garrido and Satrio (2014).

Anaerobic granular sludge was also used to prepare bio-char using higher heating temperature (650℃), whereas POS was prepared at lower heating temperature (300-350℃) as compared with others sewage sludge.

On the other hands, microwave pyrolysis of sewage sludge was studied by Huang, et al. (2015). Huang, et al. (2015) stated that microwave heating is faster than conventional heating, and thus resulting in a higher yield of product. This is because microwave heating has faster heating rate compared to conventional heating. Nonetheless, limited information is available on the optimal parameters of pyrolysis or microwave pyrolysis for the preparation of Palm Oil Sludge Bio-char (POSB).

Despite pyrolysis is widely used by many researchers, sludge based bio-char can be produced using liquefaction process. According to Leng, et al. (2015), liquefaction is a lower temperature process with a range of temperature from 280-380℃. Moreover, bio-char produced by liquefaction has larger amount of functional groups on its surface. Therefore, bio-char produced by liquefaction has better heavy metals adsorption capacity than bio-char produced by pyrolysis due to its existing great number of oxygen-containing functional groups (Leng, et al., 2015). Similarly, bio-chars produced by liquefaction with different solvent at different temperatures will have different properties as well.

As stated by Zielinska, et al. (2015), the type and condition of biomass and the pyrolysis conditions used to produce bio-char are the most significant factors that regulate the bio-chars’ properties. Zielinska, et al. (2015) reported that carbon content in sludge derived bio-char was higher compared to other biomass. Furthermore, increasing the temperature of pyrolysis will increase the ash quantity of bio-char. In addition, bio-char produced at higher temperature will have greater contribution of nutrients. In short, different pyrolysis condition will produce different properties of bio-chars.

2.3.2 Utilization of Sludge Based Bio-Char

Literatures reported many utilization of sludge based bio-char for a wide range of environmental and agricultural applications as shown in **Table 2.5**.

Table 2.5: Applications of Sludge Based Bio-Char

Applications	**References**
Carbon sequestration	Collision, et al. (2009)
Adsorbent in wastewater treatment	Abnisa, et al. (2013)
Land applications and land reclamations	Song, et al. (2014)
Soil application in agricultural	Zielinska, et al. (2015)

In the beginning, bio-char is intended to be used as soil amendment (Lehmann and Joseph, 2015). Due to its induced liming effect, it can be used to de-acidify the soil and resulting in the increase of crop productivity (Zielinska, et al., 2015). Furthermore, land application of sludge derived bio-char is able to improve soil condition owing to its high nutrients content (Song, et al., 2014).

Apart from that, Collision, et al. (2009) declared that sludge based bio-char is able to sequestrate the atmospheric carbon. It was estimated that single application of bio-char into a specified land area resulted in the sequestration of up to 0.65 giga-tons of carbon for every 10 years.

Last but not least, it can be converted into a low-cost adsorbent and being employed in wastewater treatment plants to remove heavy metals such as copper, lead, cadmium and arsenic as studied by Abnisa, et al. (2013).

2.4 Heavy Metals in Wastewater

Heavy metals are the elements found in periodic table that exhibits metallic properties. Heavy metals are characterized by 5 g/cm^3 of density or higher (Barakat, 2011). In recent decades, heavy metals are being discharged continuously into the aquatic environment due to anthropogenic activities (Tavakoly Sany, et al., 2013; Bieby, et al., 2011). These anthropogenic sources include mining, welding, semiconductors and electrical appliances manufacturing industries (Bilal, et al., 2013).

Unquestionably, presence of heavy metals can bring negative effects to human and ecosystem. In fact, according to Faruk, Hamdam and Rezaur (2015), living organisms do require several types of metals at trace amount for metabolic function purposes. These metals are zinc, iron, copper and magnesium. In vice versa, it can cause serious health disorders if ingested at exceeded concentration limits. Furthermore, nonessential metals such as mercury, nickel, cadmium and arsenic can bring irreversible damage to human body even at trace concentration. Resulting effects are including brain damage, blood circulation damage, carcinogen and nervous system damage (Barakat, 2011). For this reason, removal of toxic heavy metals from water bodies is a must.

In recent years, many methods have been proposed and being used in order to remove heavy metals from the wastewater. These methods include adsorption, chemical precipitation, coagulation, ion-exchange and membrane filtration as shown in **Table 2.6**.

Table 2.6: Advantages and Disadvantages of Conventional Methods Used for Heavy Metal

Treatment Method	Advantages	Disadvantages	References
Adsorption	• Simple operation • Cost effective technique for heavy metal removal • High quality of treated effluent • Reversible process	• Disposal problems	Amin (2010); Fu and Wang (2011)
Chemical Precipitation	• Simple process • High degree of selectivity • Cheap	• Harmful substances are still remained in waste product • Disposal problem	Farooq, et al. (2010); Metcalf and Eddy (2004)
Coagulation	• Constantly high removal efficiency of heavy metal from wastewater • Safe and effective method	• Excessive sludge production which lead to disposal problems • High operational cost • High consumption of coagulant	Metcalf and Eddy (2004); Tzoupanos and Zouboulis (2008)
Ion-exchange	• Selective heavy metal removal • Materials are generable	• Operating cost is high over long term • Microorganism cannot be removed • Bacteria has chances to culture in the deionization bed	Helfferich (1962)

Membrane filtration	• Less chemicals consumption • Selective heavy metal removal	• Membrane fouling • Frequent maintenance is required	Lewinsky (2007)

2.4.1 Copper(II) Metal Ion

Copper(II) ion is an essential element required in small amount for human growth. Nonetheless, excessive ingestion of copper(II) ion can cause vomiting, headache, liver and kidney damage as well as abdominal pain (Amin, 2010). Besides that, continuous exposure to copper(II) ion can reduce the lining of the inner nose and damage the respiratory system (Amin, 2010). Moreover, presence of copper(II) ion at excessive concentration in aquatic environment can impair the osmo-regulatory mechanism of the aquatic ecosystem (Bilal, et al., 2013).

Sources of copper(II) ion from industrial area include circuit board manufacturing, electronic plating, wire drawing and paint manufacturing (Farooq, et al., 2010). Thus, in order to protect the environment, Malaysia’s environmental law has set its permissible limits of copper(II) ion as 0.2 mg/L for standard A and 1.0 mg/L for standard B in industrial effluents. Apart from that, World Health Organization (WHO) has limits the concentration of copper(II) ion at 1.5 mg/L in drinking water supply (Bilal, et al., 2013).

2.4.2 Methods to Remove Copper(II) Ion

Table 2.6 shows conventional technologies utilized for removing copper(II) ions from wastewater. Nonetheless, each kind of treatment processes has their own distinct advantages and disadvantages when dealing with copper(II) ions. Among these, adsorption processes is recognized as an effective and economical method for copper(II) metal ion removal from wastewater (Amin, 2010). In addition, high quality of effluent can be obtained through adsorption and adsorbent that being used up can be regenerated through desorption. Over the long haul, cost of adsorbent will be reduced. Even though other treatment processes show good results in copper(II) ion removal from wastewater, money invested on these methods could be very high. For instance, membrane fouling is the major drawback of membrane filtration technology, consequently frequent maintenance is needed. Furthermore, ion-exchange and coagulation processes are uneconomic since high operational costs are required in comparison to adsorption. In overall, adsorption is an exceptional and desirable method to be selected in copper(II) metal ion removal.

2.4.3 Adsorbents Used to Remove Copper(II) Ion

Adsorption process requires the presence of an adsorbent. Table 2.7 shows types of adsorbent used for remove copper(II) ions in adsorption treatment process.

Table 2.7: Types of Adsorbent Used to Remove Copper(II) Ions from Aqueous Media

Types of adsorbent	**References**
Activated carbon	Farooq, et al. (2010)
Bio-char	Trakal, et al. (2014)
Nanoparticle: Iron oxide	Ghaemi, et al. (2015)
Geopolymer	Al-Harahsheh, et al. (2015)

According to Farooq, et al. (2010), adsorption using activated carbon is the most common method to remove copper(II) ion that applied in many treatment plants. Furthermore, Ghaemi, et al. (2015) stated iron oxide nanoparticles have a very strong affinity toward metals and obtained results have shown high efficiency in copper(II) ion removal. However, the production cost of these adsorbents are highly expensive and non-recyclable (Farooq, et al., 2010). Hence, low cost adsorbents derived from agricultural waste as well as industrial solid waste are being applied in copper(II) ion adsorption process. For example, adsorbent of fly ash based geopolymer was used by Al-Harahsheh, et al. (2015) to remove copper(II) ion from aqueous solution. Eventually, a high removal efficiency of copper(II) ion has obtained based on the results of the study. In addition, bio-char is being widely used as adsorbent in recent years due to its high affinity to copper(II) ion and organic matter (Trakal, et al., 2014).

2.5 Adsorption

As mentioned earlier, there are many reported treatment methods for heavy metal removal such as chemical precipitation, ion exchange, membrane filtration, coagulation and flocculation processes. In spite of these available treatment methods, many researches are proven that adsorption is an effective and efficient for the treatment of wastewater laden with heavy metals (Barakat, 2011; Chen, et al., 2015; Luo, et al., 2015).

Adsorption is defined as the binding of molecules on the surface of solid adsorbent (Nageeb, 2013). Adsorption is also known as a thermodynamic system in which involved components are desire to achieve equilibrium condition (Alley, 2007). During the adsorption process, heat energy will be released through the movement of adhering molecule. Hence, adsorption is an exothermic reaction (Mihaly, 2011).

According to Nageeb (2013), adsorption process can be classified into 2 types of adsorption which are physical and chemical adsorptions. Van der Waals' forces are the forces of attraction that exist in between the adsorbent and adsorbate in physical adsorption. Therefore, this type of adsorption is very weak compared to chemical adsorption since no sharing of electrons is occurring. Furthermore, the adsorbed molecule is not adhering to a specific binding site on the surface of adsorbent (Ariff, 2010). It can stack with each other and form multiple layers on the surface of adsorbent (Ariff, 2010). Obviously, the adsorption capacity of physical adsorption is much higher than chemical adsorption due to existence of multi-layer of adsorbed molecules. In addition, physical adsorption is a reversible reaction (Alley, 2007).

On the other hand, chemical adsorption is completely opposite to physical adsorption. Chemical adsorption is an irreversible reaction and has greater forces of attraction like chemical bond forces (Nageeb, 2013). Moreover, heat of adsorption in chemical adsorption is four times greater than physical adsorption (Mihaly, 2011). Besides that, chemical adsorption is a highly specific process, therefore the adsorbate can only adhere to specific site on the adsorbent's surface. Adsorption capacity of chemical adsorption is much lower compared to physical adsorption because only mono-layer can be formed on the adsorbent's surface (Ariff, 2010).

2.5.1 Characteristics of Adsorbents

Major types of conventional adsorbents are activated carbon, activated alumina, silica gel and resin (Crini and Badot, 2010). These adsorbents are generally manufactured, but the production cost is not cheap. Hence, non-conventional adsorbents have been introduced to replace the expensive one. Adsorbents particularly derived from agricultural wastes such as wheat straw, POS and brewers draff are being focused rather than those conventional adsorbents owing to their low cost and abundant availability (Farooq, et al., 2010; Trakal, et al., 2014). Furthermore, biomass adsorbents such as fungi, chitosan and algae are categorized as non-conventional adsorbent (Crini and Badot, 2010).

Typically, each adsorbent has its own unique characteristics such as surface area, pore size and charges on adsorbing surface. Understanding of these properties is crucial in order to choose the most suitable adsorbent to deal with each pollutant. First and foremost, surface area is the core factor to identify the value of an adsorbent in wastewater treatment. Amin (2010) mentioned that the surface of an adsorbent that the molecules usually bind on is known as binding sites or ligands. The surface area of adsorbent is directly proportional to its adsorption capacity. This is evident when adsorbent has greater surface area which indicates more binding sites are available to permit more adhering molecules. Therefore, adsorbent materials are typically highly porous (Alley, 2007).

Adsorbents are relegated into 3 categories based on its pore sizes. There are macropores, mesopores and micropores which proposed by International Unit of Pure and Applied Chemistry (IUPAC) (Knaebel, 2009). Scanning tunneling microscopy and mercury porosimetry techniques have been commonly used to determine the pore size distribution of adsorbents (Manocha, 2003). **Table 2.8** shows the classification of adsorbents by pore size distribution.

Table 2.8: IUPAC Classification on Pore Sizes of Adsorbent (Knaebel, 2009)

Class	Range of pore sizes (nm)
Macropores	> 50
Mesopores	2 – 50
Micropores	< 2

Interestingly, pore sizes of adsorbent's surface can influence the rate of adsorption. This is mainly because of larger adsorbate materials can only fit well in the larger diameter of pore size (Knaebel, 2009). In other word, the adsorption capacity of an adsorbent with smaller diameter pores will be lower if the present of adsorbate materials are larger in size. **Figure 2.1** is indicating smaller pore size of adsorbent only available for smaller adsorbate to attach onto its surface.

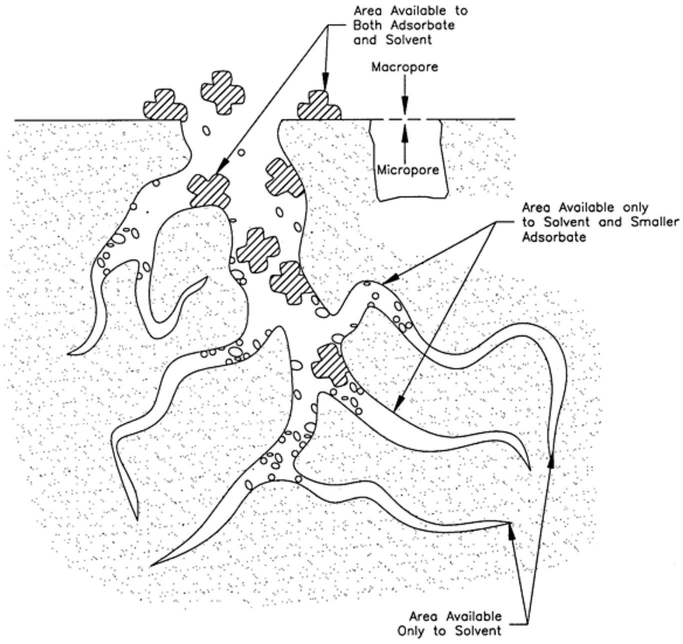


Figure 2.1: Schematic Diagram of Typical Pore Structure of an Adsorbent

Besides that, the surface of an adsorbent contains different types of functional groups such as carbonyl, carboxylic, phenolic and lactonic groups (Crini and Badot, 2010). These functional groups play an important role during the interaction between the adsorbate and adsorbent. Therefore, the adsorbing surface of adsorbent is charged mainly due to the presence of these functional groups. In overall, heavy metal adsorption performance can be greatly influenced by these physical characteristics of an adsorbent (Crini and Badot, 2010).

Apart from that, adsorption capacity is also considered as one of the most important characteristics of an adsorbent. It is employed to state the amount of adsorbate taken up by the adsorbent per unit mass (or volume) of the adsorbent. Moreover, it is useful in capital cost estimation since it can determine the exact amount of adsorbent required for treatment process (Knaebel, 2009). Adsorption capacity (q_t) can be expressed from the relationship:

$$q_t\ (mg/g) = \frac{(C_o - C_t)V}{m} \qquad (Eq. 2.1)$$

where q_t is the adsorption capacity at time t (mg/g), C_o and C_t are the initial and equilibrium concentration of metal ions in solution respectively (mg/L), V is the volume of solution (L), and m is the weight of adsorbent sample (g).

2.5.2 Adsorption Mechanism between Heavy Metals and Adsorbents

Adsorption mechanism between heavy metals and adsorbents can be described well by the chemical interaction between the metal ion and surface functional groups of adsorbent in the absence of organic matters (Wang, et al., 2009). These interactions include surface complexation reactions and electrostatic interactions. Surface complexation reactions are generally referred to as formation of inner-sphere surface complex by metal ions on the adsorbents' surface functional groups whereas formation of outer-sphere complex at a distance to the adsorbent is known as electrostatic interactions (Somasundaran, 2006).

Theoretically, specific adsorption and ion-exchange are the two basic mechanism of metal adsorption (Somasundaran, 2006). Specific adsorption is a particular type of adsorption that has adsorption energy greater than physical adsorption but lower than chemical adsorption. Even though interaction of metal ion with specific functional group on the adsorbent involves in specific adsorption, nonetheless, no chemical bond can be found in specific adsorption unlike chemical adsorption (Alley, 2007). As stated by Somasundaran (2006), heavy metals can be retained and trapped by selectively binding of the respective metal ions on the adsorbents. To distinguish specific adsorption from ion-exchange, these strong and irreversible binding forces by metal ions can become as indication of specific adsorption.

In turn for ion-exchange mechanism, protons in functional groups of adsorbent can exchange with metal ions in the aqueous phase (Wang, et al., 2009). For instance, cation exchange is occurred when the cation in aqueous solution swap with the cation from the surface of adsorbent. Therefore, cation exchange is also known as non-specific adsorption and occurs at relatively fast speed due to the nature of electrostatic interaction (Somasundaran, 2006).

2.5.3 Advantages and Disadvantages of Adsorption Process

As retrieved from various published journals, the pros and cons of adsorption process in recent years were summarized and tabulated in **Table 2.9**.

Table 2.9: Advantages and Disadvantages of Adsorption Process over the Years from Various Studies

Treatment Method	Advantages	Disadvantages	References
Adsorption process	• Simple and cost effective technique for heavy metal removal	• Disposal problems	Amin (2010)
	• Low cost • Simple operation • High metal binding capacities • Applicable at wide pH range	• Low selectivity • Exhausted adsorbents generated as waste	Barakat (2011)
	• High effectiveness for removing heavy metals	• Disposal of exhausted adsorbents • Preparation of adsorbent such as activated carbon is costly	Bilal, et al. (2013)
	• High quality product of water can be produced	• Disposal of used adsorbent has to be	Saqib and Ahsan (2014)

	in wastewater treatment	considered - Commonly used adsorbent such as activated carbon is expensive and need to be reactivate after used up	
	- High removal rate can be obtained using high adsorption capacity of adsorbent	- Interaction mechanisms of multi-component adsorption are still unknwon yet	Luo, et al. (2015)

As indicated in **Table 2.9**, adsorption is a simple, efficient and cost effective technique developed to remove contaminants from the wastewater. However, it is essential to declare that adsorption is a non-destructive technique which involves only a phase change of pollutants (Crini and Badot, 2010). Eventually, this technique will imposes further problems in the form of sludge disposal. Furthermore, low-cost adsorbents should be encouraged to replace the costly adsorbents like activated carbon.

2.6 General Factors that Influence the Adsorption Process

The major factors that will influence the adsorption process are pH, concentration of adsorbent, contact time and contact speed. These parameters that affect the efficiency of heavy metals adsorption onto adsorbent were reviewed in the following sections. Moreover, value of these parameters obtained at optimum conditions from literatures were tabulated in **Table 2.10**.

Table 2.10: Comparison of Optimal Parameters Obtained from Various Studies for Copper(II) Ion Adsorption

Adsorbents	**pH**	**Amount of dosage used**	**Contact time (minute)**	**Contact speed (rpm)**	**References**
Sawdust	8	-	5	300	Larous, Meniai and Lehocine (2005)
Chitosan	6	0.1 g/L	-	160	Kyzas, Kostoglou and Lazaridis (2009)
Peanut husk charcoal	6	-	140	-	Abdel Salam, Reiad and Elshafei (2011)
Corn straw bio-char	5	10 g/L	120	-	Chen, et al. (2011)
Hardwood bio-char	5	50 g/L	120	-	Chen, et al. (2011)
Banana peel based bio-sorbent	6	5 g/L	60	120	Hossain, et al. (2012a)
Bio-char derived from animal manure	5	0.5 g	-	-	Kolodynska, et al. (2012)
Modified ligand	7	-	-	650	Awual, et al. (2013)
Chitosan beads	4	-	120	120	Igberase, Osifo and Ofomaja (2014)
Geopolymer	6	2 g/L	60-120	100	Al-Harahsheh, et al. (2015)

2.6.1 pH

The pH of the solution plays an important role on heavy metals adsorption as it determines the surface charge of adsorbent. Apart from the surface charge of adsorbent, pH also affects the degree of ionization and speciation of the heavy metals present in the solution (Abdel Salam, Reiad and Elshafei, 2011). Theoretically, the adsorptive capacity of metal cations increases with the increase in pH of the solution (Wang, et al., 2009). Nonetheless, the relationship between adsorption capacity and the pH of solution is not linear. This is mainly due to high pH value which may cause precipitation of metal ions which should be fended off during experiments.

Based on research conducted by Kolodynska, et al. (2012), the optimal adsorption efficiency for copper(II) ions using bio-char was achieved at a pH of 5.0 as shown in **Figure 2.2**. Initially, the adsorption capacity of bio-char was very low under strong acidic condition. Wang, et al. (2009) explained that the surface binding sites of adsorbent are protonized at low pH which led to reduction of binding sites availability. As indicated in **Figure 2.2**, the adsorption capacity for copper(II) ion was increasing with the increasing pH value until the optimum point is reached. With further increase in pH, the adsorption efficiency was getting lower due to precipitation of metal ions. Solubility of metal ions will decrease at high pH and thereby precipitation will occur.

From **Table 2.10**, it is known that the optimal pH in copper(II) ion removal ranged from 4 to 8. Among these pH values, pH 5 and 6 most often were reported from many studies as compared to others. The highest pH (8) was reported by Larous, Meniai and Lehocine (2005) whereas the lowest pH (4) was reported by Igberase, Osifo and Ofomaja (2014).

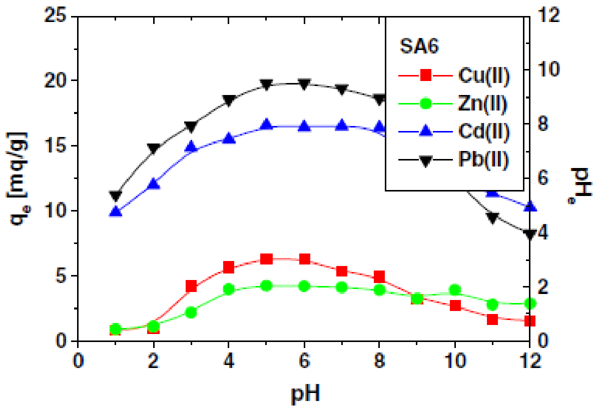


Figure 2.2: Effect of pH on Cu(II), Zn(II), Cd(II) And Pb(II) Adsorption on Bio-Char (Kolodynska, et al., 2012)

2.6.2 Adsorbent Dosage

Adsorbent dosage is a significant factor of adsorption process since it can determines the extent of decontamination and estimates the capital cost required for dosage (Crini and Badot, 2010). Hypothetically, the uptake rate of metal ion will increase with increasing the initial amount of adsorbent (Wang, et al., 2009). This is because the availability of surface binding sites of adsorbent is considered as the core element in adsorption process (Crini and Badot, 2010). Therefore, at greater amount of adsorbent, the sites available for metal ion sorption will be increase and thus, promote the adsorption process. Furthermore, it is crucial to identify the optimal concentration of adsorbent to avoid over expenditure on dosage.

Retrieved from **Figure 2.3** plotted by Chen, et al. (2015), it was clearly shown that the removal efficiency of cadmium ion increased rapidly with the increasing adsorbent dose from 0.1 to 0.5% and a slight increase was spotted after 0.5% of dosage. The removal efficiency does not increase significantly after the maximum uptake rate of metal ion is reached. Beyond the optimal removal percentage, the concentration of the metal ion becomes the limiting factor.

Based on data obtained from **Table 2.10**, the dosage required to achieve the optimum condition are ranged widely. Different amount of dosage required is mainly due to the different adsorbents used. For instance, 50 g/L of hardwood bio-char is required to obtain optimum result whereas chitosan adsorbent required the least amount which is 0.1 g/L.

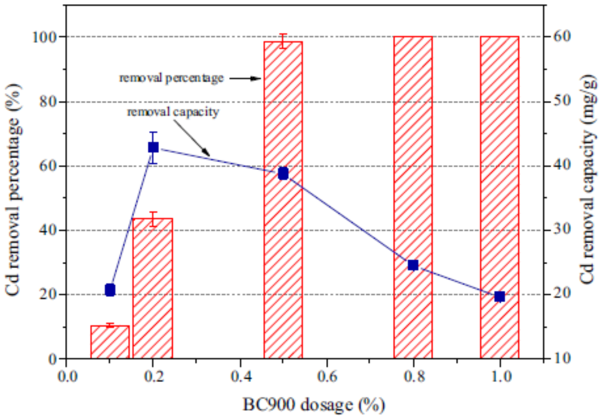


Figure 2.3: Effect of Bio-Char Dosage on Cadmium Ion (Cd^{2+}) Removal (Chen, et al., 2015)

2.6.3 Contact Time

In general, adsorption process of heavy metal by adsorbent is usually completed speedily (Abdel Salam, Reiad and Elshafei, 2011). According to Wang, et al. (2009), metal sorption can be divided into two phases which are rapid initial phase, followed by long period of slow uptake phase. Initially, the uptake rate of metal ions is very high due to the availability of binding sites. This means there are more chances of contact between the metal ions and adsorbents. After some time, the binding sites are getting lesser since the sites are occupied by adsorbate. Thus, the remaining metal ions have to compete with each other for the binding sites. Besides, the adsorbed metal ions at macrospore do require some time to traverse farther and deeper into the pores. Therefore, this scenario explained why the uptake rate of metal ion is much lower after a period of time. As illustrated in **Figure 2.4**, the copper(II) ion removal percentage for three different adsorbents was increased rapidly at initial phase until equilibrium has reached and eventually remained constant (Abdel Salam, Reiad and Elshafei, 2011).

Table 2.10 showed the capital contact time for copper(II) ion removal was in the range of 5 to 140 minutes. A number of researchers were reported 120 minutes as the best contact time for copper(II) ion removal from aqueous solution.

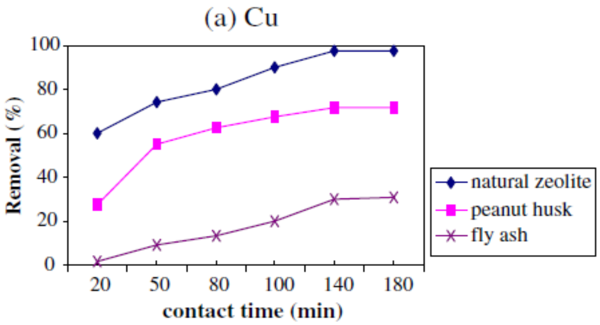


Figure 2.4: Effect of Contact Time on Copper(II) Ion Removal for Three Different Adsorbents (Abdel Salam, Reiad and Elshafei, 2011)

2.6.4 Contact Speed

In addition, contact speed is also an important parameter in any adsorption phenomena. Contact speed and contact time are the key parameters for the process design and operation control (Kolodynska, et al., 2012). In general, metal ions removal efficiency will be increases with increasing contact speed. This happens because higher contact speed will improves the diffusion of metal ions towards the surface of the adsorbents. Larous, Meniai and Lehocine (2005) have reported that adsorption capacity for copper(II) ions using sawdust boosted up sharply with the increasing contact speed as can be seen in **Figure 2.5**.

As shown in **Table 2.10**, the contact speed for copper(II) ion adsorption from various studies was typically ranged from 100 to 300 rpm. Astonishingly, the outstanding contact speed which is 650 rpm was recorded by Awual, et al. (2013). In contrast, the lowest contact speed which is 100 rpm was established by Al-Harahsheh, et al. (2015). Lichfouse, Schwarzbauer and Robert (2011) declared that shaking rate in the range of 100-200 rpm is sufficient to ensure an intimate contact between metal ions and adsorbents.

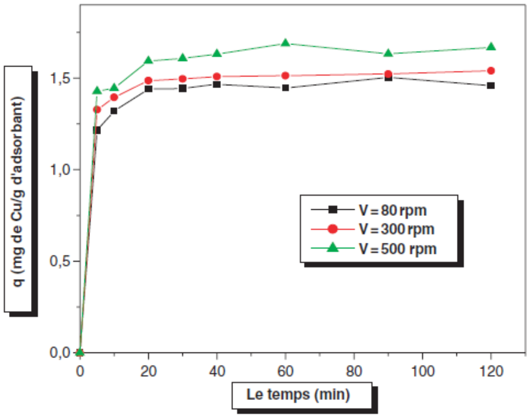


Figure 2.5: Effect of Contact Speed on Copper(II) Ion Removal by Sawdust (Larous, Meniai and Lehocine, 2005)

2.7 Adsorption Isotherms

Adsorption isotherm, also known as equilibrium relationship, is present to offer a delineation of the interaction between adsorbate and adsorbent (Bakhtiari and Azizian, 2015). Thus, adsorption isotherm is crucial for optimization of the adsorption process and adsorbents capacities. Generally, adsorption isotherm can be established by an invaluable curve that describe the fluidity of a substance (sorbate) from liquid phase (solvent) to the solid phase (sorbent) at constant pH and temperature (Foo and Hameed, 2010). In contrast with the past, there is a wide variety of equilibrium isotherm models have been formulated by scientists to analyse the sorption data. Two oldest adsorption isotherms that are still commonly used to fit the experimental adsorption data are Langmuir and Freundlich isotherms (Foo and Hameed, 2010). In addition, Foo and Hameed (2010) stated that linear least-squares method has been historically used to determine the isotherm parameters or the best fit model by analyzing the experimental data.

2.7.1 Langmuir Isotherm Model

Langmuir isotherm is one of the oldest isotherm models that scientifically developed by Irving Langmuir in 1916 (Levine, 2009). Although this model was originally used to describe the gas-solid-phase adsorption onto activated carbon, nonetheless it has been modified to compute the performance of different adsorbents (Foo and Hameed, 2010). The Langmuir model showed as:

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \qquad (Eq. 2.2)$$

where C_e is the equilibrium concentration of the adsorbate (mg/dm^3), q_e is the adsorption capacity at equilibrium (mg/g), q_m (mg/g) and K_L (dm^3/mg) are the Langmuir constants related to monolayer adsorption capacity and rate of adsorption respectively (Kolodynska, et al. 2012).

In order to use Langmuir isotherm to describe the adsorption relationship between adsorbates and adsorbents, three assumptions must be satisfied (Levine, 2009). First and foremost, surface of adsorbent is in contact with the adsorbate containing solution. Secondly, the adsorbent has the specific sites allowing adsorbates to be attached. The last assumption is that only single layer of molecules is allowed to be attached on the surface of adsorbent. For instance, it assumes that adsorption of metal ions occur at a homogenous surface by monolayer sorption (Adeyemo, Adebowale and Olu-Owolabi, 2014). Thus, the energies of adsorption on the surface of adsorbents are uniform. Nevertheless, the major drawback of this isotherm is unable to account for the surface roughness of the adsorbent (Levine, 2009).

Table 2.11 shows the isotherm models followed by adsorption of heavy metals from various literatures. It can be indicated that generally Langmuir isotherm model is followed which means that the metal ions are predominately adsorbed in monolayer.

Table 2.11: Previous Researches of the Adsorption Isotherm Studies for Heavy Metals Removal

Metal ion	**Adsorbent**	**Best fit model**	**References**
Copper(II) ion	Grape seed activated carbon	Freundlich isotherm	Ozcimen and Ersoy-Mericboyu (2009)
Copper(II) ion	Wheat based bio-sorbent	Langmuir isotherm	Farooq, et al. (2010)
Copper(II) ion	Palm oil fruit shells	Langmuir and Freundlich isotherms	Hossain, et al. (2012a)
Copper(II) ion	Animal manure based bio-char	Langmuir isotherm	Kolodynska, et al. (2012)
Copper(II) ion	Dried pinecones based bio-char	Langmuir isotherm	Adeyemo, Adebowale and Olu-Owolabi (2014)
Arsenic and Cadmium ions	Oil palm empty fruit bunch bio-char	Langmuir isotherm	Norzalina, Che and Rosenani (2014)
Copper(II) ion	Brewers draff based bio-char	Langmuir isotherm	Trakal, et al. (2014)
Copper(II) ion	Nano-porous metal organic framework	Freundlich isotherm	Bakhtiari and Azizian (2015)
Copper(II) ion	Fly ash based geopolymer	Langmuir isotherm	Al-Harahsheh, et al. (2015)

Copper(II) ion	Ion exchange fibres (IEFs)	Freundlich isotherm	Ntimbani, Simate and Ndlovu (2015)
Cadmium ion	Palm oil sludge bio-char	Langmuir isotherm	Suchithra, et al. (2015)
Copper(II) ion	Carbon nanotubes (CNTs)	Langmuir and Freundlich isotherms	Tofighy and Mohammadi (2015)

2.7.2 Freundlich Isotherm Model

In 1909, Freundlich derived an empirical equation to express the isothermal variation of adsorption of gaseous molecules adsorbed by solid adsorbent with pressure (Shafiq, et al., 2008). This equation is known as Freundlich adsorption isotherm. Freundlich isotherm model can be expressed as:

$$q_e = K_F C_e^{1/n} \qquad (Eq. 2.3)$$

where K_F is the Freundlich adsorption capacity (mg/g) and $1/n$ is the Freundlich constant related to the surface heterogeneity (Kolodynska, et al., 2012).

To be specific, Freundlich isotherm is typically used to determine the adsorption intensity of adsorbent in relation to the adsorbate assuming that the adsorption is occurring at heterogeneous surface (Adeyemo, Adebowale and Olu-Owolabi, 2014). Unlike Langmuir isotherm, Freundlich isotherm does not restricted to the formation of monolayer (Foo and Hameed, 2010). Hence, this isotherm model can be applied in multilayer adsorption with uneven distribution of adsorption heat and affinities over the surface of adsorbent (Foo and Hameed, 2010). The only limitation of this isotherm is the adsorption varies widely with pressure until saturation pressure is reached. Therefore, the performance of Freundlich isotherm will be limited at high pressure (Levine, 2009).

2.8 Adsorption Kinetic Model

Despite the fact that isotherm study is important to determine the exact amount of adsorbate removed by a given adsorbent, and yet the kinetic study plays a crucial role as well particularly in adsorption process (Oliveira, et al., 2009). This is because kinetic of the process limits the rate at which equilibrium state can be reached (Oliveira, et al., 2009). Nowadays, adsorption kinetic models were implemented in many studies as well in order to gain a holistic comprehension of the adsorption process (Deepak, Varsha and Yogesh, 2014). Kinetic models are developed to describe how fast the adsorption of a substance occurs and also investigate the mechanism of adsorption by implementing these models on the experimental data (Deepak, Varsha and Yogesh, 2014). Typically, there are three kinetic models that have been widely used which are Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion models.

2.8.1 Pseudo-first-order Model

First-order rate equation was first presented by Lagergen in 1898 so as to describe the kinetic activity of liquid-solid phase adsorption (Qiu, et al., 2009). Soon afterwards, the first-order rate equation has been called pseudo-first-order with a view to distinguish kinetic equations based on adsorption capacity. Furthermore, this equation has been widely used to describe the adsorption of heavy metals from wastewater (Qiu, et al., 2009). The pseudo-first-order kinetic equation is represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (Eq. 2.4)$$

where q_e and q_t are the adsorption capacity of particular adsorbent at equilibrium and at time t (mg/g) respectively, and k_1 is the rate constant of pseudo-first-order adsorption (1/min) (Adamczuk and Kolodynska, 2015).

2.8.2 Pseudo-second-order Model

Analogous to pseudo-first-order equation, pseudo-second-order also is a regularly used expression to describe the kinetic activity of adsorption of a substance. The only dissimilarity is that the rate limiting step is the chemical adsorption that involves valency forces through sharing or exchange of electrons (Robati, 2013). Pseudo-second-order kinetic equation is expressed as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (Eq. 2.5)$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min) (Adamczuk and Kolodynska, 2015).

The superior advantage of this model is to describe the entire kinetic experimental data accurately (Farooq, et al., 2010). Thereby, pseudo-second-order kinetic model provides the best correlation of the experimental data (Ho and Mckay, 1999). As shown in **Table 2.12**, the best fit kinetic model for copper(II) ion (Cu^{2+}) adsorption using different types of adsorbents from various studies over the years are pseudo-second-order model. As can be seen, chemical reaction does play a vital role in the rate-determining step (Ho and Mckay, 1999).

Table 2.12: Previous Researches of the Adsorption Kinetic Studies for Copper(II) Ion (Cu^{2+}) Removal

Metal ion	Adsorbent	Best fit kinetic model	References
Copper(II) ion	Peanut hull	Pseud-second-order	Oliveira, et al. (2009)
Copper(II) ion	Wheat based bio-sorbent	Pseud-second-order	Farooq, et al. (2010)
Copper(II) ion	Animal manure based bio-char	Pseud-second-order	Kolodynska, et al. (2012)
Copper(II) ion	Dried pinecones based bio-char	Pseud-second-order	Adeyemo, Adebowale and Olu-Owolabi (2014)
Copper(II) ion	Modified sand	Pseud-second-order	Deepak, Varsha and and Yogesh (2014)
Copper(II) ion	Polyaniline graft chitosan beads (PGCB)	Pseud-second-order	Igberase, Osifo and Ofomaja (2014)
Copper(II) ion	Brewers draff based bio-char	Pseud-second-order	Trakal, et al. (2014)
Copper(II) ion	Fly ash coated by chitosan (FAICS)	Pseud-second-order	Adamczuk and Kolodynska (2015)
Copper(II) ion	Nano-porous metal organic framework	Pseud-second-order	Bakhtiari and Azizian (2015)
Copper(II) ion	Fly ash based geopolymer	Pseud-second-order	Al-Harahsheh, et al. (2015)
Copper(II) ion	Ion exchange fibres (IEFs)	Pseud-second-order	Ntimbani, Simate and Ndlovu (2015)
Copper(II) ion	Carbon nanotubes (CNTs)	Pseud-second-order	Tofighy and Mohammadi (2015)

2.8.3 Intra-particle Diffusion Model

Intra-particle diffusion model was earliest presented by Weber and Morris in 1962 (Wu, Tseng and Juang, 2009). According to Robati (2013), intra-particle diffusion model is broadly used to describe the diffusion-controlled adsorption process specifically for the rapid initial adsorption period. In other words, this model is specified in order to determine the rate of adsorption depends on the velocity at which adsorbate diffuses towards adsorbent during initial time of adsorption, which can be presented by:

$$q_t = k_i t^{1/2} + C \qquad (Eq. 2.6)$$

where k_i is the intraparticle diffusion rate constant (mg/g min$^{1/2}$), $t^{1/2}$ is square root of time (min$^{1/2}$) and C is the intercept which indicates the effect of boundary layer (Adamczuk and Kolodynska, 2015).

Nonetheless, there is no kinetic study of adsorption of heavy metal using sludge based bio-char using intra-particle diffusion model has been reported yet. **Table 2.13** has shown the involvement of intra-particle diffusion model in the kinetic studies of heavy metal adsorption using other adsorbents over the years.

Table 2.13: Previous Researches of Kinetic Studies for Heavy Metal Adsorption involving Intra-particle Diffusion Model

Adsorbate	Adsorbent	References
Copper(II) ion	Chitosan	Wu, Tseng and Juang (2009)
Copper(II) ion	Modified chitosan transparent thin membrane	Cheng, et al. (2010)
Copper(II) ion	Diboron trioxide and titanium dioxide	Al-Rashdi, Tizaoui and Hilal (2012)
Lead ion	Multi-walled carbon nanotube	Robati (2013)

Copper(II) ion	Litchi pericarp	Kong, et al. (2014)
Copper(II) ion	Activated bentonite	Koyuncu and Kul (2014)
Copper(II) ion	Fly ash coated by chitosan (FAICS)	Adamczuk and Kolodynska (2015))
Nickel and copper(II) ions	γ-alumina nanoparticles	Fouladgar, Beheshti and Sabzyan (2015)

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Materials

Chemicals and materials used throughout the research studies were tabulated in **Table 3.1**.

Table 3.1: Selected Materials for Research Studies

Materials	Purity (%)	Manufacturer / Supplier	Grade
Copper(II) Sulphate-5-hydrate	98	Bendosen Laboratory	Chemically Pure
Nitric Acid	65	QRëC Chemical	Analytical Reagent
Sodium Hydroxide	99	R & M Chemical	Analytical Reagent
Hydrochloric Acid	37	QRëC Chemical	Analytical Reagent
Palm Oil Sludge	-	Tiang Siang Oil Mill (Air Kuning) Sdn. Bhd.	-
Nitrogen Gas	99	Linde Malaysia Sdn. Bhd.	-

3.2 Workplaces

In this study, experimental works were conducted at Environmental Laboratory and Engineering Workshop. These workplaces are located at Kampar campus of Universiti Tunku Abdul Rahman. Pyrolysis of POS was performed at the Engineering Workshop whereas batch adsorption studies were conducted at Environmental Laboratory.

The overall flow of the project methodology is shown in **Figure 3.1.**

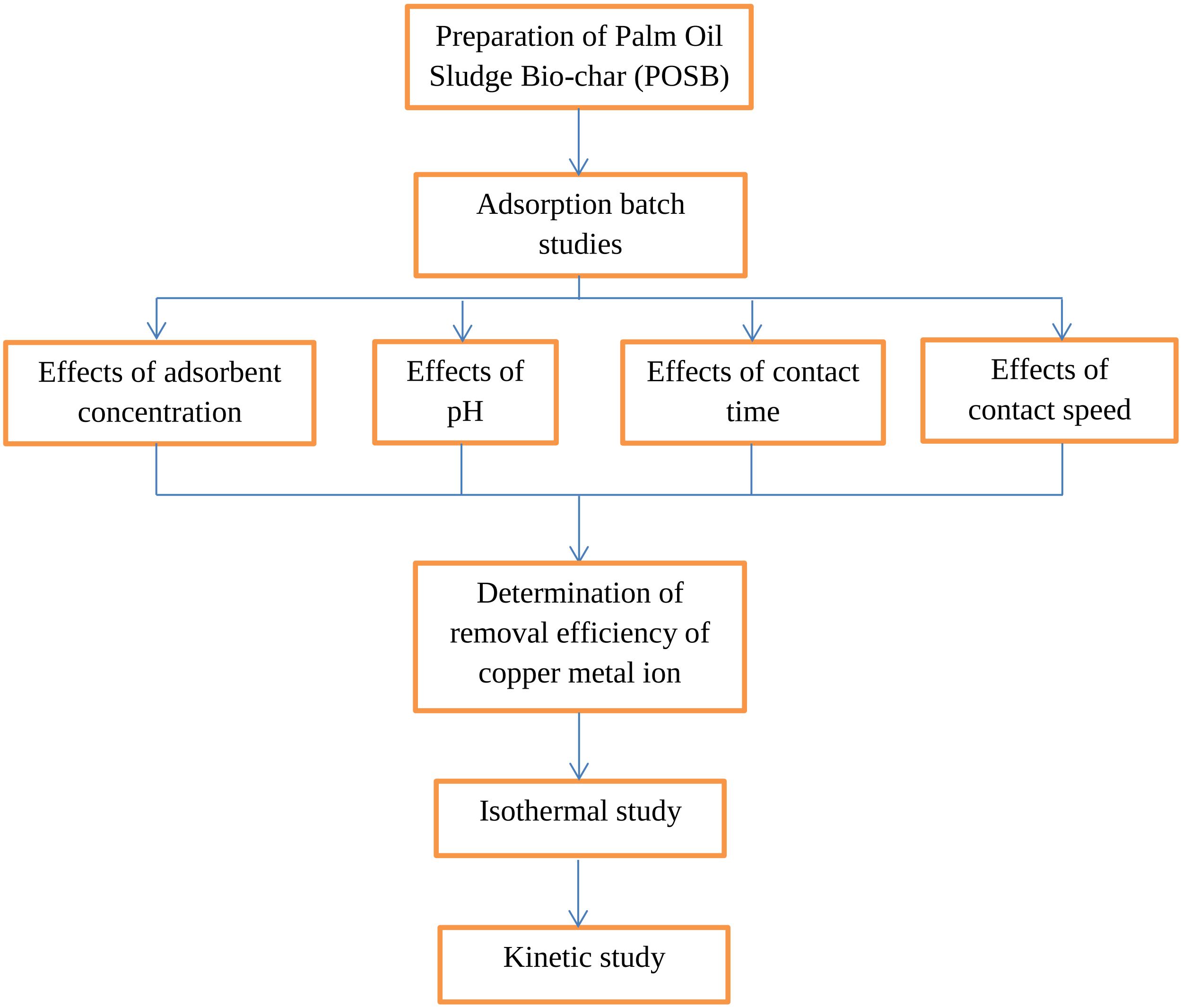


Figure 3.1: Flow Chart of Research Studies

3.3 Palm Oil Sludge (POS) Preparation

POS samples were collected from Tiang Siang Oil Mill (Air Kuning) Sdn. Bhd. located at Air Kuning, Perak, Malaysia. The sludge was the leftover after anaerobic digestion. Firstly, the sludge samples were dried under hot sun for several days. Prior to use in the pyrolysis process, the sludge samples were dried again in an oven at 105 ℃ for 24 hours in order to completely remove the moisture content of the sample. Drying was repeated till a constant weight is achieved. Finally, the dried sludge samples were kept in a plastic container for future usage and to avoid air contact.

3.4 Bio-char Preparation

The production procedure of Palm Oil Mill Sludge Bio-char (POSB) for this study was taken based on an optimized production data from the previous work done by Low (2015). The bio-char was produced in a vertical carbonizer under the following optimized conditions; temperature: 400 ℃, heating rate: 15 ℃/min and holding time: 90 mins. Throughout the POSB production, nitrogen gas was supplied continuously to maintain the anoxic condition inside the vertical carbonizer. The gas flow rate was set at 300 mL/min. The pyrolyzed samples were kept in a desiccator immediately after taken out from the carbonizer. Prior to usage it was sieved to 600 μm and kept in air-tied container for moisture control.

Figure 3.2: Carbonization Unit Used to Prepare Palm Oil Sludge Bio-Char Samples

3.5 Preparation of Synthetic Copper(II) Ion Containing Wastewater

The initial concentration of synthetic wastewater containing copper(II) ion was fixed as 10,000 ppb. 0.01 g of copper(II) sulphate-5-hydrate salt was weighted and transferred into the 1 L volumetric flask. Subsequently, deionized water was added into the volumetric flask until it reached the calibration mark. Then, the volumetric flask was shaken thoroughly to ensure complete dissolution. Deionized water was used to prepare and dilute all the solutions and reagents in the study.

3.6 Preparation of Calibration Curve

A calibration curve was prepared using three different concentrations of copper(II) ion solutions. Firstly, 0.01 g of copper(II) sulphate-5-hydrate salt was weighted and added into a 1 L of deionized water to produce a 10,000 ppb of synthetic copper(II) ion solution. Next, the 10,000 ppb of synthetic copper(II) ion solution was further diluted to required concentrations which were 10 ppb, 500 ppb and 1,000 ppb using deionized water together with 1% of nitric acid (HNO_3) for acid digestion purpose.

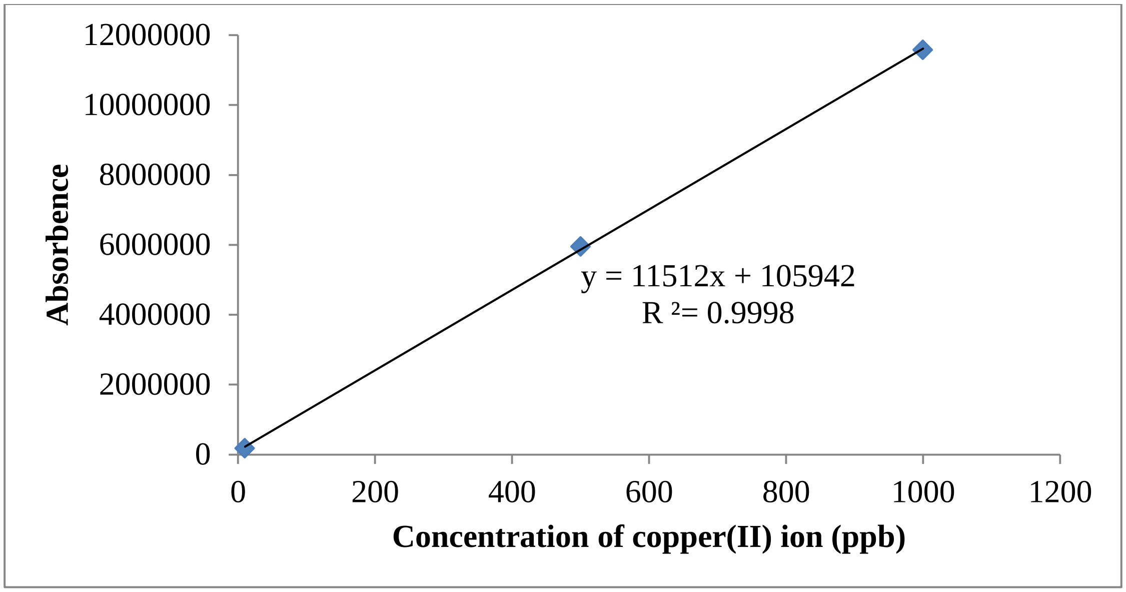


Figure 3.3: Calibration Curve

3.7 Process Parameter Study via Batch Studies

The adsorption of copper(II) ion onto the bio-char was studied using the batch experimental method. The effects of adsorbent dosage, pH, contact time and contact speed on copper(II) ion adsorption were studied based on **Table 3.1**. For each study 100 mL of 10,000 ppb copper(II) ion solution was poured in each Erlenmeyer flask. POSB samples were weighted using analytical balance and transferred into each Erlenmeyer flask accordingly. Next, all Erlenmeyer flasks were placed in an orbital shaker to agitate the solution. All the samples from each batch experiment were duplicated. After shaking, the samples were filtrated using 0.45 μm syringe membrane filter and diluted 10 times using deionised water. Later, the final concentration of copper(II) metal ion in each samples were determined by the ICP-MS. The adsorption capacity and percentage of removal for each sample were calculated using the following equations:

$$q_t\ (mg/g) = \frac{(C_o - C_t)V}{m} \qquad (Eq.3.1)$$

$$R\ (\%) = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (Eq.3.2)$$

where q_t is the adsorption capacity at time t (mg/g), C_o and C_t are the initial concentration and equilibrium concentration of metal ions at time t in solution respectively (mg/L), V is the volume of solution (L), m is the weight of adsorbent sample (g), and R is the removal percentage (%).

In order to investigate the effect of adsorbent dosage, the amount of dosage was varied according to **Table 3.1** and other parameters were fixed as following; 250 rpm of contact speed, 120 minutes of contact time and original pH. These parameters were chosen based on work done by Low (2015).

Next for the effect of contact time on copper(II) ion adsorption onto POSB, different contact times as shown in **Table 3.1** was used with fixed contact speed of 250 rpm, original pH and moderate performed dosage of POSB (0.02 g).

The effect of contact speed on copper(II) ion adsorption onto bio-char was analysed by a range of contact speed as shown in **Table 3.1**. Moderate performed dosage (0.02 g) was selected in this study. Initial pH value and contact time were kept at original pH and 240 minutes respectively.

For the pH studies, the pH value of the copper(II) ion solutions was adjusted to a range of pH 3 – 10 using 0.01 M NaOH and 0.01 M HCl and measured by pH meter. Similarly, 100 mL of 10,000 ppb concentration of copper(II) ion solution and moderate performed dosage chosen from the dosage studies were added into each flask respectively and shaken by using orbital shaker. The fixed parameters were the optimum contact time and contact speed obtained from previous studies.

Table 3.2: Varied Parameter and Fixed Parameters for each Adsorption Study

Adsorption studies	Parameter (Varied)	Parameters (Fixed)
Adsorbent dosage study	Dosage value (0.010 g – 0.080 g)	Agitation speed Contact time pH value
Contact time study	Contact time (30 min – 270 min)	Dosage value Agitation speed pH value
Agitation speed study	Agitation speed (50 rpm – 250 rpm)	Dosage value Contact time pH value
pH study	pH value (pH 3 – 10)	Dosage value Agitation speed Contact time

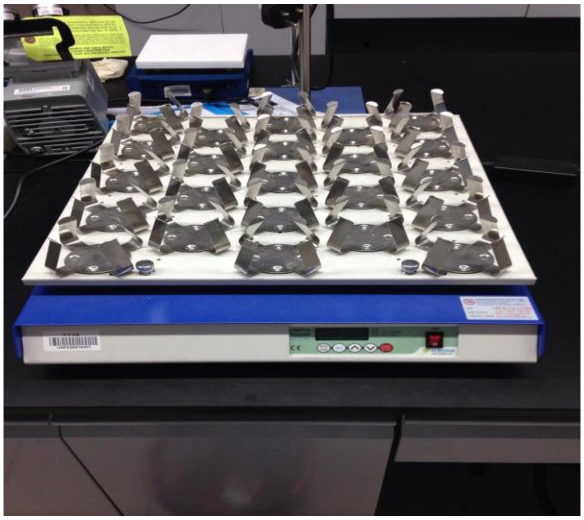


Figure 3.4: Orbital Shaker (Model: N-BIOTEK, 101M)

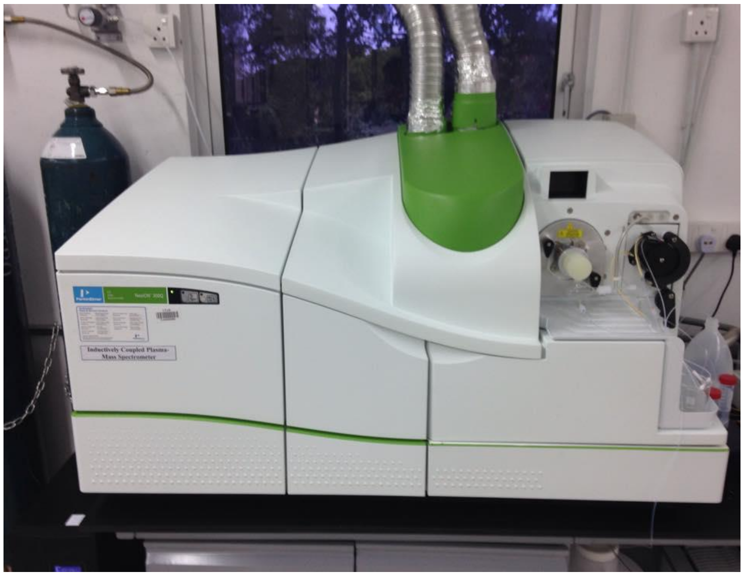


Figure 3.5: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Model: Perkin Elmer, NexION 300Q)

3.8 Equilibrium Isotherm

In order to study the interaction between the adsorbents and adsorbates, an adsorbent dosage study was conducted using optimum performed adsorption parameters obtained from **Section 3.7**. Adsorption data from the adsorbent dosage study using optimal parameters were analysed using the Langmuir and Freundlich isotherm models. Langmuir isotherm is represented by Eq. 3.3 whereas Freundlich isotherm is represented by Eq. 3.4.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (Eq. 3.3)$$

where C_e is the equilibrium concentration of the adsorbate (mg/dm^3), q_e is the adsorption capacity at equilibrium (mg/g), q_m (mg/g) and K_L (dm^3/mg) are the Langmuir constants related to maximum monolayer adsorption capacity and rate of adsorption respectively (Kolodynska, et al. 2012).

$$q_e = K_F C_e^{1/n} \qquad (Eq. 3.4)$$

where K_F is the Freundlich adsorption capacity (mg/g) and $1/n$ is the Freundlich constant related to the surface heterogeneity (Kolodynska, et al. 2012).

For Langmuir isotherm, a graph of (q_e / c_e) against q_e was plotted. Next, Langmuir constants were determined from the slope and intercept of the plotted graph. Apart from that, separation factor, R_L was calculated based on Eq. 3.5 to indicates the adsorption nature to be either unfavourable, linear, favourable or irreversible (Dada, et al., 2012). Similar procedures were repeated for Freundlich isotherm. The best isotherm model was determined based on the highest R^2 value.

$$R_L = \frac{1}{1 + (K_L + C_o)} \qquad (Eq. 3.5)$$

3.9 Kinetic Modelling

Kinetic models were used to determine the rate-controlling step of the adsorption mechanism. The kinetic models that were used in this study were pseudo-first-order, pseudo-second-order and intra-particle diffusion models. Adsorption data of contact time study using optimal parameters from **Section 3.7** were fitted into these models using the following three equations as expressed:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (Eq. 3.6)$$

where q_e and q_t are the adsorption capacity of particular adsorbent at equilibrium and at time t (mg/g) respectively, and k_1 is the rate constant of pseudo-first-order adsorption (1/min) (Adamczuk and Kolodynska, 2015).

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (Eq. 3.7)$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min) (Adamczuk and Kolodynska, 2015).

$$q_t = k_i t^{1/2} + C \qquad (Eq. 3.8)$$

where k_i is the intraparticle diffusion rate constant (mg/g min$^{1/2}$), $t^{1/2}$ is square root of time (min$^{1/2}$) and C a the intercept which indicates the effect of boundary layer (Adamczuk and Kolodynska, 2015).

For pseudo-first-order model, a graph of $log(q_e - q_t)$ against t was plotted. Rate constant, k_1 was determined from the slope and intercept of the plotted graph. Corresponding graphs were plotted for other models. Similarly, rate constants were determined for other equations. The best kinetic model was determined based on highest R^2 value from all the plotted graphs.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Batch Adsorption Studies on Process Parameters

Batch adsorption studies were conducted in order to optimize the process parameters of copper(II) ion adsorption using Palm Oil Sludge Bio-char (POSB). The parameters were dosage of POSB, contact time, contact speed and pH. The initial concentration of copper(II) ion in the aqueous solution was adjusted to 10,000 ppb for all the batch studies. Furthermore, all batch adsorption studies were carried out at constant room temperature.

4.1.1 Effect of Adsorbent Dosage on Copper(II) Ion Adsorption

Influence of adsorbent dosage on copper(II) ion adsorption was studied using a range of 0.01 g to 0.08 g of POSB. For this study, the contact time was fixed at 120 minutes whereas the contact speed was adjusted to 250 rpm as well as the initial pH of copper(II) ion solution was maintained. The original pH value of copper(II) ion solution was determined to be 8.2. **Figure 4.1** shows the removal percentage of copper(II) ion using POSB. It was noticed that the removal efficiency increased sharply from 24.85 % to 96.15 % from 0.01 g to 0.04 g. It was apparent that the applying higher amount of bio-char can provide more sorption sites to favour the adsorption of copper(II) ion. In other words, the percentage removal of copper(II) ion was increased by increasing adsorbent dosage. Nonetheless, the copper(II) ion removal has reached optimal at 0.04 g of bio-char and does not increase appreciably after the dosage of 0.05 g and above. Beyond the optimal removal percentage, the concentration of the copper(II) ion becomes the limiting factor. Similar result was also reported by Chen, et al. (2015) and Dave, Subrahmanyam and Sharma (2009).

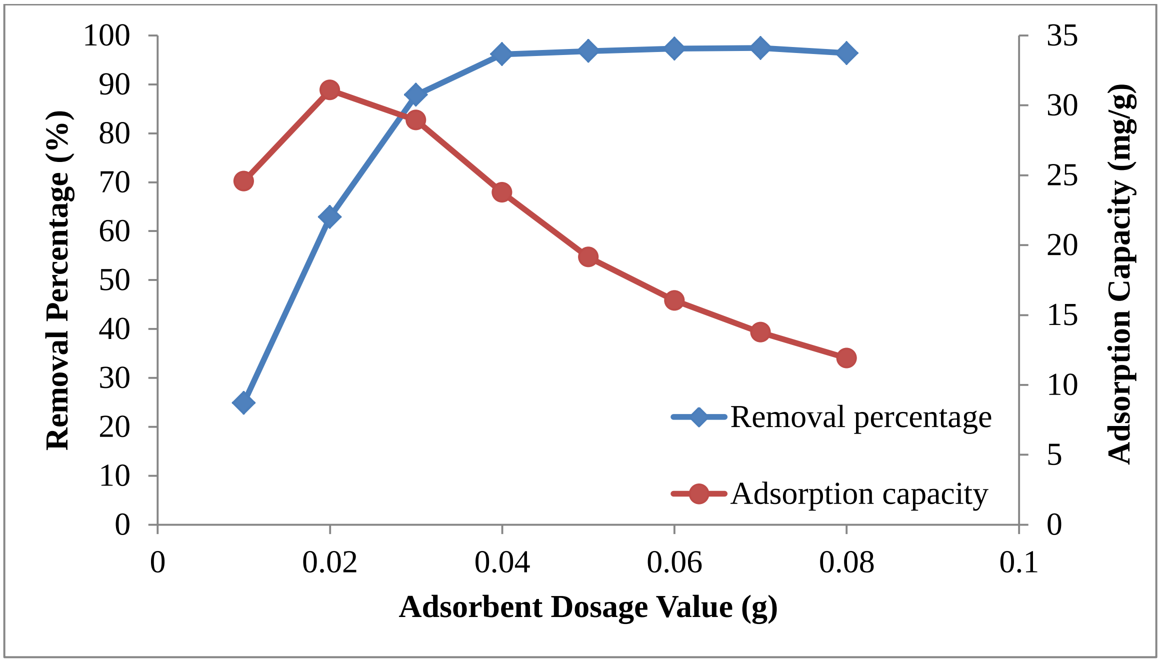


Figure 4.1: Effect of Adsorbent Dosage on Copper(II) Ion Adsorption and Adsorption Capacity of POSB

On the other hand, the adsorption capacity does not indicate similar result as percentage of copper(II) ion removal. As seen in **Figure 4.1**, the highest observed copper(II) ion adsorption capacity was 31.09 mg/g. Chen, et al. (2011) reported that copper(II) ion adsorption capacity will be decreased with the increasing of adsorbent dosage. It was evident that the adsorption capacity falls gradually between 0.02 g and 0.08 g of dosage as shown in **Figure 4.1**. This was because copper(II) ion adsorption does not increase sufficiently when the adsorbent dosage was raised beyond a certain value. Furthermore, overlapping and aggregation of adsorbent sites might occur due to the congested bio-char particles (Tumin, et al., 2008). Consequently, binding sites were shielded from copper(II) ions by the overlapped adsorbent particles (Dave, Subrahmanyam and Sharma, 2009). Therefore, uptake of copper(II) ion was getting difficult and thereby decreasing the removal efficiency as the dosage increased. This was proven with similar observation as reported by Chen, et al. (2015) and Tumin, et al. (2008). They reported that the adsorption capacity was decreased with the increase of the adsorbent dosage. As a result, 0.02 g amount of the bio-char sample was established as optimal dosage. Despite this amount of bio-char dosage performed a moderate result of copper(II) ion adsorption, but it had provided the highest value of adsorption capacity which was 31.09 mg/g. It is important to identify the optimal dosage of adsorbent to avoid over expenditure on dosage.

4.1.2 Effect of Contact Time on Copper(II) Ion Adsorption

Contact time plays a crucial role on adsorption process. The contact time study was conducted by varying the contact time from 0 to 270 minutes at 30 minutes interval. Besides, this study was conducted at contact speed of 250 rpm, dosage of 0.02 g and at original pH. The relationship between contact time and removal percentage of copper(II) ion was illustrated in **Figure 4.2**. During the first 60 minutes, the rate of copper(II) ion uptake by POSB was outstandingly high and achieved 53.42 % of copper(II) ion removal. After 60 minutes, the rate of copper(II) ion adsorption becomes slower while the copper(II) ion removal percentage increased steadily up to 75.73 % at 240 minutes. Nevertheless, there was a slight decrease from 75.73 % to 65.61 % after 240 minutes. Thus, 240 minutes was declared as the equilibrium time with the maximum percentage of copper(II) ion removal of 75.73%.

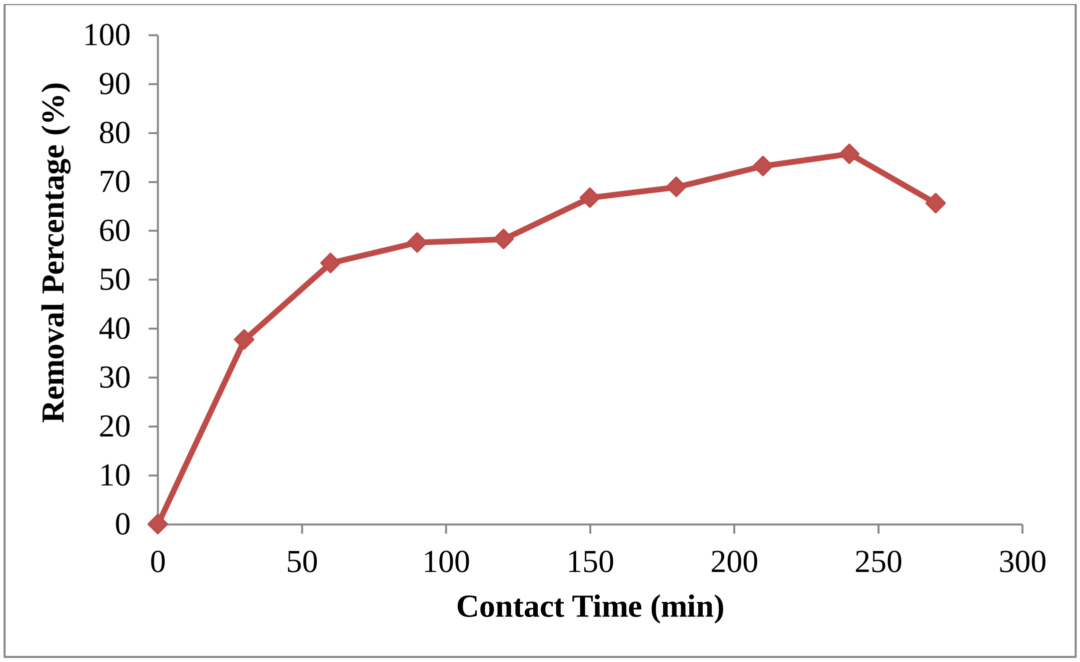


Figure 4.2: Effect of Contact Time on Copper(II) Ion Adsorption

These results may be due to the availability of binding sites was redundant during the initial phase and therefore great amount of copper(II) ions were adsorbed rapidly onto the bio-chars (Hossain, et al., 2012b). After 60 minutes, the uptake of copper(II) ion by bio-char was slower and lesser owing to the reduced numbers of sorption site and copper(II) ion. As a result, the remaining surface sites were arduous to be filled by limited copper(II) ions. Later, there was a decrement after 240 minutes and this situation happened might be due to fact that the sorption sites were saturated. In other words, the exchange sites on surface of bio-char were fully filled with adsorbed copper(II) ion. Hence, repulsion in between adsorbed copper(II) ions and free copper(II) ions would occur due to the identical charges (Hossain, et al., 2012b).

It was observed that the longer the contact time, the higher the adsorption efficiency as well as the adsorption capacity of adsorbent. Moreover, the number of contact between the adsorbent and adsorbate increased when the contact time increased. The time required for adsorption process to attain the equilibrium state was 240 minutes. The adsorption capacity of POSB at 240 minutes was 36.60 mg/g and it was the highest value among other contact time. In recent years, researchers reported similar result regarding the effect of contact time on adsorption of copper(II) and lead ions using different type of adsorbents (Farghali, et al., 2013; Shobana, Sahayaraj and Soruba, 2014; Wan, Wang and Chen, 2013).

4.1.3 Effect of Contact Speed on Copper(II) Ion Adsorption

The effect of contact speed has been studied by varying the agitation speed of orbital shaker from 50 to 250 rpm. Furthermore, contact time was fixed at optimal 240 minutes as obtained from previous study. The adsorbent dosage was fixed at 0.02 g and the initial pH of the solution was maintained as previous studies. The removal percentage of copper(II) ion by POSB was illustrated in **Figure 4.3**. Initially, the uptake of copper(II) ion by POSB increased as the agitation speed increased from 50 to 150 rpm. Theoretically, the increment of adsorption of copper(II) ion was mainly due to the effective intercourse between adsorbates and adsorbents (Rohaizar, Hadi and Wong, 2013). In short, higher rotational speed improved the diffusion of metal ions towards the surface of the POSB (Larous, Meniai and Lehocine, 2005). Later, the copper(II) ion adsorption decreased from 73.12 % at 150 rpm to 65.80 % at 250 rpm. In overall, the adsorption efficiency did not change significantly even though the contact speed increased from 50 to 250 rpm. Moreover, it was predicted that the adsorption efficiency of copper(II) ion will be lower for 300 rpm and above. Hence, the effects of 300 rpm of contact speed and above were not investigate in this study due to incapability of the equipment. Moreover, it was not feasible for commercialization.

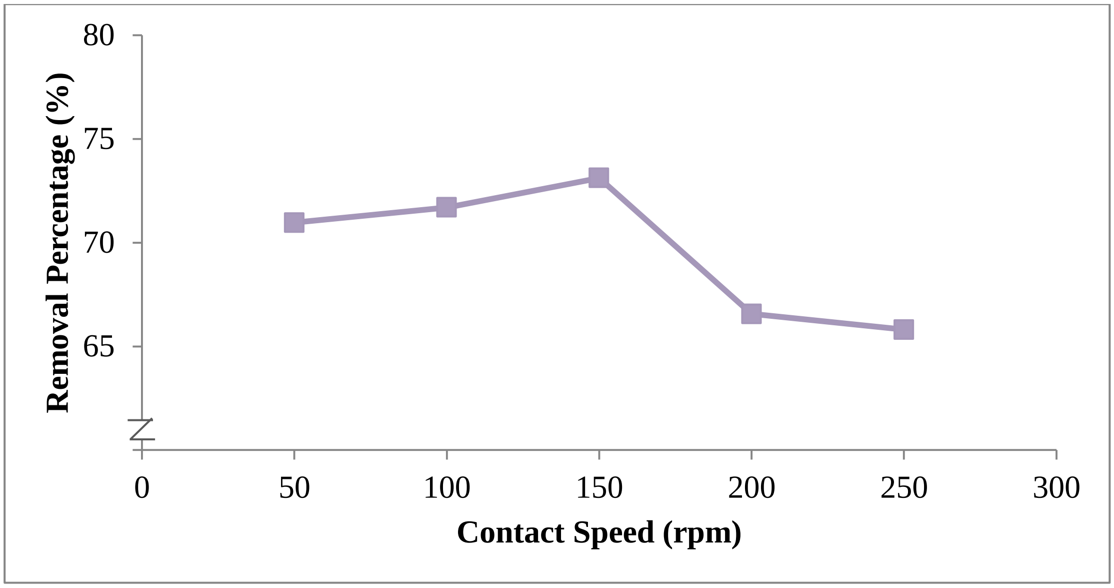


Figure 4.3: Effect of Contact Speed on Copper(II) Ion Adsorption

During the agitation period, it was observed that a portion of POSB samples sticked on the wall of Erlenmeyer flask. This issue happened for agitation speeds at 200 and 250 rpm. Hence, adsorbent which was sticked to the wall did not contribute to the adsorption process whenever the solution was rotating vigorously. As a consequence, the exchange sites were limited and thereby, reducing the chances for copper(II) ions to be adsorbed. It was evident that the copper(II) ion adsorption decreased at 200 rpm onward as indicated in **Figure 4.3**.

Moreover, desorption of copper(II) ions could occur when the agitation speed goes too high. This was probably due to the fact that higher shaking rate can breakdown the adsorbed copper(II) ions from the POSB (Bergmann and Machado, 2015). Results obtained by Choumane and Benguella (2013) showed that the cadmium ion adsorption by modified clays started to decrease at 400 rpm onward. Omri, Wali and Benzina (2012) provided another reason that suspension was not homogeneous at high agitation rate and eventually led to decrement of adsorption efficiency. Furthermore, adsorption process could not achieve the optimal condition when the agitation speed was too low or too high and therefore, identification of optimal agitation speed was crucial. According to some researches, the most favourable agitation speed for adsorption process falls between 100 to 200 rpm (Lichfouse, Schwarzbauer and Robert, 2011; Bergmann and Machado, 2015). The optimal agitation speed for copper(II) ion adsorption using POSB was reported as 150 rpm which was the range of the above mentioned range. The adsorption capacity of POSB at 150 rpm was 36.28 mg/g.

4.1.4 Effect of pH on Copper(II) Ion Adsorption

pH value of aqueous solution is a significant controlling factor for the adsorption of copper(II) ion. This is due to the fact that pH of the aqueous solution is able to control the magnitude of the electrostatic charges that are imparted by metal ions (Yang, et al., 2013). The adsorption experiment of copper(II) ions as a function of pH between 3 and 10 was conducted. In this study, the contact time was fixed at 120 minutes and the contact speed was adjusted to 250 rpm. Furthermore, the POSB dosage was fixed at 0.02 g.

As shown in **Figure 4.4**, the copper(II) ion removal percentage increased steadily from 59.12 % at pH 4 to 68.42 % at pH 5. Next, there was a sharp increase in the percentage of copper(II) ion removal between pH 5 and pH 6. The copper(II) ion adsorption then remained stable from pH 6 to pH 9. Lastly, the copper(II) ion removal percentage was increased slightly and it reached the highest removal percentage as 95.98 % at pH 10.

At lower pH value, the result of copper(II) ion adsorption was undesirable owing to the protonated surface binding sites of POSB. Wang, et al. (2009) established that the surface binding sites of adsorbents held more positive charges which led to large-scale repulsion of copper(II) ions. Furthermore, copper(II) ion needed to compete with existing hydrogen ion for the exchange sites. Adil, et al. (2014) declared that hydrogen ions are more prefer to be adsorbed on adsorbents than metal ions. This was because the concentration and mobility of hydrogen ions was higher than adsorbates at low pH

(Shobana, Sahayaraj and Soruba, 2014). This was proven in **Figure 4.4** that copper(II) ion adsorption at lower pH was much lower than higher pH.

Whereas at higher pH, the surface sites on POSB were becoming more negatively charged. This was because the protons were being released from the surface sites (Abudaia, et al., 2013). Therefore, the copper(II) ion removal was more favourable. This was proven in **Figure 4.4** that there was a sharp increment of copper(II) ion adsorption from 68.42 % at pH 5 to 94.86 % at pH 6.

However, precipitation of copper(II) hydroxide could be also triggered as the solubility of copper(II) ions decreased at pH 8 and above (Albrecht, Addai-Mendash and Fornasiero, 2011). Hence, the reduction of copper(II) ions may not be due to the adsorption alone. In **Figure 4.4**, it was apparent that the high rate of copper(II) ion removal at pH 9 and 10 due to adsorption and precipitation took place at the meantime. Thus, the optimal pH value for copper(II) ion adsorption was denoted as pH 6 and this investigation was unanimous with other similar researches (Kyzas, Kostoglou and Lazaridis, 2009; Abdel Salam, Reiad and Elshafei, 2011; Hossain, et al., 2012b; Al-Harahsheh, et al., 2015).

It can be concluded that the adsorption of metal cations increased with the increase of pH. The removal percentage increased from pH 3 and remained steady at pH 6 onwards in the study. This was in agreement with the results obtained by Abdel Salam, Reiad and Elshafei (2011) for adsorption of copper(II) ion from aqueous solution onto low-cost adsorbents.

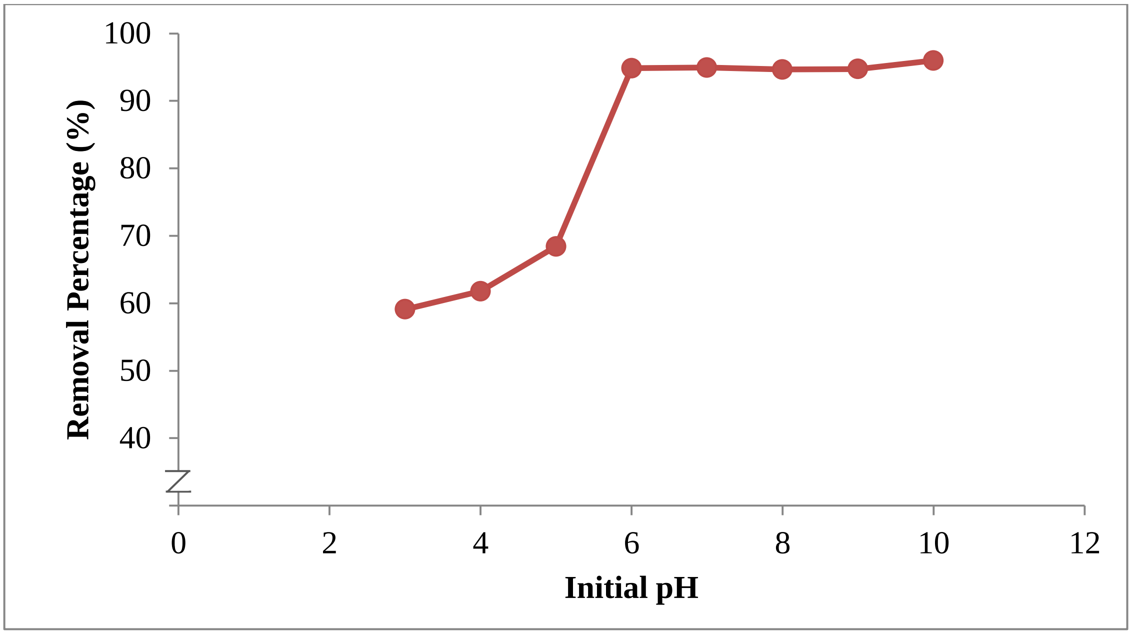


Figure 4.4: Effect of pH on Copper(II) Ion Adsorption

4.2 Equilibrium Study

Adsorption isotherm is commonly used for optimization of adsorption process and adsorbents capacities (Bakhtiari and Azizian, 2015). In this study, two well-known adsorption isotherm models were employed in order to analyse the experimental data and investigate the interaction between the POSB and copper(II) ions. These selected models were Langmuir isotherm and Freundlich isotherm.

An adsorbent dosage study was repeated for the range of 0.01 g to 0.06 g at optimized conditions in which the process parameters were fixed at 240 minutes of contact time, 150 rpm of contact speed and at original pH. The adsorption data was then analysed by the Langmuir and Freundlich models to check its equilibrium. The constant parameters and correlation coefficients were determined for both models and tabulated in **Table 4.1**. **Figure 4.5** and **4.6** show Langmuir and Freundlich plots which representing the copper(II) ion adsorption on the POSB.

Table 4.1: Parameters of the Langmuir and Freundlich Isotherms for the Adsorption of Copper(II) Ions onto the POSB

Adsorbate	**Langmuir isotherm parameters**				**Freundlich isotherm parameters**		
	K_L (L/mg)	q_m (mg/g)	R_L	R^2	K_F (L/mg)	$1/n$	R^2
Cu^{2+}	0.9596	52.36	0.0944	0.9796	24.07	0.3898	0.9186

*q_m = maximum monolayer adsorption capacity (mg/g)
*R_L = separation factor (unitless)

From **Table 4.1**, the Langmuir constant, K_L was found to be 0.9596 L/mg and the maximum monolayer adsorption capacity of POSB, q_m was 52.36 mg/g. Moreover, the calculated separation factor, R_L was 0.0944. Due to the separation factor was greater than 0 but less than 1, it indicated that Langmuir isotherm was favourable for the copper(II) ion adsorption onto the POSB (Dada, et al., 2012).

Alternatively, the Freundlich constant, K_F which indicates the selective uptake of copper(II) ion and affinity of POSB was 24.07 L/mg and *1/n* value was determined as 0.3898 as presented in **Table 4.1**. Ghazi, et al. (2013) stated that higher K_F value indicated better adsorption capacity and Rohaizar, Hadi and Wong (2013) reported that *1/n* value is related to the adsorption energies distribution of binding sites. If the *1/n* value is greater than 1, the K_F value will increase with the increase of metal concentration in solution (Rohaizar, Hadi, and Wong, 2013). On the contrary, K_F will decrease with metal concentration in solution as low energy sites are utilized when 1/n value is smaller than 1. Furthermore, the smaller the value of *1/n*, the stronger the adsorption bond and vice versa. The *1/n* value obtained from the present study was lesser than 1. Therefore, the adsorption bond was quite strong and K_F value decreased with copper(II) ion concentration in aqueous solution.

According to Rohaizar, Hadi, and Wong (2013), the value of correlation coefficient, R^2 is an indication of aptness of adsorption data on the isotherm models. In other words, the closer the R^2 value to 1, the better the model fitted to the adsorption data (Nagy, et al., 2014). Results from **Table 4.1** showed that the adsorption data was preferably represented by Langmuir isotherm based on R^2 value. This was because the R^2 value of Langmuir model was higher than the R^2 value from Freundlich model. This proved that uptake of copper(II) ions on a homogeneous surface of POSB and occurred as monolayer adsorption (Al-Harahsheh, et al., 2015). In other words, there was only a single layer of molecules allowed to be formed on the surface of POSB, provided all the adsorption sites were equally probable (Levine, 2009). Moreover, the energies of adsorption on the surface of POSB were uniform (Adeyemo, Adebowale and Olu-Owolabi, 2014). Apart from that, several researchers also reported that copper(II) ion adsorption onto other adsorbents was well described by Langmuir isotherm model (Farooq, et al., 2010; Kolodynska, et al., 2012; Trakal, et al., 2014; Al-Harahsheh, et al., 2015). From this equilibrium study, maximum adsorption capacity of Palm Oil Sludge Bio-char (POSB) was found to be 45.31 mg/g.

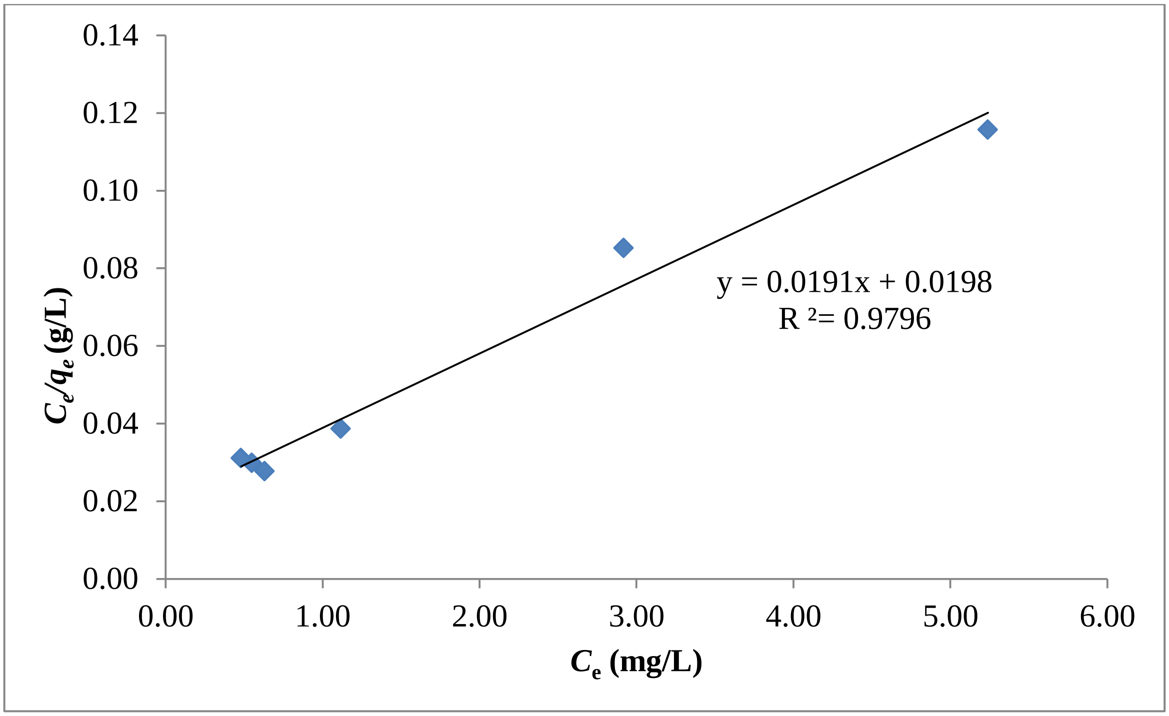


Figure 4.5: Linear Plot of Langmuir Equation

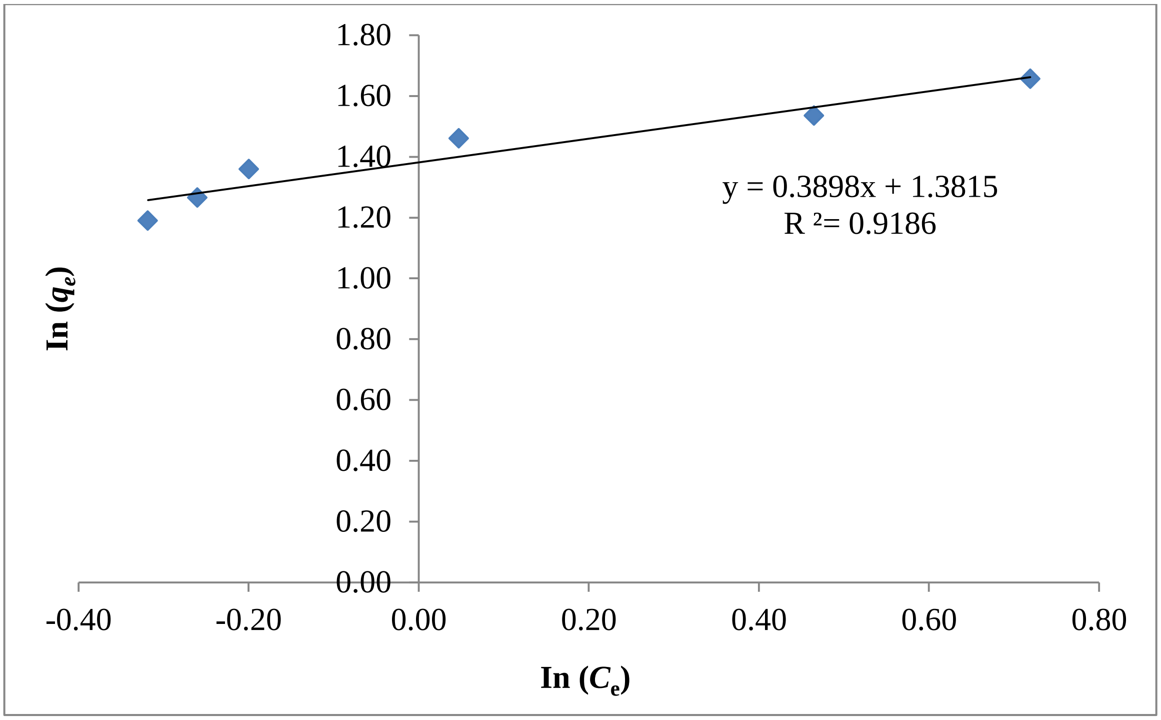


Figure 4.6: Linear Plot of Freundlich Equation

4.3 Kinetic Study

Adsorption kinetic generally expresses the potential rate controlling steps (Ho and Mckay, 1999). Thus, in order to examine how fast the copper(II) ion adsorption occurs on POSB and the adsorption mechanism, a kinetic study has been performed. Three most popular kinetic models were utilized in this study, which were Pseudo-first-order model, Pseudo-second-order model and Intra-particle diffusion model.

For the kinetic study, a contact time study has been conducted for 0 until 240 minutes. This study was carried out at optimized conditions in which the process parameters were fixed at 150 rpm of contact speed, 0.04 g of adsorbent dosage and at original pH. The experimental data from contact time study was then fitted into these three models. All the kinetic parameters and correlation coefficients were calculated and tabulated in **Table 4.2**. On top of that, the results of linear regressions for all three models were illustrated in **Figures 4.7**, **4.8** and **4.9** respectively.

Table 4.2 Kinetic Parameters of Copper(II) Ion Adsorption on POSB for Three Proposed Models

Adsorbate	$q_{e.exp}$ **(mg/g)**	**Pseudo-first-order parameters**			**Pseudo-second-order parameters**			**Intra-particle diffusion parameters**	
		K_1 (min^{-1})	$q_{e.cal}$ (mg/g)	R^2	K_2 (g/mg.min)	$q_{e.cal}$ (mg/g)	R^2	K_i (mg/g. min^{-1})	R^2
Cu^{2+}	45.00	0.01336	21.27	0.8080	0.0009183	48.30	0.9973	1.3888	0.9111

It was noted in **Table 4.2** that the Pseudo-second-order kinetic model showed higher correlation coefficient, R^2 than the Pseudo-first-order model which expressed the adsorption data was well-fitted by the former. Furthermore, R^2 value obtained from Intra-particle diffusion model was smaller than the Pseudo-second-order model. On top of that, the calculated adsorption capacity at equilibrium, $q_{e.cal}$ for Pseudo-second-order model was much nearer to the actual adsorption equilibrium, $q_{e.exp}$ compared to the Pseudo-first-order model. Based on the obtained results, it was proved that the adsorption process followed second order of kinetics. In this case, adsorption mechanisms involved in copper(II) ion adsorption on POSB can be concluded as inner-sphere complexation and precipitation based on Kolodynska, et al. (2012) finding. These results may due to the fact that Pseudo-first-order model was not suitable to be applied for a prolonged contact time (240 minutes). In the light of Ho and Mckay (1999), Pseudo-first-order equation fits well only for the contact time of first 30 minutes of the adsorption process. Furthermore, Pseudo-second-order equation was employed with a view to cope with the longer period of contact time. In addition, surface adsorption that was well described by Pseudo-second-order model usually involved chemical reactions which actually take longer time to complete than physical adsorption (Robati, 2013). Therefore, it can be concluded that the chemical adsorption between the two phases was the rate determining step in the present study. Nevertheless, the uptake rate may be controlled by the rate of intra-particle diffusion once the surface sites of adsorbents were being fully occupied (Cheng, et al., 2010; Mobasherpour, Salahi and Ebrahimi, 2014).

The results from this study were in agreement with result obtained in adsorption of copper(II) ions using animal manure based bio-char (Kolodynska, et al., 2012). Besides, adsorption kinetic results of copper(II) ion onto the palm oil fruit shell obtained by Hossain, et al. (2012b) were indicated that the Pseudo-second-order model acquired the highest R^2 value compared with other models. In overall, this is strongly proposed that the adsorption of copper(II) ion onto the POSB can be suitably manifested by Pseudo-second-order kinetic model.

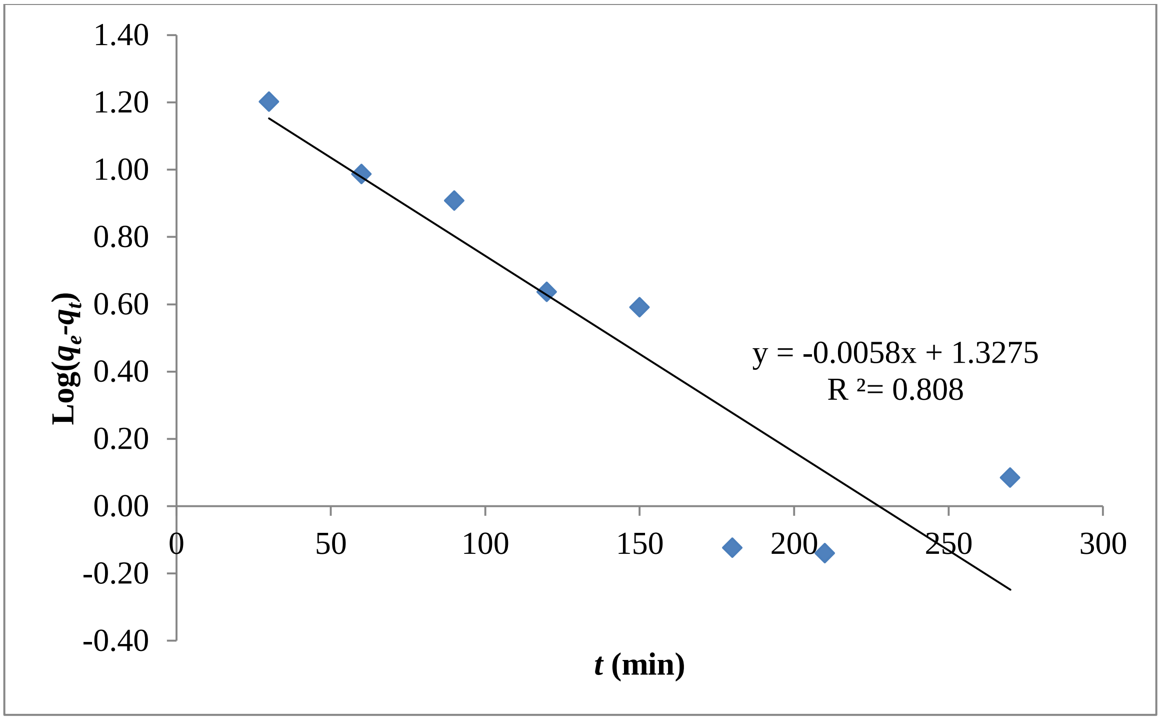


Figure 4.7: Linear Plot of Pseudo-first-order Model

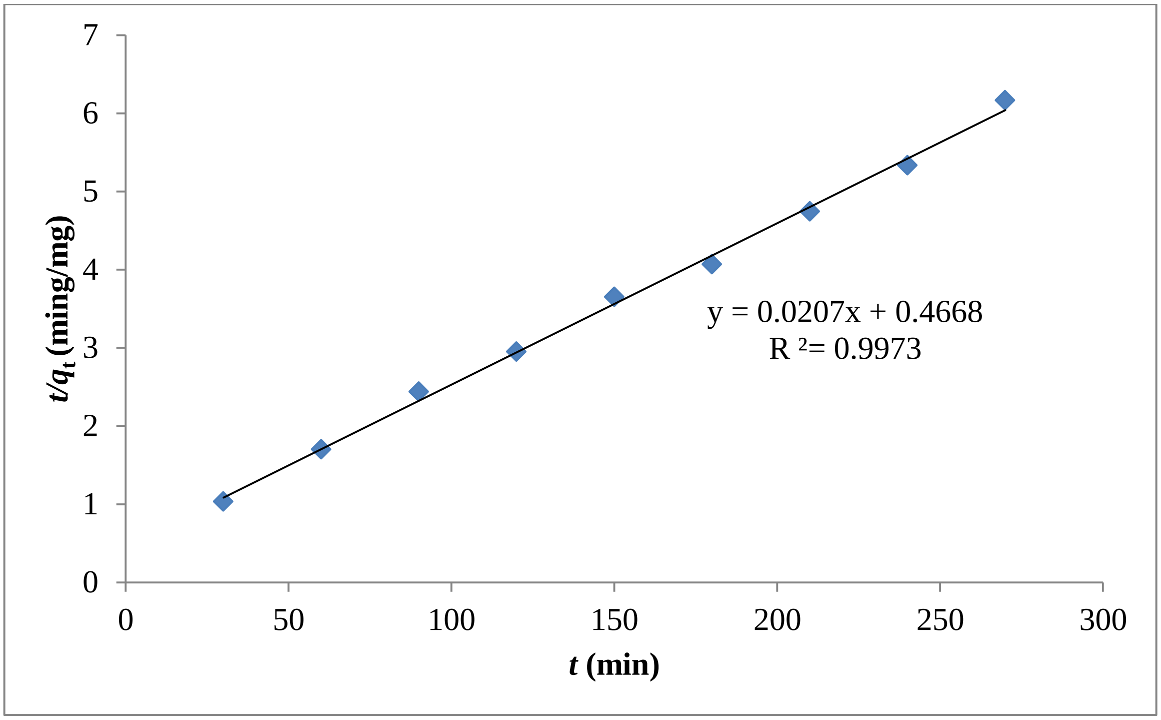


Figure 4.8: Linear Plot of Pseudo-second-order Model

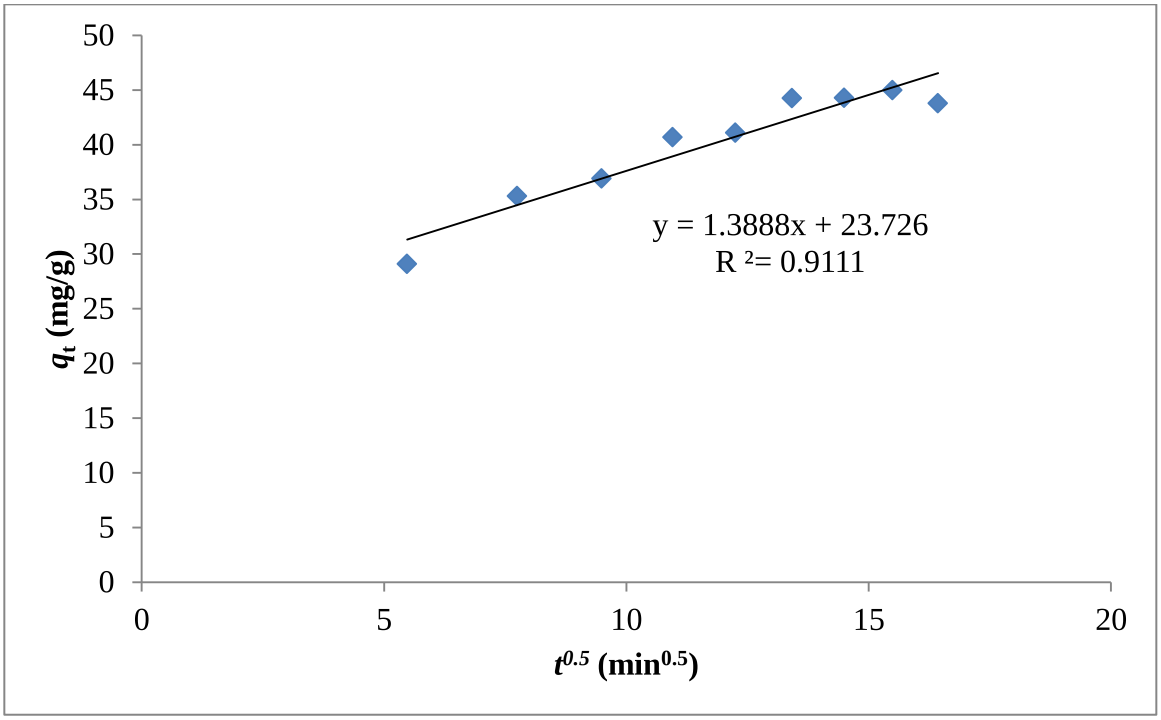


Figure 4.9: Linear Plot of Intra-particle Diffusion Model

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study clearly indicated that bio-char prepared from dried Palm Oil Sludge (POS) can be employed as an effective adsorbent for copper(II) ion removal from aqueous solution. Adsorption process parameters such as adsorbent dosage, contact time, contact speed and pH were optimized using batch method at constant room temperature. Removal of copper(II) ion using the adsorption process is affected by these tested parameters. Overall, the percentage of copper(II) ion removal increased with the increased in dosage, contact time, contact speed and pH till the adsorption reaches the equilibrium state. Apart from that, the optimum conditions of copper(II) ion adsorption obtained from these studies were: 0.04 g of adsorbent dosage, 240 minutes of contact time, 150 rpm of contact speed and pH of 6.

The equilibrium study was established using both Langmuir and Freundlich isotherm models. As a result, Langmuir model denoted the best description of copper(II) ion adsorption mechanism. From the study, the maximum adsorption capacity of Palm Oil Sludge Bio-char (POSB) was found to be 45.31 mg/g. Thus, it is assumed that a single layer of molecules was allowed to be formed on the surfaces of bio-chars. On the other hand, kinetic study indicated that the adsorption kinetics of copper(II) ion on POSB obeyed the Pseudo-second-order kinetic model. In other words, chemisorption was the rate-determining step in the copper(II) ion adsorption process.

In conclusion, results from these adsorption studies indicated the potential usage of biochar derived from POS on large-scale for heavy metal removal from water. By doing this, the goals of waste recycle, reduce and reuse as well as development of sustainable environment can be achieved.

5.2 Recommendations for Future Research

In order to further enhance the adsorption efficiency and capacity of POS Bio-char, several proposals are listed below:

- Thermal study can be conducted to investigate the effect of temperature on metal ion adsorption using POSB.
- The sizes of POS should be standardized prior to pyrolysis to ensure even heating of the sludge.
- POSB can be modified using acids and bases to increase the numbers of functional groups since adsorption process is highly dependent on availability of functional groups.
- Instead of using conventional pyrolysis method to produce bio-char, liquefaction method is strongly suggested because it requires lesser time and heat energy. Bio-char produced by liquefaction has more functional groups compared to conventional pyrolysis.
- In future, studies to determine the possibility of Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) removal from wastewater using POSB should be tested to verify the adsorption data.

REFERENCES

Abdel Salam, O.E., Reiad, N.A. and Elshafei, M.M., 2011. A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *Journal of Advanced Research*, 2, pp. 297-303.

Abnisa, F., Arami-Niya, A., Wan Daud, W.M.A., Sahu, J.N. and Noor, I.M., 2013. Utilization of oil palm tree residues to produce bio-oil and bio-char via pyrolysis. *Energy Conversion and Management*, 76, pp. 1073-1082.

Abudaia, J.A., Sulyman, M.O., Elazaby, K.Y. and Ben-Ali S.M., 2013. Adsorption of Pb (II) and Cu (II) from aqueous solution onto activated carbon prepared from dates stones. International *Journal of Environmental Science and Development*, 4(2), pp. 191-195.

Adamczuk, A. and Kolodynska, D., 2015. Equilibrium, thermodynamic and kinetic studies on removal of chromium, copper, zinc and arsenic from aqueous solutions onto fly ash coated by chitosan. *Chemical Engineering Journal*, 274, pp. 200-212.

Adeeb, H., Zahangir, A., Mirghani, M.E.S., Nassereldeen, A.K., Noor Irma Nazashida, M.H., Yosri, M.S. and Shawaluddin, T., 2010. Sludge palm oil as a renewable raw material for biodiesel production by two-step processes. *Bioresource Technology*, 101, pp. 7804-7811.

Adeyemo, A.O., Adebowale, K.O. and Olu-Owolabi, B.I., 2014. Adsorption of copper by biochar. *International Research Journal of Pure & Applied Chemistry*, 4(6), pp. 727-736.

Adil, S., Mashiatullah, A., Asma, M., Ghaffar, A., Khan, S. and Abid, J., 2014. Adsorption of heavy metals by bio-chars produced from pyrolysis of paper mulberry from simulated industrial wastewater. *The Nucleus*, 51(3), pp. 323-327.

Al-Harahsheh, S., Kamel, A.Z., Leema, A., Muhannad, H. and Mehaysen, M., 2015. Fly ash based geopolymer for heavy metal removal: A case study on copper removal. *Journal of Environmental Chemical Engineering*, 677, pp. 1-9.

Al-Rashdi, B., Tizaoui, C. and Hilal, N., 2012. Copper removal from aqueous solutions using nano-scale diboron trioxide/titanium dioxide (B_2O_3/TiO_2) adsorbent. *Chemical Engineering Journal*, 183, pp. 294-302.

Albrecht, T.W.J., Addai-Mensah, J. and Fornasiero, D., 2011. *Effect of pH, concentration and temperature on copper and zinc hydroxide formation/precipitation in solution*. PhD. University of South Australia.

Ali, M.F., Heng, L.Y., Ratnam, W., Nais, J. and Ripin, R., 2004. Metal distribution and contamination of the Mamut River, Malaysia, caused by copper mine discharge. *Environmental Contamination and Toxicology*, 73, pp. 535-542.

Alley, E.R., 2007. *Water quality control handbook*. 2nd ed. New York: McGraw-Hill.

Amin, B.A., 2010. *Simultaneous removal of copper and lead from an aqueous solution using low-cost adsorbents*. Universiti Malaysia Pahang.

Ariff, B.K., 2010. *Removal of heavy metal from industrial wastewater using ultrasonic assisted by tea waste as adsorbent*. Universiti Malaysia Pahang.

Awual, M.R., Yaita, T., El-Safty, S., Shiwaku, H. and Suzuki, S., 2013. Copper(II) ions capturing from water using ligand modified a new type mesoporous adsorbent. *Chemical Engineering Journal*, 221, pp. 322-330.

Aziz, H.A., Yusoff, M.S., Adlan, M.N., Adnan, N.H. and Alias, S., 2004. Physico-chemical removal of iron from semi-aerobic landfill leachate by limestone filter. *Waste Management*, 24, pp. 353-358.

Bakhtiari, N. and Azizia, S., 2015. Adsorption of copper ion from aqueous solution by nanoporousMOF-5: A kinetic and equilibrium study. *Journal of Molecular Liquids*, 206, pp. 114–118.

Barakat, M.A., 2011. New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, 4, pp. 361-377.

Batool, S., Akib, S., Ahmad, M., Balkhair, K.S. and Muhammad Ashraf, A., 2014. Study of modern nano enhanced techniques for removal of dyes and metals. *Journal of Nanomaterials*, 1, pp.1-20.

Bergmann, C.P. and Machado, F., 2015. *Carbon nanomaterials as adsorbents for environmental and biological applications*. Switzerland, Springer International Publishing.

Bieby, V.T., Siti Rozaimah, S.A., Hassan, B., Mushrifah, I., Nurina, A. and Muhammad Mukhlisin, 2011. A review on heavymetals (As, Pb, and Hg) uptake by plants through phytoremediation. *International Journal of Chemical Engineering*.

Bilal, Jehanzeb, A.S., Tayyab, A., Syed Mubashar, H.G., Adnan, A.T., Arshid, P., Hajira H. and Qaisar, M., 2013. Waste biomass adsorbents for copper removal from industrial wastewater - A review. *Journal of Hazardous Materials*, 263, pp. 322-333.

Chan, N.W., 2009. Issues and challenges in water governance in Malaysia. *Journal of Environmental Health and Science*, 9(3), pp. 143-152.

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B. and Hay, A.G., 2011. Adsorp-tion of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Biores Technology*, 102, pp. 8877–8884.

Chen, T., Zhou, Z., Han, R., Meng, R., Wang, H. and Lu, W., 2015. Adsorption of cadmium by biochar derived from municipal sewage sludge: Impact factors and adsorption mechanism. *Journal of Chemosphere*, 134, pp. 286-293.

Cheng, Z., Liu, X., Han, M. and Ma, W., 2010. Adsorption kinetic character of copper ions onto a modified chitosan transparent thin membrane from aqueous solution. *Journal of Hazardous Materials*, 182, pp. 408-415.

Choumane, F.Z. and Benguella, B., 2013. Effects of algerian clays properties on the adsorption of Cd (II). *Journal of Environmentally Friendly Processes*, 1(2), pp. 10-21.

Collision, M., Collision, L., Sakrabani, R., Tofield, B. and Zoe, W., 2009. *Biochar and carbon sequestration: A regional perspective*. University of East Anglia.

Crini, G. and Badot, P., 2010. *Sorption processes and pollution: conventional and non-conventional sorbents for pollutant removal from wastewaters*. Presses Univ. Franche-Comté.

Dada, A.O., Olalekan, A.P., Olatunya, A.M. and Dada, O., 2012. Langmuir, freundlich, temkin and dubinin–radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. *Journal of Applied Chemistry*, 3(1), pp. 38-45.

Datusahlan, M., Wan Ishak, W.M.F. and Makky, E.A., 2013. Biodegradation of wastewater oil pollutants, identification and characterization: A case study – Galing River, Kuantan Pahang, Malaysia. *International Journal of Bioscience, Biochemistry and Bioformatics*, 3(6).

Dave, P.N., Subrahmanyam, N. and Sharma, S., 2009. Adsorption of cadmium by biochar derived from municipal sewage sludge: Impact factors and adsorption mechanism. *Indian Journal of Chemical Technology*, 16, pp. 234-239.

Deepak, G., Varsha, S. and Yogesh, C.S., 2014. Kinetic and thermodynamic studies on the removal of Cu(II) ions from aqueous solutions by adsorption on modified sand. *Journal of Industrial and Engineering Chemistry*, 20, pp. 841-847.

Farghali, A.A., Bahgat, M., Enaiet, A. and Khedr, M.H., 2013. Adsorption of Pb(II) ions from aqueous solutions using copper oxide nanostructures. *Beni-Suef University Journal of Basic and Applied Sciences*, 2, pp. 61-71.

Farooq, U., Kozinski, J.A., Khan, M.A. and Athar, M., 2010. Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature. *Bioresource Technology*, 101, pp. 5043-5053.

Faruk, H., Hamdan, S. and Rezaur, R., 2015. Review on the risk assessment of heavy metals in Malaysian clams. *The Scientific World Journal*, 2015.

Foo, K.Y. and Hameed, B.H., 2010. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156, pp. 2-10.

Fouladgar, M., Beheshti, M. and Sabzyan, H., 2015. Single and binary adsorption of nickel and copper from aqueous solutions by γ-alumina nanoparticles: Equilibrium and kinetic modelling. *Journal of Molecular Liquids*, 211, pp. 1060-1073.

Fu, F. and Wang, Q., 2011. Removal of Heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, 92, pp. 407-418.

Ghaemi, N., Madaeni, S.S., Daraei, P., Rajabi, H., Zinadini, S., Alizadeh, A., Heydari, R., Beygzadeh, M. and Ghouzivand, S., 2015. Polyethersulfone membrane enhanced with iron oxide nanoparticles for copper removal from water: Application of new functionalized Fe3O4 nanoparticles. *Chemical Engineering Journal*, 263, pp. 101-112.

Ghazi, H.I., Chan, N.W., Haliza, A.R. and Zakaria, N.A., 2013. Freundlich isotherm equilibrium equastions in determining effectiveness a low cost absorbent to heavy metal removal in wastewater (leachate) at Teluk Kitang landfill, Pengkalan Chepa, Kelantan, Malaysia. *Journal of Geography and Earth Science*, 1(1), pp. 1-8.

Hassan, S., Kee, L.S. and Hussain, H.A., 2013. Experimental study of palm oil mill effluent and oil palm frond waste mixture as an alternative biomass fuel. *Journal of Engineering Science and Technology*, 8(6), pp. 703-712.

Helfferich, F.G., 1962. *Ion exchange*. New York: McGraw-Hill.

Ho, Y.S. and Mckay, G., 1999. Pseudo-second order model for sorption processes. *Process Biochemistry*, 34, pp. 451-465.

Hossain, M.A., Ngo, H.H., Guo, W.S. and Nguyen, T.V., 2012a. Palm oil fruit shells as bio-sorbent for copper removal from water and wastewater: experiments and sorption models. *Biores Technol*, 113, pp. 97–101.

Hossain, M.A., Ngo, H.H., Guo, W.S. and Nguyen, T.V., 2012b. Biosorption of Cu(II) from water by banana peel based biosorbent: Experiments and models of adsorption and desorption. *Journal of Water Sustainability*, 2(1), pp. 87-104.

Huang, Y.F., Shih, C.H., Chiueh, P.T. and Lo, S.L., 2015. Microwave co-pyrolysis of sewage sludge and rice straw. *Energy*, 87, pp. 638-644.

Igberase, E., Osifo, P. and Ofomaja, A., 2014. The adsorption of copper(II) ions by polyaniline graft chitosan beads from aqueous solution: Equilibrium, kinetic and desorption studies. *Journal of Environmental Chemical Engineering*, 2, pp. 362-369.

Igwe, J.C. and Onyegbado, C.C., 2007. A review of palm oil mill effluent (pome) water treatment. *Global Journal of Environmental Research*, 1(2), pp. 54-62.

Indah Water Konsortium (IWK), 2011. *Sustainability report 2011*.

Inyang, M., Gao, B., Pullammanappallil, P., Ding, W. and Zimmerman, A.R., 2010. Biochar from anaerobically digested sugarcane bagasse. *Bioresource Technology*, 101, pp. 8868-8872.

Jarup, L., 2003. Hazards of heavy metal contamination. *Journals of British Medical Bulletin*, 68(1), pp. 167-182.

Japan Sanitation Consortium, 2008. *Country sanitation assessment in Malaysia report*. [Online] Available at: <http://www.jsanic.org/news/Release%20of%20Sanitation%20Assessment%20Report%20in%20Malaysiax.html> [Accessed 29 May 2015].

Knaebel, K.S., 2009. *Adsorbent selection*. Dublin, Ohio: Adsorption Research, Inc.

Kolodynska, D., Wnetrzak, R., Leachy, J.J., Hayes, M.H.B., Kwapinski, W. and Hubicki, Z., 2012. Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal*, 197, pp. 295-305.

Kong, Z., Li, X., Tian, J., Yang, J. and Sun, S., 2014. Comparative study on the adsorption capacity of raw and modified litchi pericarp for removing Cu(II) from solutions. *Journal of Environmental Management*, 134, pp. 109-116.

Koyuncu, H. and Kul, A.R., 2014. An investigation of Cu(II) adsorption by native and activated bentonite: Kinetic, equilibrium and thermodynamic study. *Journal of Environmental Chemical Engineering*, 2(3), pp. 1722-1730.

Kyzas, G.Z., Kostoglou, M. and Lazaridis, N.K., 2009. Copper and chromium(VI) removal by chitosan derivatives—Equilibrium and kinetic studies. *Chemical Engineering Journal*, 152, pp. 440-448.

Larous, S., Meniai, A.H. and Lehocine, M.B., 2005. Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust. *Desalination*, 185, pp. 483-490.

Leng, L., Yuan, X., Huang, H., Shao, J., Wang, H., Chen, X. and Zheng, G., 2015. Bio-char derived from sewage sludge by liquefaction: Characterization and application for dye adsorption. *Applied Surface Science*, 346, pp. 223-231.

Lehmann, J. and Joseph, S., 2015. Biochar for environmental management: An introduction. *Biochar for environmental management: Science, technology and implementation*. Routledge.

Levine, I.N., 2009. *Physical chemistry*. 6th ed. Boston: McGraw-Hill.

Lewinsky, A.A., 2007. *Hazardous materials and wastewater: treatment, removal and analysis*. New York: Nova Science Publisher, Inc.

Lichfouse, E., Schwarzbauer, J. and Robert, D., 2011. *Environmental chemistry for a sustainable world: Volume 2: Remediation of air and water pollution*. Springer.

Liu, W.J., Zeng, F.X., Jiang, H. and Zhang, X.S., 2011. Preparation of high adsorption capacity bio-chars from waste biomass. *Bioresource Technology*, 102, pp. 8247-8252.

Liu, T., Liu B. and Zhang, W., 2014. Nutrients and heavy metals in bio-char produced by sewage sludge pyrolysis: Its application in soil amendment. *Pollution Journal of Environmental Studies*, 23(1), pp. 271-275.

Low, S.L, 2015. *Preparation, characterization and utilization of palm oil sludge biochar for copper removal*. Undergraduate Final Year Project. Universiti Tunku Abdul Rahman.

Luo, X., Zhang, Z., Zhou, P., Liu, Y., Ma, G. and Lei, Z., 2015. Synergic adsorption of acid blue 80 and heavy metal ions (Cu^{2+}/Ni^{2+}) onto activated carbon and its mechanisms. *Journal of Industrial and Engineering Chemistry*, 27, pp. 164-174.

Malaysian Palm Oil Board, 2014. *Malaysian palm oil industry*. [Online] Available at: <http://www.palmoilworld.org/about_malaysian-industry.html> [Accessed 12 June 2015].

Manocha, S.M., 2003. Porous carbons. *Sadhana*, 28(1), pp. 335-348.

Metcalf and Eddy, 2004. *Wastewater engineering, treatment and reuse*. 4th ed. Singapore: Mc Graw Hill.

Metosen, N.S., 2009. Uptake of heavy metals by water spinach from sludge amended. Universiti Malaysia Sarawak.

Mihaly, P., 2011. *Air pollution control: Adsorption*. [Online] Available at: <https://www.ara.bme.hu/oktatas/tantargy/NEPTUN/BMEGEATAG04/ENGLISH_course/2011-2012-I/ea_lecture/BMEGE%C1TAG04_part12_Adsorption.pdf> [Accessed 20 June 2015].

Mitra, M., Hasfalina, C.M., Ali, H. and Phang, L.Y., 2010. Treatment of wastewater from rubber industry in Malaysia. *African Journal of Biotechnology*, 9(38), pp. 6233-6243.

Mobasherpour, I., Salahi, E. and Ebrahimi, M., 2014. Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto multi-walled carbon nanotubes. *Journal of Saudi Chemical Society*, 18, pp. 792-801.

Nageeb, R., 2013. *Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater, Organic Pollutants-Monitoring, Risk and Treatment*. [Online] Available at: <http://www.intechopen.com/books/organic-pollutants-monitoring-risk-and-treatment/adsorption-technique-for-the-removal-of-organic-pollutants-from-water-and-wastewater> [Accessed 20 June 2015].

Nagy, B., Manzatu, C., Maicaneanu, A., Indolean, C., Lucian, B.T. and Majdik, C., 2014. Linear and nonlinear regression analysis for heavy metals removal using Agaricus bisporus macrofungus. *Arabian Journal of Chemistry*, pp. 1-11.

Norazlina, A.S., Che, F.I. and Rosenani, A.B., 2014. Characterization of oil palm empty fruit bunch and rice husk biochars and their potential to adsorb arsenic and cadmium. *American Journal of Agricultural and Biological Sciences*, 9(3), pp. 450-456.

Ntimbani, R.N., Simate, G.S. and Ndlovu, S., 2015. Removal of copper ions from dilute synthetic solution using staple ion exchange fibres: Equilibrium and kinetic studies. *Journal of Environmental Chemical Engineering*, 3, pp. 1258-1266.

Nuhoglu, Y. and Oguz, E., 2003. Removal of copper(II) from aqueous solutions by biosorption on the cone biomass of Thuja orientalis. *Process Biochemistry*, 38, pp. 1627-1631.

Oliveira, F.D., Paula, J.H., Freitas, O.M. and Figueiredo, S.A., 2009. Copper and lead removal by peanut hulls: Equilibrium and kinetic studies. *Desalination*, 248, pp. 931-940.

Omri, A., Wali, A. and Benzina, M., 2012. Adsorption of bentazon on activated carbon prepared from Lawsonia inermis wood: Equilibrium, kinetic and thermodynamic studies. *Arabian Journal of Chemistry*, pp. 1-11.

Ozcimen, D. and Ersoy-Mericboyu, A., 2009. Removal of copper from aqueous solutions by adsorption onto chestnut shell and grapeseed activated carbons. *Journal of Hazardous Material*, 168, pp. 1118–1125.

Parveen, F.R., Rajeev, P.S., Ibrahim, M.H. and Norizan, E., 2010. Review of current palm oil mill effluent (pome) treatment methods: Vermicomposting as a sustainable practice. *World Applied Sciences Journal*, 11(1), pp. 70-81.

Qiu, H., Lv, L., Pan, B.C., Zhang, Q.J., Zhang, W.M. and Zhang, Q.X., 2009. Review: Critical review in adsorption kinetic models. *Journal of Zhejiang University Science A*, 10(5), pp. 716-724.

Randall, L., 2008. Malaysia: Water & wastewater treatment. U.S. Commercial Service. *Asia-Pacific Economic Cooperation*. [Online] Available at:

<http://egs.apec.org/more-articles/155-malaysia-water-a-wastewater-treatment> [Accessed 21 June 2015].

Reckamp, J.M., Garrido, R.A. and Satrio, J.A., 2014. Selective pyrolysis of paper mill sludge by using pretreatment processes to enhance the quality of bio-oil and biochar products. *Biomass and Bioenergy*, 71, pp. 235-244.

Reem, A.A., Nik Norulaini, N.A.R., Ahmad, A., Norli, I. and Omar, A.K., 2013. Characterization of oily and non-oily natural sediments in palm oil mill effluent. *Journal of Chemistry*, 2013, pp. 1-11.

Robati, D., 2013. Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube. *Journal of Nanostructure in Chemistry,* 3(55).

Rohaizar, N.A., Hadi, N. and Wong, C.S., 2013. Removal of Cu(II) from water by adsorption on chicken eggshell. *International Journal of Engineering & Technology*, 13(1), pp. 40-45.

Saqib, N. and Ahsan, 2014. Comparison of physico-chemical, advanced oxidation and biological techniques for the textile wastewater treatment. *Alexandria Engineering Journal*, 53, pp. 717-722.

Sari, N.A., Ishak, C.F. and Bakar, R.A., 2014. Characterization of oil palm empty fruit bunch and rice husk biochars and their potential to adsorb arsenic and cadmium. *American Journal of Agricultural and Biological Sciences*, 9(3), pp. 450-456.

Shafiq, Ranjiha, A.M., Yaseen, M., Mehdi, S.M. and Hannan, A., 2008. Comparison of freundlich and langmuir adsorption equations for boron adsorption on calcareous soils. *J. Agric. Res.*, 46(2).

Shi, L., Zhang, G., Wei, D., Yan, T., Xue, X., Shi, S. and Wei, Q., 2014. Preparation and utilization of anaerobic granular sludge-based biochar for the adsorption of methylene blue from aqueous solutions. *Journal of Molecular Liquids*, 198, pp. 334-340.

Shobana, R., Sahayaraj, A.P. and Soruba, R., 2014. Adsorption study on copper(II) ions from aqueous solution using chemically activated Couroupita guianensis (J.K. AUBLET) carbon. *Research Journal of Recent Sciences*, 3, pp. 375-379.

Silbey, R.J., Alberty, R.A. and Moungi, G.B., 2005. *Physical Chemistry*. 4th ed. Wiley.

Somasundaran, P., 2006. *Encyclopedia of surface and colloid science, Volume 3*. 2nd ed. CRC Press. Taylor & Francis Group.

Song, X.D., Xue, X.Y., Chen, D.Z., He, P.J. and Dai, X.H., 2014. Application of biochar from sewage sludge to plant cultivation: Influence of pyrolysis temperature and biochar-to-soil ratio on yield and heavy metal accumulation. *Chemosphere*, 109, pp. 213-220.

Suchithra, T., Wail, M.A.A., Dinesh, J., Sahu, J.N., Mubarak, N.M. and Nizamuddin, S., 2015. Utilization of palm oil sludge through pyrolysis for bio-oil and bio-char production. *Bioresource Technology*, 178, pp. 65-69.

Tavakoly Sany, S.B., Salleh, A., Rezayi, M., Saadati, N., Narimany, L. and Tehrani, G.M., 2013. Distribution and contamination of heavy metal in the coastal sediments of Port Klang, Selangor, Malaysia. *Water Air Soil Pollut*, 224, pp. 1476.

Tofighy, M.A. and Mohammadi, T., 2015. Copper ions removal from water using functionalized carbon nanotubes–mullite composite as adsorbent. *Material Research Bulletin*, 68, pp. 54-59.

Trakal, L., Sigut, R., Sillerova, H., Faturikova, D. and Komarek, M., 2014. Copper removal from aqueous solution using biochar: Effect of chemical activation. *Arabian Journal of Chemistry*, 7, pp. 43-52.

Tumin, N.D., Chuah, A.L., Zawani, Z. and Rashid, S.A., 2008. Adsorption of copper from aqueous solution by elais guineensis kernel activated carbon. *Journal of Engineering Science and Technology*, 3(2), pp. 180-189.

Tzoupanos, N.D. and Zouboulis, A.I., 2008. *Coagulation-flocculation processes in water/wastewater treatment: The application of new generation of chemical reagents*. Aristotle University of Thessaloniki.

Wan, M.W., Wang, C.C. and Chen, C.M., 2013. The adsorption study of copper removal by chitosan-coated sludge derived from water treatment plant. *International Journal of Environmental Science and Development*, 4(5), pp. 545-551.

Wang, L.K., Chen, J.P., Hung, Y. and Shammas, N.K., 2009. *Heavy metals in the environment*. CRC Press. Talyor & Francis Group, United State.

Wu, F.C., Tseng, R.L. and Juang, R.S., 2009. Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. *Chemical Engineering Journal*, 153, pp. 1-8.

Yachigo, M. and Sato, S., 2013. Chapter 15: Leachability and vegetable absorption of heavy metals from sewage sludge biochar. *Soil Processes and Current Trends in Quality Assessment*.

Yahaya, S.M. and Lau, S., 2013. Palm oil mill effluent (pome) from Malaysia palm oil mills: waste or resource. *International Journal of Science, Environment and Technology*, 2(6), pp. 1138-1155.

Yang, Y., Lin, X., Wei, B., Zhao, Y. and Wang, J., 2013. Evaluation of adsorption potential of bamboo biochar for metal-complex dye: equilibrium, kinetics and artificial neural network modeling. *International Journal of Environmental Science and Technology*.

Yuan, H., Lu, T., Wang, Y., Chen, Y. and Lei, T., 2016. Sewage sludge biochar: Nutrient composition and its effect on the leaching of soil nutrients. *Geoderma*, 267, pp. 17-23.

Zielinska, A., Oleszczuk, P., Charmas, B., Skubiszewska-Zieba, J. and Pasieczna-Patkowska, S., 2015. Effect of sewage sludge properties on the biochar characteristic. *Journal of Analytical and Applied Pyrolysis*, 112, pp. 201-213.

APPENDICES

Appendix A: Tables of Concentrations and Removal Efficiencies from Batch Adsorption Studies

Table A1: Copper(II) Ion Concentration and Removal Efficiency of POSB from Dosage Study

Dosage Value (g)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal Percentage (%)	Adsorption Capacity (mg/g)
0.01	9.8852	7.4289	24.85	24.56
0.02	9.8852	3.6674	62.90	31.09
0.03	9.8852	1.2020	87.84	28.94
0.04	9.8852	0.3807	96.15	23.76
0.05	9.8852	0.3155	96.81	19.14
0.06	9.8852	0.2651	97.32	16.03
0.07	9.8852	0.2539	97.43	13.76
0.08	9.8852	0.3572	96.39	11.91

Table A2: Copper(II) Ion Concentration and Removal Efficiency of POSB from Contact Time Study

Contact Time (minute)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal Percentage (%)	Adsorption Capacity (mg/g)
0	0	0	-	-
30	9.7227	6.0517	37.76	18.36
60	9.7227	4.5289	53.42	25.97
90	9.7227	4.1216	57.61	28.01
120	9.7227	4.0553	58.29	28.34
150	9.7227	3.2317	66.76	32.46
180	9.6669	3.0006	68.96	33.33
210	9.6669	2.5889	73.22	35.39
240	9.6669	2.3461	75.73	36.60
270	9.6669	3.3240	65.61	31.71

Table A3: Copper(II) Ion Concentration and Removal Efficiency of POSB from Contact Speed Study

Contact Speed (rpm)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal Percentage (%)	Adsorption Capacity (mg/g)
50	9.9231	2.8816	70.96	35.21
100	9.9231	2.8082	71.70	35.57
150	9.9231	2.6673	73.12	36.28
200	9.9231	3.3179	66.56	33.03
250	9.9231	3.3933	65.80	32.65

Table A4: Copper(II) Ion Concentration and Removal Efficiency of POSB from pH Study

Initial pH	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal Percentage (%)	Adsorption Capacity (mg/g)
3	9.8830	4.0406	59.12	29.32
4	9.8830	3.7761	61.79	30.53
5	9.8830	3.1209	68.42	33.81
6	9.8830	0.5081	94.86	46.87
7	9.8830	0.5002	94.96	46.91
8	9.8830	0.5271	94.67	46.78
9	9.8830	0.5212	94.73	46.81
10	9.8830	0.3969	95.98	47.43

Appendix B: Tables of Equilibrium Isotherms and Kinetics Models

Table B1: Langmuir and Freundlich Isotherm Models

Bio-char Dosage (g)	**C_o (mg/L)**	**C_e (mg/L)**	**q_e (mg/g)**	**C_e/q_e (g/L)**	**In (C_e)**	**In (q_e)**
0.01	9.7704	5.2397	45.31	0.1156	0.7193	1.65619
0.02	9.7704	2.9181	34.26	0.08518	0.4651	1.53479
0.03	9.7704	1.1151	28.85	0.03865	0.04731	1.46015
0.04	9.7704	0.6316	22.85	0.02764	-0.1996	1.35889
0.05	9.7704	0.5493	18.44	0.02979	-0.2602	1.26576
0.06	9.7704	0.4804	15.48	0.03103	-0.3184	1.18977

Table B2: Pseudo-first-order, Pseudo-second-order and Intra-particle Diffusion Models

Contact Time (minute)	**C_o (mg/L)**	**C_t (mg/L)**	**q_t (mg/g)**	**q_e (mg/g)**	**Log (q_e - q_t)**	**t/q_t (min. g/mg)**	**$t^{0.5}$ ($min^{0.5}$)**
30	9.6443	3.8254	29.09	45.00	1.2016	1.0311	5.4772
60	9.6443	2.5833	35.31	45.00	0.9866	1.6995	7.7460
90	9.6443	2.2616	36.91	45.00	0.9078	2.4381	9.4868
120	9.6443	1.5102	40.67	45.00	0.6364	2.9505	10.9545
150	9.6443	1.4235	41.10	45.00	0.5906	3.6493	12.2474
180	9.6443	0.7945	44.25	45.00	-0.1244	4.0679	13.4164
210	9.6443	0.7891	44.28	45.00	-0.1403	4.7430	14.4914
240	9.6443	0.6452	45.00	45.00	-	5.3339	15.4919
270	9.6443	0.8872	43.79	45.00	0.0844	6.1664	16.4317