HYDROTHERMAL PREPARATION OF BIOCHAR FROM LIGNOCELLULOSIC BIOMASS FOR THE PRACTICAL AMENDMENT OF HEAVY METAL CONTAMINATED WASTEWATER

by

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LIST OF ABBREVIATIONS

AC	Activated Carbon
As	Arsenic
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Hanlenda
Cd	Cadmium
CEC	Carbon Exchange Cation
CKB	Coconut Kernel Derived Biochar
CNT	Carbon Nanotubes
CO_2	Carbon Dioxide
COOH	Carboxylic Groups
Cr	Chromium
Cu	Copper
$Cu(OH)_2$	Copper (II) Hydroxide
FAO	Food And Agricultural Organization
FOB	Free On Board
FTIR	Fourier Transform Infrared Spectroscopy
Hg	Mercury
HTC	Hydrothermal Carbonization
IBI	The International Biochar Initiative
ICF	Individual Contamination Factor
MCL	Maximum Contaminant Levels

LIST OF ABBREVIATIONS (Continue)

MPOB	Malaysian Palm Oil Board
MSW	Municipal Solid Wastes
MTC	Malaysia Timber Council
Ni	Nickel
OH	Hydroxyl Groups
PAC	Polyaluminium Chloride
PAHs	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PCBs	Polychlorinated Biphenyls
PHE	Phenanthrene
RMSD	Root Mean Square Deviation
SEM	Scanning Electron Microscope
SO_3H	Sulphonic Group
USEPA	United State Environmental Protection Agency
WHO	World Health Organization
Zn	Zinc

LIST OF SYMBOLS

A_T	Temkin isotherm equilibrium binding constant (L/g)
b	Langmuir isotherm constant (dm^3/mg)
b_T	Temkin isotherm constant
C_e	Equilibrium concentration (mg/L)
C_o	Adsorbate initial concentration (mg/L)
K_F	Freundlich isotherm constant (mg/g) $(dm^3/g)^n$ related to adsorption capacity
K_L	Langmuir isotherm constant (L/mg)
n	Adsorption intensity
q_e	Amount of adsorbate in the adsorbent at equilibrium (mg/g)
q_{cal}	Calculated adsorbate concentration at equilibrium (mg/g)
q_{exp}	Measured adsorbate concentration at equilibrium (mg/g)
R^2	Correlation coefficient
K	Kelvin
S_{BET}	Specific Surface Area
V_T	Total Pore Volume

LIST OF SYMBOLS (Continue)

D_{ap}	Average pore size
Q_o	Monolayer adsorption capacity
	Angstroms
Cu^{2+}	Copper (II) ions
^{o}C	Temperature
ΔG°	Free Gibbs Energy
ΔH°	Enthalpy
ΔS°	Entropy

PENYEDIAAN BIOCAR HIDROTERMA DARIPADA BIOJISIM LIGNOSELLULOSA UNTUK KAJIAN PRAKTIKAL SISA AIR TERCEMAR LOGAM BERAT

ABSTRAK

Biocar daripada penyediaan hidroterma sisa inti kelapa telah dijalankan. Potensi biocar yang disediakan untuk rawatan praktikal sisa air tercemar logam berat, khususnya kandungan ion kuprum (Cu^{2+}) telah dikaji. Sifat-sifat fizikal dan kimia biocar inti kelapa (CKB) dinilai menggunakan analisis struktur liang, pengimbasan mikroskop, analisis unsur, dan jelmaan Fourier spektroskopi inframerah. Analisis unsur menggambarkan kandungan C, O, H, N, dan S adalah 65.33%, 20.89%, 5.02%, 8.75%, dan 0.01% masing-masing. Experimen penjerapan dijalankan dengan mengubah dos bahan penjerap, kepekatan logam awal dan masa sentuhan, dan pH. Keputusan eksperimen menunjukkan bahawa penyingkiran serapan Cu^{2+} meningkat selaras dengan peningkatan dos bahan penjerap, kepekatan awal dan masa sentuhan, dan pH. Penyingkiran Cu^{2+} secara maksima dapat dilihat pada pH 5.5 bersamaan dengan pengambilan serapan iaitu 2.17 mg/g dan penyingkiran serapan adalah 99.65% masing-masing. Data-data eksperimen telah dianalisis dengan menggunakan model isoterma Langmuir, Freundlich, dan Temkin. Data penjerapan bersesuaian dengan model Langmuir dengan menunjukkan pekali korelasi, R^2 dan RMSD yang lebih baik iaitu 0.999 dan 0.152 masing-masing, dengan kapasiti penjerapan monolayer maksimum bagi ion Cu^{2+} adalah 88.08 mg/g. Analisis termodinamik mencadangkan bahawa penjerapan Cu^{2+} oleh biocar inti kelapa yang digunakan adalah sesuai dilaksanakan untuk alam semula jadi dengan ΔG^o -7.696 kJ/mol sehingga -11.081 kJ/mol, dan ΔH^o dan ΔS^o adalah 43.61 kJ/mol dan -160.40 J/mol K, masing-masing. Hasil kajian menunjukkan biocar inti kelapa berpotensi sebagai penjerap bio mesra alam untuk pemulihan in-situ pencemaran air adalah yang terbaik.

HYDROTHERMAL PREPARATION OF BIOCHAR FROM LIGNOCELLULOSIC BIOMASS FOR THE PRACTICAL AMENDMENT OF HEAVY METALS CONTAMINATED WASTEWATER

ABSTRACT

The hydrothermal preparation of biochar from spent coconut kernel has been attempted. The potential of the prepared biochar for the practical treatment of heavy metals contaminated wastewater, specifically copper ions (Cu^{2+}) was examined. The physical and chemical properties of coconut kernel derived biochar (CKB) were evaluated by pore structural analysis, scanning electron microscope, elemental analysis, and Fourier transform infrared spectroscopy. The elemental analysis illustrated that the content of C, O, H, N, and S was 65.33%, 20.89%, 5.02%, 8.75%, and 0.01% respectively. Adsorption experiments were carried out by varying the adsorbent dosage, initial metal concentrations and contact time, and pH. Experimental results manifested that the adsorptive removal of Cu^{2+} increased with increasing the adsorbent dosage, initial concentration and contact time, and pH. Maximum Cu^{2+} removal was observed at pH 5.5, corresponding to the adsorptive uptake of 2.17 mg/g and adsorptive removal of 99.65%, respectively. Experimental data were analyzed using Langmuir, Freundlich, and Temkin isotherm models. Adsorption data fitted to the Langmuir model, with the correlation coefficient, R^2 and RMSD of 0.999 and 0.152, respectively, anticipated a maximum monolayer adsorption capacity for Cu^{2+} ions of 88.08 mg/g. Thermodynamics analysis suggested that adsorption of Cu^{2+} onto CKB was feasible and in nature, with the ΔG^o of -7.696 kJ/mol to -11.081 kJ/mol, and ΔH^o and ΔS^o were 43.61 kJ/mol and -160.40 J/mol K, respectively. The findings revealed the potential of spent coconut kernel biochar as an eco-friendly biosorbent for the in-situ remediation of water pollutants were best.

CHAPTER 1

INTRODUCTION

1.1 The emerging heavy metals contamination concern in Malaysia

Rapid industrialization and uncontrolled urbanization around many cities have raised an alarming environmental concern due to the anthropogenic pollutions from the semiconductor, fertilizer, and metal plating industries. Accordingly, the discharge of heavy metal ions into the waterways has increased tremendously (Bao, 2013; Naji *et al.*, 2010). Among those industries, semiconductor industry has been identified as the top heavy metals producing industry (Mat *et al.*, 1999). Semiconductor industry has shown a profound impact as it is the major support of technical equipment, ranging from personal computers, mobile phones, to home appliance such as dish washer and microwave ovens. In Malaysia, semiconductor industry plays a critical role, contributing about 41% of the Malaysia's total Electrical and Electronic sector output, with approximately 62 semiconductor companies are currently in operation (Cardas Research and Consulting, 2012).

A large variety of chemicals are involved during the operation, and more than 2 USD per pound of management cost are required (Pacific Northwest Pollution Prevention Resource Center, 2008). The growth rate of waste generation in electronic and semiconductor sectors was estimated at 5% per annum from 1987-1992 and a high content of this waste is heavy metals (Hamid and Sidhu, 1993). These heavy metals, including both essential and non-essential elements show a particular significance in ecotoxicology, due to their highly persistence and potential toxic effects to the living organisms (Storelli *et al.*, 2005). These heavy metals could exist in soluble forms, present mainly as suspended colloids or fixed by organic and mineral substances (Kabata-Pendias and Pendias, 2001).

Sediments are important sinks for many pollutants such as pesticides and heavy metals which play a crucial role in mobilization of contaminants in aquatic systems under favorable conditions (Ikem *et al.*, 2003). Heavy metals contaminant affect not only river system, but also ecosystem such as lakes, and soils. Ebrahimpour and Mushrifah (2008) conducted a study to determine the concentration of heavy metals, cadmium, copper, and lead, in water and sediment at Tasik Chini, Malaysia. Results showed that cadmium and lead have higher potential mobilization at the exchangeable and acid reduction fraction, while the individual contamination factor (ICF) showed a greater risk. In the previous studies, an open pit copper mine located in the Northwest of Sabah, East Malaysia has been known to pollute its surroundings with the release of heavy metals (Murtedza *et al.*, 1989). Therefore, the enforcement of regulations and specific guidelines for the reduction of chemical contaminants as stated in the Environmental Quality (Sewage and Industrial Effluents) Regulations 2009, (Environmental Quality Act, 1974) is required.

1.2 The generation of lignocellulosic biomass in Malaysia

Malaysia has a large quantity of lignocellulosic biomass from agriculture waste, forest residues, and municipal solid waste (Goh *et al.*, 2010). Oil palm is one of the most abundantly available sources of lignocellulosic biomass, where Malaysia has approximately 362 of palm oil mills to process 82 million tons of fresh fruit bunch, with an estimated 33 million tons of crop residue annually, chiefly in the form of empty fruit bunch, fiber and shell, MPOB (Malaysian Palm Oil Board, 2009d). Malaysia has become the most important agricultural country to export palm oil, cocoa and rubber (Goh *et al.*, 2010). Continuous efforts and researches are focused on biomass as an alternative source for power generation, whereby numerous agricultural and forest residues are turned into useful energy and applicable bioproducts (Mekhilef *et al.*, 2011). The conversion of these unwanted wastes into valuable products is a strategic move to become a self-sustained country in the future (Goh *et al.*, 2010).

Another potential of lignocellulosic biomass generation is the forest residues, woods, straws from pulp and paper industries, and logging activities (Goh *et al.*, 2010). According to the Malaysia Timber Council, Malaysia has generated free on board (FOB) value of more than 18 million from January to October 2008 by logging activities (MTC, 2008a), where, pulp and paper industries reach the production threshold of 1 million tons in 2002 (FAOSTAT, 2008). While these vigorous industries generate profits, an enormous quantity of waste is produced. Other than agriculture wastes and forest residues, municipal solid wastes (MSW), animal manures and food processing residue are another option of feedstock (Goh *et al.*, 2010). In many countries, the MSW is segregated into several fractions, thus the biodegradable organic components of MSW which consisting of paper and cardboard, kitchen waste and garden waste, could be converted into biofuel (Li *et al.*, 2007). These wastes can be fully matched with the input requirements of the process which MSW includes wastes generated from residential, commercial, and municipal services (Goh *et al.*, 2010).

1.3 The utilization of lignocellulosic biomass as renewable sources of biochars

1.3.1 Lignocellulosic biomass

Biomass is defined as: "organic matter that can be converted into energy which the organic matter refers to food crops, crop residues, wood waste and byproducts, and animal manure" (Bracmort, 2012). In recent years, the naturally transformation of biomass into coal or peat takes from hundreds to millions of year and presumably, wet biomass treated under geothermal conditions of high pressure and temperature converts to coal (Reza *et al.*, 2014). Lignocellulosic biomass, the most abundant organic materials on earth, has enormous potential as a feedstock for the production of fuel, heat and electrical power (Liu *et al.*, 2012) and the attractiveness of lignocellulosic biomass has increased in recent years due to rapid depletion of conventional fossil fuels and growing concerns of environmental pollution and climate change.

Biomass is known to be the only source of renewable carbon, shows great promise for the large-scale economical production of renewable energy and chemicals (Kim *et al.*, 2013). Biomass is an extremely abundant resource that can be produced in many forms such as agriculture, forestry and microbial system (Foust *et al.*, 2008). Kim *et al.* (2013) stated that the utilization of biomass as a renewable energy requires a proper energy conversion process because of its recalcitrance which this trait results from compositional biomass resistance to deconstruction from microbes and enzymes has made it difficult to be used as an energy resource. The two major conversion technologies used for lignocellulosic biomass such as thermochemical and biological conversion but with the advanced of technology and innovation the researchers have begun to uncertain the coal's natural formation is mainly a chemical process, instead of biological process (Liu *et al.*, 2012; Reza *et al.*, 2014). This is because thermochemical process has benefits that require short processing times with high product yields compared to biological process (Liu *et al.*, 2012). Thermochemical processes are classified into pyrolysis, gasification, combustion and hydrothermal preparation. The lignocellulosic biomass will be upgrading through the chemical process called hydrothermal carbonization (HTC) as to yield high products of HTC biochar. This biochar is potentially a valuable product since it provides a mean for effective carbon sequestration and environmental management besides its application in soils as both a beneficial soil amendment in terms of increasing cation exchange, and helps retain plant nutrients that would otherwise been lost by runoff, which facilitates in maintaining water quality as well (Abdel-Fattah *et al.*, 2014).

1.3.2 The compositions of lignocellulosic materials

Lignocellulosic materials have been known as photomass because they are a result of photosynthesis and the composition of lignocellulic biomass can be classified into different components which are cellulose, hemicellulose, and lignin (Mohamad Nor *et al.*, 2013) which have high content of hydroxyl groups (Nguyen *et al.*, 2013). Consequently, they have good abilities to attach heavy metals (Okoro and Okoro, 2011). Chemical composition of common lignocellulosic materials is presented in Table 1.1. Cellulose which constitutes about 35-50% of lignocellulosic materials is a linear polymer of β-D-glucopyranose sugar units with average chain has a degree of polymerization of about 9000-10,000 units. Approximately 65% of the cellulose is highly oriented and crystalline with no accesibility to water and other solvents, while the rest is composed of less oriented chains which have association with hemicellulose that constitutes about 20-35% and lignin constitutes 15-20% of lignocellulosic materials.

Table 1.1: Typical compositions of lignocellulosic materials (Mood *et al.*, 2013)

Composition	Percentage (%)
Cellulose	35-50
Hemicellulose	20-35
Lignin	15-20
Ash and Other	15-20

As its partial availability to water and other solvents, the molecular structure of cellulose gives a variety of characteristics such as hydrophilicity, chirality, and degradability. Moreover, chemical reactivity is strongly a function of the high donor reactivity of the OH groups in cellulose molecules. With lower degree of polymerization than cellulose, the hemicellulose includes a group of polysaccharide polymers and the hemicelluloses which are not crystalline vary in structure and polymer composition depending on the source (Abdolali *et al.*, 2014). Figure 1.1 shows a schematic illustration of cellulose chain, and Figure 1.2 shows a diagram of hemicellulose. Unlike cellulose, hemicellulose consist of different monosaccharide units and the polymer chains of hemicelluloses have short branches and are amorphous. The morphology of amorphous made hemicelluloses known to be soluble in water (Reza, 2011).

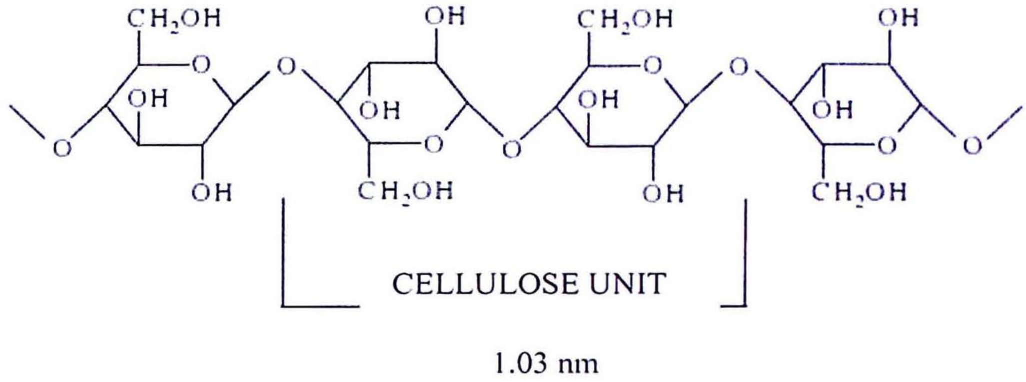


Figure 1.1: Cellulose chain unit

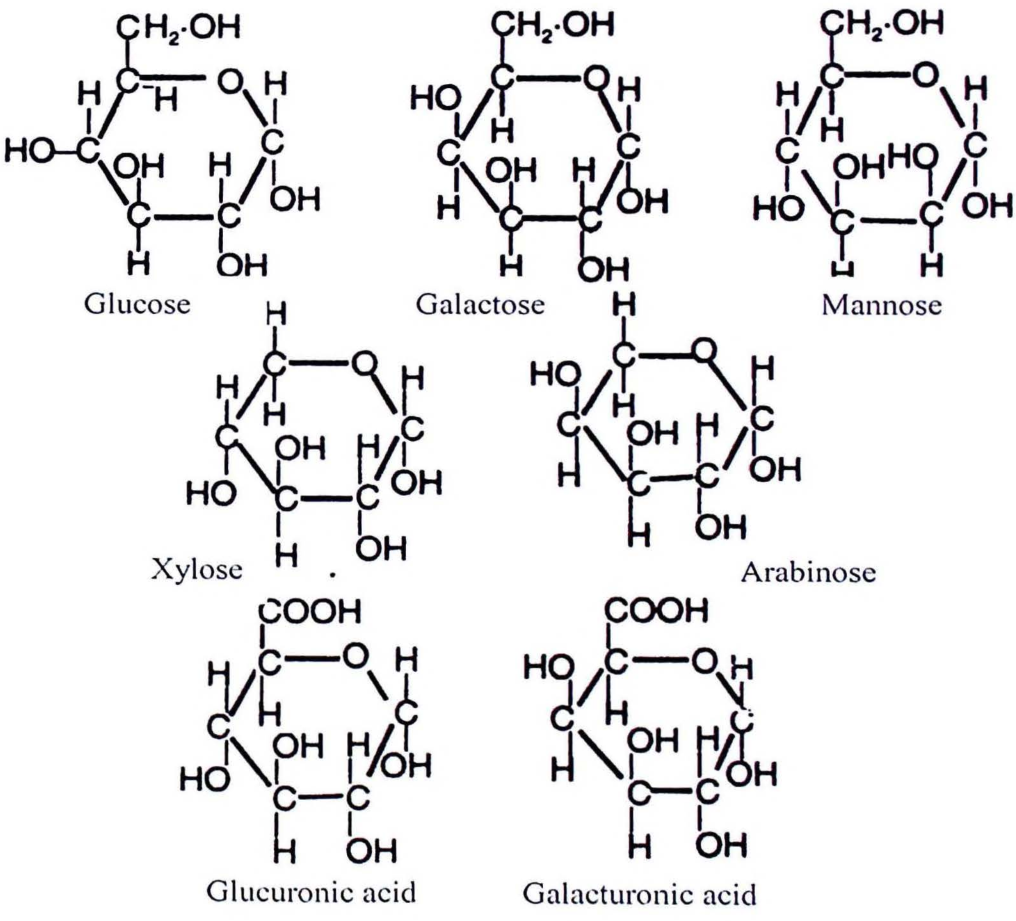
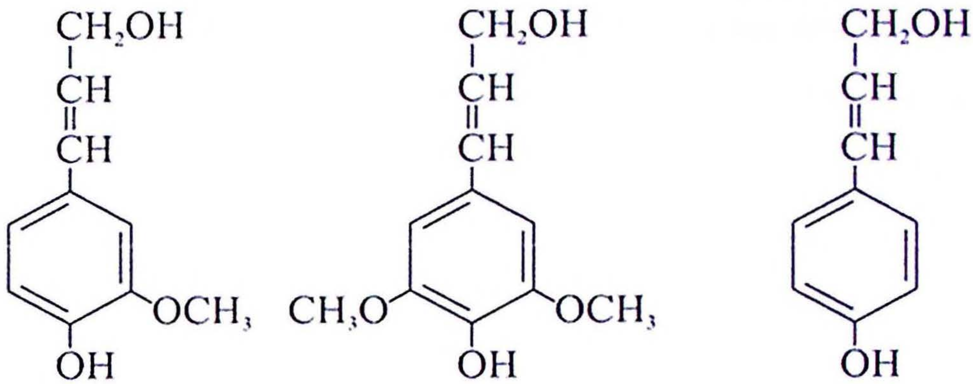


Figure 1.2: Schematic illustration of sugar groups of hemicellulose

The third most abundant natural polymer present in nature after cellulose and hemicellulose is lignin, where it is expected to play a crucial role as raw material for the world's bio-based economy for the production of bioproducts and biofuels (Buranov and Mazza, 2008). Lignins are highly branched without crystalline structure and are composed of nine carbon units derived from substituted cinnamyl alcohol of which the structure and chemical composition are a function of their source (Abdolali *et al.*, 2014). Among the three, lignin is the one recognized as the main component in lignocellulosic biomass that accountable for the adsorption process (Cagnon *et al.*, 2009). Due to the rich carbon content of lignin, lignocellulosic biomass is a good option to be used as precursor for producing adsorbent (Demirbas, 2004; Allen *et al.*, 2005).

In previous studies, lignin presented initially the highest carbon content and the lowest oxygen content compared to cellulose and hemicellulose, but those three basic compounds of lignocellulosic material have similar contents of water and hydrogen and close to 6% weight (Cagnon *et al.*, 2009). There are three main groups of lignins such as the lignins of softwoods, the lignins of hardwoods and the lignins of grasses. Lignin provides rigidity, internal transport of water and nutrients and protection against attack by microorganisms (Buranov and Mazza, 2008). The lignin structure is composed of coniferyl alcohol which holds about 35%-49%, sinapyl alcohol is 40%-61% and *p*-coumaryl alcohol units which is 4%-15% (Mood *et al.*, 2013).



Coniferyl alcohol Sinapyl alcohol *p*-coumaryl alcohol

Figure 1.3: Chemical structures of the phenylpropanoid alcohols used to construct the lignin polymer (Lignoworks, 2014)

Cagnon *et al.* (2009) reported that components of lignocellulosic materials have contributed to the mass and the porous properties of chars and activated carbons. The proper characteristics and structural compounds of lignocellulosic biomass have made it able to adsorb heavy metal ions on their surface binding sites through interaction with the chemical functional groups (Abdolali *et al.*, 2013). These functional groups substitute hydrogen ions for metal ions in solution or donation of an electron pair to form complexes with the metal ions in solutions. Due to abundant binding groups, lignocellulosic biomass could be an enormous potential source of adsorbent materials for decontaminating heavy metals from wastewater (Jimenez-Cedillo *et al.*, 2013; Marin-Rangel *et al.*, 2012; Zafar *et al.*, 2007).

Guo *et al.* (2008) investigated the adsorption of metal ions such as Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) on lignin which extracted from black liquor and the result showed that lignin has affinity with those ions in such sequence Pb(II) > Cu(II) > Cd(II) > Zn (II) > Ni(II), where it was found that lignin surfaces has two main types of acid sites which attributed to carboxylic- and phenolic- type surface groups. Among these two, phenolic sites show a higher affinity for metal ions compared to carboxylic sites, whereby the adsorption of metal ion onto deprotonated carboxyl and phenolic sites was important mechanism that will able to explain the observed adsorption behavior (Guo *et al.*, 2008).

1.4 Problem statement

Environmental pollution is currently one of the most important issues which has been growing exponentially in the past few years, and reached an alarming level in terms of its effects on the living creatures (Renge *et al.*, 2012). Heavy metals have been excessively released into the environment, following the rapid industrialization (Wan Ngah and Hanafiah, 2008). Those heavy metals such as cadmium, zinc, copper, nickel, lead, mercury and chromium are used in various industries, and some of the micronutrients are necessary for the living organisms at the trace level (Hossain *et al.*, 2014). Unlike organic wastes, heavy metals are non-biodegradable, and can be accumulated in the living tissues, to cause various disorders (Wan Ngah and Hanafiah, 2008). With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries, and pesticides, heavy metals wastewaters are directly or indirectly discharged into the environment (Fu and Wang, 2011).

Among heavy metals, copper plays a huge role in semiconductor industry, because of its abundance and low price tag (Pappas, 2014) and it is of the hazardous heavy metals used in different industries such as mining and smelting, plating, brass manufacture, petroleum refining, electroplating industies, and Cu-based agrichemicals in which Cu(II) ions are released with various concentrations. Although copper is an essential metal for living beings at lower concentration, it is potentially toxic at the higher concentration level (Singha and Das, 2013). Heavy metals occur naturally in rock-forming and ore minerals and so a range of normal background concentrations is associated with each of these elements in soils, sediments, waters and living organisms (O'Connel *et al.*, 2008). Hossain *et al.* (2014) stated that the removal of heavy metal ions from wastewater is now a major global concern for both industry and environmental protection agencies. Hence, it is crucial to control heavy metals level in wastewater before discharged into the nature. Traditional water treatment technologies such as precipitation, ion-exchange, membrane filtration, coagulation-flocculation, and flotation, have been found to be effective in reducing heavy metal concentrations (Akbal and Camci, 2011; Boudrahem *et al.*, 2011; Malamis *et al.*, 2011). Each process has its own pros and cons, however, these physico-chemical processes involve the requirement of costly reagents (Popuri *et al.*, 2009; Nghiem *et al.*, 2006).

Among these techniques, adsorption has been proved to be an excellent way to treat industrial wastewater, which offers significant advantages such as low-cost, availability, profitability, easy to operate and efficient, compared to other conventional methods especially from economical and environmental points of view (Hashem *et al.*, 2007; Ravikumar *et al.*, 2005; Allen *et al.*, 2005; Mittal *et al.*, 2005). Adsorption process is widely used to efficiently remove heavy metals from wastewater with high solute loadings and even at dilute concentrations (<100 mg/L) (Popuri *et al.*, 2009). Adsorption has progressed as a defense front line for pollutants which are hard to remove by other methods such as selective adsorption by biological materials, mineral oxides, activated carbon, or polymer resins. Although activated carbon is suitable and efficient to remove water contaminants, it is costly to make (Mohan *et al.*, 2014). In spite of its prolific use, activated carbon remains an expensive material as the higher the quality of activated carbon, the greater its cost. Activated carbon also requires such complexing agents to improve its removal performance for inorganic matters, therefore, this situation makes it lesser attractive to be widely used in small-scale industries because of cost inefficiency (Babel and Kurniawan, 2003). Due to the problems mentioned previously, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years, and low cost-adsorbents have been evaluated for the heavy metal removal (Chaiyasith *et al.*, 2006) and there is an effective environmental management tool which has been introduced as to replace the activated carbon called biochar.

Typical biochar is less carbonized than activated carbon and more hydrogen and oxygen remain in its structure along with the ash originating from the biomass. A unique opportunity has been provided by biochar to enhance the fertility of soil and nutrient-use efficiency, in a sustainable way (Mohan *et al.*, 2014). Evidence has suggested that biochar has a high potential to adsorb to both inorganic and organic pollutants (Cao *et al.*, 2009; Beesley *et al.*, 2010; Wang *et al.*, 2010). The term biomass (Greek, bio, life + maza or mass) is referred to wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous species, wood wastes, bagasse, industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, food processing waste, aquatic plants, algae animal wastes, and a host of other materials (Demirbas, 2000). Adsorbent materials derived from low-cost agricultural wastes can be employed for the effective removal and recovery of heavy metal ions from wastewater streams (Kratochvil and Volesky, 1998; Pagnanelli *et al.*, 2003; Volesky, 2003; Shin and Rowel, 2005; Park *et al.*, 2006). The removal of heavy metal ions using low-cost abundantly available adsorbents include agricultural wastes such as sawdust (Ajmal *et al.*, 1998; Zarraa, 1995), coconut husk (Babarinde, 2002; Tan *et al.*, 1993), banana and orange peels (Annadurai *et al.*, 2002), and rice husk. One of the main factors that sprightly influences whether an agricultural waste or by-product is practical or not is the availability itself, for example sugarcane bagasse as biosorbent exhibited very high potential in heavy metal uptake during wastewater treatment (Aloma *et al.*, 2012; Liu *et al.*, 2012).

The capacity of biosorption of sugarcane bagasse could be noticeably improved by carboxyclic, amine and other functional groups into the surface materials (Pereira *et al.*, 2010) or by removing soluble organic compounds and increasing the metal sorption efficiency (Martin-Lara *et al.*, 2010). Raw biosorbents such as lignocellulosic biomass, were modified by various methods to increase their sorption capacities because metal ion binding by lignocellulosic biosorbents is believed to take place through chemical functional groups such as carboxyl, amino, or phenolics (Demirbas, 2008). Modified lignin extracted from lignocellulosic biomass is used for the removal of certain metal ions such as lead and zinc from effluent (Pasticarkova, 2004; Morita *et al.*, 1987; Verma *et al.*, 1990; Lalvani *et al.*, 1997; Sun *et al.*, 1998; Demirbas, 2004). According to Dobrovol`skii (2006) lignin is known to adsorb many heavy metal ions. Agricultural wastes are usually composed of lignin and cellulose as major constituents and may also include polar functional lignin groups, such as alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution (Pagnalelli *et al*, 2003). There are varieties of thermochemical or biological processes that could be employed for the conversion of biomass in the absence of oxygen to value added products with high degrees of carbon content than the original biomass (Libra *et al.*, 2011). Gas or liquid products (biogas or bioalcohol) predominate in the transformation of biochemical, while solids called charcoal are the major commercial products of the thermochemical conversion of pyrolysis process (Antal and Groli, 2003).

During pyrolysis, the organic matter in the biomass is thermochemically decomposed by heating in the absence of oxygen. If it is carried out in the presence of subcritical liquid water, it is often called hydrous pyrolysis or hydrothermal carbonization (HTC) (Libra *et al.*, 2011). Hydrothermal carbonization (HTC) is said to be an efficient pre-treatment process to yield a solid lignite-like fuel, which for hydrothermal treatment, biomass is covered with hot water (Erlach *et al.*, 2012). The solid product yields with a high calorific value and good dewatering properties make it favorable for combustion, pyrolysis (Chang *et al.*, 2013), and gasification (Tremelet *et al.*, 2012). The purpose of the carbonization of biomass by using dry or wet pyrolysis is to yield products with higher carbon contents (Libra *et al.*, 2011) and to provide significant benefits for the conversion of biomass which include the lack of an energy extensive drying process, high conversion efficiency and relatively low operation temperature compared to other thermal methods (Liu *et al.*, 2013).

1.5 Research objectives

The objectives of this study are listed as below:

1. To synthesis a low cost biochar from lignocellulosic biomass by hydrothermal carbonization (HTC).
2. To characterize the physical, chemical and physiochemical behavior of the biochar.
3. To expand the application of biochar for the practical amendment of heavy metals contaminated wastewater.
4. To determine the best treatment conditions.
5. To establish the modeling of the treatment process.
6. To study the thermodynamics of the treatment process.

1.6 Scope of the study

This study focused on the hydrothermal preparation of biochar from lignocellulosic biomass for the removal of heavy metal contaminated wastewater. The proposed raw precursor was spent coconut kernel, a food waste abundantly available locally. Hydrothermal preparation method (HTC), an efficient pre-treatment process with high solid yield was applied. The obtained biochar was examined for the practical treatment of Cu(II) metal ions. The effects of treatment conditions, adsorbent dosage, initial concentration and contact time, and pH were evaluated. The modeling and thermodynamics of the adsortion process were elucidated. Additionally, various characterization technique, SEM, FTIR, and nitrogen adsorption-desorption analyzer for the determination of physical, chemical and physio-chemical properties have been adopted.

1.7 The organization of thesis

This thesis is organized by five chapters which each chapter has its own characterization. Chapter 1 is known as introduction, with a highly focused review of the literature, and is normally the prospectus that a comittee approves before the proposal to start research is approved. After the prospectus is approved, some of the review of literature may be moved into Chapter 2, which then becomes part of the proposal to do research. Chapter 1 consists of introduction of the topic chosen, problem statement, the objectives of research and the scope of study. Chapter 2 is the literature review which the purpose of the review is to prove that no one has studied the gap in the knowledge outlined in Chapter 1. The topic in the literature review should have been introduced in the problem statement in Chapter 1.

Chapter 3 discussed the materials and methods to be used in this research. In this chapter, the instruments and the equipments used are also mentioned including the flow chart of research activities. Chapter 4 describes the results and data of the experiments which the results are collected and then processed in response to the problems posed in Chapter 1 of this dissertation. This chapter presents the results of the experiments that were conducted based on the methods described in Chapter 3. The data obtained throughout the experiments were analyzed and interpreted. Summaries of results are generally presented in figures and tables. Typical graphs relating to the experiments was provided in this chapter, and all tables of raw data and complete results relating to the experiments conducted are also shown in Chapter 4. The last chapter of this dissertation is Chapter 5, which is conclusions and recommendations. Conclusion usually includes a comprehensive summary of the findings and it ends with a statement which will lead to the recommendations section. Recommendations are based on the conclusions of the study. Give a detailed description of the suggestion for future action based on the significance of findings. It includes implications for future use of findings and recommendation for future research.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy metals contaminated wastewater

2.1.1 Definition and classification of contaminants

Anthropogenic activities are largely the main responsible for the emission of heavy metals into the nature. Examples of industries related with the release of metals are mining, metallurgy, electroplating, and other surface finishing industries, leather and tanning industries, production of energy and pigment and battery manufacturing (Eduardo and Helena, 2012). Heavy metals are known as elements that have atomic weight between 63.5 and 200.6, with a specific gravity greater than 5.0 (Srivastava and Majumder, 2008). 'Heavy metals' is a general collective term applying to the group with an atomic density greater than 6 g cm^{-3} (O'Connel *et al.*, 2008). The term heavy metal is referred to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations (Renge *et al.*, 2012).

Although it is only a loosely defined term, it is widely recognised and has been applied to the elements such as Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel), Pb (lead) and Zn (zinc) which are commonly associated with pollution and toxicity problems (O'Connel *et al.*, 2008). Among them, heavy metals are element groups on the "heavier" end of the periodic table of elements that have specific weight characteristics (Yu *et al.*, 2014). The existence of metal ions in marine environment has been of great concern because of their toxicity and non-biodegradable nature and some of them are cumulative poisons, capable of being assimilated and stored in the tissues of organisms, causing noticeable adverse physiological effects (Gupta and Ali, 2000; Lagadic *et al.*, 2001; Mohan *et al.*, 2006; Mohan and Singh, 2002). The toxic characteristics of heavy metals are described as follows: (1) the toxicity can resist for a long term in nature, (2) some heavy metals even could be transformed from relevant low toxic species into more toxic forms in a certain environment, mercury in such a case, (3) the bioaccumulation and bioaugmentation of heavy metal by food chain might damage normal physiological activity and threaten human life finally, (4) metals can only be transformed and changed in valence and species, but cannot be degraded by any methods including biotreatment, (5) the toxicity of heavy metals exists even in low concentration (Chen and Wang, 2008).

2.1.2 Environment and health implications

Heavy metals pose a risk to public health because of their toxicity and non-biodegradable nature and widespread occurence in natural and human-altered environments (Inyang *et al.*, 2012). Heavy metals cannot be eliminated during pyrolysis, in contrast to organic compounds. Since they may have a toxic risk potential, the heavy metals fate has to be followed and their possible accumulation in the solid phase, especially if they can affect the food chain and has to be taken into consideration (Libra *et al.*, 2011). Due to the release of large quatities of metal-contaminated wastewater, industries bearing heavy metals such as Cd, Cr, Ni, Cu, As, Pb, and Zn are the most hazardous among the chemical-intesive industries and because of its high solubility in the aquatic environments, heavy metals are able to be absorbed by living organism (Barakat, 2011). To a small extent heavy metals pass through our bodies via food, drinking water and air, however at high concentrations they can lead to poisoning. The poisoning of heavy metals could result, for instance, from drinking-water contamination (eg: lead pipes), high ambient air concentrations near emission sources, or intake via the food chain (Renge *et al.*, 2012). Once they enter the food chain, large heavy metals concentrations may accumulate in the human body (Barakat, 2011). If the metals are ingested over the permitted concentration, they can cause serious health disorders (Babel and Kurniawan, 2004). Potential hazards to human's health would be caused once overtaking or a long period of contact of them. The following symptoms of heavy metal toxicity such as mental confusion, pain in muscles and joints, headaches, short term memory loss, gastrointestinal upsets, food intolerances, vision problems, chronic fatigue, and others (Yu *et al.*, 2014). Some heavy metals are essential trace minerals in the human body, whereas some are non-essential and even can damage to health when consuming in excess amounts more (Yu *et al.*, 2014).

A large number of elements fall into this category, but the ones listed in Table 2.1 are those of relevance in the environmental context (Barakat, 2011). Taking lead poisoning as examples, the nervous system, gastrointestinal system, cardiovascular system, blood production, kidneys, and even reproductive system would be affected (Yu *et al.*, 2014). The build up of nickel in human body will lead to many diseases and disorders that might include lung fibrosis, cardiovascular and kidney disease and increased malignant tumors risks (Denkhaus and Salnikow, 2002). Zinc is known as one of the trace elements that is necessary for human health and it is considered crucial for the physiological functions of living tissue and regulates many biochemical processes, however excessive consume of zinc can lead to eminent health problems, such as stomach cramps, skin irritation, vomiting, nausea and anemia (Oyaro *et al.*, 2007). While many of the heavy metals are essential by plants at the micronutrient level, higher concentrations are said to produce a various of toxic effects (O'Connel *et al.*, 2008). Several past disasters due to the contamination of heavy metals in aquatic streams are Minamata tragey in Japan due to methylmercury contamination and "Itai-Itai" because of the contamination of cadmium in Jintsu river of Japan (Sud *et al.*, 2008). Minamata tragedy was unprecendeted in human history in terms of health damage it caused through environmental pollution and the level of spread and severity in endangering the natural environment, leaving behind adverse effects across the local communities that lasted for protracted time period (Ministry of Environment Japan).

Minamata disease is known to be a toxic nervous disease which caused by eating seafood that has been contaminated with methylmercury compounds that emitted from the Minamata plant of Shin-Nippon Chisso Hiryo and its major symptoms include sensory disturbance, ataxia, concentric constriction of the visual field, and auditory nerves (Ministry of Enviroment Japan). According to Khezami and Capart (2005) chromium presents in the aquatic environment mainly in two forms which are Cr(III) and Cr(IV), where Cr(IV) is known to be more toxicity than Cr(III) and it can affect human physiology, and be accumulated in food chain and cause severe health problems ranging from simple skin irritation to lung carcinoma. Renge *et al.* (2012) stated that heavy metals are hazardous because they tend to bioaccumulate which means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Therefore, the maximum contaminant levels (MCL) for those heavy metals established by USEPA (Babel and Kurniawan, 2003) are summarized in Table 2.1.

Table 2.1: The MCL standards for the most hazardous heavy metals (Babel and Kurniawan, 2003).

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

2.1.3 Copper (II) metal ions, Cu^{2+}

Copper is one of the most widespread heavy metal contaminants in the environment, and known to be very toxic to the living organisms (Pellera *et al.*, 2012). It is an essential micro-nutrient needed by human beings, animals and plants at the low levels, while it turns to be toxic once the permittable have been exceeded (Tong *et al.*, 2011). Copper has been recognized as the most common toxic metals, which finds its way to the water stream from the emerging industries such as electroplating, mining, electrical and electronics, iron and steel production, the non-ferrous metal plants, the printing and photographic factories and metalworking and finishing processes (Mukhopadhyay *et al.*, 2007; Zhu *et al.*, 2008). However, the divalent copper (Cu^2) ions are said to be carcinogenic when they are consumed in excess through ingestion.

The imprudent Cu^{2+} intake may lead to the deposition in liver, subsequent by vomiting, headache, nausea, respiratory problems, abdominal pain, liver and kidney failure and finally gastrointestinal bleeding (Akar *et al.*, 2009). The excessive contents of Cu^{2+} in the fresh water resources and aquatic ecosystem could destroy the oxmo-regulatory mechanism of the aquatic ecosystem to induce mutagenesis in humans (Lee *et al.*, 2010; Shawabkeh *et al.*, 2004). The United State Environmental Protection Agency (USEPA) has suggested the permissible limit for Cu^{2+} as 1.3 mg/L in the industrial effluents (Shawabkeh *et al.*, 2004), while the World Health Organization (WHO) has defined the permissible limit of Cu^{2+} as 1.5mg/L in the drinking water (Kalavathy *et al.*, 2005).

2.1.4 Current treatment technologies

Unlike organic pollutants, metals and their salts are recognized as non-degradable but rather they remain indefinitely in the environment (Eduardo and Helena, 2002) and they can build up in living tissues, causing various diseases and disorders, therefore they must be eliminated before discharge (Wan Ngah and Hanafiah, 2008). Those metals such as copper, mercury, lead, zinc, and arsenic are the most common toxic heavy metals in water system, and the release of heavy metals in the environment is an important matter which poses a different kind of challenge for remediation and due to that, heavy metals contaminated wastewater needs to be pretreated (Wang *et al.*, 2012; Pang *et al.*, 2013; Zolfaghari *et al.*, 2013). Faced with more and more strict and rigid regulations, nowadays heavy metals are the environmental priority contaminants and are becoming one of the most critical environmental problems (Fu and Wang, 2011).

Many methods have been emerged to address these rigid environmental regulations which necessitate removal of heavy metal compounds from wastewater (Inyang *et al.*, 2012). Physicochemical technologies, such as chemical precipitaion, ion-exchange, adsorption, membrane filtration, flotation and electrochemical technologies have been used to treat wastewater containing heavy metals (Eduardo and Helena, 2002). Chemical precipitation is widely used for heavy metal remedy from inorganic effluent and this process involves hydroxide precipitation and sulfide precipitation (Fu and Wang, 2011). The most widely used chemical precipitation technique is hydroxide precipitation because of its relatively simplicity, low cost and ease of pH control (Huisman *et al.*, 2006). In precipitation process, chemicals react