ADSORPTION OF COPPER(II) AND NICKEL(II) IONS ONTO CHEMICALLY TREATED CANDLENUT SHELL

by

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LIST OF ABBREVIATIONS AND SYMBOLS

$1/n$	Adsorption intensity/heterogeneity factor
ΔG^{o}	Gibbs free energy (kJ mol^{-1})
ΔH^{o}	Enthalpy change (kJ mol^{-1})
ΔS^{o}	Entropy change (J mol^{-1} K^{-1})
AAS	Atomic Absorption Spectrometry
C_e	Equilibrium concentration in milligram per liter (mg L^{-1})
C_o	Initial metal ions concentration in milligram per liter (mg L^{-1})
D-R	Dubinin-Radushkevich isotherm
E	Mean energy of adsorption in kilojoule per mole (kJ mol^{-1})
EDX	Energy Dispersive X-ray spectroscopy
ε	Polanyi constant
FTIR	Fourier Transform-Infrared
h	Initial adsorption rate in milligram per gram per minute (mg g^{-1} min^{-1})
k_1	First-order kinetic constant In one per minute (min^{-1})
k_2	Second-order kinetic constant in gram per milligram per minute (g mg^{-1} min^{-1})
K_F	Adsorption capacity in milligram per gram (mg g^{-1})
K_L	Langmuir equilibrium constant in liter per milligram (L mg^{-1})
pH_{zpc}	pH zero point of charge
q_e	Adsorption capacity at equilibrium in milligram per gram (mg g^{-1})
$q_{e\ cal}$	Calculated equilibrium adsorption capacity in milligram per liter (mg g^{-1})
$q_{e\ exp}$	Experimental equilibrium adsorption capacity in milligram per gram (mg g^{-1})
q_{exp}	Experimental adsorption capacity in milligram per gram (mg g^{-1})
Q_e	Amount adsorbed at equilibrium in mole per gram (mol g^{-1})
q_m	Maximum monolayer adsorption capacity in milligram per gram (mg g^{-1})
Q_m	Maximum adsorption capacity in mole per gram (mol g^{-1})
q_t	Adsorption capacity at time t in milligram per gram (mg g^{-1})
R	Gas constant in kilojoule per mole (kJ mol^{-1} K^{-1})
R_L	Separation factor (unitless)
R^2	Correlation coefficient

RCS	Raw candlebutshell
SEM	Scanning Electron Microscopy
T	Adsolute temperature in Kelvin (K)
TCS	Treated candlenutshell
TOC	Total organic Carbon (TOC)
V	Volume of the metal ions solution in liter (L)
W	Weight of TCS in gram (g)

PENJERAPAN ION KUPRUM(II) DAN NIKEL(II) DENGAN KULIT BUAH KERAS TERAWAT KIMIA

ABSTRAK

Kulit buah keras daripada industri makanan telah dirawat dengan pelbagai jenis bahan kimia untuk mengkaji potensi dan prestasinya sebagai penjerap bagi penyingkiran ion Cu^{2+} dan Ni^{2+} dalam larutan akueus. Penjerap kulit buah keras terawat (TCS) telah dikaji dengan analisis COD, TOC, pH_{zpc}, FTIR, SEM-EDX, luas permukaan, size dan isipadu liang pada untuk tujuan pencirian. Tiga penjerap terbaik iaitu TCS – NaOH (TOC 3.928 g L^{-1}; kapasiti penjerapan, q_m 13.63 mg g^{-1} bagi ion Cu^{2+}), TCS – HCHO (TOC 4.173 g L^{-1}; kapasiti penjerapan, q_m 9.55 mg g^{-1} bagi ion Cu^{2+}) dan TCS – K_2HPO_4 (TOC 3.871 g L^{-1}; kapasiti penjerapan, q_m 8.94 mg g^{-1} bagi ion Cu^{2+}) yang mempunyai larut lesap organik yang rendah selepas perawatan kimia dan kapasiti penjerapan tinggi yang dianggari daripada isoterma penjerapan Langmuir telah dipilih daripada lapan penjerap TCS. Eksperimen penjerapan berkelompok telah dijalankan ke atas ketiga-tiga penjerap TCS terbaik ini bagi mengkaji kesan pH awalan, masa sentuhan, kepekatan ion logam awal dan suhu. Hasil kajian menunjukkan bahawa pH awalan optima untuk penjerapan Cu^{2+} dan Ni^{2+} adalah masing-masing pada pH 5.5 dan pH 6.0. Kapasiti penjerapan maksimum terhadap kedua-dua ion logam telah dicapai selepas dua jam. Data penjerapan pada keseimbangan lebih padan kepada model kinetik tertib pseudo-kedua yang menunjukkan penjerapan kimia adalah penyumbang utama dalam langkah penentuan kadar untuk proses penjerapan. Empat jenis isoterma penjerapan iaitu Langmuir, Freundlich, Dubinin-Radushkevich (D-R) dan Sips telah digunakan untuk menganalisis data keseimbangan. Ketiga-tiga penjerap TCS menunjukkan afiniti yang lebih baik terhadap ion Cu^{2+} berbanding dengan ion Ni^{2+}. Antara ketiga-tiga penjerap TCS ini, TCS – NaOH menunjukkan prestasi penjerapan yang lebih baik ke atas ion Cu^{2+} (kapasiti penjerapan, q_m 19.72 mg g^{-1}) dan ion Ni^{2+} (kapasiti penjerapan, q_m 19.72 mg g^{-1}) pada suhu 323K.. Parameter termodinamik seperti tenaga bebas Gibbs (ΔG^o), entalpi (ΔH^o), dan entropi (ΔS^o) telah ditentukan melalui plot Van Hoff dan keputusan menunjukkan bahawa penjerapan ion Cu^{2+} dan Ni^{2+} ke atas penjerap TCS adalah spontan (nilai ΔG^o dalam -20 to -80 KJ mol^{-1}), endotermik (positif nilai ΔH^o) dan melibatkan penjerapan fizikal dan penjerapan kimia. Analisis FTIR menunjukkan bahawa kumpulan berfungsi yang terlibat dalam penjerapan kedua-dua ion logam ini adalah kumpulan hidroksil, karbonil, dan amino. Pertukaran ion dicadangkan sebagai mekanisme utama dalam penjerapan ion logam ini ke atas penjerap TCS.

ADSORPTION OF COPPER(II) AND NICKEL(II) IONS ONTO CHEMICALLY TREATED CANDLENUT SHELL

ABSTRACT

The candlenut shell from food industry was treated with different types of chemicals to evaluate their potential and performance adsorbents in the removal of Cu^{2+} and Ni^{2+} metal ions in aqueous solution. Treated candlenut shell (TCS) adsorbents were subjected to COD, TOC, pH_{zpc}, FTIR, SEM-EDX, surface area, surface pore size and pore volume analysis for characterization purpose. The best three TCS adsorbents, namely TCS – NaOH (TOC 3.928 g L^{-1}; adsorption capacity, q_m 13.63 mg g^{-1} of Cu^{2+} ions), TCS – HCHO (TOC 4.173 g L^{-1}; adsorption capacity, q_m 9.55 mg g^{-1} of Cu^{2+} ions) and TCS – K_2HPO_4 (TOC 3.871 g L^{-1}; adsorption capacity, q_m 8.94 mg g^{-1} of Cu^{2+} ions) in terms of lower organic leaching after the chemical treatment as well as higher adsorption capacities estimated from Langmuir isotherm model were selected from the eight TCS adsorbents produced. Batch adsorption studies were conducted on these three best TCS adsorbents to investigate the effect of initial pH, contact time, initial metal ion concentration and temperature. Results obtained showed that the optimum initial pH for the adsorption of Cu^{2+} and Ni^{2+} ions were at pH 5.5 and pH 6.0, respectively. The maximum adsorption capacity was achieved after 2 hours for both of the metal ions studied. The adsorption equilibrium data were fitted better with pseudo-second order kinetic model indicating that chemisorption was predominant in the rate limiting step of the adsorption process. The data were then fitted with four isotherm models namely Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Sips to analyze the equilibrium data. The three TCS adsorbents showed better affinity towards Cu^{2+} ions than Ni^{2+} ions. Among these three best TCS adsorbents, TCS – NaOH showed better adsorption performance with highest adsorption capacities on Cu^{2+} (adsorption capacity, q_m 19.72 mg g^{-1}) and Ni^{2+} ions (adsorption capacity, q_m 19.72 mg g^{-1}) at temperature 323K. Thermodynamic parameters such as Gibbs free energy (ΔG^{o}), enthalpy (ΔH^{o}) and entropy (ΔS^{o}) were determined via Van Hoff plots and the results obtained showed that the adsorption of Cu^{2+} and Ni^{2+} ions onto TCS adsorbents were spontaneous (ΔG^{o} at a range of -20 to -80 KJ mol^{-1}), endothermic (positive ΔH^{o} values) in nature and governed by both physisorption and chemisorption. FTIR analysis indicated the main functional groups involved in these two metal ions adsorption were hydroxyl, carbonyl and amino groups. Ion exchange was suggested as the main mechanism in the adsorption of these metal ions onto TCS adsorbents.

CHAPTER 1

INTRODUCTION

1.1 Water pollution

As a result of industrialization and urbanization, the presence of heavy metal ions in water streams has readily increased in the last 50 years. Heavy metals are nowadays among the most prevailing pollutants in surface and ground water in view of their bio-magnification, persistence and toxicity (Kadirvelu et al. 2001; Ricordel et al., 2001). Heavy metal contamination exists in wastewater of various industries, such as metal plating and cleaning, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries, storage batteries manufacture, agricultural activities, as well as municipal wastewater disposal (Demirbas, 2008; Imamoglu & Tekir, 2008; Javaid et al., 2011; Wan Ngah & Hanafiah, 2008;). Heavy metals get distinguished from other toxic pollutants, due to their non-biodegradability and can accumulate in living tissues, thus becoming concentrated throughout the food chain and can be readily absorbed into the human body. Study shows even a trace amount of heavy metals can cause serious physiological or neurological damages to the human body (Mohan & Sreelakshmi, 2008).

In Malaysia, the major sources of heavy metals contamination are industries dealing in electroplating, etching, electronics, batteries and metal treatment, which are usually located in the western coast of the Peninsular Malaysia such as Klang Valley, Malacca, Johor Bahru, and Penang areas (Noor Azhar et al., 2007; Onundi et al., 2010).

1.2 Heavy metals

Generally, heavy metals is a term applied to the group of metals and metalloids with an atomic density greater than 6 g cm^{-3} or atomic weight greater than sodium (Na), such as cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) which are usually related with environmental pollution and toxicity problems (Duffus, 2002; Keane, 1998). Heavy metals cannot be degraded or destroyed. Some heavy metals such as Cu and Zn are essential to maintain the metabolism of the human body in trace amounts. However, they can lead to poisoning at higher concentrations. Cu and Ni were selected in this study because both are widely used especially in electroplating industry (Ghaee et al., 2012; Kleinubing et al., 2012; Kumar et al., 2010).

1.2.1 Copper

The first element in Group IB in the periodic table, copper (Cu) has an atomic number of 29, atomic weight of 63.54, and valences of +1 and +2. The average abundance of Cu in the earth's crust is 68 ppm; in soils is 9 to 33 ppm; in streams is 4 to 12 ppb; and in groundwater is less than 0.1 ppm. Cu is commonly occurs in its native state as the free metal and in various minerals as compounds such as those containing sulfides (e.g., chalcopyrite, CuS.FeS), oxides (e.g., cuprite, Cu_2O), and carbonates (e.g., malachite, $Cu_2CO_3(OH)_2$). Most cupric Cu^{2+} salts dissolve readily in water to form an aquo complex $Cu(H_2O)_4^{2+}$, and the water molecules can then be replaced by various organic and inorganic ligands in forming different complexes (Clesceri et al., 1998). Cu is found in all living organisms in the oxidized Cu(I) and Cu(II) states as an essential trace metal for the human diet. It is required for survival serving as a significant catalytic cofactor in redox chemistry for proteins that perform fundamental biological functions needed for growth and development. The main sources of Cu are seeds, grains, nuts, and beans and the recommended intakes of Cu by a human adult, is 0.6 to 1.6 mg per day (Tapiero et al., 2003; Theophanides & Anastassopoulou, 2002). Excessive intake of Cu by humans can cause serious toxicological concerns as it can be deposited in the brain, skin, liver and pancreas. It will then cause nausea, vomiting, headache, kidney and liver damage, hair loss, insomnia, hypoglycemia, increase heart rate, widespread capillary damage and central nervous system irritation followed by depression (Benaissa & Elouchdi, 2007; Kuniarwan et al., 2006; Rozaini et al., 2010).

Cu is one of the most common heavy metal contaminants in the environment. It is usually found in wastewaters from various industries such as metal plating, engine manufacturing, alloy manufacturing, batteries, petroleum refining, mining and smelting (Demirbas et al., 2009; Ghaee et al., 2012; Kleinubing et al., 2012; Kumar et al., 2010). The limitation of Cu in industrial effluent in catchment area and inland water have been fixed to 0.20 mg L^{-1} and 1.0 mg L^{-1}, respectively by Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations in Environmental Quality Act (Department of Environment–DOE, 1979). Furthermore, the maximum concentration for Cu in drinking water regulated by Engineering Services Division, Ministry of Health Malaysia by referring to WHO Drinking Water Guideline, 2008 is 1.0 mg L^{-1}.

1.2.2 Nickel

Nickel (Ni) is the third element in Group VIII in the periodic table with an atomic number of 28 and atomic weight of 58.69. Ni can exist in the oxidation states ranging from +1 to +4, dominated by the +2 (nickelous) state. The average abundance of Ni in the earth's crust is 1.2 ppm; in soils is 2.5 ppm; in streams is 1 ppb; and in groundwater is less than 0.1 ppm. Ni is obtained mainly from pentlandite ($(FeNi)_9S_8$) and garnierite ($(NiMg)_6Si_4O_{10}(OH)_8$). Ni^{2+} is the most common aqueous species. Insoluble sulfides can be formed in reducing conditions, while Ni complexes with hydroxide, carbonates, phosphates, halides and organic ligands can be formed in aerobic conditions (Clesceri et al., 1998).

Studies identify that Ni is a potential essential trace element for plants and animals. However, Ni compounds show toxic effects to organisms too, especially at high concentrations. Ni intake occurs through inhalation, ingestion and dermal adsorption (Denkhaus & Salnikow, 2002; Schaumlöffel, 2012). The estimated body burden of a healthy non-exposed adult is about 7.3 g Ni/kg body weight. High Ni intake can lead to birth defects, embolism, chronic bronchitis, several lung, cardiovascular and kidney diseases, the most serious concern is Ni has carcinogenic potential (Denkhaus & Salnikow, 2003; Futalan et al., 2011; Kasprzak et al., 2003; Schaumlöffel, 2012).

Ni is extensively used in industries such as mining, refining, alloy production, electroplating, welding, metal coating, battery production, catalysts, manufacturing of sulphate and porcelain enamelling (Kasprzak et al., 2003; Malamis & Katzou, 2013; Schaumlöffel, 2012). Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations in Environmental Quality Act (Department of Environment–DOE, 1979) has set the limitation for Ni in industrial effluent in catchment area and inland water to 0.20 mg L^{-1} and 1.0 mg L^{-1}, respectively. By referring to WHO Drinking Water Guideline, the Engineering Services Division, Ministry of Health Malaysia stated that the maximum acceptable concentration for Ni in drinking water is 0.02 mg L^{-1}.

1.3 Technologies used to remove heavy metals from wastewater

Till recent years, heavy metals are still being used widely in various industries due to their technological significance. The treatment of heavy metals is of distinctive concern due to their recalcitrance and persistence in the environment. Numerous methods for heavy metals removal from wastewater has been studied extensively in recent years.

Chemical precipitation is the most widely applied method to remove heavy metals from wastewater because it is relatively simple and inexpensive (Djedidi et al., 2009; Ku & Jung, 2001). Generally, chemical precipitation process involves adding chemicals such as hydroxide (OH^-), sulfide (S^{2-}), or synthesized chelator with heavy metal ions to form insoluble precipitates (Matlock et al., 2002; Mirbagher & Hosseini, 2004; Özverdi & Erdem, 2006). The precipitates formed will then be separated from water by sedimentation or filtration. However, chemical precipitation is usually applied in treating wastewater containing high concentration of heavy metal ions and it is ineffective when the concentration of heavy metal ions is low. In addition, chemical precipitation can generate large quantity of sludge to be treated with great difficulties (Fu & Wang, 2011).

The application of ion exchange process on the removal of heavy metals from wastewater has been widely studied due to their various advantages, such as high treatment capacity, high removal efficiency, and fast kinetic rates (Kang et al., 2004). Synthetic or natural solid ion-exchange resin, has the specific ability to exchange its cations with the metal ions in the wastewater. Strongly acidic resins with sulfonic acid groups (–SOH) and weekly acidic resins with carboxylic acid groups (–COOH) are the most common cation exchangers used. However, chemical reagents must be used to regenerate the exhausted ion exchange resin and the regeneration can result in serious secondary pollution. Also, they cannot be used at large scale especially when treating a large amount of wastewater with low concentration of heavy metal ions because of the relatively high cost (Fu & Wang, 2011).

Other methods that have been extensively used in removing heavy metal ions from wastewater are coagulation-flocculation, flotation, membrane filtration and electrochemical treatment. However, most of these methods have several limitations and disadvantages, such as high initial capital, maintainence and operation costs, chemical consumption, ineffective at low concentration of heavy metal ions and produce toxic sludge or secondary waste during the process (O'Connel et al., 2008).

1.4 Adsorption

In 1881, Kayser used the term "adsorption" to explain the condensation of gases on surfaces to differentiate the term of gas absorption in which gas molecules penetrate the bulk phase of the absorbing solid. Adsorption is a mass transfer process at which implies the presence of an "adsorbent" solid that binds molecules (the adsorbates) from the liquid phase on it's surface by physical attractive forces, ion exchange, or chemical binding (Dermibas, 2008; Kurniawan et al., 2006).

Adsorption can be categorised into physical adsorption (physisorption) or chemical adsorption (chemisorption) depending on the types of forces of interaction between the adsorbate and the adsorbent. Physisorption is relatively non-specific and is due to the operation of weak forces such as Van der Waals forces between adsorbate and adsorbent. Meanwhile, chemisorption involves a chemical reaction either in covalent or ionic binding with functional groups on certain sites of the adsorbent (Berger & Bhown, 2011; Xiong et al., 2011).

The most important distinguishing features between physisorption and chemisorption can be summarised by the following factors (Rouquerol, 1999):

i) Physisorption is a common phenomenon with a relatively low degree of specificity, whereas chemisorptions is specific and it depends on the reactivity of the adsorbent and adsorbate.

ii) Generally, physisorption occurs as a multilayer at relatively high pressure. Chemisorbed adsorbates are linked to reactive parts on the surface of the adsorbent, thus, the adsorption is necessarily confined to a monolayer.

iii) A physisorbed molecule keeps its identity and returns to the fluid phase in its original form by desorption, whereas a chemisorbed molecule undergoes reaction or dissociation, it loses its identity and cannot be recovered by desorption.

iv) Physisorption is always exothermic, the energy involved is usually not much larger than the energy of condensation of the adsorptive. However, it is appreciably enhanced when physisorption takes place in very narrow pores. The energy of chemisorption is the same order of magnitude as the energy change in a similar chemical reaction.

v) Generally, physisorption systems achieve equilibrium relatively more rapid, but equilibration may be slow if the transport process is rate-determining. Chemisorption often involves an activation energy as the system may not have adequate thermal energy to reach thermodynamic equilibrium at low temperature.

1.4.1 Adsorption Isotherm

Proper analysis and design of adsorption separation processes require relevant equilibrium data as one of the important information. In equilibrium, a certain relationship prevails between adsorbate concentration in the solution and adsorbed state, for example, the amount of adsorbate adsorbed per unit mass of adsorbent are a function of temperature. This adsorption equilibrium relationship at a given temperature is referred as adsorption isotherm. Adsorption isotherm gives important information about how the adsorbate molecules distribute between the liquid phase as well as solid phase when reaching the equilibrium state. Several adsorption isotherm models which were first applied for gas phase adsorption are available after adopted to correlate with adsorption equilibria in heavy metal ions adsorption (Febrianto et al, 2009; Wan Ngah & Fatinathan, 2010). Freundlich and Langmuir are the most commonly used among all isotherm models (Anirudhan & Suchithra, 2008; Azouaou et al., 2010; Escudero et al., 2008; Febrianto et al., 2009; Jadhav, 2011; Wang & Qin, 2005).

1.4.1(a) Freundlich isotherm

In 1906, the earliest known sorption isotherm equation was presented by Freundlich. Freundlich isotherm is an empirical isotherm model used for adsorption on heterogeneous surfaces or surfaces supporting sites of vary affinities. It describes multilayer coverage of adsorbent by the solutes and assumes that different adsorption sites involve different adsorption energies (Escudero et al., 2008; Fenriatnto et al., 2009; Ho et al. 2002; Ho et al., 2005; Jadhav, 2011). Freundlich equation is written in the following form:

$$q_e = K_F C_e^{1/n} \tag{1.1}$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentrations (mg L^{-1}), K_F is the adsorption capacity ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) when the metal equilibrium concentration equal to 1.00 mg L^{-1} and *1/n* is the adsorption intensity, which varies with the heterogeneity of the adsorbent. Commonly, a favourable adsorption tends to have Freundlich constant, n between 1 and 10 or *1/n* between 0.1 and 1. Larger value of *n* or smaller value of *1/n* implies stronger interaction between adsorbent (chemisorption) and heavy metal ions while *1/n* equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites (physisorption) (Al-Degs et al., 2006; Febrianto et al., 2009; Foo & Hameed, 2010; Site, 2001).

1.4.1(b) Langmuir isotherm

Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. This isotherm based on assumptions that adsorption is limited to monolayer coverage at which the adsorbed layer is only as thick as one molecule, all adsorption sites are energetically identical and can only accommodate one adsorbed atom and the capability of a molecule to be adsorbed on a given site is independent of its neighbour sites occupancy (Akhtar et al., 2006; Febrianto et al., 2009; Foo & Hameed, 2010; Ho et al., 2002; Li and Bai, 2006). The Langmuir equation can be written in the following form:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{1.2}$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentrations (mg L^{-1}), q_{max} is the monolayer adsorption capacity (mg g^{-1}) and K_L is the equilibrium constant (L mg^{-1}). The Langmuir isotherm model used to estimate the maximum adsorption capacity values which could not be reached experimentally. The value of K_L constant represents the affinity between the adsorbate and adsorbent, where a higher value of K_L reflects in the steeper initial slope of the adsorption isotherm, indicating desirable high affinity for the adsorbent to bind on the binding sites on the adsorbent surface (Guibal et al., 1999; Vijayaraghavan et al., 2006).

To determine whether the adsorption process is favorable or unfavorable, the essential characteristics of the Langmuir equation can be expressed in term of R_L, a dimensionless separation factor, defined as follows:

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{1.3}$$

where C_0 (mg L^{-1}) is the initial concentration of the metal ions solution. The values of R_L define the favourability of the adsorption systems studied towards Langmuir isotherm model at which the adsorption system is irreversible when $R_L = 0$, favorable when R_L lies between 0 and 1, linear when $R_L = 1$ or unfavorable when R_L is more than 1 (Azouaou et al., 2010; Hameed et al., 2007).

1.4.1(c) Sips isotherm

In 1948, Sips proposed an expression which is the combination of both Langmuir and Freundlich isotherms to avoid the problem of continuing increase in the adsorbed amount with a rising concentration as observed for Freundlich model. Therefore, it is also known as Langmuir-Freundlich isotherm. Sips isotherm equation is usually used to confirm the heterogeneity of an adsorbent and is express as follow:

$$q_e = \frac{q_m (bC_e)^{\frac{1}{n}}}{1+(bC_e)^{\frac{1}{n}}} \qquad (1.4)$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentrations (mg L^{-1}), q_m is the adsorption capacity (mg g^{-1}), b is the median association constant and $1/n$ is the heterogeneity factor indicating that the adsorbent has heterogeneous binding sites when $1/n$ is less than 1, while the adsorbent is homogeneous adsorbent when $1/n$ is closer or even to 1 (Vijayaraghavan et al., 2006).

1.4.1(d) Dubinin-Radushkevich (D-R) isotherm

The adsorption mechanism is expressed by estimating the characteristic porosity and the Gaussian energy distribution onto a heterogeneous surface by applying D-R isotherm (Foo & Hameed, 2010, Sheha & Metwally, 2007). The D-R isotherm equation can be written as follows:

$$Q_e = Q_m \exp(-K\varepsilon^2) \qquad (1.5)$$

where Q_e (mol g^{-1}) is the amount of metal ions adsorbed per unit mass of adsorbent, Q_m (mol g^{-1}) is the maximum adsorption capacity, K is the D-R constant (mol kJ^{-1}) used to calculate the adsorption energy, and ε is the Polanyi potential that can be estimated as follows:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \qquad (1.6)$$

where R is the gas constant (J^{-1} mol^{-1} K^{-1}), T is the absolute temperature (Kelvin) and C_e (mol L^{-1})is the equilibrium concentration of metal ions in the solution.

The K (mol^2 kJ^{-2}) is a constant used to calculate the mean energy adsorption, E (kJ mol^{-1}). E is the mean energy adsorption when 1 mol of ions is transferred to the surface of the adsorbent from infinity in the metal ions solution (Sheha & Metwally, 2007). It is defined by the following equation:

$$E = \frac{1}{\sqrt{2K}} \qquad (1.7)$$

The adsorption process is referred as ion exchange process if the value of E obtained lies between 8 and 16 kJ mol^{-1}. However, the adsorption process is defined as physical in nature if $E < 8$ kJ mol^{-1} (Anirudhan & Suchithra, 2008; Azouaou et al., 2010; Sheha & Metwally, 2007; Vijayaraghavan et al., 2006; Wan Ngah & Hanafiah, 2008).

1.4.1 Adsorption kinetics

Large adsorption capacity and fast adsorption rate are the main requirements of a good adsorbent for wastewater treatment. Hence, the adsorption rate is another vital factor to be taken into account in adsorption studies. Adsorption kinetics is defined as the adsorbate removal rate that controls the residence time of the adsorbate in the solid-solution interface. Modelling of experimental kinetic data gives information to compare among different adsorbents under different operational conditions for the removal of pollutant from the wastewater system. Therefore, it is the fundamental for the industrial application of adsorption. The rate of adsorption onto adsorbent surface depends on several parameters such as: initial concentration of the adsorbate, structural properties of the adsorbent, and the interaction between the adsorbate and the active sites of the adsorbent. The pseudo-first-order kinetic model (Lagergren model) and pseudo-second-order kinetic model (Ho and McKay model) are two kinetic models that have been widely applied in the adsorption studies (Elangovan et al., 2008; Febrianto et al., 2009; Jadhav, 2011).

1.4.2(a) The pseudo-first-order kinetic model

In 1898, a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal was presented by Lagergren, this kinetic model is trusted to be the earliest model used to relate the adsorption rate based on the adsorption capacity (Qiu et al., 2009). Generally, the pseudo-first-order kinetic equation is defined as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (1.8)$$

where q_e and q_t are the adsorption capacity (mg g^{-1}) at equilibrium and at time t, respectively. k_1 is the equilibrium rate constant of pseudo first-order adsorption (L min^{-1})., The calculated q_e are not equal to the experimental q_e, indicates that the pseudo-first-order model is unable to fit the kinetics of heavy metal ions adsorption data as the calculated q_e values are lower than that of the experimental q_e values causing the disagreement occurs for most systems. This is mostly caused by the occurance of boundary layer or external resistance that control at the beginning of the adsorption process. However, this model is still widely applied to data modeling, though no adsorption mechanisms are available (Febrianto et al., 2009).

1.4.2(b) The pseudo-second-order kinetic model

In 1995, Ho derived another rate equation which was then named as pseudo-second-order rate equation. The equation is defined as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{1}{q_e} t \qquad (1.9)$$

where q_e and q_t are the adsorption capacity (mg g^{-1}) at equilibrium and at time t, respectively. k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The correlation coefficients obtained were higher than 0.98 in most adsorption systems. Furthermore, the estimated q_e values correlated very well with the experimental q_e values. By comparing it to pseudo-first-order kinetic model, this model is believed to be more suitable to represent the kinetic data in adsorption systems at which the rate limiting step in the adsorption of heavy metal ions are chemisorption that involves valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate. This equation has been successfully applied to study the adsorption kinetics of various pollutants such as dyes, metal ions, oils, herbicides, and organic substances from aqueous solutions (Febrianto et al., 2009; Qiu et al., 2009; Wan Ngah & Hanafiah, 2008).

1.4.3 Thermodynamic parameters of adsorption

Since K_L from Langmuir isotherm model is an equilibrium constant, it can be changed with temperature and thus gives valuable information about the thermodynamic parameters, such as changes in the Gibbs free energy (ΔG°), enthalpy energy (ΔH°) and entropy energy(ΔS°) associated to the adsorption processes (Azouaou et al., 2010; Şölener et al., 2008; Wan Ngah & Hanafiah, 2008). These thermodynamic parameters can be estimated by using following equations:

$$\Delta G^{\circ} = -RT \ln K_L \qquad (1.10)$$

$$\ln K_L = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (1.11)$$

where R is the universal gas constant, 8.3145 J mol^{-1} K^{-1}, and T is the absolute temperature in K.

1.4.4 Alternative low-cost adsorbents

Adsorption is defined as a better technology in removing heavy metal ions from wastewater due to its simplicity and high efficiency even at a low concentration of heavy metal ions. Activated carbon (AC) is a well-known adsorbent used and accepted to be the best adsorbent effective for the treatment of heavy metal ions from wastewater. However, due to its relatively high price and the cost associated with the regeneration as a result of high-degree of losses in real process, the application of AC is infeasible (Fu & Wang, 2011; Park et al., 2006). Consequently, treatment of heavy metal ions with agricultural waste and its industrial by-products has been widely explored due to its low cost and the abundance of agricultural-related materials such as peanut skins, plant wastes and nut shells (Demirbas, 2008). An adsorbent can be categorized as a low-cost adsorbent if it is abundantly available in nature or a byproduct of waste material from waste industry which requires little processing steps (Bailey et al., 1999). In addition, these low-cost adsorbents are usually containing lignin and cellulose as major constituents. Other polar functional groups such as alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups that are able to form complexes with the metal ions by donating the electron pairs in solution may also contained in these adsorbents (Demirbas, 2008). As a result, adsorbents derived from low-cost agricultural wastes can be utilized as an alternative path in the treatment or recovery heavy metal ions from wastewater at the same time solving environmental problems.

1.4.5 Candlenut shell and its applications

The candlenut (*Aleurites moluccana*), is a native tree from the family of Euphorbiaceae (Figure 1.1), also known as "Kemiri" in Indonesia, "Buah keras" in Malaysia, "candleberry", "Indian walnut", "Varnish tree" or "Kukui nut tree". The tree is indigenous to Malaysia, Indonesia, Hawaii, and other tropical countries. The nut has an oval-like shape, 4-6 cm in diameter, off-white in colour; the seed inside has a very hard seed coat with 60 % oil content and burns easily with a smoky flame, which allows it to be used as a candle, indicated by its name. The nut is often used in Indonesia and Malaysia cuisines, as curry pastes, and as meat tenderizer. Several parts of the plant have been used in traditional medicine in treating tumors and several diseases. The oil extracted from the candlenut can be used for industrial purpose such as the production of paint, resin, soap, medicine and also for cosmetics (Nik Norulaini et al., 2004; Seedman, 1992; Siddique et al., 2011).

Recent study on the chemical composition and antioxidant properties of candlenut oil extracted by supercritical carbon dioxide, CO_2 (Nik Norulaini et al., 2004; Siddique et al., 2011), biodiesel production from candlenut oil (Martín et al., 2010; Sulistyo et al., 2008), and evaluation of candlenut oil for controlling termites (Nakayama & Osbrink, 2010) have been reported. They concluded that the candlenut oil could be an acceptable substitute for high stearic, linoleic, and oleic oils. Also, the oil can be used in both food and industrial applications to meet the current growing needs for edible oils as well as being a potential alternative for renewable energy sources.

Figure 1.1 Candlenut tree (Photo downloaded from National Library of Medicine, http://www.nlm.nih.gov/nativevoices/exhibition/healing-ways/medicine-ways/healing-plants/images/ob1687.html).

Typically, the candlenuts (Figure 1.2) are mechanically cracked and the oil-rich kernel is manually separated from the shells (Figure 1.3), resulting in the accumulation of over 1 kg of nutshells for every 1L of biodiesel produced (Klein et al., 2010). Presently, the abundance of agricultural wastes (agro-wastes) in Malaysia poses serious impacts to both environment and society. Every year, five million tons of agro-wastes are estimated to be produced in Malaysia (Pang et al., 2006). Agro-wastes are usually disposed by dumpling in the landfill or open burning which will cause the existing air pollution to be worsen. Agro-wastes are not categorized as hazardous materials, but they create a huge amount of waste substances (Kuan & Liong, 2008). Thus, agro-wastes processing to be value added products like being utilized as an alternative adsorbent to remove heavy metal ions in wastewater is helping to minimize these disposal problems. Most of the literatures reported the use of the nut from candlenut as mentioned above. However, there are not many details on the usage of the candlenut shell which posed as a waste. Candlenut shell is widely available in Malaysia and Indonesia presenting a disposal problem with no economic value. Production of activated carbon from candlenut shell by CO_2 activation and accelerated solvent extraction of lignin from candlenut shell were studied by Turmuzi et al. (2003) and Klein et al. (2010), respectively. The resulting lignin extracted from candlenut shells was found containing high hydroxyl and phenolic hydroxyl groups (Klein et al., 2010). The urge of using the candlenut shells as the adsorbent in removing heavy metal ions in this study is due to its sustainability, carbon neutral and potential to decrease the production cost.

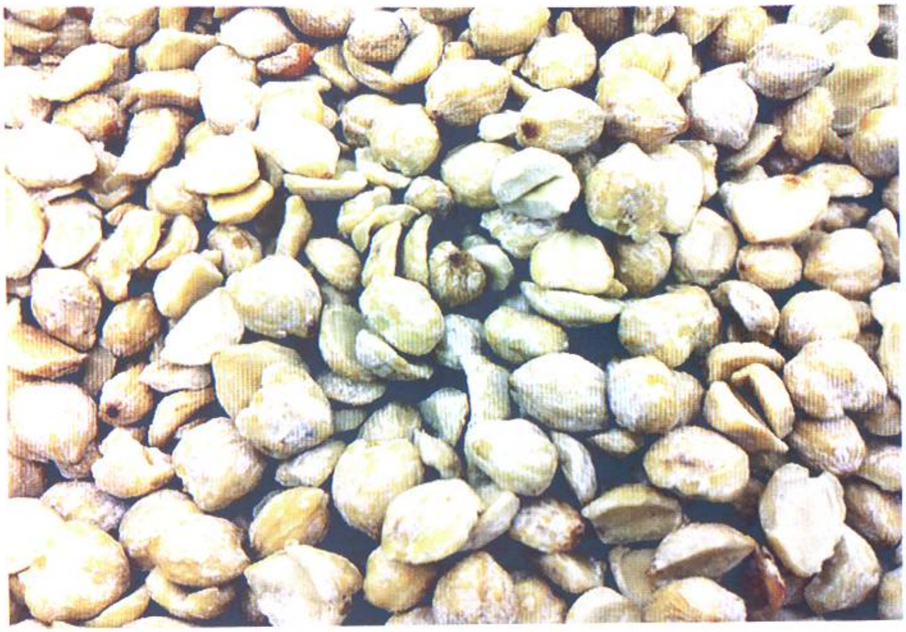

Figure 1.2 The raw candlenuts (Photo taken in Tesco Hypermarket on March 2013).

Figure 1.3 The raw candlenut shells.

1.4.6 Chemical Modification of Adsorbents

The use of agro-wastes as adsorbents in removing heavy metals from wastewaters was extensively studied in recent years due to various advantages such as the simplicity of the wastewater treatment process requiring a few processing steps and freely available with very low cost. Most of the adsorption studies were focused on untreated or unmodified agro-wastes such as tea waste and coffee, hazelnut shells, and different bark samples (Demirbas, 2008). Nevertheless, the use of agro-wastes as adsorbents potentially will incur certain problems such as high chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC) due to the release and leaching of soluble organic compounds contained in the agro-wastes. Also, it can be observed that the solution mixture after adsorption changed to a yellowish, greenish or brownish colour. Such an increase of soluble organic contamination can cause secondary pollution retarding the adsorption technology in water and wastewater treatment at the same time causing the depletion of oxygen content in water and can threaten the aquatic life (Chen & Yang, 2005; Gaballah & Kilbertus, 1998; Wan Ngah & Hanafiah, 2007). Therefore, chemical treatment or modification to the raw adsorbents is needed before the application for the decontamination of heavy metal ions to reduce organic leaching of adsorbents during adsorption by extracting soluble organic compounds from the adsorbents, at the same time, enhance the adsorption efficiency.

There are two common methods applied for chemical treatment on adsorbents: encapsulation or entrapment and surface modification. For encapsulation, various supporting materials such as poly(vinyl alcohol), collagen fiber, and alginate are often used as immobilization matrixes to encapsulate the adsorbents to prevent the organic leaching . However, the mass transfer is usually reduced. The surface of raw adsorbents was modified by using acids such as hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid, orthophosphoric acid; alkalis such as sodium hydroxide, potassium hydroxide, calcium hydroxide, aluminium hydroxide, sodium carbonate; organic compounds such as ethylenediamine, formaldehyde, methanol; oxidizing agent such as hydrogen peroxide to remove soluble organic compounds, eliminate colouration of the aqueous solutions and enhance efficiency of metal ions adsorption on the adsorbents. This method is more cost-effective, as the modification agents are usually less expensive than entrapment materials, the mass transfer is not affected, and the adsorption capacity is enhanced (Chen & Yang, 2005; Gaballah & Kilbertus, 1998; Nadeem et al., 2008; Wan Ngah & Hanafiah, 2007).

1.5 Problem statements

The increase of heavy metal pollution in wastewater results in the rise of interest in using agro-wastes to remove heavy metal ions in wastewater. However, agro-wastes without pretreatment will create secondary pollution to the wastewater treated due to the organic compounds leached from the agro-wastes. Therefore, this study was completed mainly to evaluate the performance of chemically treated candlenut shell as a novel and environmentally friendly adsorbent to remove Cu^{2+} and Ni^{2+} ions from aqueous solution.

This study will be able to determine the best adsorbent produced from candlenut shell in terms of lower organic leaching during adsorption process with highest adsorption capacity towards the heavy metal ions studied after achieving the mentioned objectives.

1.6 Research objectives

The objectives of this study are set as follow:

1. To produce chemically treated adsorbents for the study of heavy metal ions removal in aqueous solution.
2. To characterize the adsorbents produced using FT-IR analysis, pH of zero point charge, SEM – EDX analysis, surface area, pore size, and pore volume analysis.
3. To study the effect of different chemical treatment methods on candlenut shell for the prevention of organic leaching during adsorption and the enhancement of heavy metal removal.
4. To determine the type of adsorption process and mechanisms of the adsorption of Cu^{2+} and Ni^{2+} ions from aqueous solutions based on the thermodynamic, kinetic and isotherm models from the effects of initial pH, contact time, initial metal ions concentration and temperature.

CHAPTER 2

MATERIALS AND METHODS

2.1 Chemicals and reagents

The nickel(II) sulfate hexahydrate ($NiSO_4.6H_2O$), copper(II) sulfate pentahydrate ($CuSO_4.5H_2O$), and sodium hydroxide (NaOH) were purchased from QRec, formaldehyde (HCHO, 37%) and hydrochloric acid(HCl, 37%) were purchased from R&M Chemicals, while di-potassium hydrogen orthophosphate anhydrous (K_2HPO_4) was purchased from Bendosen. The IR graded potassium bromide (KBr) was procured from Merck. All the chemicals and reagents used for the experiments were analytical grade and used without purification.

2.2 Preparation of metal solutions

Standard stock solutions of heavy metal (1000 mg L^{-1}) were prepared by dissolving 3.929 g of copper(II) sulfate pentahydrate and 4.478 g of nickel(II) sulfate hexahydrate, respectively with distilled water and then top up to 1000 mL in a volumetric flask. Desired concentration (5 – 100 mg L^{-1}) of heavy metal solutions were prepared by subsequent dilutions of the stock solution. For the batch adsorption studies, the pH of each test solution was adjusted using 0.1 M sodium hydroxide and 0.1 M nitric acid to the desired pH with reference to a pH meter (Lab 850, Schott Instrument).

2.3 Preparation of candlenut shell adsorbent

Candlenut *(Aleurites moluccana)* shell was kindly provided by Bangkatan Rice Mill (Sei Rampah, North Sumatera, Indonesia). The shells were washed with tap water and rinsed with distilled water for several times to remove impurities, such as soil and dirt, and dried to constant mass at room temperature. The dried shells were crushed, grinded, sieved into 400 μm mesh size and labeled as raw candlenut shell (RCS)

2.3.1 Screening of chemical treatment methods

One gram of raw candlenut shell (RCS) was reacted with 100 mL of each chemical solution listed in Table 2.1 for 24 hours at room temperature. The treated candlenut shell (TCS) was then separated from the solution mixture through filtration, washed with distilled water to a constant pH, and dried to constant mass at room temperature. The weight-loss percentage (W %) due to the chemical modification was determined by

$$W\ \% = \frac{W_i - W_f}{W_i} \times 100 \tag{2.1}$$

where W_i is the dry weight of RCS (g) and W_f is the dry weight of TCS (g).

Table 2.1. List of chemical solutions used for RCS modification [x]

Method index	Description
a	Distilled water
b	0.1 M NaOH
c	0.1 M HCl
d	0.2 % formaldehyde
e	2.0 % formaldehyde
f	10.0 % formaldehyde
g	0.1 M K_2HPO_4
h	0.2 M K_2HPO_4

[x] Note: the pretreatment contact time was 24 hours and the solid-to-liquid ratio (S/L) was 10 g L^{-1}.