

REMOVAL OF COPPER(II) AND NICKEL(II) IN AQUEOUS SOLUTION
BY MODIFIED *RHIZOPHORA APICULATA* BARKS ADSORBENT

By

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LIST OF ABBREVIATION AND SYMBOLS

ABS	: Absorbance
BET	: Brunauer, Emmet, and Teller
FTIR	: Fourier Transform Infrared Spectroscopy
FW	: formula weight
MBA	: Modified bark in acidic condition
MBB	: Modified bark in basic condition
C_o	: Initial heavy metal ion concentration (mg L^{-1})
C_e	: Equilibrium heavy metal ion concentration (mg L^{-1})
C	: The intercept of the line which is proportional to the boundary layer thickness (mg g^{-1})
t	: Time (min)
q_e	: Adsorption capacity at equilibrium (mg g^{-1})
q_t	: The amount of solute adsorbed on the surface of adsorbent at any time t (min)
q_m	: D-R adsorption capacity
q_o	: maximum adsorption capacity (mg g^{-1})
M	: Weight of adsorbent dosage (g)
V	: Volume of heavy metal solution (mL)
h	: The initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) at $t \rightarrow 0$
K	: Langmuir constant (L mg^{-1})
K_F	: Freundlich constant (mg g^{-1})
k	: D-R constant related to adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$)

k_{id}	: The intraparticle diffusion constant ($\text{mg g}^{-1} \text{min}^{-0.5}$)
k_1	: The rate constant of a pseudo-first-order equation (min^{-1})
k_2	: The rate constant of a pseudo-second-order adsorption ($\text{g min}^{-1} \text{min}^{-1}$)
n	: Freundlich constant related to adsorption intensity
R_L	: Dimensionless separation factor
P/P_0	: Relative pressure
S_{BET}	: Surface area BET ($\text{m}^2 \text{g}^{-1}$)
R^2	: Correlation coefficient
ε	: Polanyi potential
R	: Gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
T	: Temperature (K)
h	: Initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)
E	: Mean of adsorption energy (mg g^{-1})
pH_{zpc}	: pH zero point of charges
ΔpH	: Difference in pH
pH_0	: pH of Sodium Hydroxide solution before adsorbent was added
pH_f	: Final pH of the mixture after filtration

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PENYINGKIRAN KUPRUM(II) DAN NIKEL(II) DALAM LARUTAN AKUEUS DENGAN PENJERAP KULIT KAYU *RHIZOPHORA APICULATA* TERUBAHSUAI

ABSTRAK

Bahan buangan kulit kayu *Rhizophora apiculata* telah diubahsuai dalam keadaan yang berbeza untuk digunakan sebagai penjerap bagi penyingkiran ion kuprum(II) dan nikel(II) daripada larutan akueus. Kulit kayu *Rhizophora apiculata* terdiri daripada 48% selulosa, 53% lignin, 46% ekstrakatif dan 13% kandungan abu. Ubahsuai kimia telah dilakukan dengan menggunakan formaldehid sebagai agen perangkai silang dalam keadaan berasid dan beralkali. Pencirian kimia dan fizikal bahan-bahan penjerap ini telah dilakukan dengan spektroskopi FTIR, pH_{zpc} dan analisis BET menunjukkan bahawa bahan penjerap yang dihasilkan adalah tidak larut dalam air dan mempunyai tekstur berliang mikro. Kesan pH, kepekatan awal ion logam, dos penjerap, masa sentuhan serta suhu bagi penyingkiran ion Cu(II) dan Ni(II) daripada larutan akueus telah dikajidengan keadaan keseimbangan telah dicapai selepas goncangan selama 60 minit menggunakan 1 g dos penjerap pada pH 5. Perubahan pada tekstur permukaan bahan penjerap dinilai menggunakan mikroskop elektron imbasan selepas proses pengubahsuaian. Proses penjerapan telah dijelaskan dengan baik menggunakan model isoterma Freundlich dengan kapasiti penjerapan ekalapisan bagi penyingkiran ion Cu(II) adalah 6.16 mg g^{-1} dan 5.80 mg g^{-1} , masing-masing bagi keadaan berasid dan beralkali. Manakala kapasiti penjerapan ekalapisan bagi penyingkiran ion Ni(II) adalah 1.50 mg g^{-1} dan 11.67 mg g^{-1} , masing-masing bagi keadaan berasid dan beralkali. Data kinetik didapati paling baik menurut kinetik tindak balas tertib kedua. Data termodinamik

menunjukkan bahawa penjerapan ion Cu(II) dan Ni(II) oleh penjerap kulit kayu *Rhizophora apiculata* terubahsuai adalah spontan dan endotermik. MBA dan MBB boleh digunakan untuk penyingkiran air buangan penyaduran elektrik dengan 65% kecekapan penyingkiran.

REMOVAL OF COPPER(II) AND NICKEL(II) IN AQUEOUS SOLUTION BY MODIFIED *RHIZOPHORA APICULATA* BARKS ADSORBENT

ABSTRACT

Waste mangrove barks of *Rhizophora apiculata* has been chemically modified in different conditions to be used as adsorbents to remove Cu(II) and Ni(II) ions from aqueous solution. *Rhizophora apiculata* bark mainly consists of 53% cellulose, 48% lignin, 46% extractive and 13% ash content. Chemical modifications were done using formaldehyde as cross linking agent in acidic and basic conditions. The adsorbents were chemically and physically characterised by FTIR spectroscopy, pH_{zpc} and BET analysis shows that the adsorbent produced are insoluble in water and have micro porous texture. The effects of pH, initial heavy metal ion concentration, adsorbent dosage, contact time and temperature on the removal of Cu(II) and Ni(II) were studied with equilibrium was established after shaking for 60 min using 1 g of adsorbent dosage at pH 5. Changes in the texture surface of the adsorbent were evaluated by using scanning electron microscopy after modification process. The adsorption process was described well by the Freundlich isotherm models with monolayer adsorption capacity of Ni(II) was 6.16 mg g^{-1} and 5.80 mg g^{-1} for acidic condition and basic condition, respectively. Meanwhile the monolayer adsorption capacity of Cu(II) was 1.50 mg g^{-1} and 11.67 mg g^{-1} for acidic condition and basic condition, respectively. Kinetics data were best described by pseudo-second order model. Thermodynamic parameters showed that the adsorption of Cu(II) and Ni(II) ions onto modified *Rhizophora apiculata* barks were spontaneous and endothermic. MBA and MBB may be applied for removal of electroplating wastewater with 65% removal efficiency.

CHAPTER ONE

INTRODUCTION

1.1 Heavy Metal Ions as Pollutant

Pollution is an undesirable state of the natural environment being contaminated with harmful substances. It occurs as an effect of human activities when pollutants exceed the natural level, and cause disorder to the nature. These activities have caused adverse effect to the community with depletion of food resources, animal extinction, global warming, acid rains, hazardous waste disposal problem and bio-accumulation in the food chain causing health problem to the mankind (Spellman, 2010).

The increase of world population and development of industrial sectors have raised the pollution rate and the large volume of industrial discharges adds to the amount of untreated human wastes. Both solid and liquid wastes are discharged after it has been used as variety of application. Wastewater is released to the environment through sewer pipes, soil erosion and surface run-off. It will then spread out to other places via water streams. The presence of excess heavy metal ion in wastewater has resulted in environmental imbalance. Apparently, studies on pollution of heavy metals in the urban environment became prominent after the mid sixties, concurrent with enhanced urbanization and industrialization processes worldwide. One of the earlier cases was

happened at Minamata Bay, Japan around mid fifties where mercury poisoning occurred associated with fishes consumed by the local residence (Khaniki et al., 2005).

Heavy metals are toxic even when they are discharged in very small quantities. Moreover, these heavy metals are not biodegradable and their toxicity increases due to bioaccumulation and biomagnifications in ecological system. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can endanger public health and the environment. Therefore, heavy metal ions should not be discharged without adequate treatment (O'Connell et al., 2008).

Nickel is a silvery white, hard and ductile transition element which the most dominant species, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ exist as soluble salt at neutral pH, a greenish solution in aqueous media. Nickel is present in crude oil in varying concentrations and burning of petroleum products, either in combustions processes or in vehicle fuel, which then introduces the metal into the environment. It also enters surface water by the natural weathering and leaching processes of minerals and rocks. Nickel compounds are important in modern industry and are used in electroplating, electroforming, and for the production of nickel–cadmium batteries and electronic equipment. Nickel alloys, like stainless steel, are used in the production of tools, machinery, and electrical device, besides used to cast coins, to produce jewelry and medical prostheses.

Nickel is an omnipresent element on earth and due to its abundance; nickel depletion is unlikely to occur. Nickel has been shown to be essential for the growth of some microorganisms. The growth of blue-green algae *Oscillataria spp.* and of the bacterium *Alcaligenes eutrophus* has been proven to depend on the presence of nickel in specially purified media. Nickel depletion in rats resulted in modification of grooming behavior, liver development and decreased growth. Depletion of the element also causes anemia that is manifested in decreased hemoglobin and hematocrit values as well as lowering specific activities of many enzymes involved in carbohydrate and amino acid metabolism. However, uptake of large quantities of nickel may lead to higher chances of development of lung cancer, lung embolism, respiratory failure, birth defects, asthma, chronic bronchitis, gastrointestinal distress (nausea, vomiting and diarrhea), pulmonary fibrosis and renal edema, allergic reactions such as skin rashes and heart disorders (Denkhaus and Salnikow, 2002).

Copper is a reddish element, malleable and tensile material. It has good conductivity properties and high electrical resistance. Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. Human activities that releases copper to the environment includes mining, metal production, wood production and phosphate fertiliser production.

Copper is used mainly in the production of alloys with zinc, nickel and tin, as a catalyst in the chemical industry, in the electrochemical industry where it is used in wires,

generators, transformers and heat exchangers, and of course in the production of piping for water supply. Copper salts are used as pigments and fungicides, and also biocides for controlling slime and in human and animal waste (Li et al., 2009).

The adsorption of copper is necessary because it is a trace element that is essential for human health. Depletion of copper resulted to Menkes disease or the milder Occipital Horn Syndrome, characterised by progressive neurological impairment and death in infancy (Tapiero et al., 2003). Moreover, copper-containing enzymes and even many copper complexes are capable of protecting the organism against reactive oxygen species ($O_2^{\bullet-}$) implicated in many chronic diseases. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. The 1983 Food Act in Malaysia allows only 30 mg kg^{-1} of copper in food. Excessive copper uptake would cause irritation, headaches, stomachaches, dizziness, vomiting, diarrhea, liver damage and insomnia. Chronic copper poisoning will lead to Wilson's disease, characterised by a hepatic cirrhosis, brain damage, demyelination, renal disease, and copper deposition in the cornea.

Different treatment techniques for heavy metal ions removal from wastewater have been developed in recent years. Although various treatments such as chemical precipitation, coagulation–flocculation, reverse osmosis, ultra-filtration, electro-dialysis flotation and ion exchange can be employed to remove heavy metals from contaminated wastewater, they have their inherent advantages and limitations in application. These methods are only effectively applied to high concentration of heavy metal ions solutions and

considered as expensive for removal of trace heavy metal ions. Adsorption has become one of the alternative treatment techniques due to its effectiveness to remove these heavy metal ions even at low concentration. Furthermore, adsorption is more economical and a lot of easily available material can be used as adsorbents (O'Connell et al., 2008).

1.2 Adsorption

Adsorption is described as a process of transferring material of gaseous or liquid components of mixtures (adsorbate) from the external and/or internal surface onto the surface of a porous solid (adsorbent). Adsorption happens due to the increased free surface energy of the solids due to their extensive surface (Inglezakis and Pouloupoulos, 2006). According to the second law of thermodynamic, energy cannot be created nor destroyed. This energy is conserved by converting it to another form. Therefore, this free energy is converted by capturing external adsorbate into the adsorbent to reduce its surface tension.

Adsorption can be categorised into two types, depending on bonding of the interaction. Physical adsorption (physisorption) is characterised by relatively weak van der Waals interaction of the adsorbate attached into the surface. Only intermolecular attraction between favorable energy takes place in the interaction and there is no exchange of electrons observed. Consequently, there is no dependence on the electronic properties of the molecules. The process is reversible. Multiple layers may be formed rapidly with

approximately the same heat of adsorption. The heat of adsorption for physisorption is generally small, 5 - 40 kJ mol⁻¹ (Argun et al., 2007). In chemical adsorption (chemisorption), the interaction energies between the surface and the adsorbate are comparable to the strength of chemical bonds (more than 40 kJ mol⁻¹). It is much stronger and more stable at high temperatures when compared to physisorption. Chemical bonds can be divided into two broad categories: ionic bonds and covalent bonds. Ionic compound formed by transferring of electron between atoms to give charge particle that attract each other. Covalent bonds are formed by the sharing of electron between atoms. The chemical nature of the adsorbent may be altered by surface reaction in such a way that the original species cannot be recovered; in this sense, the process is irreversible. Electrostatic sorption (ion exchange) is a term reserved for Coulomb attractive forces between ions and charged functional groups. It is a reversible reaction involving chemically equivalent quantities. The principle is a redistribution of ions between two phases by diffusion, and chemical factors which are less significant or even absent. The heat is usually very small to negligible, often less than 10 kJ mol⁻¹ (Brady, 1990)

Adsorption process depends on the nature of adsorbate and adsorbent surface. Surface properties are characterised by surface area and porosity via adsorption isotherm test. Generally, six types of isotherm identified by International Union of Pure and Applied Chemistry (IUPAC) as shown in Figure 1.1. Brunauer, Emmett and Teller (BET) classified five of the isotherm (type I-V), while type VI is additional which represent stepwise monolayer adsorption on a porous surface. Type I associated with microporous

solid known as Langmuir isotherm corresponding to monolayer adsorption. Type II and III isotherm normally related to multilayer adsorption which describes adsorption on macroporous solid. Type IV and V represents adsorption isotherm with hysteresis loop which associated with capillary condensation in mesopores.

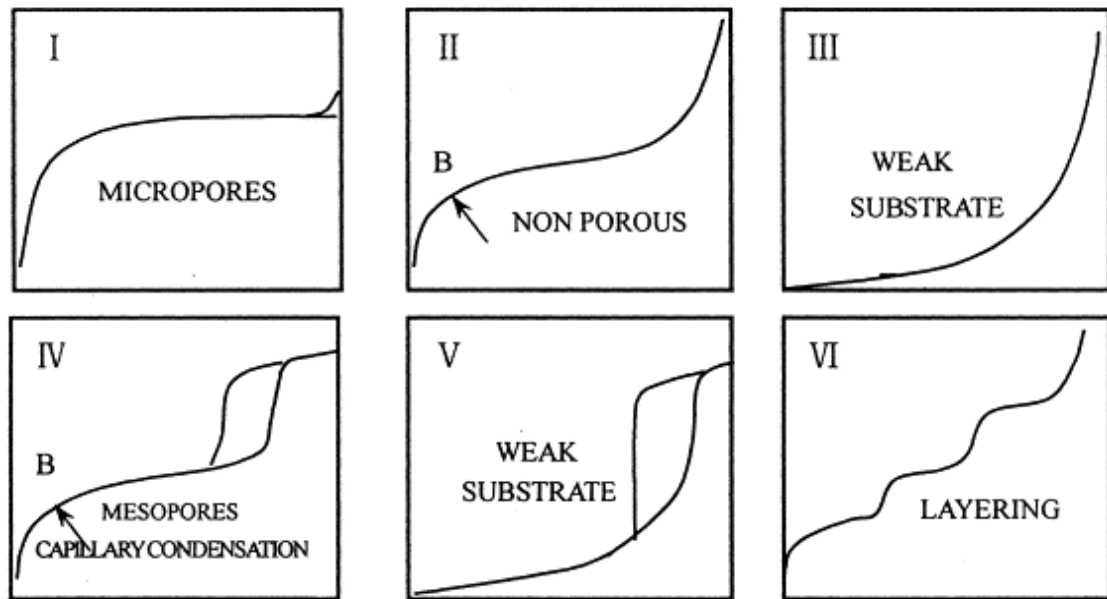


Figure 1.1 Six type of isotherm defined by IUPAC (Ryuet al., 1999)

Currently, material widely used as adsorbent is activated carbon for removing not only heavy metal ions, but also other organic and inorganic pollutant such as phenol, pesticides, dyes and many other chemicals and organisms. Studies have shown that activated carbons are effective and commercially applicable in industrial and wastewater treatment (Cotoruelo et al., 2010). However, usage of this material is constrained by the high cost of producing the adsorbent and disposal problem of the used activated carbon. Once this activated carbon has been exhausted, it has to be regenerated for further use and the most common method is thermal regeneration. Regeneration process results in a

loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with the original activated carbon. Due to the high energy and cost used for the thermal regeneration of activated carbon, several attempts have been done by various workers to prepare low cost alternative adsorbents (Ali and Gupta, 2007) which may replace activated carbons in pollution control through adsorption process.

1.3 Alternative Low-cost Adsorbent

Among various ways of treating heavy metal ions is to utilise as much as possible our resources including inexpensive and low-cost waste to be converted into adsorbent. The advantages of the low-cost adsorbents over activated carbon adsorbents is it could be employed effectively for the removal of pollutants, depending on the characteristics of the adsorbent and the concentration of the adsorbate. Further, due to the abundant and readily availability of the materials, the adsorbents are much cheaper compared to activated carbon and it required only simple alkali or acid treatment before application.

Many materials have been tested for heavy metal ions removal. Certain waste products from industries and agricultural operations, natural materials and bioadsorbents represent potentially economical alternative adsorbents.

Some review articles discussing low-cost alternative adsorbents such as coconut, rice bran, sawdust, banana peel and chitosan have already been available. For example, a

comprehensive data on the removal of metals by low-cost adsorbents has been reviewed by Bailey et al. (1999). An overview of low-cost adsorbents for heavy metal removal has been presented by Babel and Kurniawan (2003).

The category of adsorbent produced can be categorised into natural materials, biosorbent and waste materials or by-products from agriculture and industry. Natural materials are generally the ones existing in nature and used as such or with minor treatment. Examples of some of the materials used are clay, silica beads and zeolite. The term biosorption is used for the accumulation of pollutants from aqueous solutions by the use of biological materials. Materials such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass, are used as chelating and complexing adsorbents in order to remove pollutants from wastewater (Liu and Liu, 2008). The waste materials or by-products from the agriculture and industries such as various types of tree barks, rice husk, sugarcane bagasse and sawdust could be assumed to be the low-cost adsorbents since they are abundant in nature, inexpensive, and require little processing. Agricultural waste materials are usually composed of lignin and cellulose as the main constituents. Other components are hemicelluloses, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups are present in the binding process. Bark is an abundant forest residue which has been found to be effective in removing heavy metal ions from water solutions. Due to its low cost and high availability, bark is very suitable to function as an adsorbent (Catinon et al., 2009).

1.4 Chemical Composition of Bark

Bark portion consist of 20 – 35 % with regard of the whole tree and the second most important tissue of a trunk. Bark is a very complex tissue that is composed of two principal zones: the inner bark and the outer bark. The bark is divided from the wood or xylem by the vascular cambium layer. The chemical composition of bark is complex and varies between and within species, and also between the inner and outer bark.

Proximate chemical analysis of bark from different species indicates that the chemical constituents of bark can be classified into four major groups: polysaccharides (cellulose, hemicelluloses, and pectic materials); lignin and polyphenols; hydroxy acid complexes (suberin); and extractives (fats, oils, phytosterols, resin acids, waxes, tannins, terpenes, phlobaphenes, and flavonoids).

The major carbohydrate portion of bark is composed of cellulose and hemicelluloses polymers (homocelluloses). Cellulose polymers (Figure 1.2) are made up of simple sugars, mainly, D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-glucuronic acid, and lesser amounts of other sugars such as L-rhamnose and D-fucose. Cellulose has been used in the form of wood and cotton for thousands of years as an energy source, a building material and for clothing. Cellulose has a ribbon shape which allows it to twist and bend in the direction out of the plane, so that the molecule is moderately flexible. This molecular structure gives cellulose its characteristic properties of hydrophilicity, chirality and degradability. Chemical reactivity is largely a function of

the high donor reactivity of the OH groups (Klemm et al., 2005). These polymers are rich in hydroxyl groups that are responsible for moisture sorption through hydrogen bonding.

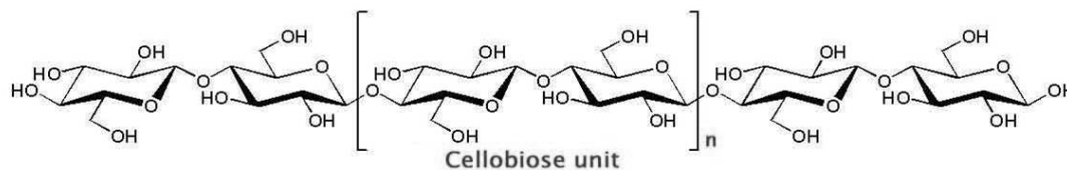


Figure 1.2 Structure of Cellulose

Hemicellulose is a heterogeneous group of compounds that in plant-cell walls form part of the matrix within which cellulose fibers are embedded. Hemicelluloses comprise almost one-third of the carbohydrates in woody plant tissue. The chemical structure of hemicelluloses consists of long chains of a variety of pentoses, hexoses, and their corresponding uronic acids.

Hemicelluloses usually consists of more than one type of sugar unit and is sometimes referred to the sugars contain, for example, galactoglucomanan, arabinoglucuronoxylan, arabinogalactan, and glucomannan. The two principal structural types are polymers of D-xylose and of glucose and mannose, known respectively as xylans and glucomannans (Figure 1.3), they are intimately associated with cellulose and contribute to the structural components of the tree (Roubroeks et al., 2001).

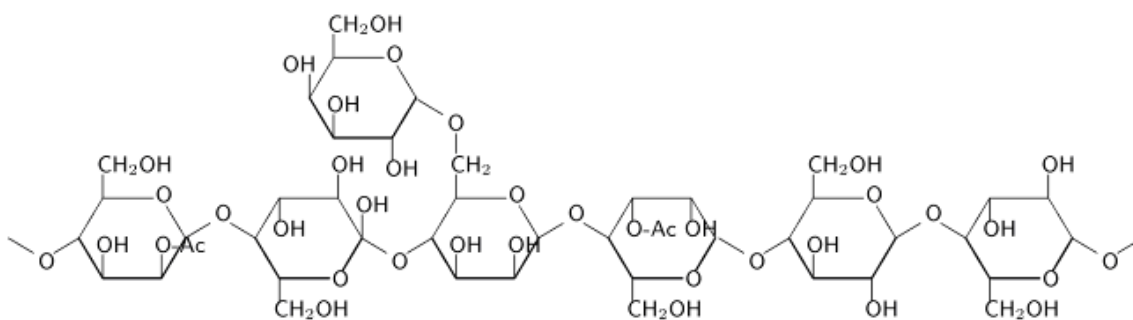


Figure 1.3 Structure of glucomannan hemicellulose

Lignin is the second most abundant natural raw material and nature's most abundant aromatic (phenolic) polymer. Lignin is amorphous, highly complex, mainly aromatic polymers of phenylpropane units. It functions to regulate the circulation of liquid in the living plant (partly by reinforcing cell walls and keeping them from collapsing, partly by regulating the flow of liquid), and it enables trees to grow. The three-dimensional polymer is made up of C–O–C and C–C linkages. The precursors of lignin biosynthesis are shown in Fig 1.4 as, coniferyl alcohol, coumaryl alcohol and sinapyl alcohol (Vanholme et al., 2010).

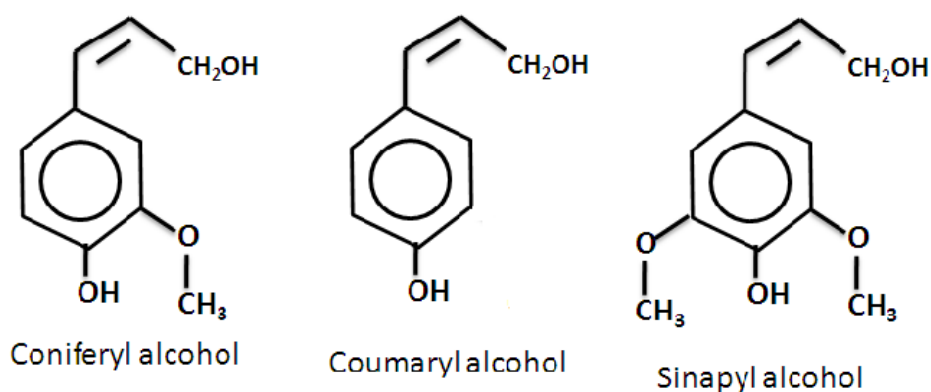


Figure 1.4 Monomers of lignin

Tannins are polyphenols obtained from various parts of different plants belonging to multiple species. It is found in abundance in the tree bark, wood, fruit, leaves and roots (Hernes and Hedges, 2004). Their main characteristic is that they bind and precipitate proteins. Tannins are usually found in large quantities in the bark of trees where they act as a barrier for micro-organisms like bacteria and fungi and protect the tree. Tannins can be classified into two broad groups which are hydrolysable tannins and condensed tannins. Condensed tannins (Fig 1.5) also known as polyflavonoids or proanthocyanidins comprise of a group of polyhydroxyflavon-3-ol oligomers and polymers linked by carbon-carbon bonds between flavanol subunits. Typical materials used for bark tanning include any of the oaks, fir, certain willows, chestnut, sumac leaves, oak galls, canaigre root, birch, alder, hemlock, Bearberry (leaves), heather, bloodroot, alfalfa and tea. Currently, tannin mostly obtained from extracted Quebracho, Chestnut or Mimosa. In Malaysia, tannin extracted from mangrove barks *Rhizophora apiculata* (Heredia and Martín, 2009).

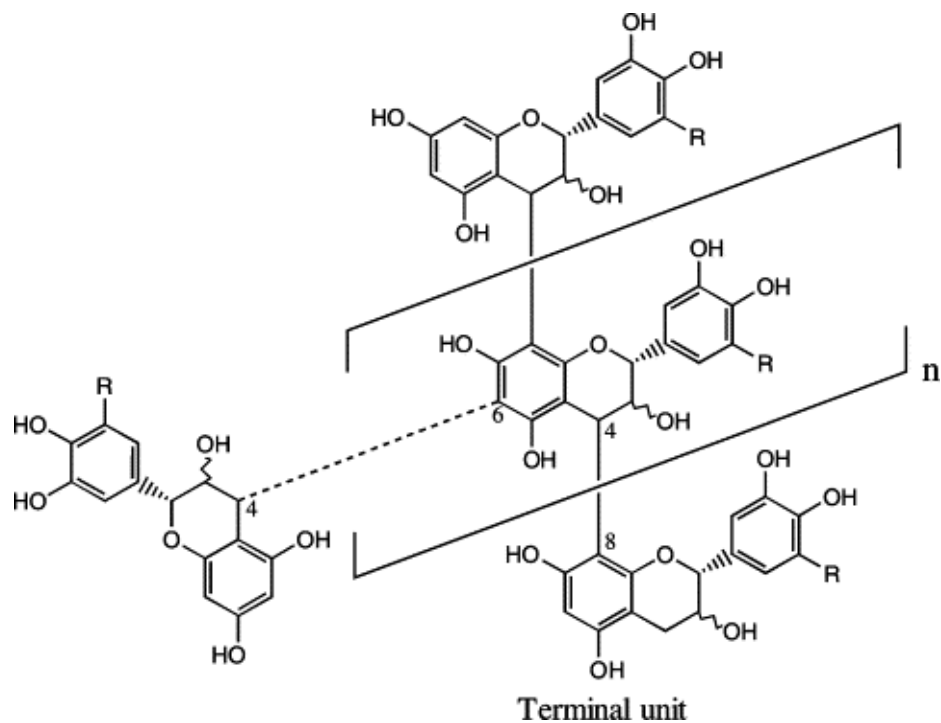


Figure 1.5 Structure of condensed tannin

1.5 Mangrove *Rhizophora apiculata*

Mangroves dominate three quarters of tropical coastlines. Trees and shrubs that grow abundantly in saline soil and brackish water subject to periodic fresh- and salt-water inundation in the tropics and subtropics are known as mangroves. Mangrove trees have specific characteristics such as tough root systems, special bark and leaf structures and other unique adaptations to enable them to survive in their natural environment. Mangrove trees of the genus *Rhizophora* from family Rhizophoraceae, a genus of tropical mangrove trees was the most well-known mangrove. Mangroves are a unique and dominant ecosystem comprised of inter-tidal marine plants, mostly found at bordering margins of tropical coastlines around the world, especially estuaries and deltas. It protects the coastlines from erosion and strong coastal winds and at the same

time protecting the inlands from floods and tsunamis. Mangrove forest is a very productive ecosystem, providing resources for coastal communities and is an important breeding ground for many marine species such as fishes, prawns and crabs. Other than that, mangroves also act as natural filter to retain, concentrate and recycle nutrients and also to remove toxicants.

Mangrove forests can provide many benefits and therefore, proper management and conservation is necessary to ensure the continued existence of mangrove forests. In Malaysia, there are several mangrove forestsgazette as reserved forestssuch as the Matang Forest Reserve in Perak, the Kuala Selangor Nature Park in Selangor, Bako National Park in Sarawak, the Kota Kinabalu City Bird Sanctuary and Sepilok Forest Reserve in Sabah. The harvesting of mangrove poles (usually *Rhizophora* spp.) for piling purposes is still an important part of mangrove utilization. The mangrove timbers are also used for the production of charcoal, firewood and woodchips.

Mangrove bark *Rhizophora apiculata* species are waste product from charcoal industry and it is abundantly available. The barks contain polyhydroxy phenol groups which will act as the active species in the adsorption process. The uptake of cationic takes place by ion exchange by displacing the adjacent phenolic hydroxyl groups forming a chelate. The main problem associated with tannin rich material is the de-coloration of water, resulting from the solubility of phenol.

Chemical pretreatment of barks has been tried by numerous researchers to prevail this problem, Randall et al.(1974) carried out a comparative study of bark adsorption with formaldehyde modification operates in the same manner and with the same efficiency as the non-modified product. Thus, the tree bark acts as an absorbent for heavy metal ions in wastewater through chemical or physical reaction. Reaction of tannin as well as other phenolic compounds with formaldehyde has been done in acidic or basic catalyst conditions. Palma et al. (2003) said that the main role of formaldehyde in the modification reaction is to immobilise the phenolic polymers in the tannin and bark (Figure 1.6 and 1.7).

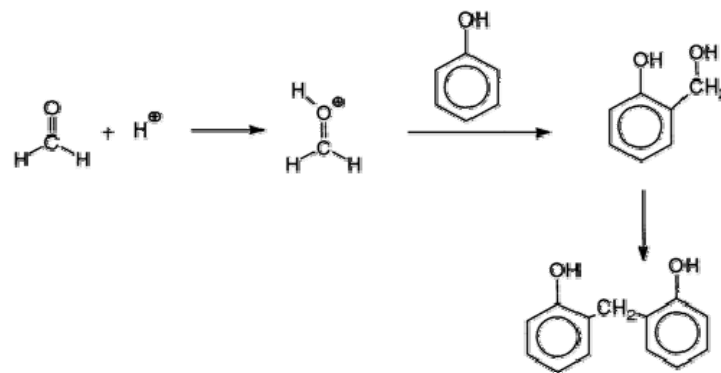


Figure 1.6 Typical reaction between phenol and formaldehyde

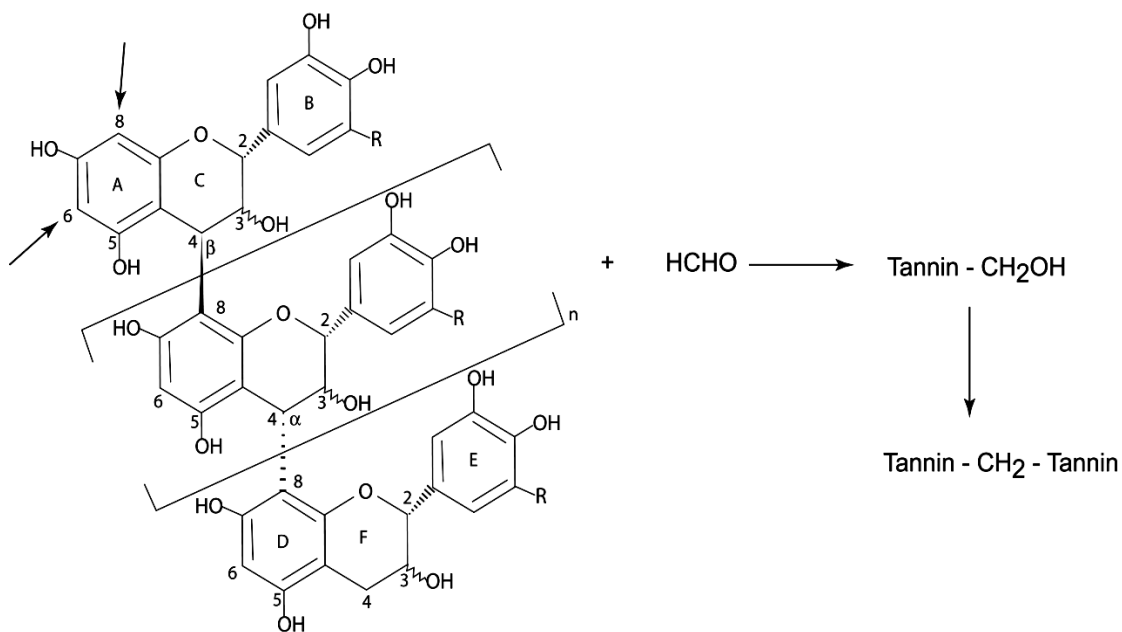


Figure 1.7 Reaction of tannins with formaldehyde

The advantage of chemical pretreatment is no increment in BOD was found as there were no discharges of pigment and other organic compound. Furthermore, the modified tree bark even removes even trace amounts of heavy metal ions. Present environmental standards require removal of even these trace amounts, which are considered to be hazardous to the health of humans and other animals.

1.6 Adsorption Isotherms

It is fundamental to correlate equilibrium data between adsorbates and adsorbent in order to assess the adsorption capacity for different adsorbates. The adsorbates can range from dyes to heavy metal ions. Besides, adsorption isotherm gives information on adsorption mechanisms, surface properties and affinity of an adsorbent towards the

adsorbate (Ho et al., 2002). The adsorption isotherm is a prerequisite for the design of commercial treatment system (Gerente et al., 2007).

In this study, three isotherm models were applied, which were Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models.

1.6.1 Langmuir Isotherm

Adsorbents that exhibit the Langmuir isotherm behavior are supposed to contain fixed individual sites, each of which equally adsorbs only one molecule, forming thus a monolayer with the thickness of a molecule.

$$\frac{C_e}{q_e} = \frac{1}{q_o K} + \frac{C_e}{q_o} \quad (1.1)$$

Where C_e is the solute concentration at equilibrium (mg L^{-1}), q_e the adsorption capacity at equilibrium (mg g^{-1}), K the Langmuir adsorption constant (L mg^{-1}), and q_o is the maximum adsorption capacity retained by the adsorbent (mg g^{-1}).

1.6.2 Freundlich Isotherm

Adsorption process which follow the Freundlich isotherm equation are assumed to have a heterogeneous surface consisting of sites with different adsorption potentials, and each type of site is assumed to adsorb molecules.

The Freundlich isotherm model is given by following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (1.2)$$

Where C_e is solute concentration at equilibrium (mg L^{-1}), K_F represents Freundlich constant (mg g^{-1}) and n is constant related to adsorption intensity.

1.6.3 Dubinin-Radushkevich Isotherm

The third isotherm model used to interpret data in this study is Dubinin-Radushkevich (D-R) isotherm model. It is given as:

$$\ln q_o = \ln q_m - k\varepsilon^2 \quad (1.3)$$

where q_o (mg g^{-1}) is the maximum adsorption capacity, q_m (mg g^{-1}) is the D-R adsorption capacity, k is related with adsorption energy ($\text{mol}^2 \text{kJ}^2$) and ε is a Polanyi potential.

The Polanyi potential (ε) is given as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (1.4)$$

Where R is a gas constant $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, T is the temperature (K) and C_e is the equilibrium heavy metal ion concentration (mg L^{-1}).

D-R isotherm describes adsorption by single and uniform pores. This isotherm gives information about the chemical or physical properties of the sorption by the value of calculated mean energy of adsorption, E. It represents the free energy for the transfer of one mole of adsorbate to the adsorbent surface from infinity. The linearised form of the D–R model is given in Eq. 1.3 and 1.4.

E(kJ mol⁻¹) is calculated using the following equation:

$$E = \frac{1}{\sqrt{-2k}} \quad (1.5)$$

These isotherm models will be discussed in detail in section 3.6.

1.7 Kinetic of Adsorption

In order to investigate the mechanisms of adsorption and potential rate-limiting steps such as mass transport and chemical reaction process, kinetics model have been used to test the experimental data. Three types of kinetics models were applied in this study, which are:

(i) pseudo-first-order kinetic model

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1.6)$$

(ii) pseudo-second-order kinetic model

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (1.7)$$

$$h = k_2 q_e^2 \quad (1.8)$$

(iii) intraparticle diffusion kinetic model

$$q_t = k_{id} t^{0.5} \quad (1.9)$$

Based on the equations, q_e is the adsorption capacity at equilibrium (mg g^{-1}), q_t is the amount of solute adsorbed on the surface of adsorbent at any time t (min), k_1 is the rate constant of a pseudo-first-order equation and k_{id} is intraparticle diffusion constant ($\text{mg g}^{-1} \text{min}^{-0.5}$), h is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) as $t \rightarrow 0$, and k_2 is the rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) for pseudo-second-order adsorption.

These kinetic models will be discussed in detail in section 3.5.

1.8 Thermodynamic of Adsorption

The thermodynamic studies were conducted to determine the nature of the adsorption process whether it is exothermic or endothermic. The values of Gibbs free energy change (ΔG^0) and entropy change (ΔS^0) give the information regarding the spontaneity of the adsorption process and the affinity between adsorbent and adsorbate, respectively.

The following equations were used to obtain the thermodynamic parameters:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (1.10)$$

$$\Delta G^\circ = -RT \ln K \quad (1.11)$$

where K is the Langmuir constant (L mol⁻¹), R is the gas constant (8.314 J K⁻¹ mol⁻¹), ΔH° is enthalpy change (kJ mol⁻¹), ΔS° is entropy change (J K⁻¹ mol⁻¹), ΔG° is Gibbs free energy (kJ mol⁻¹) and T is temperature in Kelvin.

This topic will be discussed in detail in section 3.7

1.9 Objective of the Research

Mangrove bark *Rhizophora apiculata* is a waste from charcoal industry and it can be used as possible adsorbent because of its availability and chemical composition. During the processing of wood to produce charcoal, bark is considered as a waste and disposed via burning method or accumulation which will cause contamination of air and occupation of land space. Due to greater demands of low-cost alternative adsorbent for heavy metal ions removal, waste bark *Rhizophora apiculata* which contain polyhydroxy phenol groups are found to be a very attractive alternative adsorbent for this purpose.

Thus, the objectives of this research are:

- To analyse the chemical composition of mangrove bark.
- To produce and characterise a low-cost adsorbent from waste mangrove bark for copper(II) and nickel(II) removal from aqueous solution.
- To determine adsorption capacities of bark adsorbent towards copper(II) and nickel(II) through batch experiment studies.
- To determine kinetics, thermodynamics and adsorption mechanism of copper(II) and nickel(II) onto bark adsorbent.
- To determine adsorption capacities of the bark adsorbent towards copper(II) and nickel(II) from industrial wastewater.

CHAPTER TWO

MATERIALS AND METHODS

2.1 Chemicals and Instruments Used for the Research

2.1.1 List of Chemicals

Chemicals used in this study were:

1. Acetic acid, 99.8 % (System)
2. Aceton (QRĕC)
3. Formaldehyde, 37 % (Merck)
4. Toluene (QRĕC)
5. Ethanol (QRĕC)
6. Sodium chlorite (R&M Chemical)
7. Hydrochloric acid, 37 % (Lab Scan)
8. Nitric acid, 65 % (System)
9. Sodium hydroxide (System)
10. Sulphuric acid, 95-98 % (Mallinckrodt Chemicals)
11. Copper (II) sulphate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Riedel de Hĕen)
12. Nickel (II) sulphate hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (APH Chemical)

All chemicals used are analytical grade and were used without any purification.