

**POTENTIAL OF MODIFIED GAMBIR AS ADSORBENT FOR THE
REMOVAL OF SELECTED HEAVY METAL IONS FROM
AQUEOUS SOLUTIONS**

by

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**POTENSI GAMBIR TERUBAHSUAI SEBAGAI PENJERAP UNTUK
PENYINGKIRAN ION LOGAM BERAT TERPILIH DARIPADA
LARUTAN AKUEUS**

ABSTRAK

Dalam kajian ini, ekstrak gambir dan pulpa gambir telah masing-masing diubahsuai secara kimia dengan formaldehid (FGA) dan asid hidroklorik (AGPA). Bahan penjerap telah dicirikan secara fizikal dan kimia dengan FTIR, BET, TGA, SEM, EDS dan pH_{pzc} . Permukaan FGA didapati berbentuk butiran dan sesarang lebah manakala AGPA adalah dalam bentuk bulat dan padatan. Nilai pH_{pzc} untuk FGA dan AGPA masing-masing ialah 3.90 and 3.62. Hidroksil (-OH) dan karbosisil kumpulan (-COOH) telah dikesan oleh FTIR. Kesan pH, dos bahan penjerap, kepekatan awal, tempoh pengadukan dan suhu terhadap penjerapan telah dikaji. Keadaan optimum pH untuk penjerapan logam ion pada FGA dan AGPA masing-masing ialah pH 5.0 (Cu^{2+} , Pb^{2+} ion) dan pH 6.0 (Ni^{2+} , Co^{2+} ion). Manakala, keadaan optimum dos bahan penjerap untuk penjerapan logam ion pada FGA masing-masing ialah 6.00 g/L (Cu^{2+} ion), 10.00 g/L (Pb^{2+} ion), 16.00 g/L (Ni^{2+} , Co^{2+} ion) dan pada AGPA masing-masing ialah 10.00 g/L (Pb^{2+} ion), 12.00 g/L (Ni^{2+} ion), 16.00 g/L (Cu^{2+} , Co^{2+} ion). Proses penjerapan awal adalah pantas dan mencapai keseimbangan dalam masa tidak melebihi 90 min untuk semua ion logam. Empat jenis model kinetic telah digunakan untuk menganalisis data kinetik iaitu tertib pseudo-pertama, tertib pseudo-kedua, Elovich and resapan intrapartikal. Tertib pseudo-kedua adalah model yang menepati data kinetik dan menunjukkan bahawa proses pengjerapan adalah secara kimiajerapan. Sementara itu, resapan intrapartikal menyatakan bahawa terdapat lebih daripada satu proses penyebaran dalam kajian ini. Isotherma pengjerapan telah dimodelkan dengan menggunakan model isotherma Langmuir,

Freundlich, Temkin dan Dubinin-Radushkevich. Nilai-nilai muatan penjerapan maksimum Cu^{2+} , Pb^{2+} , Ni^{2+} and Co^{2+} ion untuk FGA pada suhu optimum masing-masing ialah 10.10 mg/g, 6.41 mg/g, 6.38 mg/g dan 4.45 mg/g. Walau bagaimanapun, nilai-nilai muatan pengjerapan maksimum bagi Cu^{2+} , Pb^{2+} , Ni^{2+} dan Co^{2+} ion untuk AGPA ditemui di suhu optimum yang berbeza dengan masing-masing ialah 3.99 mg/g (343 K), 8.01 mg/g (343 K), 9.75 mg/g (303 K) dan 4.81 mg/g (313 K). Nilai-nilai negatif ΔG° dan ΔH° untuk FGA dan AGPA tersirat bahawa proses penjerapan adalah eksotermik, berlaku secara spontan. Walau bagaimanapun, terdapat kes-kes yang luar biasa di mana penjerapan telah menunjukkan sebagai endotermik oleh sebab ΔH° bernilai positif. Tiga jenis asid termasuk HCl, HNO_3 dan EDTA dengan pelbagai kepekatan antara 0.10 M – 0.001 M telah digunakan untuk kajian penyahjerapan. Hasil kajian menunjukkan bahawa penggunaan 0.10 M HCl menghasilkan prestasi menyahjerap yang lebih baik berbanding dengan HNO_3 dan EDTA. Penjanaan semula ion logam untuk kedua-dua FGA dan AGPA menyimpulkan bahawa kitaran pertama dan kedua menunjukkan hasil yang memberangsangkan. Kitaran ketiga, bagaimanapun, didapati agak rendah dan tidak berkesan. Ini dapat disimpulkan bahawa FGA lebih baik untuk penjerapan Cu^{2+} ion dan AGPA lebih baik untuk penjerapan Pb^{2+} and Ni^{2+} ion. Manakala, kedua-dua FGA dan AGPA menunjukkan prestasi penjerapan yang rendah terhadap Co^{2+} ion.

**POTENTIAL OF MODIFIED GAMBIR AS ADSORBENT FOR THE
REMOVAL OF SELECTED HEAVY METAL IONS FROM
AQUEOUS SOLUTIONS**

ABSTRACT

In this study, gambir extracted and gambir pulp has been chemically modified with formaldehyde (FGA) and hydrochloric acid (AGPA), respectively. Adsorbents were physically and chemically characterized by FTIR, BET, TGA, SEM, EDS and pH_{pzc} . The surface of FGA was found to be granular and honeycombed shape while AGPA was in spherical and compacted shape. The pH_{pzc} values for FGA and AGPA were found to be 3.90 and 3.62, respectively. Hydroxyl (-OH) and carboxyl (-COOH) groups were detected by FTIR. The effects of pH, adsorbent dosage, initial concentration, contact time and temperature on adsorption were studied. The optimum conditions of pH for metal ions adsorption onto both FGA and AGPA were found to be pH 5.0 (Cu^{2+} , Pb^{2+} ions) dan pH 6.0 (Ni^{2+} , Co^{2+} ions), respectively. Meanwhile, the optimum conditions of adsorbent dosage for metal ions adsorption onto FGA were found to be 6.00 g/L (Cu^{2+} ions), 10.00 g/L (Pb^{2+} ions), 16.00 g/L (Ni^{2+} , Co^{2+} ions) and for AGPA were found to be 10.00 g/L (Pb^{2+} ions), 12.00 g/L (Ni^{2+} ions), 16.00 g/L (Cu^{2+} , Co^{2+} ions), respectively. The initial adsorption process was rapid and reached equilibrium within 90 min for all metal ions. Four types of kinetic models were applied to analyze kinetic data particularly pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion. Pseudo-second order was found to be the best model that fitted well the kinetic data and predicted that chemisorptions took place in the process. Meanwhile, the intraparticle diffusion stated that there was more than one diffusion process as in this study. Adsorption isotherm was studied by using Langmuir, Freundlich, Temkina and Dubinin-

Radushkevich models. The highest maximum adsorption capacities of Cu^{2+} , Pb^{2+} , Ni^{2+} and Co^{2+} ions for FGA at optimum temperature (333 K) were found to be 10.10 mg/g, 6.41 mg/g, 6.38 mg/g and 4.45 mg/g, respectively. However, the highest maximum adsorption capacities of Cu^{2+} , Pb^{2+} , Ni^{2+} and Co^{2+} ions for AGPA were found at different optimum temperatures; 3.99 mg/g (343 K), 8.01 mg/g (343 K), 9.75 mg/g (303 K) and 4.81 mg/g (313 K), respectively. The negative values of ΔG° and ΔH° for FGA and AGPA implied that the adsorption process was exothermic and spontaneous in nature. However, there are exceptional cases where the adsorption was suggested to be endothermic with positive value of ΔH° . Three types of acid including HCl, HNO_3 and EDTA with various concentration ranging from 0.10 M – 0.001 M were applied for desorption study. The results showed that the use of 0.10 M HCl resulted in a better desorption performance compared to HNO_3 and EDTA. The regeneration of metal ions for both FGA and AGPA concluded that the first and second cycles showed a promising outcome. The third cycle, however, was found to be quite low and not efficient. This can be concluded that FGA is more favorable for adsorption of Cu^{2+} ions and AGPA is more favorable for the adsorption of Pb^{2+} and Ni^{2+} ions. Meanwhile, both FGA and AGPA showed a low adsorption performance against Co^{2+} ions.

CHAPTER ONE

INTRODUCTION

1.1 Water Pollution

Water is one of the basic necessities required for the sustenance and continuation of life. It is often being described as “the universal solvent” or “the liquid of life”. However, millions of people worldwide are suffering with the shortage of fresh and clean drinking water. Over the past several decades, the exponential growth of population, social civilization expansion, resources use, and continuing progress of the industrialization and technologies have been accompanied by a sharp modernization and metropolitan growth. Environmental pollution problem has been always a serious issue that gained human great concern. The main sources of freshwater pollution can be attributed to the discharge of untreated sanitary and toxic industrial wastes. It is well known that 70-80% of all illness in developing countries are related to water contamination, particularly susceptible for women and children (Husein et al., 2011; WHO/UNICEF, 2000). The scientific and technical communities, the public opinion, the national governments and the international institutions are aware of the negative impacts of industrial activities on the population’s health (Gaballah and Kilbertus, 1998).

These industrials waste commonly generate both organic and inorganic pollutants such as phenols, dyes, detergents, insecticides, pesticides and heavy metals (Bhatnagar and Sillanpää, 2009). Among all the pollutants, heavy metals are considered to be particularly dangerous pollutants. Their presence in the wastewater of several industrial

processes, such as electroplating, metal finishing, metallurgical work, tanning, chemical manufacturing, mining, battery manufacturing, wood preservatives production, fertilizers and pesticides, has brought about more environmental concerns due to their toxicity even at low concentrations (Abu Al-Rub, 2006; Kang et al., 2007).

Industrial effluent has been always gained human great concern because of its toxicity and harmful effect on human and also on plants, animals and marine life (Cheng et al., 2010). Unlike organic wastes, these inorganic pollutants are of considerable concern because they are non-biodegradable, cannot be broken down by bacterial action, accumulated in living tissues, cause various diseases and disorders, and have a probable carcinogenic effect (Cimino et al., 2000).

1.2 Heavy Metal from Industrial Effluent

In the environment, one element can be present in different chemical forms, which differ in their chemical behavior, bioavailability and toxicity. Some elements such as iron (Mulaudzi et al., 2002), arsenic (Balaji, 2002), manganese (Qian et al., 2001) and chromium (Xue et al., 2000) are mainly present in natural water in two oxidation states. For instance chromium(VI), arsenic(III) and arsenic(V) are known as carcinogens, while ferum(II), ferum(III), manganese(II), manganese(VII) and chromium(III) are essential micronutrients for organisms and plants. However, the effluents of industrial wastewater often contain considerable amounts of toxic and polluting heavy metals.

A summary of permissible limits and health effects of various toxic heavy metals is shown in Table 1.1. Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. However, metal ions are being added to the water stream at a much higher concentration than the prescribed limits by industrial activities, thus leading to health hazardous and environmental degradation.

Table 1.1: Permissible limits and health effects of various toxic heavy metals (Xue et al., 2000; Pasavant et al., 2006; Oliveira et al., 2005)

Metal contaminant	Permissible limits by international bodies (µg/L)			Health effects
	WHO ^a	USEPA ^b	MNG ^c	
Arsenic	10	50	10	Carcinogenic, producing liver tumors, skin and gastrointestinal effects
Mercury	1	2	1	Corrosive to eyes, skin and muscle, dermatitis, anorexia, kidney damage and severe muscle pain
Cadmium	3	5	3	Causes lung fibrosis, dyspnea and weight loss
Lead	10	15	10	Carcinogenic, anemia, muscle and joint pains, diminishing Intelligence Quotient, kidney problem, and high blood pressure
Nickel	50	50	-	Causes chronic bronchitis, lung cancer and nasal sinus
Chromium	50	100	50	Carcinogenic, producing lung tumors and allergic dermatitis
Zinc	100	100	300	Causes short-term illness called " metal fume fever" and restlessness
Copper	1500	1300	1000	Causes irritation of nose, mouth, eyes, headache, dizziness and diarrhea
Cobalt	1500	2000	-	Causes cardiomyopathy, lung irritations, bone defects and low blood pressure

^a World Health Organization

^b United State Environment Protection Agency

^c Malaysia National Guidelines for Drinking Water Quality

1.2.1 Copper

The potential sources of Cu^{2+} ions in industrial effluents come from metal cleaning and plating baths, pulp and paper board mills, wood pulp production, fertilizer industry, mining manufacturing, steel-works, paints and pigments, etc. (Gupta, 1998; Ng et al., 2002). Cu^{2+} ion is one of the essential micronutrients that are needed by human body in trace quantities. It is found primarily in bloodstream, in various enzymes and in copper based pigments (Ajmal et al., 2005; Beppu et al., 2004). However, like all heavy metals it has been reported to cause stomach and intestine problems, neurotoxicity and jaundice at high amounts (over 5.0 mg/L) (Xianfang and Ruckenstein, 1996). For examples, continued inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers, lesions in the central nervous system, Wilson's disease, gastrointestinal disturbance that includes vomiting and nausea, liver damage, neurological abnormalities, hemolytic anemia, corneal opacity, etc. (Dinesh et al., 2006; Kurniawan et al., 2006; Maria et al., 2011; Yu et al., 2000). Therefore, too much of copper element contains in water has been found to damage marine life (Hasanur et al., 2009). The World Health Organization (WHO) recommended a maximum acceptable concentration of Cu^{2+} ions in drinking water of 1.5 mg/L.

1.2.2 Lead

Lead is one of the most widespread metal pollutants in soil. The contamination of Pb^{2+} ions in soil has received much attention in recent years due to its toxicity (Chrysochoou et al., 2007; Saifullah et al., 2009). The primary source of Pb^{2+} ion is galena (PbS), and it

is widely used in many industrial application, such as mining operation, plumbing, automobile battery, petrochemical industries, photographic materials, explosive manufacturing, coating, textile dyeing, ceramic and glass industries, etc. (Iqbal and Edyvean, 2004; Jalali et al., 2002; Özacar et al., 2008). Basically, Pb^{2+} ions are highly toxic and cumulative poison accumulates mainly in bones, brain, kidney and muscles. Pb^{2+} ions poisoning in human causes severe damage to kidney, nervous and reproductive systems, liver and brain (Naiya et al., 2009). The presence of Pb^{2+} ions in drinking water even at low concentration may cause such diseases as anemia, encephalopathy, hepatitis and nephritic syndrome (Deng et al., 2010; Gupta et al., 2011; Özer, 2007). The permissible limit for Pb^{2+} ions in wastewater as set by Environmental Protection Agency (EPA) is 0.05 mg/L and in drinking water intended for drinking as set by Europe (EU), United Stated (US) EPA and WHO are 0.010, 0.015 and 0.010 mg/L, respectively (Balaria and Schiewer, 2008; Bhattacharjee et al., 2003).

1.2.2 Nickel

Nickel is also a common environmental pollutant which is considered as toxic (over concentration 15 mg/L), especially to activated sludge bacteria, and its presence is detrimental to the operation of anaerobic digesters used in wastewater treatment plants (Srivastava et al., 2006b). Ni^{2+} ions are frequently encountered in various industrial wastewaters such as mine drainage, electroplating, paint and ink industries, stainless steel, silver refineries, zinc base casting, jewelry and coinage, etc. (Anoop Krishnan et al., 2011; Kadirvelu et al., 2001). People often suffer from allergy due to exposure to nickel-containing materials and the carcinogenic effects of nickel have also been well

documented (Boujelben et al., 2009). The main symptoms of Ni²⁺ ions effect on human health are headaches, dizziness, vomiting, chest pain, dry cough, rapid respiration, cyanosis and extreme weakness (Kadirvelu et al., 2001; Parker, 1980). The permissible limit for Ni²⁺ ions in drinking water as set by both WHO and European Economic Community is 0.05 mg/L (Demirbaş et al., 2002).

1.2.3 Cobalt, Co(II)

Cobalt is a key constituent of cobalamin (vitamin B₁₂) and also an essential element to human health (Wang et al., 2011). The increasing usage of Co²⁺ ions in nuclear power plants and in many industries such as mining, metallurgy, electroplating, paints and pigments and electronic industries (Manohar et al., 2006) has caused the Co²⁺ ions finding its way to natural bodies of water. The excess intake of Co²⁺ ions can result in paralysis, diarrhea, low blood pressure, lung irritations, bone defects, imparting neurotoxicological disorders, genotoxicity, cardiomyopathy and bronchial asthma (Baun and Christensen, 2004; Krishnan and Anirudhan, 2008).

1.3 Wastewater Treatment Technologies

Heavy metals pose serious environmental risks, lethal effects on all form of life and, therefore, their removal from wastewaters particularly has been examined extensively. Owing to the toxic effects, industries are advised that their waste waters must be treated systematically to remove/minimize the metal contents in their wastes.

Various methods exist for the removal of heavy metal ions from industrial wastewater which include chemical precipitation, coagulation/flocculation, membrane filtration technology, electrolytic reduction, ion exchange, and adsorption (Wang et al., 2003). However, there is no single technique which is most suitable for all conditions, as each of them have its advantages and limitations. The advantages and disadvantages associated with each method are listed in Table 1.2.

Table 1.2 Advantages and limitations of physicochemical treatments of industrial wastewater

Technology	Advantages	Disadvantages	Reference
Chemical precipitation	<ul style="list-style-type: none"> • Inexpensive • Most of the metal can be removed • Simple operation 	<ul style="list-style-type: none"> • Large amount of sludge produced • Disposal problems • High maintenance cost 	(Aderhold et al., 1996; Ahluwalia and Goyal, 2007)
Ion exchange	<ul style="list-style-type: none"> • High regeneration • Less time consuming • Metal selective 	<ul style="list-style-type: none"> • Not all ion exchange resins are suitable for metal removal • High maintenance cost 	(Aderhold et al., 1996)
Ultrafiltration	<ul style="list-style-type: none"> • Smaller space requirement • Metal selective • Low solid waste generation • Low chemical consumption 	<ul style="list-style-type: none"> • Prone to membrane fouling • High operational cost • Limited flow rates • Low removal percentage with the presence of other metals 	(Ahn et al., 1999; Qin et al., 2002; Vigneswaran et al., 2005)
Electrochemical treatment	<ul style="list-style-type: none"> • Able to work under both acidic and basic conditions • Can treat effluent with metal concentration > 2000 mg/L 	<ul style="list-style-type: none"> • High capital and operational costs • Production of hydrogen gases • Formation of metal hydroxide 	(Kongsricharoen and Polprasert, 1996; Subbaiah et al., 2002)

Table 1.2 (Continue)

Technology	Advantages	Disadvantages	Reference
Coagulation-flocculation	<ul style="list-style-type: none"> • Shorter time to settle out suspended solids • Bacterial inactivation capability 	<ul style="list-style-type: none"> • Chemical consumption • Increase sludge volume generation • Extra operational cost for sludge disposal 	(Aderhold et al., 1996; Ayoub et al., 2001; Semerjian and Ayoub, 2003)
Dissolved flotation	<ul style="list-style-type: none"> • Low cost • Shorter hydraulic retention time • Removal of small particles • Metal selective 	<ul style="list-style-type: none"> • High initial capital costs • High maintenance costs 	(Lazaridis et al., 2001; Rubio et al., 2002)
Adsorption (granular activated carbon)	<ul style="list-style-type: none"> • Wide variety of target pollutants • Fast kinetics • High capacity 	<ul style="list-style-type: none"> • Performance depends on type of adsorbent • Chemical derivation to improve its sorption capacity 	(Crini, 2005)

Chemical precipitation of metal ions is perhaps the simplest and most widely used technique of heavy metal removal from aqueous solutions (Sheikholeslami and Bright, 2002). In this approach, the dissolved metal ions are converted to the insoluble solid phases via a chemical reaction with a precipitant. The precipitate then is separated from water by sedimentation or filtration (Matis et al., 2004). Traditionally, hydroxide precipitant such as lime and caustic soda have been favored over their sulfide counterparts, due to the higher cost of chemically produced hydrogen sulfide and

associated hazards (Tünay, 2003). The conceptual mechanism of heavy metal removal by chemical precipitation is presented below (Tünay, 2003):

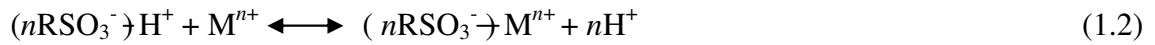


where M^{2+} and OH^{-} represent the dissolved metal ions and hydroxide precipitant, respectively, and $M(OH)_2$ is the metal hydroxide.

In spite of its advantages, the chemicals consumption of chemical precipitation process is extremely higher than other treatments in order to reduce the metals to an acceptable level for discharge (Jüttner et al., 2000). Xu et al. (2011) stated that the chemical precipitation treatment is not ideal because different heavy metal hydroxides will be precipitated at different pH levels. This is due to some metal ions may bond with other ions in a multi-metal ions solution. During the treatment process, the heavy metal ions may be leaking from the precipitates when pH solution decreased and cause secondary pollution. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling and the long-term environmental impacts of sludge disposal (Bose et al., 2002; Wingenfelder et al., 2005; Yang et al., 2001).

Ion exchange process has been widely applied to remove the heavy metal ions from industrial wastewater (Kang et al., 2004). In ion exchange, a reversible interchange of ions between the solid and liquid phases occurs, where an insoluble substance (resin) removes ions from aqueous solution (Rengaraj et al., 2001). The common cation exchangers are strongly acid resins with sulfonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups ($-COOH$) (Gode and Pehlivan, 2006). The hydrogen

ions from both sulfonic and carboxylic groups of the resin can serve as exchangeable ions with metal cation. The physicochemical interactions between resins and metal ions during the process can be expressed as follows (Dąbrowski et al., 2004):



where $(-\text{RSO}_3^-)$ and M^{n+} represent the anionic groups attach to the ion exchange resin and metal cation, respectively, while n is the coefficient of the reaction component, depending on the oxidation state of metal ions.

Ultrafiltration utilizes permeable membrane to separate heavy metals, macromolecules and suspended solid from inorganic solution on the basis of the pore size 5-20 nm. These unique specialties enable ultrafiltration to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules. Ultrafiltration presents some advantages such as lower driving force and a smaller space requirement due to its high packing density. However, the decrease in ultrafiltration performance due to membrane fouling has hindered it from a wider application in wastewater treatment (Choi et al., 2005). In addition, this has limited ultrafiltration to separate smaller pollutants like heavy metal ions. The micellar enhanced ultrafiltration (MEUF) was proposed to obtain high removal efficiency of metal ions. MEUF is a physico chemical membrane separation technique aimed at improving the performance of ultrafiltration membrane by capturing the small size pollutants into larger structures called micelles (Husein et al., 2011).

Coagulation and flocculation followed by sedimentation and filtration is also employed to remove the heavy metal ions from industrial wastewaters. Principally, the coagulation

process destabilizes colloidal particles by adding a coagulant and results in sedimentation of pollutants (Semerjian and Ayoub, 2003). Many coagulants are widely used in the conventional wastewater treatment processes such as aluminium, ferric chloride and ferrous sulfate, resulting in the effective removal of wastewater impurities by enmeshment the impurities on the formed amorphous metal hydroxide precipitates. To increase the particle, coagulation is followed by the flocculation of the unstable particles into bulky flocculants (Licskó, 1997).

Flocculation is the action of polymers to form bridge between the floccules and bind the particles into large agglomerates or clumps. In general, coagulation-flocculation can treat inorganic effluent with a metal concentration of less than 100 mg/L. Like chemical precipitation, pH ranging from 11.0 to 11.5 has been found to be effective to improve the heavy metal removal percentage (Charerntanyarak, 1999; Li et al., 2003).

However, coagulation-flocculation processes are unable to treat the heavy metal wastewater completely. Therefore, coagulation-flocculation must be followed by other techniques (Plattes et al., 2007). This process also has limitations such as high operational cost due to high chemical consumption (Ayoub et al., 2001).

1.4 Problem Statement

In Malaysia, water is needed for many kinds of use such as drinking supply, sanitation, agriculture, urbanization, industrialization, transportation and to produce hydroelectric power. However, like other countries in the world, the heavy metal pollution level of fresh water bodies in Malaysia, especially rivers, is no longer within the safe limits for human consumption (Thanapalasingam, 2005). To solve this serious environmental problem, industrial processes that use significant amount of water are required to treat its wastewater before discharging into the river. A significant majority of recent developments relate to biological processes and advanced treatment technologies such as electrolysis and adsorption. Adsorption of heavy metals by activated carbon is a powerful technology among all wastewater treatment for treating domestic and industrial wastewater. However, the high cost of activated carbon and its loss during regeneration restricts its application. From an economic point of view, it is infeasible to utilize activated carbon for commercial wastewater treatment. To that end, the focus of removal of heavy metals studies has been altered toward natural materials which are eco-friendly and available in vast amounts, as well as certain waste products from agricultural industrial or biomass. Agricultural waste materials particularly with the presence of cellulose, hemicelluloses, lignin, and starch containing a variety of functional groups that facilitates metal complexation may help for the sequestering of heavy metals (Bailey et al., 1999; Hashem et al., 2005b; Pavasant et al., 2006; Vieira and Volesky, 2000). Gambir (*Uncaria gambir*) is known as a common medicine plant which consisted of several polyphenolic and flavonoid components. Up to date, there is no record of researches studying the application of gambir as adsorbent on the removal of heavy

metal ions from aqueous solution except the research group of Prof. Dr. Mohd Jain Noordin in Univerisiti Sains Malaysia whom applied gambir on dyes adsorption study. Gambir contains of polyphenolic compounds which act as antioxidant in human metabolisms. This polyphenolic compound has the ability to quench metal cations and form metal complexes. Thus it is possible to apply gambir on the removal of heavy metal ions from aqueous solutions in order to meet the requirement of eco-friendly and low cost adsorbent.

1.5 Research Objectives

This study aims to evaluate the potential of gambir extract and pulp as adsorbent for the application in removing copper, lead, nickel and cobalt ions from aqueous solutions. In order to achieve the aim, the work was divided into following objectives:

- i. To extract gambir with several types of solvents and analyze its total phenolic, total flavonoid, and condensed tannin components.
- ii. To chemically modify the gambir extract and waste gambir pulp into water insoluble adsorbent and determine the characteristic of formaldehyde modified gambir adsorbent (FGA) and acid modified gambir pulp adsorbent (AGPA).
- iii. To optimize the adsorption conditions including solution pH, adsorbent dosage, initial concentrations and contact time of FGA and AGPA for copper, lead, nickel and cobalt metal ions.
- iv. To evaluate the adsorption experimental data of FGA and AGPA by isotherms and kinetics model.
- v. To determine the thermodynamic parameters of the adsorption.
- vi. To investigate desorption and regeneration process of FGA and AGPA.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction of Adsorption

Adsorption is defined as the accumulation of a substance at the interface between two phases such as solid and liquid or solid and gas. It is also explained as a separation process in which some material, is concentrated from a bulk vapor or liquid phase onto the surface of a porous solid (Bhatnagar and Sillanpää, 2010). Besides, Kurniawan and Babel (2003) has stated that the adsorption process is a mass transfer from the liquid phase to surface of solid compound, and becomes bound by physical and/or chemical interactions. The substance that is being removed from liquid or gas phase at the interface is called adsorbate. The substance to be adsorbed (before it is on the surface) is called adsorpt or adsorptive. Adsorbent is the solid, liquid or gas phase onto which the adsorption takes place. Figure 2.1 shows the definitions of adsorbent, adsorptive, and adsorbate. It has been universally recognized that adsorption of a species on a solid surface followed by three steps, (i) transport of the adsorbate (ions in case of solutions) from the bulk to the external surface of the adsorbent, (ii) passage through the liquid film attached to the solid surface, and (iii) interactions with the surface atoms of the solid (Gupta et al., 1998). Although adsorption is used at the solid-air and solid-liquid interface, only the case of adsorption at the solid-liquid interface will be discussed in this study.

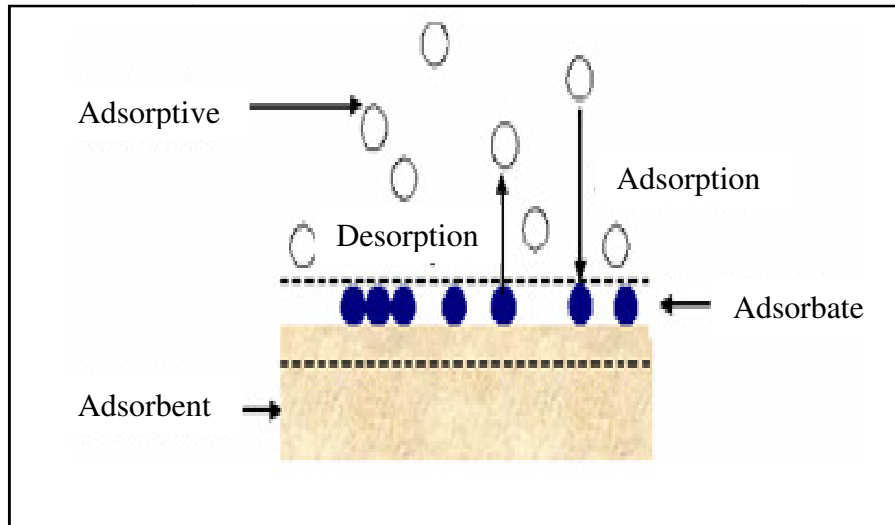


Figure 2.1: Definitions of adsorbent, adsorptive, and adsorbate (Butt et al., 2011)

2.2 Classification of Adsorption

Basically, adsorption process depends upon the nature of force existing between adsorbate molecules and adsorbent. Adsorption can be classified into physical adsorption (physisorption) and chemical adsorption (chemisorptions). If the forces of attraction existing between adsorbate and adsorbent are van der Waal's forces, the adsorption is called physisorption. Meanwhile, if the forces of attraction existing between adsorbate particles and adsorbent are almost the same strength as chemical bonds, the adsorption is known as chemisorptions (Rouquerol, 1999).

Physisorption is completely nonspecific reversible under high temperature and pressures. A physisorption molecules is not affixed to a particular site on the solid surface, where it can spontaneously leave the surface after a certain time (Sawyer et al., 2002). In chemisorptions, the formation of a chemical linkage (often covalent) between

the adsorbent and adsorbate gives a shorter bond length and higher bond energy (Montgomery, 1985). The properties and characteristics of chemisorptions and physisorption are listed in Table 2.1.

Table 2.1 Properties of physisorption and chemisorption (Atkins, 1994)

Properties	Chemisorption	Physisorption
Adsorption temperature	This type of adsorption increases with the increase of temperature	This type of adsorption decreases with the increase of temperature
Adsorption energy	Always exothermic < 40 kJ/mol	Exothermic or endothermic, chemical bond forms 40-200 kJ/mol
Nature of adsorption	Often dissociative and irreversible in many cases	Non-dissociative and reversible
Saturation	Limited to monolayer	Often occurs as multilayer
Adsorption process	Activated and slow	Non-activated and rapid
Desorption process	Desorption is impossible (adsorbed molecule keeps its identity)	Desorption is possible (adsorbed molecule keeps its identity)

2.3 Adsorbents from Agricultural Waste and Biomass

Adsorption has been commented as an effective and versatile technique for heavy metal ion removal, even at low concentrations. However, the high price of adsorbent (commonly activated carbon) is regarded as the major obstacle for industrial application. Thus, alternative adsorbents have been investigated by researchers in order to solve the major problem.

Searching for low-cost and abundant adsorbents to remove heavy metals has become a main research focus. To date, thousand of studies on the use of low-cost adsorbent has been published. Agricultural waste and biomass are the most popular adsorbent that highlighted among all researchers. Studies reveal that numerous agricultural waste materials and biomass such as rice and wheat waste (Zafar et al., 2007), tea and coffee waste (Dubey and Gopal, 2007), coconut waste (Horsfall, 2005), peanut and groundnut waste (Amarasinghe and Williams, 2007), fruit peels (Memon et al, 2008), seed waste (Gupta and Babu, 2009), wood sawdust (Kadirvelu and Namasivayam, 2000), sugar beet pulp (Reddad et al., 2003), plants leaf (Saliba et al., 2005), fresh water green microalgae (Rao et al., 2005; Vilar et al., 2007), marine red and brown macroalgae (Romera et al., 2007), bacteria (Ziagova et al., 2007), fungi (Dursun, 2006) etc have been tried and gave an efficient adsorption capacity. The carboxyl, hydroxyl, amino and sulfate groups in agricultural waste and biomass act as binding sites for metal ions. The agricultural waste and biomass characteristics, physicochemical properties of the target metals and solution pH have a large impact on the adsorption performance. Table 2.2 shows the summary of unmodified and chemically modified agricultural waste as adsorbent for the removal of heavy metal ions from aqueous solution with the maximum adsorption capacities (Q_{max}).

Table 2.2 Summary of unmodified and chemically modified agricultural waste as adsorbent for the removal of heavy metal ions from aqueous solution

Agricultural waste	Modifying agent (s)	Metal ions	Q _{max} (mg/g)	References
Poplar wood sawdust	Unmodified	Cu(II) Zn(II) Cd(II)	6.88 0.967 0.157	(Šćiban et al., 2007)
Maple wood sawdust	Unmodified	Cu(II)	9.19	(Rahman and Islam, 2009)
Bamboo sawdust	Unmodified	Cu(II)	NA	(Zhao et al., 2012)
Linden wood sawdust	Unmodified	Cu(II) Zn(II) Ni(II) Cd(II) Mn(II) Fe(II)	9.9 2.2 4.6 3.5 1.0 NA	(Božić et al., 2009)
Mansonia sawdust	Unmodified	Cu(II)	28.6	(Ofomaja, 2010a)
Meranti sawdust	Hydrochloric acid	Cu(II) Cr(III) Ni(II) Pb(II)	32.05 37.88 35.97 34.25	(Rafatullah et al., 2009)
Poplar sawdust	Sulfuric acid	Cu(II)	13.5	(Acar and Eren, 2006)
Poplar sawdust	Sodium hydroxide	Cu(II) Zn(II)	6.92 15.83	(Šćiban et al., 2006)
Oak sawdust	Hydrochloric acid	Cu(II) Ni(II) Cr(VI)	3.22 3.29 1.70	(Argun et al., 2007)

Table 2.2 (Continue)

Agricultural waste	Modifying agent (s)	Metal ions	Q _{max} (mg/g)	References
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Sawdust	Sodium hydroxide	Pb (II)	0.89	(Asadi et al., 2008)
		Cd(II)	0.84	
		Zn(II)	0.80	
		Cu(II)	0.82	
	Hydrochloric acid	Ni(II)	0.66	
		Pb(II)	0.37	
		Cd(II)	0.13	
		Zn(II)	0.69	
	Heat	Cu(II)	0.62	
		Ni(II)	0.49	
		Pb(II)	0.76	
		Cd(II)	0.63	
		Zn(II)	0.65	
		Cu(II)	0.62	
Ni(II)	0.45			
Rice bran	Unmodified	Ni(II)	0.15	(Oliveira et al., 2005)
		Cr(III)	0.32	
		Cr(VI)	0.15	
Rice bran	Unmodified	Zn(II)	18.31	(Wang et al., 2006)
Rice bran	Sulfuric acid	Ni(II)	46.51	(Zafar et al., 2007)
Rice bran	Sodium chloride	Cd(II)	0.28	(Farajzadeh and Reza Vardast, 2003)
		Pb(II)	6.00	
		Zn(II)	0.26	
		Ni(II)	1.20	
		Cu(II)	1.40	
		Fe(III)	NA	
Rice hulls	Unmodified	Cu(II)	11.83	(Jeon, 2011)
Rice husk	Sodium hydroxide	Cu(II)	29.00	(Wang et al., 2003)
		Pb(II)	108.00	
Rice husk	Sodium hydroxide, 2%	Cu(II)	4.77	(Hasanur et al., 2009)
Rice husk	Unmodified	B(III)	4.23	(Hasfalina et al., 2012)
Wheat straw	Citric acid	Cu(II)	78.13	(Gong et al., 2008)
Wheat straw	Citric acid	Cu(II)	39.17	(Han et al., 2010)
Wheat straw	Unmodified	Cu(II)	16.08	(Aydın et al., 2008)

Table 2.2 (Continue)

Agricultural waste	Modifying agent (s)	Metal ions	Q _{max} (mg/g)	References
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Sugarcane bagasse	Sulfuric acid and carbon disulfide	Cd(II) Pb(II) Ni(II) Zn(II) Cu(II)	219.20 327.40 147.90 156.90 184.90	(Homagai et al., 2010)
Sugarcane bagasse	Unmodified	Ni(II)	2.23	(Alomá et al., 2012)
Bagasse	Acrylonitrile, Sodium hydroxide hydroxylamine chloride	Cu(II)	101.01	(Jiang et al., 2009)
Sugarcane bagasse	Sodium hydroxide and ethylenediaminetetraacetic dianhydride	Cu(II) Cd(II) Pb(II)	92.60 149.00 333.00	(Júnior et al., 2009)
Sugarcane bagasse	Succinic acid	Cu(II) Cd(II) Pb(II)	123.50 164.00 295.10	(Gurgel et al., 2008)
Sugar beet pulp	Sodium hydroxide and citric acid	Cu(II)	119.43	(Altundogan et al., 2007)
Sugar beet pulp	Unmodified	Cu(II)	31.40	(Aksu and İšoğlu, 2005)
Kudzu (<i>Pueraria lobata ohwi</i>)	Unmodified	Cu(II) Cd(II) Zn(II)	32.00 15.00 35.00	(Brown et al., 2001)
<i>Ulmus carpinifolia</i> leaves	Sodium hydroxide	Tl(I)	54.60	(Zolgharnein et al., 2011)
<i>Withania frutescens</i> leaves	Unmodified	Cd(II) Cu(II) Pb(II) Zn(II)	0.002 0.078 0.24 0.64	(Chiban et al., 2012)
<i>Cinnamomum camphora</i> leaves	Unmodified	Cu(II)	17.87	(Chen et al., 2010)
Sunflower leaves	Unmodified	Cu(II)	89.37	(Benaïssa and Elouchdi, 2007)

Table 2.2 (Continue)

Agricultural waste	Modifying agent (s)	Metal ions	Q _{max} (mg/g)	References
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Areca waste	Sodium hydroxide and sulfuric acid	Cd(II) Cu(II)	1.12 2.84	(Zheng et al., 2008)
Rubber (<i>Hevea brasiliensis</i>) leaves	Sodium hydroxide	Cu(II)	14.97	(Nghah and Hanafiah, 2008)
Cogon (<i>Imperata cylindrical</i>) leaves	Sodium hydroxide	Cu(II)	11.64	(Hanafiah et al., 2009)
Cogon (<i>Imperata cylindrical</i>) leaves	Sodium hydroxide	Ni(II)	6.96	(Hanafiah et al., 2010)
<i>Carpobrotus edulis</i> stems and leaves	Unmodified	Pb (II) Cd(II)	175.00 28.00	(Chiban et al., 2011)
Neem (<i>Azadirachta indica</i>) leaves	Unmodified	Cu(II)	33.30	(Bhattacharyya et al., 2010)
(Red pepper) <i>Capsicum annuum</i> seeds	Unmodified	Cu(II)	28.40	(Özcan et al., 2005)
Chickpea (<i>Cicer arietinum</i> L.) leaves, stems and fruit peelings	Unmodified	Pb(II)	25.59 25.51 9.17	(Nadeem et al., 2006)
Okra waste	Unmodified	Pb(II)	5.74	(Moshen, 2007)
Sesame leaves	Unmodified	Pb(II)	279.86	(Liu et al., 2012)
<i>Salvinia</i> plant biomass	Unmodified	Cr(IV) Ni(II) Cd(II)	39.68 41.32 39.06	(Dhir and Kumar, 2010)
Tea waste	Unmodified	Cu(II) Pb(II)	48.00 65.00	(Amarasinghe and Williams, 2007)
Tea waste	Unmodified	Ni(II)	15.26	(Malkoc and Nuhoglu, 2005)
Papaya (<i>Carica papaya</i>) seed	Unmodified	Zn(II)	19.88	(Ong et al., 2012)

Table 2.2 (Continue)

Agricultural waste	Modifying agent (s)	Metal ions	Q_{\max} (mg/g)	References
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<i>Psidium guvajava</i> leaves	Unmodified	Cd(II)	31.15	(Rao et al., 2010)
Coriander (<i>Coriandrum sativum</i>) seeds	Unmodified	Cu(II) Pb(II) Zn(II)	5.60 47.70 3.33	(Rao and Kashifuddin, 2012)
Orange peels	Cross-linked with calcium hydroxide and sodium hydroxide, followed by graft polymerization with ceric ammonium nitrate and methyl acrylate	Cu(II)	289.00	(Feng et al., 2009)
Orange peels	Sodium hydroxide and calcium chloride	Cu(II) Pb(II) Zn(II)	70.73 209.80 56.18	(Feng and Guo, 2012)
Orange peels	Nitric acid	Cd(II) Cu(II) Pb(II)	13.70 15.27 73.53	(Lasheen et al., 2012)
Citrus peels	Unmodified	Pb(II)	480.70	(Schiewer and Balaria, 2009)
Ponkan mandarin peels	Unmodified	Ni(II) Co(II) Cu(II)	112.68 80.73 83.25	(Pavan et al., 2006)
Lemon peels	Thermally activated	Co(II)	22.00	(Bhatnagar et al., 2010)
Cassava (<i>Manihot esculenta</i>) peels	Unmodified	Cu(II)	41.77	(Kosasih et al., 2010)
Banana peels	Unmodified	Cu(II)	8.24	(Liu et al., 2012)
Mango peels	Unmodified	Cd(II) Pb(II)	67.08 96.32	(Iqbal et al., 2009)
Pomegranate (<i>Punica granatum</i>) peels	Unmodified	Ni(II)	52.00	(Bhatnagar and Minocha, 2010)

Table 2.2 (Continue)

Agricultural waste	Modifying agent (s)	Metal ions	Q _{max} (mg/g)	References
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