UTILIZATION OF MANGO LEAF AS LOW-COST ADSORBENT FOR THE REMOVAL OF CU(II) ION FROM AQUEOUS SOLUTION

By

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ABSTRACT

The potential of mango leaves as a low-cost adsorbent for the removal of Cu(II) ions from aqueous solution was investigated in this study. The influences of pH, contact time, initial metal concentration, agitation rate, particle size and presence of chelating agent were studied in batch experiments at room temperature. The mango leaves used in this study were characterized by FTIR spectroscopy and it was found that O-H, C-H, C=C and C-O stretching were present. Maximum sorption for metal was found to be at pH 5. The adsorption was rapid at the first 5 minutes of contact, with uptake of more than 90%, and equilibrium was achieved in 60 minutes of agitation. Kinetic studies showed good correlation coefficient for a pseudo-second order kinetic model. The uptake was found to increase with higher agitation rate and smaller size of adsorbent. The presence of chelating agent EDTA and NTA suppressed the uptake of Cu(II) ions, with the earlier having a stronger suppressing effect. Langmuir, Freundlich, and BET isotherm models were applied to describe the biosorption of Cu(II) ions onto mango leaves. Langmuir model fitted the equilibrium data better, giving correlation coefficient of 0.9918 and a maximum adsorption capacity of 15.77 mg/g. This indicates monolayer coverage on adsorbent. The results showed that mango leaves have the potential to be applied as alternative low-cost biosorbent in the remediation of heavy metal contamination in waste water.

ABSTRAK

Potensi daun mangga sebagai penjerap berkos rendah dalam penyihkiran ion Cu(II) daripada larutan akues telah dikaji. Pengaruhan pH, masa sentuhan, kepekatan ion permulaan, kadar agitasi, saiz zarah, dan kehadiran agen chelate telah dikaji secara kelompok dalam suhu bilik. FTIR spektroskopi telah dijalankan ke atas daun mangga yang digunakan dan regangan O-H, C-H, C=C and C-O telah dijumpai. Keupayaan sorpsi maksimum telah dijumpai pada pH 5. Penyikiran ion adalah cepat dalam 5 minit sentuhan pertama, dengan penjerapan lebih daripada 90%, dan keseimbangan telah dicapai dalam masa 60 minute. Kajian kinetik menunjukkan korelasi yang bagus bagi model kinetik pseudo kadar kedua. Penjerapan telah didapati meningkat dengan kadar agitasi yang lebih tinggi dan saiz zarah yang lebih kecil. Kehadiran agen chelate EDTA dan NTA merendahkan penjerapan ion Cu(II). Model-model isoterma Langmuir, Freundlich, dan BET telah digunakan untuk menggambarkan penjerapan ion Cu(II) ke atas daun mangga. Model Langmuir menunjukkan keputusan yang lebih memuaskan, dengan korelasi 0.9918 dan keupayaan penjerapan maksimum 15.77 mg/g. Ini menunjukkan lingkupan lapisan mono ke atas daun mangga. Keputusan kajian menunjukkan daun mangga mempunyai potensi sebagai penjerap berkos rendah alternatif dalam memulihkan air sisa yang dicemarkan oleh logam berat.

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APPROVAL SHEET

I certify that, this project report entitled "**UTILIZATION OF MANGO LEAF AS LOW-COST ADSORBENT FOR THE REMOVAL OF CU(II) ION FROM AQUEOUS SOLUTION**" was prepared by **ONG PICK SHEEN** and submitted in partial fulfilment of the requirements for the degree of Bachelor of Science (Hons.) in Chemistry at Universiti Tunku Abdul Rahman.

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PERMISSION SHEET

It is hereby certified that **ONG PICK SHEEN** (ID No: **08ADB05723**) has completed this report entitled "**UTILIZATION OF MANGO LEAF AS LOW-COST ADSORBENT FOR THE REMOVAL OF CU(II) ION FROM AQUEOUS SOLUTION**" under the supervision of **ASST. PROF. DR. ONG SIEW TENG** from the Department of Chemical Sciences, Faculty of Science.

I hereby give permission to my supervisor to write and prepare manuscript of these findings for publishing in any form, if did not prepare it within six (6) months time from this date provided that my name is included as one of the authors for this article. Arrangement of my name depends on my supervisor.

DECLARATION

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

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Date:

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ΔG Standard free energy (kJ/mol)

Cu(II)   Copper(II)

C_e Concentration of Cu(II) ions at equilibrium (mg/L)

C_o Initial concentration of Cu(II) ions (mg/L)

Cs   Solute concentration at the saturation of all layers (mg/L)

EDTA   Ethylenediaminetetraacetic acid

FTIR   Fourier Transform Infrared

h   Initial sorption rate(mg/g min)

k_1 Pseudo first-order rate constant (min^{-1})

k_2 Pseudo second-order rate constant (g/mg min)

K_B BET constant

K_F Freundlich indicative of relative adsorption capacity of adsorbent ($mg^{1-1/n} L^{1/n}g^{-1}$)

K_L Langmuir constant related to free energy of adsorption (L/mg)

m   Mass of adsorbent (g)

n	Freundlich indicative of the intensity of adsorption
NTA	Nitrilotriacetic acid
rpm	Revolution per minute
q_e	Amount of Cu(II) ions adsorbed at equilibrium (mg/g)
q_m	Maximum adsorption capacity (mg/g)
q_t	Amount of Cu(II) ions adsorbed at time t (mg/g)
R_2	Correlation coefficient
R_L	Dimensionless separation factor
t	Adsorption time in minute
V	Volume of solution used in L

CHAPTER 1

INTRODUCTION

1.1   Heavy metal

Heavy metal contamination exists in aqueous waste streams of many industries such as metal purification, metal finishing, chemical manufacturing, mining operations, smelting, battery manufacturing, and electroplating. (Liang *et al*., 2009; Issabayeva *et al*., 2010; Lu and Gibb, 2006). As a result of industrial activities and technological development, the amount of heavy metal ions discharged into streams and rivers by industrial and municipal wastewater have been increasing incessantly (Serencam *et al*., 2007). Heavy metals are member of a loosely-defined subset of elements that exhibit metallic properties, which mainly includes the transition metals, some metalloids, lanthanides, and actinides.

Certain heavy metals such as iron, copper (Cu), zinc and manganese are required by humans for normal biological functioning. However, heavy metals such as mercury, lead, cadmium are toxic to organisms. Most of the health disorders are linked with specific tendency of heavy metals to bioaccumulate in living tissues and their disruptive integration into normal biochemical processes (Issabayeva *et al*., 2010). Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contains high level of toxic heavy metals and their presence poses environmental-disposal problems due to their non-degradable and persistence nature (Ahluwalia and Goyal,

2005). Table 1.1 shows the permissible limits and health effects of various toxic heavy metals.

Most heavy metals are cations, carrying a positive charge, such as zinc and cadmium. Soil particles tend to have a variety of charged sites on their surfaces, some positive while some negative. The negative charges of these soil particles tend to attract and bind the positively charged metal cations, preventing them from becoming soluble and dissolve in water. The soluble form of metals is more dangerous because it is easily transported, hence more readily available to plants and animals. Metal behavior in the aquatic environment is surprisingly similar to that outside a water body. Sediments at the bed of streams, lakes and rivers exhibit the same binding characteristics as soil particles mentioned earlier. Hence, many heavy metals tend to be sequestered at the bottom of water bodies. Yet, some of these heavy metals will dissolve. The aquatic environment is more susceptible to the harmful effects of heavy metal pollution. Metal ions in the environment bioaccumulate and are biomagnified along the food chain. There, their toxic effect is more pronounced in animals at higher trophic levels (Ahluwalia and Goyal, 2005)

1.2   Cu-usage, health impact, and environmental aspect

Pure Cu is rather soft and malleable, and a freshly exposed surface has a pinkish or peachy color. Its unique chemical and physical properties have made it

Table 1.1: permissible limits and health effects of various toxic heavy metals

Metal contaminant	Permissible limits by international bodies (µg/L)		Health hazards
	WHO	USEPA	
Arsenic	10	50	Carcinogenic, producing liver tumors, skin and gastrointestinal effects
Mercury	01	02	Corrosive to skin, dermatitis, anorexia, and severe muscle pain
Cadmium	03	05	Carcinogenic, causes lung fibrosis
Lead	10	05	Suspected carcinogen, loss of appetite, diminishing IQ, cause sterility, kidney problem and high blood pressure
Chromium	50	100	Suspected human carcinogen, producing lung tumors
Nickel	-	-	Causes chronic bronchitis, reduced lung function, and nasal sinus
Zinc	-	-	Causes short-term illness called "metal fume fever' and restlessness
Copper	-	1300	Long term exposure causes irritation of nose, mouth, eyes, headache, stomachache, dizziness, diarrhea

Source: Sud *et al*., 2008

one of the most commercially important metals. Since Cu is malleable, ductile, and a good conductor of heat and electricity, it is commonly used as a thermal conductor, electrical conductor, building material, and constituent of various metal alloys.

Cu compounds are commonly encountered as salts of Cu(II) ions (Cu^{2+}), which often impart blue or green colors to minerals. Cu(II) ions are soluble in water, where they function at low concentration as bacteriostatic substances, fungicides, and wood preservatives. In sufficient amounts, Cu salts can be poisonous to even higher animals and plants lives. However, Cu(II) ions at lower concentrations are essential trace nutrient to all higher organisms. In animals, including humans, it is found widely in tissues, especially in the liver, muscle, and bone, functioning as a co-factor in various enzymes and in copper-based pigments.

1.2.1   Commercial usage of Cu

Cu is heavily used in metal industries such as plating, mining and smelting, brass manufacture, electroplating industries, petroleum refining, and excessive use of Cu-based agrichemical mining (Demirbas *et al*., 2008). About 98% of all Cu is used as metal, taking advantage of its distinctive physical properties by being malleable and ductile, a good conductor of both heat and electricity, and being resistant to corrosion.

1.2.1.1.1 Electrical and electronic devices

In manufacturing electrical and electronic devices, the safe and economical distribution of electrical energy is always a constant challenge, which is the reason why Cu is widely used in this industry. Cu has the highest electrical conductivity of all metals with the exception of silver, and also has excellent corrosion resistance, strength, ductility and good workability. Cu is routinely refined to 99.98% purity before it is acceptable for many electrical applications.

By far the most important usage of Cu is in electrical wiring. With its exceptional current carrying capacity, Cu is more efficient than any other electrical conductor. Cu exceptional strength, compared to aluminum conductors, is another reason why it has remained the conductor of choice in wiring systems throughout the building industry. Cu, with its superior tensile strength can prevent dangerous overheating and wastage of energy. The pure Cu used in building wire is described by corrosion specialists as noble metal, indicating that it is not subject to galvanic corrosion when connected to other less noble metals and alloys. Cu wiring will also resist corrosion from moisture, humidity, industrial pollution and other atmospheric influence.

In electronic industry, firms such as IBM have been replacing aluminum with Cu in the computer chips they manufacture (Copper Development Association, 2011). Due to Cu superior electrical conductivity, this breakthrough

technology enables conductor channel lengths and widths to be significantly reduced, resulting in much faster operating speeds.

1.2.1.2   Cu pipes for water supply

Due to its ability to withstand earthquakes, flexibility and environmental friendly characteristic, Cu pipes are extensively used for underground and internal building pipelines. Because it resists corrosion and conducts heat well, Cu is widely used in plumbing and heating applications. Cu pipes and tubing are used to distribute hot and cold water through houses and other buildings.

1.2.1.3   Household utensils

Because Cu is an excellent conductor of heat, it is used to make cooking utensils such as saute and fry pans. An even temperature across the pan bottom is important for cooking as this ensures the food does not burn or stick to hot spots. The insides of the pans must be coated with tin, however, because too much Cu in our food is toxic.

1.2.1.2   Alloys

Since Cu is often too soft for its applications, so it is incorporated in numerous alloys. Brass, for example, is an alloy of Cu and zinc. It can be cast or machined into everything from candle sticks to cheap, gold-imitating jewelry.

Another example is bronze, which is an alloy of Cu and tin. Bronze was especially suitable for use in boat and ship fittings prior to the wide employment of <u>stainless steel</u> owing to its combination of toughness and resistance to salt water corrosion

1.2.2   Cu in human health

Cu is one of the relatively small groups of metallic elements which are essential to human health. These elements, along with amino and fatty acids as well as vitamins, are required for normal metabolic processes. Cu is a natural element that is an essential micronutrient to ensure the well being of all aerobic life forms. It plays a vital part in the development and performance of the human nervous and cardiovascular systems, as well as the skin, bone, immune and reproductive systems. Cu can also inhibit the growth of microbes, thus providing protection against harmful germs and bacteria in many environments. However, as the body cannot synthesize Cu, the human diet must supply regular amounts for absorption. The American Medical Association has recommended 1.2 − 1.3 mg/day as the dietary requirements for Cu.

On the average, drinking water accounts for less than 5% of our daily Cu intake. The U.S. Environmental Protection Agency (U.S. EPA) has determined that Cu level in drinking water should not exceed 1300 ug/L. In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine safe levels of chemicals in drinking water which do or may cause health problems. These non-enforceable levels, based solely on possible health risks and exposure,

are called Maximum Contaminant Level Goals. The MCLG for Cu has been set at 1.3 parts per million (ppm) because EPA believes this level of protection would not cause any of the potential health problems resulting from excess level of Cu. EPA has found Cu to potentially cause several health effects when people are exposed to it at elevated levels above the Action Level. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting. Long-term exposure to Cu can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Use of water that exceeds the Action Level over many years could cause liver or kidney damage.

1.2.3 Cu in the environment

Because Cu is released both naturally and through human activity, it is very widespread in the environment. Due to disposal of Cu-containing wastewater, rivers are depositing Cu –contaminated sludge on their banks. Most Cu compounds will settle and be bound to either water sediment or soil particles. When Cu ends up in soil, it strongly attaches to organic matter and minerals. In surface water Cu can travel great distances, either suspended on sludge particles or as free ions. Cu does not break down in the environment, thus it accumulates in plants and animals when it is found in soils.

Soil that is rich in Cu is not suitable for agriculture purpose as only a limited number of plants have a chance to survive. This explains why there is not much plant diversity near Cu-disposing factories. Due to the effects upon plants,

Cu is a serious threat to the productions of farmlands. It can seriously influence the proceedings of certain farmlands, depending upon the acidity of the soil and the presence of organic matter. Cu can interrupt the activity in soils as it negatively influences the activity of microorganisms and earthworms. When soils of farmland are polluted with Cu, animals will also absorb concentration of Cu that is damaging to their health.

1.3 Treatment of wastewater containing heavy metals

Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms (Aslam *et al*., 2004). Several techniques such as chemical precipitation, oxidation, reduction, coagulation, solvent extraction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies, evaporation recovery, and adsorption have been commonly employed for the removal of metal ions (Rengaraj *et al*., 2004; Ahluwalia and Goyal, 2005). Table 1.2 lists some of the common methods utilized to remove heavy metals in industrial wastewater and their corresponding advantages as well as disadvantages.

1.4 Adsorption Process

Adsorption techniques for wastewater treatment have become popular in recent years due to their efficiency in the removal of pollutants that are too stable to

Table 1.2 Conventional metal removal technologies

Method	Advantages	Disadvantages
Chemical precipitation and filtration	- cost effective - simple - requires low maintenance	- resulting in generation of large volume of sludge - affected by low pH and presence of other salts
Chemical oxidation or reduction	- ease of operate - mineralization	requires chemicals addition
Electrochemical treatment	- pure metal can be recovered for recycle - no reagents involved	require quite large amount of electricity
Reverse osmosis	- minimal maintenance - effective	not cost efficient
Evaporation	does not require addition of chemical reagent	- energy intensive - high operating cost
Ion exchange	- effective - pure effluent metal recovery is possible	- expensive resins - highly sensitive to pH of solutions

Source: Volesky, 2000

be removed by biological methods. Adsorption is a process that occurs when a gas or liquid solute adheres to a surface (adsorbent), forming a molecular or atomic film (adsorbate). This process differs from absorption, in which a substance diffuses into a liquid or solid to form a solution.

Adsorption occurs naturally, but industrialists have perfected adsorption methods to clean up hazardous waste in wastewater or purify drinking water. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Uddin *et al*., 2009). Just like surface tension, adsorption is resulted from surface energy. Atoms on the surface of adsorbent are not wholly surrounded by other adsorbent atoms. Hence, they can attract adsorbates. Adsorption can be classified into two types, which are physisorption and chemisorption, both differs in the nature of bonding. The difference between physisorption and chemisorptions is listed in Table 1.3.

1.5   Types of adsorbent

An adsorbent is a substance, usually porous in nature and with a high surface area that can adsorb substances onto its surface by intermolecular forces. The most common industrial adsorbents are activated carbon, silica gel, and alumina, because they present enormous surface areas per unit weight..

Table 1.3: Difference between physisorption and chemisorptions

Physisorption	Chemisorption
• Involves van der Waals force between adsorbate and adsorbent	• Involves formation of chemical bonds between adsorbate and adsorbent
• Low enthalpy of adsorption	• High enthapy of adsorption
• May formed multi-molecular layer	• Monolayer is formed
• Reversible process	• Irreversible process
• A general phenomenon, occurs in any solid/fluid or solid/gas system.	• A highly specific process
• Perturbation of the electronic states of adsorbent and adsorbate is minimal	• Changes in the electronic states may be detectable by suitable physical means.
• Typical binding energy is about 10–100 meV.	• Typical forms bonding with energy of 1–10 eV.
• No activation energy is invovled	• Often involves activation energy
• Equilibrium can be achieved quickly	• May take a longer time to achieve equilibrium

Source: Butt *et al*., (2003); Myers, (1999)

1.5.1 Activated carbon

The main adsorbent used in industry is activated carbon. Adsorption of heavy metal ions onto activated carbon is an efficient and well established method for their removal from contaminated waters, but high costs limit its widespread use (Zuorro and Lavacchia, 2010).

The manufacturing process consists of two phases, which are carbonization and activation. The carbonization process includes drying and then heating to separate by-products from the raw materials such as tars and other hydrocarbons, as well as to drive off any gases generated. The process is completed by heating the material over 400 ℃ in an oxygen-free atmosphere that cannot support combustion.

The carbonized particles are then "activated" by exposing them to an oxidizing agent, usually steam or carbon dioxide at high temperature. This agent burns off the pore blocking structures created during the carbonization phase to develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is larger when the exposure time is longer. The technology for manufacturing good quality activated carbon is still very cost-prohibited and the regeneration or disposal of the spent carbon is often problematic (Bhattacharyya and Sharma, 2003).

1.5.2   Silica gel

Silica gel is a matrix of hydrated silicon dioxide. It is a chemically inert, nontoxic, polar and dimensionally stable amorphous form of silicon dioxide. It is prepared by the reaction between sodium silicate and acetic acid, which is followed by a series of after-treatment processes such as aging, pickling that results in various pore size distributions.

1.5.3   Zeolite

Zeolites are crystalline solid containing silicon, aluminium and oxygen atoms which have a repeating pore network and release water at high temperature. Zeolites are polar in nature. They are manufactured by hydrothermal synthesis of sodium aluminosilicate or another silica source in an autoclave followed by ion exchange with certain cations such as sodium, lithium and calcium ions. Then, it is followed by drying of the crystals, which can be pelletized with a binder to form macroporous pellets.

1.5.4   Alumina

Alumina is mined or precipitated aluminum oxide and hydroxide. Alumina is made from bauxite, a naturally occurring ore containing variable amounts of hydrous aluminum oxides. In the industrial process, activated alumina is produced from dehydroxylating of aluminium hydroxide. Activated aluminas are basically

porous materials that consist of water and alumina in various proportions. Activated alumina's usage as an adsorbent is more or less determined by its surface functionality. The nature of this internal surface area means that the activated alumina adsorbent would attract and gather molecules from a gas or liquid to which it is exposed to. This is what is referred to as adsorption.

1.6   Biosorption

Recently, considerable attention has been given to removal of heavy metals by biosorption, which is, in simplest terms, a process of passive cations binding by biological material (Serencam *et al*., 2007). Biosorption is a complex process, mainly comprising of ion exchange, chelation and adsorption by physical forces and entrapment in inter and intra-fribillar capillaries and space of the structural polysaccharide network as a result of the concentration gradient and diffusion.

The process of biosorption has many attractive features including the selective removal of metals over a broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operation cost (Ahluwalia and Goreyal, 2005). Due to higher affinity of the sorbent for the sorbate species, the later is attracted and removed by different mechanisms. The process continues till equilibrium is established between amount of solid-bound sorbate species and its portion remaining in solution. (Das *et al*., 2007)

1.6.1   Mango leaves as adsorbent

Mango is a fruit which is indigenous to the Indian subcontinent, belonging to the genus *Mangifera* and family Anacardiaceae. It is native to southern Asia, especially Burma and eastern India. Mango exists in two races, one from India and another from the Philippines and Southeast Asia. The Indian race is intolerant of excess moisture, has flushes of bright red new growth that are subject to mildew, bearing monoembryonic fruit of high color and regular form. The Philippine race, on the other hand, is able to tolerate humidity, has pale green or red new growth and resists mildew. Although there are various Magnifera species being grown many countries, the spesies *Magnifera indica*, also known as the Indian Mango or Common Mango, is the only mango tree commonly cultivated in many tropical and subtropical regions.

Mango trees are long-lived evergreen trees that grow 35–40 m tall, with a crown radius of 10 m. Mango fruits are popular with people around the world due to their sweet pleasant flavor and essential vitamins and dietary minerals provided such as vitamins A, B, B6, C, E and K. Mature mango leaves are dark green above and pale below; the leaves are orange-pink when they are young, rapidly changing to a dark gloss red. The midrib is pale and conspicuous and the many horizontal veins distinct.

Leaves of different trees are very versatile natured chemical species as these contain a variety of organic and inorganic compounds. Cellulose,

16

hemicellulose, pectins and lignin present in the cell wall are the most important sorption sites (Qaiser et al, 2007). The important feature of these compounds is that they contain hydroxyl, carboxylic, carbonyl, amino and nitro groups which are important sites for metal sorption (Qaiser et al, 2007). Pineapple leaves, for instance, which are used in the study of Weng et al. (2009) for removal of methylene blue, contained majorly cellulose (70-80%), lignin (5-12%), and hemicelluloses.

1.7 Problem Statement

Granular activated carbon has been the most popular adsorbent in wastewater treatment application throughout the world due to its highly porous texture and large capacity to adsorb pollutants. However, adsorbent-grade activated carbon is cost-prohibited and regeneration of the used carbon is not straightforward (Bhattacharyya and Sharma, 2003). Therefore, it is no longer an attractive choice of adsorbent for small-scale industries due to cost inefficiency.

Many researches have been conducted to develop inexpensive and effective adsorbents of metal ions from plentiful sources of natural wastes in order to replace the conventional metal-removing methods available. Table 1.4 listed some low-cost and efficient biological materials which have been selected as adsorbent in recent studies.

Table 1.4: Biosorbents investigated in recent studies

Biosorbent	References
Agarose	Pandey *et al*., 2007
Banana peel	Anwar *et al*., 2009
Chitosan	Wu *et al*., 2009
Crab Shell	Dong, 2004
Grape stalk	Villaescusa *et al*., 2003
Green alga	Deng *et al*., 2006
Seaweed	Cuizano *et al*., 2009
Neem leaf	Sharma and Bhattacharyya, 2005
Palm kernel fibre	Ho and Ofomaja, 2006
Soursoup seed	Oboh. and Aluyor, 2008

The local demand for mango in 2006 was estimated at 61,570 metric tones (mt). The major consumers are the processing factories, which accounted for 54% of the total consumption while consumption by households accounted for 45% of total consumption as illustrated in Table 1.5. The amount of mango supplies in Malaysia from year 2004-2008 is listed in Table 1.6.

Table 1.5: Domestic Demands of Mango in Malaysia

Consumers (mt)	21,361	21,916	22,486	23,069	23,516
Households	854	982	1,130	1,300	1,309
Institution	28,698	33,003	37,954	43,648	43,948
Factory	50,913	55,901	61,570	68,017	68,773
TOTAL	6,898	10,487	5,499	5,871	6,243
Export (mt)	21,361	21,916	22,486	23,069	23,516

Source: *Department of Agriculture Sarawak (2011)*

Table 1.6: Supplies of mango (mt) during the period of 2004-2008 in Malaysia

Year	**2004**	**2005**	**2006**	**2007**	**2008**
Import	47,945	74,787	49,909	53,498	57,088
Production	40,414	25,142	54,102	61,200	59,192
TOTAL SUPPLY	88,359	99,929	104,011	114,698	116,280

Source: *Department of Agriculture Sarawak (2011)*

With the production of mango fruits, tons of mango leaves are produced annually. Most of the excess mango leaves wastes are discarded or composted as they have no commercial purpose, resulting in environmental pollution. Hence, the utilization of mango leaves as an adsorbent to remove heavy metals from industrial effluent can greatly reduce the amount of waste produced. This adsorbent is easy to obtain and inexpensive as well. Therefore, this study was conducted to

investigate the utilization of mango leaf as low-cost adsorbent in removal of Cu(II) ions from aqueous solution.

1.8   Objectives

The aims of this study are as follows:

- To find an inexpensive and effective adsorbent to replace commercial methods in removing heavy metals from aqueous effluent.

- To investigate the possible use of mango leaves as a low cost adsorbent for removal of Cu(II) ions.

- To study the effect of pH, effect of initial concentration of Cu(II) ions and contact time, effect of agitation rate, effect of particle size and effect of chelating agent on the adsorption of Cu(II) ions on mango leaves.

1.9   Scope of Study

Heavy metal contaminants are present in wastewater from many industries such as metal manufacturing, electroplating, dye and paint, chemicals and fertilizer. Heavy metal removal has become a serious environmental concern due to the toxic and cumulative nature of heavy metals in various life forms. Mango leaves are a low-cost agriculture waste which could be used for adsorption of heavy metals in wastewater. Hence, this study focused on the adsorption capabilities of dried mango leaves powder under various conditions.

CHAPTER 2

LITERATURE REVIEW

The contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem (Ajmal *et al*., 2002). Adsorption process using activated carbon as an adsorbent is one of the effective conventional methods used to remove heavy metals from industrial effluent. However, adsorbent-grade activated carbon is expensive and the regeneration of the used carbon is often difficult, resulting in low feasibility for small scale industries. Hence, considerable attention has been given to the use of agriculture waste materials as an alternative to replace the conventional adsorbents. Agriculture waste materials are inexpensive and available in large quantities, thus they can be disposed without concerning expensive regeneration process.

2.1   Previous study using mango leaves as adsorbent

Murugan *et al*. (2010) investigated the potential of mango leaves powder for removal of Grey BL dye from aqueous solution. Scanning electron micrograph showed the presence of a rough surface morphology with pores of different sizes on mango leavss. It was found out that the percentage of dye adsorbed increased as the initial pH increased from pH 2 to 7, reaching a maximum value of 64.25 of dye removal at pH 7. The experimental data obtained fitted well to both Langmuir (R^2 = 0.998) and Freundlich (R^2 = 0.997) isotherm model. The maximum adsorption capacity (q_m) calculated based on Langmuir isotherm model was 33.7 mg/g.

Kinetic study of the adsorption showed that equilibrium was reached within 1 hour of contact and the adsorption kinetic followed the pseudo second-order model.

The comparison of adsorption capacities of guava and mango leaves powder for adsorption of Methylene Blue dye was studied by Patel and Vashi (2009). They reported that the best adsorption for both leaves was obtained at basic pH. The amount of dye adsorbed decreased with rising temperature from 310 K to 360 K, indicating the exothermic nature of the process. The adsorption kinetic and equilibrium fitted the pseudo second-order and Langmuir isotherm models respectively. The q_m obtained based on Langmuir isotherm model was 315.6 mg/g for guava and 304.6 mg/g for mango leaves.

2.2 Other studies using agriculture wastes for heavy metals removal

2.2.1 Almond shell

Mehrasbi et al. (2008) studied the adsorption of Pb(II) and Cd(II) ions from aqueous solution by using alkali-modified, acid-modified and water-modified almond shells. It was found that almond shells which had been alkali-modified had a much higher adsorption capacities than acid-modified and water-modified shells, which was 2-9 mg/g for Pb(II) ion and 2-7 mg/g for Cd(II) ion. The best pH for adsorption was between 5 and 6 and the adsorption values decreased with decreasing pH. The best dosage for adsorption was 1 to 3 g/L. The experimental data obtained fitted well with Langmuir isotherm, with R^2 of 0.997 for Pb(II) ion

and R^2 of 0.969 for Cd(II) ion. The value of q_m for adsorption of Pb(II) and Cd(II) ions was 8.13 mg/g and 7.19 mg/g respectively, indicating that the affinity of almond shells for Pb(II) ion is stronger than that of Cd(II) ion. The values of standard free energy (ΔG) for adsorption of Pb(II) and Cd(II) ions was -33.5 kJ/mol and -25.5 kJ/mol respectively, showing that the adsorption process was thermodynamically spontaneous under natural condition.

2.2.2   Bael tree leaves

Chakravarty *et al*. (2009) investigated the adsorption of Pb(II) ion from aqueous solution onto bael leaves. They found out that the percentage uptake increased with higher pH values, with pH 4 as the optimum pH for adsorption, having uptake of approximately 97%. Above pH 4, the percentage uptake of Pb(II) ion decreased. The optimum bael leaves dose was 0.2 g for concentration of 48.2 mg/L, 87.8 mg/L and 180.2 mg/L. The experimental data obtained fitted well with Langmuir isotherm ($R^2 = 0.97$) compared to Freundlich isotherm ($R^2 = 0.80$), indicating a monolayer adsorption. An analysis on the experimental data suggested that the kinetic for adsorption of Pb(II) ion onto bael leaves followed the pseudo second-order model.

A similar study was conducted by Kumar *et al*. (2009). They found out that the optimum pH for adsorption of Pb(II) ion onto bael leaves was pH 5, with highest removal rate of 84.93%. Above pH 6, metal precipitation occurred. The maximum removal of Pb(II) was obtained at adsorbent dosage of 20 g/L for 50

mg/L of Pb(II) ion. In thermodynamic study, negative values of ΔG were obtained from 30℃ to 60℃, indicating the feasibility and spontaneous nature of the adsorption. Four isotherm equations were tested in the study, which were Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The results obtained by Kumar *et al*. (2009) agreed with the study of Chakravarty *et al*. (2009), in which Langmuir isotherm was the preferred model, having R^2 value of 0.993 and q_m of 4.065 mg/g. The pseudo second-order kinetic model agreed well with the dynamical behavior for the adsorption of Pb(II) ion onto bael leaves. They concluded that bael leaves powder may be used as an low-cost and abundant source to remove Pb(II) ion from wastewater.

Kumar and Kirthika (2010) conducted a study to remove Zn(II) ion from aqueous solution by using bael leaves. They found out that the maximum removal of Zn(II) ion was obtained in the adsorbent dosage of 20 g/L for 50 mg/L of Zn(II) ion and the adsorption process reached equilibrium in 30 minutes. The experimental data fitted well with Langmuir isotherm as well, with q_m of 2.083 mg/g at 25 ℃. The kinetic processes of Zn(II) ion adsorption onto bael leaves obeyed the pseudo second-order model (R^2 = 0.972), suggesting that chemisorption could be the rate-limiting step.

2.2.3   Coconut shell

The potential of sulfuric acid-carbonized coconut shell to be used as a low-cost adsorbent for removal of Pb(II) ion was studied by Sekar *et al* (2004). The

24

coconut shell carbon exhibited the highest adsorption of Pb(II) ion at pH 4.5. Above and below this pH, the extent of adsorption of Pb(II) ion was rather low. The kinetic of Pb(II) ion adsorption onto coconut shell carbon followed the first-order reversible kinetic, where the forward rate constants for removal of Pb(II) ion were much higher than the backward rate constants for desorption process. Adsorption isotherms were generated by using Langmuir, Freundlich and Tempkin isotherm models and the experimental data fitted well to all three isotherms. The q_m obtained from Langmuir isotherm at pH 4.5 was 26.5 mg/g. They concluded that the activated carbon prepared from coconut shell was efficient in removing Pb(II) ion from aqueous solution.

Gaikwad (2004) evaluated the ability of activated charcoal prepared from coconut shell in removing Cd(II) ion from aqueous solution. In the study, pH 6 and control time of 80 minutes were found to be optimum. The extent of removal increased linearly from pH 2 to 6 and decreased beyond that due to formation of soluble hydroxy complexes. The Freundlich and Langmuir isotherms were plotted at temperature range from 27 ℃ to 50 ℃. It was observed that the Freundlich isotherm with higher values of regression coefficients was better obeyed by the system. This indicated the heterogeneous surface energy of coconut shell activated carbon. The ∆G values were negative at all temperature and increased with increasing temperature, suggesting that the adsorption process is spontaneous in nature and the spontaneity decreased with higher temperature.

2.2.4   Grape stalk

The use of grape stalk wastes generated in wine production process for removal of Cu(II) and Ni(II) ions from aqueous solutions was investigated by Villaescusa *et al*. (2003). They discovered that the adsorption process was relatively fast and reached equilibrium after about 60 minutes of contact time. Fourier transform infrared spectroscopy (FTIR) analysis indicated a strong C-O bond at wavenumber 1058 cm^{-1} due to the lignin structure present which might be responsible for the metal binding. The adsorption process was pH-dependant, with the maximum adsorption occurred at pH 5.5 to pH 6. Villaescusa *et al*. (2003) studied the effect of sodium chloride concentration on metal uptake and they found out that a higher concentration of sodium chloride caused a reduction in adsorption of Cu(II) and Ni(II) ions onto grape stalks due to competition of sodium cation with metal cations. The q_m obtained from Langmuir model at pH 6 were 1.593 X 10^{-4} mol/g and 1.818 X 10^{-4} mol/g for Cu(II) and Ni(II) ions respectively. Besides single metal system, equilibrium batch sorption studies were also performed using a two metal system containing Cu(II) and Ni(II) ions. Based on the extended Langmuir model, in the binary system, the q_m values of Cu(II) ion was similar to that in single system while that of Ni(II) ion was slightly lower. The significant release of cations including Ca(II), Mg(II) and K ions from grape stalks after uptake of Cu(II) and Ni(II) ions indicated that ion exchange took place in the sorption process.

2.2.5 Mango peel

Mango peel waste was evaluated as a new sorbent for adsorption of Cd(II) and Pb(II) ions from aqueous solution by Iqbal *el at*. (2008). FTIR analysis revealed that carboxyl and hydroxyl groups were the principle functional sites taking part in the adsorption process. Sorption kinetic and equilibrium followed the pseudo second-order and Langmuir isotherm model respectively. The R^2 with respect to Cd(II) ion were noted to be 0.998 and 0.952 respectively for Langmuir and Freundlich models, while that for Pb(II) ion were 0.996 and 0.975 respectively. The q_m of Cd(II) and Pb(II) ions were found to be 68.92 mg/g and 99.05 mg/g respectively. Chemical blocking of carboxyl and hydroxyl groups of the mango peels indicated that 72.46% and 76.26% removal of Cd(II) and Pb(II) ions respectively, was due to carboxylic group, while 26.64% and 23.74% was due to hydroxylic group. The Energy Dispersive X-ray analysis showed the release of Ca(II) and K ions after uptake of Cd(II) and Pb(II) ions by mango peels, indicating the involvement of ion exchange mechanism. The study also showed that mango peels could be reused for five cycles without significant loss of adsorption capacity, proving its effectiveness.

2.2.6 Orange peel

Liang *et al*. (2009) conducted a comparative study of Pb(II) ion removal by orange peel and orange peel xanthate. Xanthation was performed by reacting the hydroxyl group in orange peel with carbon disulfide under caustic condition. FTIR

analysis identified the presence of sulfur groups in orange peel xanthate. The Freundlich model fitted better with the isotherm data obtained for orange peel, whereas the opposite was the case for orange peel xanthate. After xanthation of orange peel, the q_m value was found to be 204.50 mg/g at 30 °C, pH 5, which was 50% more than before xanthation. The kinetic study showed that equilibrium was achieved within 20 minutes of contact and best-fit pseudo second-order model. Temperature had little effect on the adsorbed amount and this suggested that the adsorption of Pb(II) ion by orange peel xanthate was chemisorption. The authors concluded that orange peel xanthate had much potential to be used as an efficient adsorbent for the removal of Pb(II) ion from wastewater.

2.2.7 Peanut shell

In the study of Witek-Krowiak *et al*. (2010), peanut shell was used as a low-cost biosorbent to adsorb Cu(II) and Cr(III) ions from aqueous solutions. The metal uptake increased with rising pH from the range of 2 to 5, reaching a maximum value at pH 5. It was observed that the maximum removal of Cu(II) and Cr(III) ions took place within the first 20 minutes. The kinetics of the biosorption was examined and the process was best described using the pseudo second-order model. The study demonstrated q_m of 25.30 mg/g for Cu(II) ion and 27.86 mg/g for Cr(III) ion under optimum conditions of pH 5, 10 g/L of peanut shells, temperature of 20 °C and contact time of 1 hour. The results obtained from this study suggests that peanut shells biomass is a potential low-cost biosorbent for removal of Cu(II) and Cd(III) ions from aqueous media.

Liu *et al.* (2010) investigated the adsorption of Hg(II) and Cd(II) ions from aqueous solution by EDTA modified peanut shells as a function of initial pH, adsorption time and initial metals concentration. FTIR analysis showed that amine and hydroxyl groups were involved in the modification process. The removal rates of Hg(II) and Cd(II) by peanut shells were tested at pH range of 2 to 7 and it was found that the adsorption rates increased with raise in pH. The equilibrium time for the adsorption of Hg(II) and Cd(II) onto peanut shells was 30 minutes and 2 hours respectively, with the uptake rate of Hg(II) much higher than that of Cd(II). The adsorption kinetic and equilibrium were best described by pseudo second-order and Langmuir models respectively. Langmuir isotherm model indicated q_m values of 14.17 mg/g for Cd(II) ion and 30.72 mg/g for Hg(II) ion.

2.2.8 Pomelo peel

Saikeaw *et al.* (2009) conducted a study on the adsorption of Cd(II) ion from aqueous solution onto pomelo peel. They examined the influence of pH, initial Cd(II) ion concentration and contact time on the sorption process. The biosorption of Cd(II) ions increased with increasing pH from pH 1-5 and reached a maximum value at pH 5. Adsorption isotherms were generated based on Langmuir and Freundlich isotherms and it was noted that at pH 5, the experimental data fitted better with Langmuir isotherm ($R^2 = 0.97$) than Freundlich isotherm ($R^2 = 0.86$). Based on the Langmuir isotherm, the q_m obtained was 21.83 mg/g. The kinetic study showed a very fast increase in biosorption rate of Cd(II) ions by the pomelo peel at the first 30 minutes and the equilibrium was reached at around 60

minutes. Biosorption kinetics study was carried out at pH 3 and pH 5, and the pseudo second-order gave high R^2 values at both pH.

2.2.9 Potato peel

Aman *et al*. (2007) examined the use of potato peels as solid waste for the removal of Cu(II) ion from aqueous solution. The potato peels were burned in furnace at 947 K to obtained charcoal of the peels. The optimum pH for the adsorption process was found to be pH 6. The adsorption data fitted well to both Langmuir and Freundlich isotherm models. Thermodynamic study on the adsorption of Cu(II) ion onto potato peels charcoal at temperature range of 303 K to 343 K indicated the stable, exothermic and spontaneous nature of the sorption process.

Later, the potential of potato peels waste in removing Ni(II) ion was evaluated by Prasad and Abdullah (2009). They discovered the maximum biosorption efficiency was obtained at pH 7, with removal of 67.75%. The adsorption data fitted both Langmuir ($R^2 = 0.975$) and Freundlich ($R^2 = 0.983$) as well, with q_m of 13.09 mg/g. The Separation factor (R_L) value obtained was 0.368 and 0.088 at initial concentration of 20 mg/L and 120 mg/L respectively, showing favourable biosorption process. The pseudo second-order kinetic model described the experimental data better than the pseudo first-order model, suggesting the involvement of chemisorption.

2.2.10 Rice husk

Naiya *et al.* (2008) conducted a study on the sorption of Pb(II) ion onto rice husk ash, a solid obtained from rice processing mill after burning of rice husk. Experiments were conducted from pH 2 to 6 to avoid metal hydroxides precipitation and it was found out that at pH around 5, maximum amount of Pb(II) ion was removed. The adsorption equilibrium was achieved by 1 hour of contact time when 10 mg/L of Pb(II) ion was used. The experimental data was best described by Langmuir isotherm model as evident from high R^2 value of 0.9986 and the q_m obtained was 91.74 mg/g. Adsorption of Pb(II) ion onto rice husk ash followed the pseudo second-order model. Thermodynamic parameters from the study showed the endothermic and spontaneous nature of the adsorption.

Competitive adsorption of Cd(II) and Ni(II) ions from aqueous solution was carried out by Srivastava *et al.* (2008) by using rice husk ash obtained from paper mill. The adsorption of Cd(II) and Ni(II) ions increased with increasing pH from pH 2 to 6. At pH greater than 6, the adsorption of both metal ions was maximum and constant, with the amount of adsorbed Ni(II) ion larger than that of Cd(II) ion. The single metal ion equilibrium sorption data was represented by non-competitive Redlich-Peterson and Freundlich models. The simultaneous adsorption of Cd(II) and Ni(II) ions from binary system was also investigated and it was noted that the combined effect of Cd(II) and Ni(II) ions on the total sorption was antagonistic in nature and best represented by the extended Freundlich model.

As a conclusion, in both binary and single-component system, the affinity of rice husk ash for Ni(II) ion was greater than that for Cd(II) ion.

2.2.11 Rubber leaves

Hanafiah *et al*. (2006) carried out an investigation on the ability of rubber leaves powder to adsorb Pb(II) ion from aqueous solution through batch experiments. The adsorption kinetic was best represented by pseudo second-order model, with the theoretical values of q_e agreed well with that from the experiment and indicated that chemisorptions may be the rate-limiting step. Both Langmuir and Freundlich isotherm models described the equilibrium data well and the q_m was found to be 46.73 mg/g at 303 K. The adsorption process was evident to be exothermic and spontaneous in nature.

Ngah and Hanafiah (2007) studied the adsorption of Cu(II) ion from aqueous solution by rubber leaves powder. They reported that equilibrium was achieved at about 60 minutes of contact and the optimum pH for adsorption was around pH 4-5. The adsorption of Cu(II) ion by rubber leaves followed the pseudo second-order kinetic model. Langmuir isotherm model gave q_m value of 8.92 at pH 4. The thermodynamic study suggested that the adsorption process was more favourable at lower temperature due to decreasing value of ΔG from -1.48 kJ/mol at 320 K to -3.38 kJ/mol at 300 K.

2.2.12 Seaweed

Cuizano *et al*. (2009) studied the application of brown seaweeds *Lessonia nigrescens Bory* (L13) and *Macrocystis integrifolia Bory* (S12) in removing Pb(II) ion from aqueous solution. Scanning electron micrograph revealed a homogeneous surface texture for both seaweeds, with a very well defined organization of polysaccharide chains. Batch experiments reported a maximum adsorption capacity at pH 4 and pH 5 for seaweed L13 and S12 respectively. The adsorption of Pb(II) ion was analyzed using the models given by Langmuir and Freundlich isotherm and the equilibrium data from both seaweeds followed the Langmuir isotherm at all different masses of L13 and S12 utilized. The q_m of seaweed L13 was 893 mg/g whereas that of S12 was 730 mg/g. An increment in the ionic strength of solution, represented by sodium nitrate, resulted in adverse effect on the adsorption of Pb(II) ion by both seaweeds due to competition of sodium ion and Pb(II) ion for adsorption sites.

2.2.13 Sunflower leaves

The potential use of dried sunflower leaves to remove Cu(II) ion from aqueous solution was examined by Bena ïssa and Elouchdi (2006). Maximum Cu(II) ion sorption occurred around pH 5 to 6. The adsorption equilibrium and kinetic were best described using Langmuir isotherm and pseudo second-order kinetic models. The q_m of dried sunflower leaves at natural pH was found to be 89.37 mg/g based on the Langmuir isotherm model.

2.2.14 Spent tea leaves

Zuorro and Lavecchia (2010) evaluated the removal efficiency of Pb(II) ion by spent leaves of green and black tea using batch adsorption experiments. They reported removal efficiency up to 98%-99% using spent tea leaves as adsorbent. Physiochemical characterization showed that both leaves were rich in crude fiber (36.2% w/w) and protein (22.6%). The experimental data fitted well to Langmuir isotherm model, yielding q_m of 83.3 mg/g and 101.0 mg/g at 40 ℃ for green and black tea leaves respectively. The percent removal of Pb(II) by black tea leaves was found to be 98.4% and that of green tea leaves was 98.0% at 25 ℃ whereas at 40 ℃, the percent removal was 99.3% and 98.0% for black and green tea leaves respectively. They concluded that spent tea leaves was more effective in removing Pb(II) than conventional adsorbents such as activated carbon.

CHAPTER 3

MATERIALS AND METHOD

3.1   Preparation of adsorbent

Mango leaf was selected as adsorbent for removal of Cu(II) ion in this study. The leaves were obtained from a Chokanan Mango tree located in local house yard at Sekinchan, Malaysia. Mature mango leaves were collected and each leaf was washed thoroughly under running tap water to remove dust and any adhering particles. The leaves were then dried under sunlight for a few days and then in oven at 80 ℃ until it became crisp. The dried leaves were crushed and blended to powder form using a blender. The mango leaves powder was boiled and washed for several times until it was free of colour and turbidity. Then, the powder was dried in oven at 80 ℃ overnight and stored in an airtight plastic for further use to avoid contact with moisture in atmosphere.

Figure 3.1: Mature mango leaves (left); dried mango leaves (right)
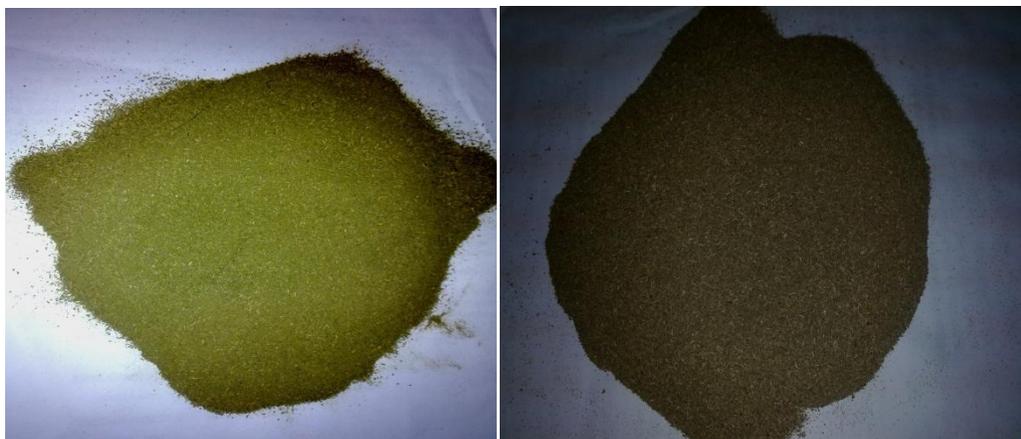
Figure 3.2: Mango leaves powder, before washing (left); after washing (right)

3.2 Preparation of Cu(II) ions solution

Cu(II) ion was used as the adsorbate in this study. A 100 mg/L Cu(II) stock solution was prepared by dissolving accurately weight amount of copper(II) nitrate trihydrate $(Cu(NO_3)_2.3H_2O)$ in deionised water. Appropriate dilution of the stock solution was carried out in order to obtain the desired concentration of Cu(II) solution used later in the experiment.

3.3 Batch experiments

Batch experiments were carried out at room temperature by shaking a mixture of 0.1 g of mango leaves powder and 20 mL of Cu(II) solution in a centrifuge tube, at agitation rate of 150 rpm for 2 hours until equilibrium was reached unless otherwise stated. All samples were carried out in duplicate under the same conditions and the average results were taken. After agitation, the powder

was removed by filtration using filter paper. The concentration of Cu(II) in the filtrates as well as in the control samples were determined by using flame atomic absorption spectroscopy (FAAS) spectrometer.   The uptake of Cu(II) was calculated using the equation 3.1:

$$\text{Uptake (\%)} = \frac{C_o - C_e}{C_o} \times 100\% \qquad [3.1]$$

where C_o = Initial concentration of Cu(II) (mg/L)

C_e = Concentration of Cu(II) at equilibrium state (mg/L)

3.3.1   Effect of pH

The effect of pH on Cu(II) adsorption was studied by agitating 0.1 g of mango leaves powder and a series of 20 mL Cu(II) solution with concentration of 10 mg/L at different pH value, ranging from pH 2-10. The samples were agitated for 2 hours to reach equilibrium and agitation speed was maintained at 150 rpm. The pH of Cu(II) solution was adjusted to the desired value by drop wise addition of hydrochloric acid (HCl) or sodium hydroxide (NaOH) of various molarity.

3.3.2   Effect of initial concentration and contact time

The effect of initial concentration and contact time was investigated by agitating 0.1 g of mango leaves powder in 20 mL of 5 mg/L of Cu(II) solution over time periods of 5, 10, 15, 30, 60, 120, 180 and 240 minutes at constant

agitation speed of 150 rpm. The above step was then repeated using 10 mg/L and 20 mg/L of Cu(II) solution respectively.

3.3.3 Effect of agitation rate

In this study, 0.1 g of mango leaves powder was agitated at 50 rpm in 20 mL of 10 mg/L of Cu(II) solution over time periods of 5, 10, 15, 30, 60 and 120 minutes. The above step was then repeated using agitation speed of 100 rpm and 200 rpm.

3.3.4 Effect of particle size

The effect of particle size was studied by using four different sizes of mango leaves powder, which are <106 μm, 106-250 μm, 250-425 μm, 425 μm-1mm. 0.1g of mango leaves powder which were sieved into desired size was agitated at 150 rpm in 20 mL of 10 mg/L of Cu(II) solution over time periods of 5, 10, 15, 30, 60, and 120 minutes.

3.3.5 Effect of chelating agent

The chelating agents used in this study were sodium salt of ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). 10 mg/L of EDTA was added to a mixture of 0.1 g of mango leaves powder and 20 mL of Cu(II) solution and the mixture was agitated at 150 rpm over time periods of 5, 10,

15, 30, 60 and 120 minutes. The above step was repeated by using 30 mg/L of EDTA, 10 mg/L of NTA and 30 mg/L of NTA respectively.

3.3.6   Study of sorption isotherm

The equilibrium isotherm was determined by using a range of different concentration of Cu(II) solution (10, 20, 30 ,40 ,50, 60, 70, and 80 mg/L). Mixture of 0.1 g of mango leaves powder and 20 mL of Cu(II) solution was contacted at agitation speed of 150 rpm for 32 hours, which was sufficient to reach equilibrium. The amount of Cu(II) adsorbed at equilibrium (q_e) was calculated by using the equation 3.2:

$$q_e = \frac{(C_o - C_e)\, V}{m} \qquad\qquad [3.2]$$

where   V = volume of solution (L)

   m = mass of adsorbent (g)

Chapter 4

Results and Discussion

4.1   Fourier Transform Infrared (FTIR) Analysis

FTIR analysis was carried out in order to identify the different functional groups present in mango leaves which were responsible for adsorption process. The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wavenumbers as reported in literatures.

Figure 4.1 shows the FTIR spectrum of mango leaves before adsorption. The broad and intense peak at 3448 cm^{-1} was attributed to the stretching of O-H group due to inter- and intramolecular hydrogen bonding of polymeric compounds such as alcohols or phenols as in pectin, hemicelluloses, cellulose and lignin (Iqbal *et al.*, 2008). The peak observed at 2925 cm^{-1} was associated with the stretching vibrations of C-H bond of methyl, methylene and methoxy groups (Feng *et al.*, 2008). The peaks around 1654 cm^{-1} corresponded to the C=C stretching which might be attributed to the presence of lignin aromatic bond (Florido *et al.*, 2009). The intense peak at 1057 cm^{-1} corresponded to the C-O stretching of alcohol or carboxylic acid (Ngah & Hanafiah, 2007).

The FTIR spectrum of mango leaves loaded with Cu(II) ions was presented in Figure 4.2. It was observed that the peaks at 3438, 2925, 1654, and 1057 cm^{-1}
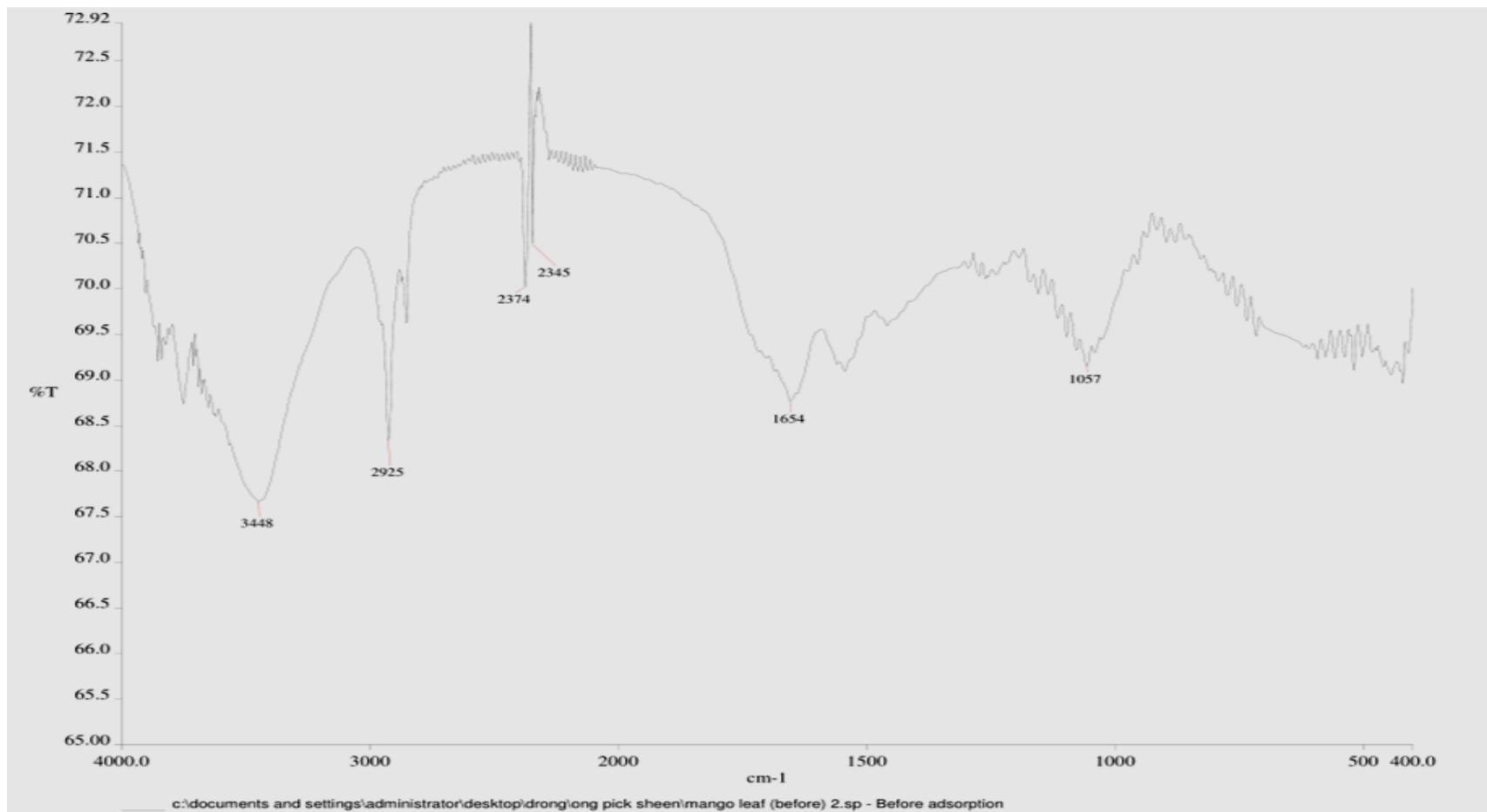
Figure 4.1: FTIR spectrum of mango leaves before adsorption
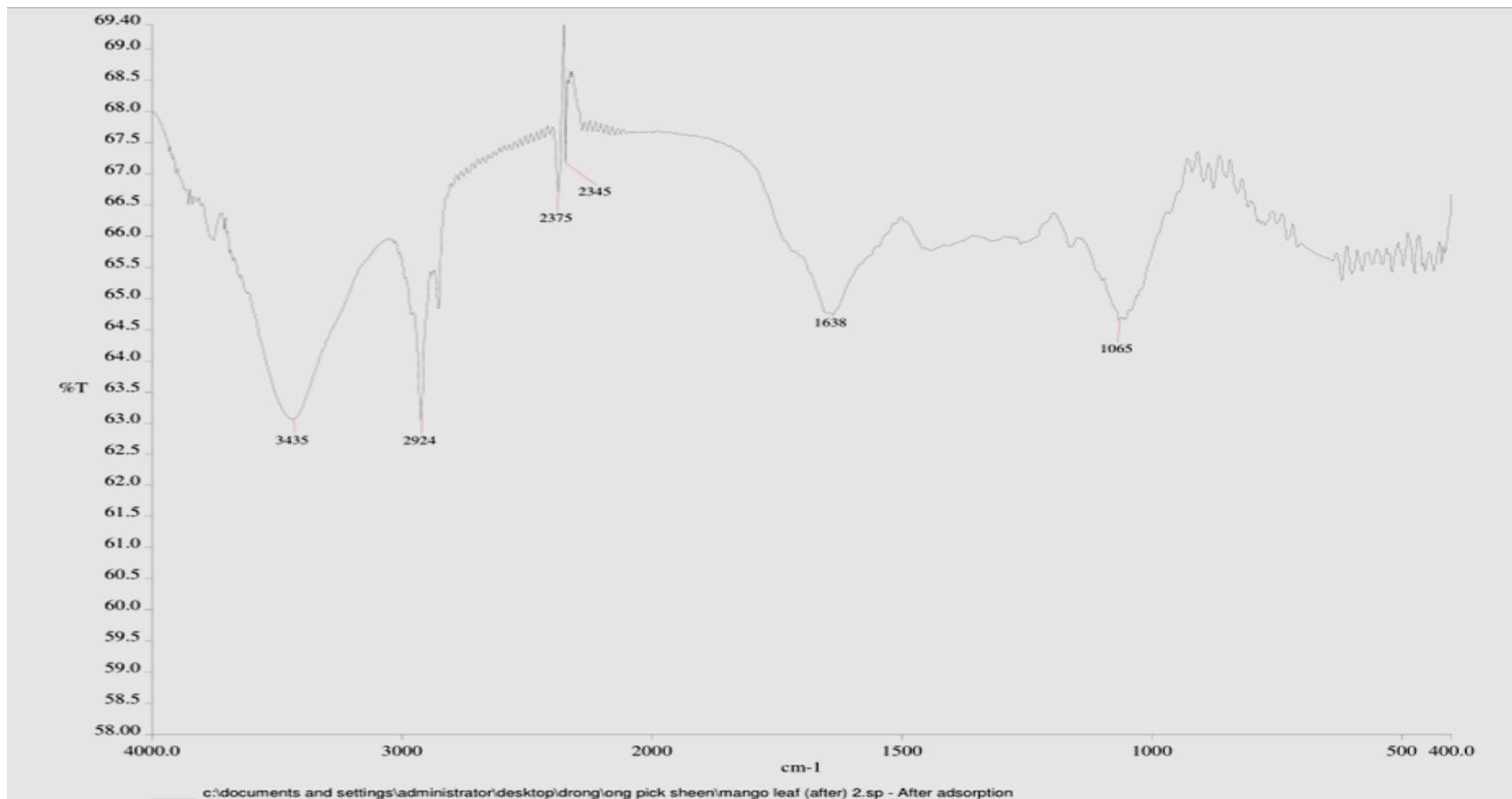
Figure 4.2: FTIR spectrum of mango leaves loaded with Cu(II) ions

before adsorption had shifted to 3435, 2924, 1638, and 1065 cm^{-1} respectively. This was due to the participation of these functional groups in the binding of Cu(II) ions (Ngah & Hanafiah, 2007).

The comparison of band positions of various functional groups in mango leaves before and after Cu(II) ions adsorption was given in Table 4.1.

Table 4.1: Comparison of FTIR band positions before and after Cu(II) ions adsorption

Assignment	Wavenumber (cm^{-1})	
	Before adsorption	**After adsorption**
O-H stretching	3448	3435
C-H stretching	2925	2924
C=C stretching	1654	1638
C-O stretching	1057	1065

4.2   Effect of pH

pH of aqueous solution is an important parameter governing the adsorption process as it not only affects the surface charge of adsorbents, but also influences the degree of ionization of metal ions in solution. The effect of solution pH on the

43

adsorption of Cu(II) ions onto mango leaves was evaluated in the pH range of 2 to 10 and the result was showed in Figure 4.3. At pH 2, which had the highest acidity, Cu(II) ions uptake by mango leaves was the lowest, which was only 15.19%. The uptake increased rapidly to 89.77% at pH 3. At the range of pH 4 to 10, the uptake became consistent, ranging between 95.14% and 97.75%. The maximum adsorption was found to be 97.75% for Cu(II) ions at pH 5.

The low adsorption of Cu(II) ions at pH 2 was due to high concentration and high mobility of H^+ ions, which competed with Cu(II) ions for the adsorption sites, hindering the adsorption of Cu(II) ions by adsorbent. Protonated adsorption sites were incapable of binding Cu(II) ions due to electrostatic repulsion between positively charged Cu(II) ions and positive charged sites. Hence, only low percentage of Cu(II) ions were adsorbed. As the pH increased, there were fewer H^+ ions present in the solution and consequently more negatively charged sites were made available and this facilitated greater Cu(II) ions uptake by electrostatic attraction.

Similar optimum pH value was also reported for adsorption of Cu(II) ions by other leaf materials, such as rubber leaves in the study carried out by Ngah and Hanafiah (2007), sunflower leaves used in the investigation of Benaïssa and Elouchdi (2006), and *Tectona Grandis* leaves utilized in the study by Kumar *et al*. (2006).
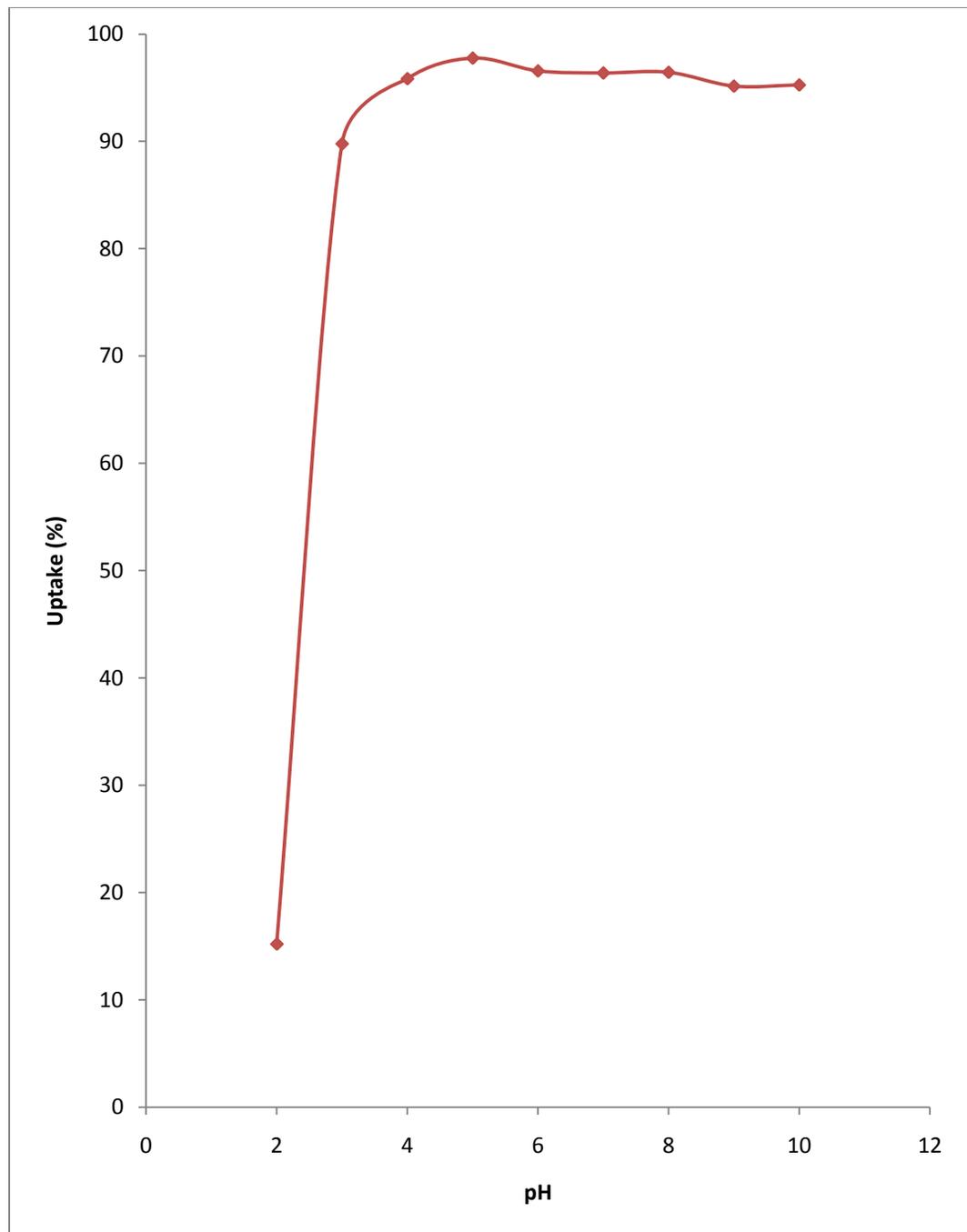
Figure 4.3: Effect of pH on uptake of Cu(II) ions by mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 10 mg/L of Cu(II) solution at 150

rpm for 2 hours.

4.3   Effect on initial metal ion concentration and contact time

Figure 4.4 shows the dependence of the percentage uptake on the initial metal ions and contact time. The data obtained from the adsorption of Cu(II) ions onto mango leaves showed that the adsorption increased with increasing contact time. The plots in Figure 4.4 show a rapid uptake of Cu(II) ions during the first 5 minutes of agitation, after which the rate of sorption became slower, attaining equilibrium in 60 minutes. Further increase in contact time had negligible effect on the amount of ions adsorbed. The rapid metal uptake was 93.59%, 92.76% and 92.48% for the total sorption of Cu(II) solutions with initial concentration of 5 mg/L, 10 mg/L and 20 mg/L respectively.

The fast initial uptake occurred in the early stage of adsorption was due to the fact that most of the binding sites on mango leaves were free which allowed quick binding of Cu(II) ions on the biomass (Gupta *et al*., 2008). As the binding sites became exhausted, the uptake rate slowed down due to competition for decreasing availability of actives sites by metal ions. According to the test results, agitation time was fixed at 120 minutes for the rest of the batch experiment to ensure equilibrium was achieved. The plots of metal uptake as a function of time are single, smooth, and continuous, suggesting the possibility of the formation of monolayer coverage of Cu(II) ions at the outer surface of adsorbent (Pimentel *et al*., 2007).
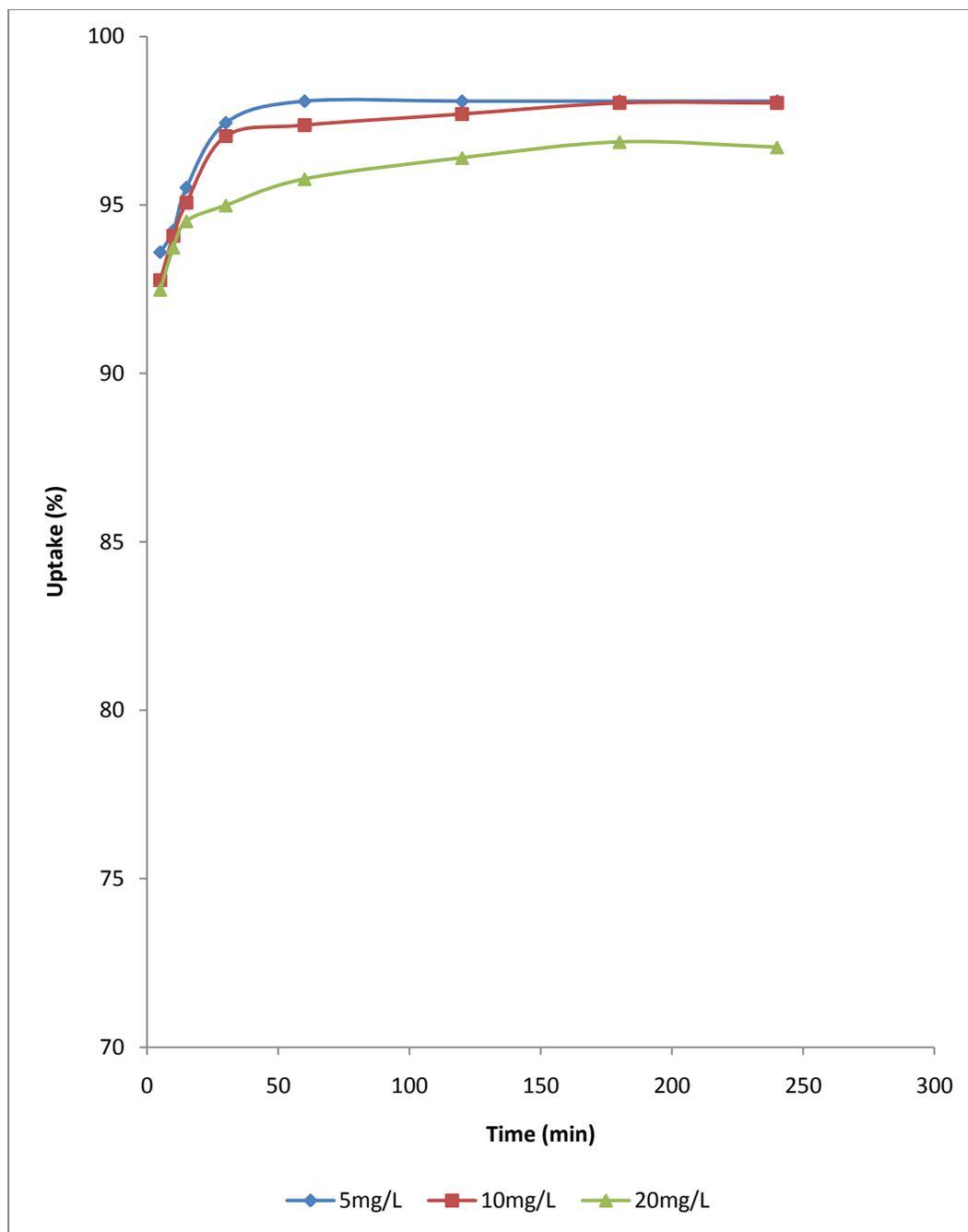
Figure 4.4: Effect of initial metal ion concentration and contact time on uptake of Cu(II) ions by mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 5 mg/L, 10 mg/L and 20 mg/L of

Cu(II)   solution   at   150   rpm   for   2   hours.

The two-phase metal uptake process had been extensively reported in previous reports on the biosorption of heavy metal with different sorbents. Chen *et al*. (2009) investigated the adsorption of Cu(II) ions by cinnamomum camphora leaves and reported a similar two-stages adsorption. The sorption rate was rapid in the beginning of their experiment with more than 90% of adsorption took place in the first 10 minutes, and thereafter adsorption proceeded at slower rate, reaching equilibrium within 30 minutes.

Figure 4.4 showed that the uptake of Cu(II) ions decreased from 98.08% to 96.71% with the increment of initial Cu(II) ions concentration from 5 mg/L to 20 mg/L. According to SenthilKumar *et al*. (2010), at lower metal ions concentration, the percentage uptake was higher due to larger surface area of adsorbent being available for adsorption. When the concentration of Cu(II) ions became higher, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites. At a higher concentration of Cu(II) ions, the ratio of initial number of moles of Cu(II) ions to the adsorption sites available was higher, resulting in lower adsorption percentage.

However, different from the percentage uptake, with the increasing initial Cu(II) ions concentration from 5 mg/L to 20 mg/L, the amount of Cu(II) ions adsorbed at equilibrium (q_e) increased from 0.8182 mg/g to 3.3048 mg/g. This occurred due to increase in driving force of the concentration gradient to overcome all mass transfer resistance of Cu(II) ions between aqueous and solid phases and

accelerate the probable collision between metal ions and sorbents, thus resulting in higher uptake of Cu(II) ions (Chen *et al*., 2005).

4.3.1   Adsorption kinetic study

The study of adsorption kinetics in wastewater treatment is important as it not only provides valuable insight into the reaction pathways and the mechanism of sorption reactions, but also describes the solute uptake rate, which in turn control the residence time of sorbate uptake at the solid-solution interface (Ho and Mckay, 1998). The kinetics data obtained from adsorption of Cu(II) ions onto mango leaves was studied by using two common kinetic models, which are the pseudo-first order kinetic model and pseudo-second order kinetic model. The best fit model was selected based on the linear regression correlation coefficient (R^2), which is a measure of how well the predicted values from a forecast model match with the experimental data.

4.3.1.1   Pseudo-first order kinetic model

The pseudo-first order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo-first order equation was expressed in equation 4.1 (Lagergren, 1898):

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad\qquad [4.1]$$

Where

q_e = Amount of Cu(II) ions adsorbed at equilibrium (mg/g)

q_t = Amount of Cu(II) ions adsorbed at time t (mg/g)

k_1 = pseudo first-order rate constant (min^{-1})

By applying the boundary conditions of t = 0 and t = t and correspondingly q_t = 0 and $q_t = q_t$ and integrating equation 4.1 gave:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1 t}{2.303} \tag{4.2}$$

The resultant equation 4.2 in linear form was:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{4.3}$$

Figure 4.5 showed the linear plots of $\log(q_e\text{-}q_t)$ against t at initial Cu(II) ions concentration of 5 mg/L, 10 mg/L and 20 mg/L. The k_1 and q_e values were determined from the slope and intercept of the linear plots in Figure 4.5 respectively. Table 4.2 gave the values of k_1, experimental and calculated values of q_e, as well as the R^2 values for the pseudo-first kinetic plots. As can be seen, although the R^2 values obtained from the plots were high. The theoretical values of q_e were far lower than the corresponding experimental data obtained. This suggested a poor fit between the kinetics data and the pseudo-first order model.
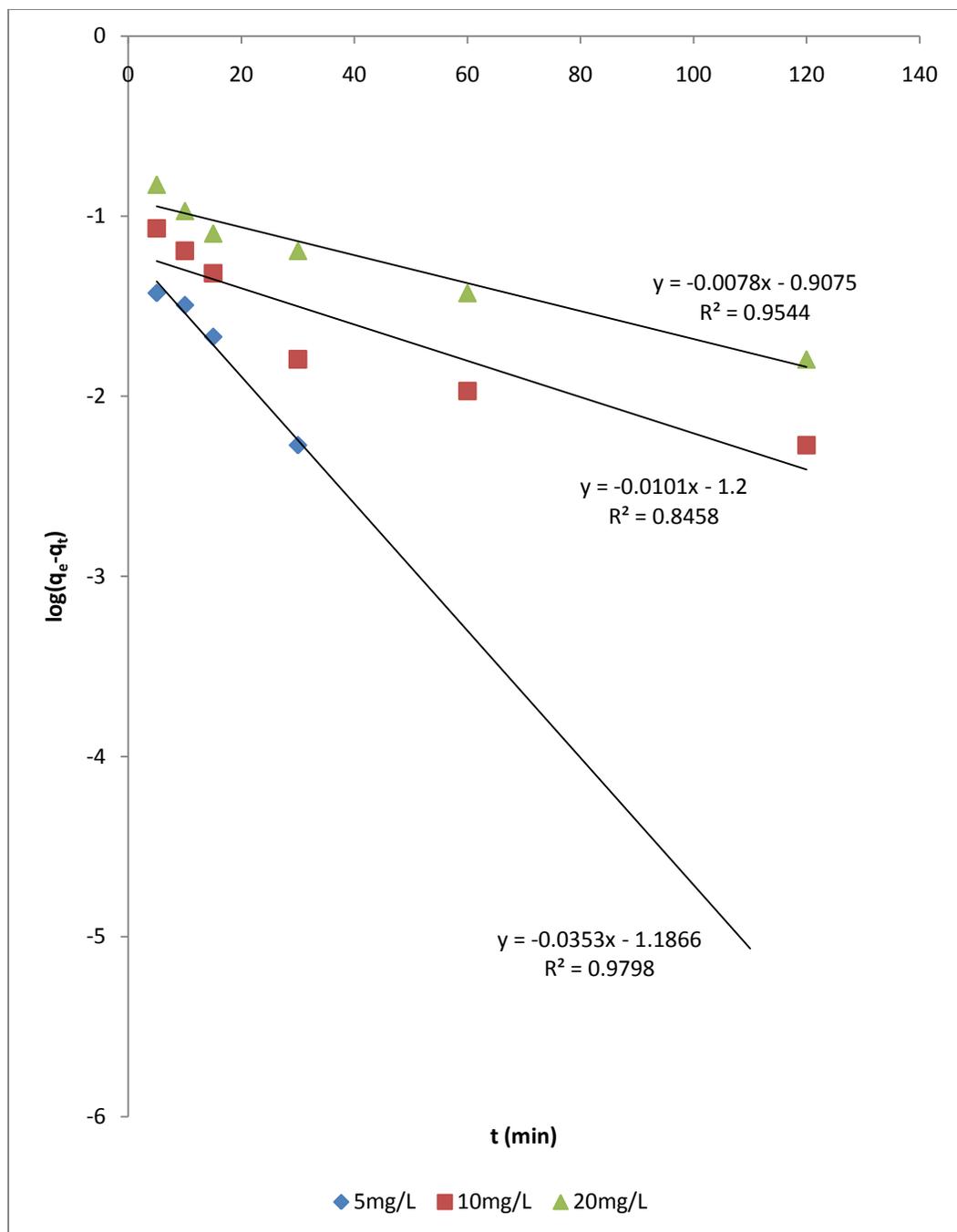
Figure 4.5: Pseudo-first order plot for the sorption of Cu(II) ions onto mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 5 mg/L, 10 mg/L, and 20 mg/L of

Cu(II) solution at 150 rpm for 2 hours.

4.3.1.2 Pseudo-second order kinetic model

The pseudo second order is based on the assumption that the rate limiting step may be chemical sorption involving valence forces through sharing or exchange of electrons between heavy metal ions and adsorbent. The pseudo-second order kinetic rate equation was expressed as (Ho & Mckay, 1998):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad\qquad [4.4]$$

where k_2 is the pseudo second-order rate constant (g/mg min). Integrating equation 4.4 and applying the boundary conditions of $t = 0$ and $t = t$ and correspondingly $q_t = 0$ and $q_t = q_t$ gave:

$$\left(\frac{1}{q_e - q_t}\right) = \frac{1}{q_e} + k_2 \qquad\qquad [4.5]$$

Equation 4.5 was rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \qquad\qquad [4.6]$$

where $h = k_2\, q_e^2$ (mg/g min) is the initial sorption rate. Figure 4.6 showed the linear plots of $\dfrac{t}{q_t}$ against t at initial Cu(II) ions concentration of 5 mg/L, 10 mg/L, and 20
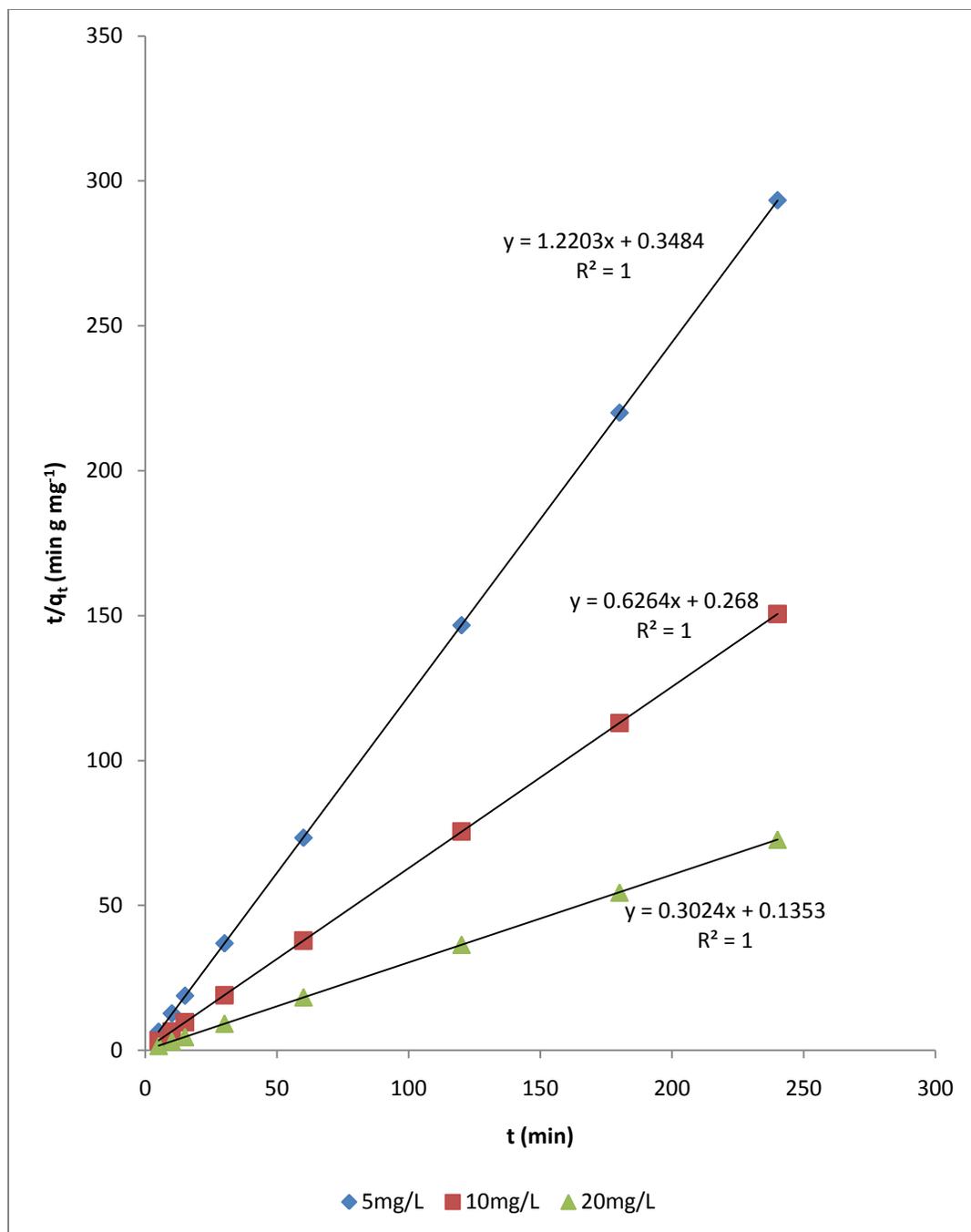
Figure 4.6: Pseudo-second order plot for the sorption of Cu(II) ions onto mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 5 mg/L, 10 mg/L and 20 mg/L of Cu(II) solution at 150 rpm for 2 hours.

mg/L. The values of q_e and h were calculated from the slope and intercept of the plots respectively. . Table 4.2 gives the values of k_2, experimental and calculated values of q_e, as well as the R^2 values for the pseudo-second order plots. It was observed that all three linear plots with different initial concentration in Figure 4.6 showed R^2 values of 1. This indicated that the kinetics data fitted perfectly well with the pseudo-second order model. In addition to the high values of R^2, the calculated q_e values also agreed well with the experimental data obtained from the pseudo-second order kinetics.

From Table 4.2, it was observed that the values of h increased from 2.79 mg/mg min to 6.63 mg/mg min when the initial concentration of Cu(II) ions increased from 5 mg/L to 20 mg/L. This was because the higher the initial concentration of Cu(II) ions, the higher the chances of collision with the binding sites of adsorbent and hence, leads to a higher initial sorption rate. Apart from that, it was obvious that the values of k_2 was higher than the corresponding values of k_1. This was because the pseudo-second order kinetic model assumed that the sorption rate is proportional to the square of number of unoccupied sites (Gupta *et al.*, 2008). The values of k_2 decreased from 4.15 g/mg min to 0.60 g/mg min with increasing initial Cu(II) ions concentration from 5 mg/L to 20 mg/L. This occurred because at higher concentration of metal ions, the competition for surface active sites was high and consequently lower sorption rates are obtained (SenthilKumar *et al.*, 2010)

Table 4.2: Pseudo-first order and pseudo second-order kinetic models parameters for sorption of Cu(II) ions onto mango leaves at different initial concentration

Initial concentration (mg/L)	Pseudo first-order				Pseudo second-order				
	k_1 (min^{-1})	q_e (mg/g) exp	calc	R^2	k_2 (g/mg min)	q_e (mg/g) exp	calc	h (mg/mg min)	R^2
5	0.081	0.81	0.07	0.980	4.288	0.83	0.82	2.870	1
10	0.023	1.59	0.06	0.846	1.469	1.59	1.60	3.731	1
20	0.018	3.30	0.12	0.954	0.677	3.30	3.31	7.391	1

The pseudo-second order kinetic model was also reported to fit well with the kinetics data from studies of a number of authors, including the adsorption of Cd(II) ions onto pomelo peel (Saikaew et al., 2009), adsorption of Cu(II) ions onto Tectona grandis leaves (Kumar et al., 2006), adsorption of Pb(II) ions onto pumpkin seed shell activated carbon (Okoye et al., 2010), adsorption of Ni(II) ions onto potato peel (Prasad and Abdullah, 2009), and adsorption of Cr(VI) ions onto cooked tea dust (Dhanakumar et al., 2007).

The term of q_e, k_2 and h could be expressed as a function of initial Cu(II) ions concentration, C_o as followed:

$$q_e = \frac{C_o}{A_q C_o + B_q} \qquad\qquad [4.7]$$

$$k_2 = \frac{C_o}{A_k C_o + B_k} \qquad\qquad [4.8]$$

$$h = \frac{C_o}{A_h C_o + B_h} \qquad\qquad [4.9]$$

The values of q_e, k_2, and h against C_o in the corresponding linear plots of pseudo-second order equation were regressed to obtain expression for these values in term of the initial Cu(II) ions concentration.

The generalized predictive models for Cu(II) ions sorbed at any contact time and initial concentration within given range with the relationship of q_t, C_o and t could be represented by substituting the following equation:

$$q_t = \frac{C_o t}{A_h C_o + B_h + (A_q C_o + B_q)t} \qquad [4.10]$$

By substituting the constant values into equation 4.10, the theoretical model for Cu(II) ions - mango leaves system was represented as:

$$q_t = \frac{C_o t}{0.0951 C_o + 1.3325 + (0.0052 C_o + 6.1044)t} \qquad [4.11]$$

A comparison of the experimental data and predicted theoretical values by using equation 4.11 was shown in Figure 4.7. As can be seen, the theoretically generated plots agreed well with the experimental curves.

4.4   Effect of agitation rate

Agitation is an important parameter in adsorption phenomena as it influences the distribution of the solute in the bulk solution and the formation of the external boundary film (Crini *et al*., 2006). The effect of agitation rate on sorption was investigated by conducting experiments at agitation rate of 50 rpm to
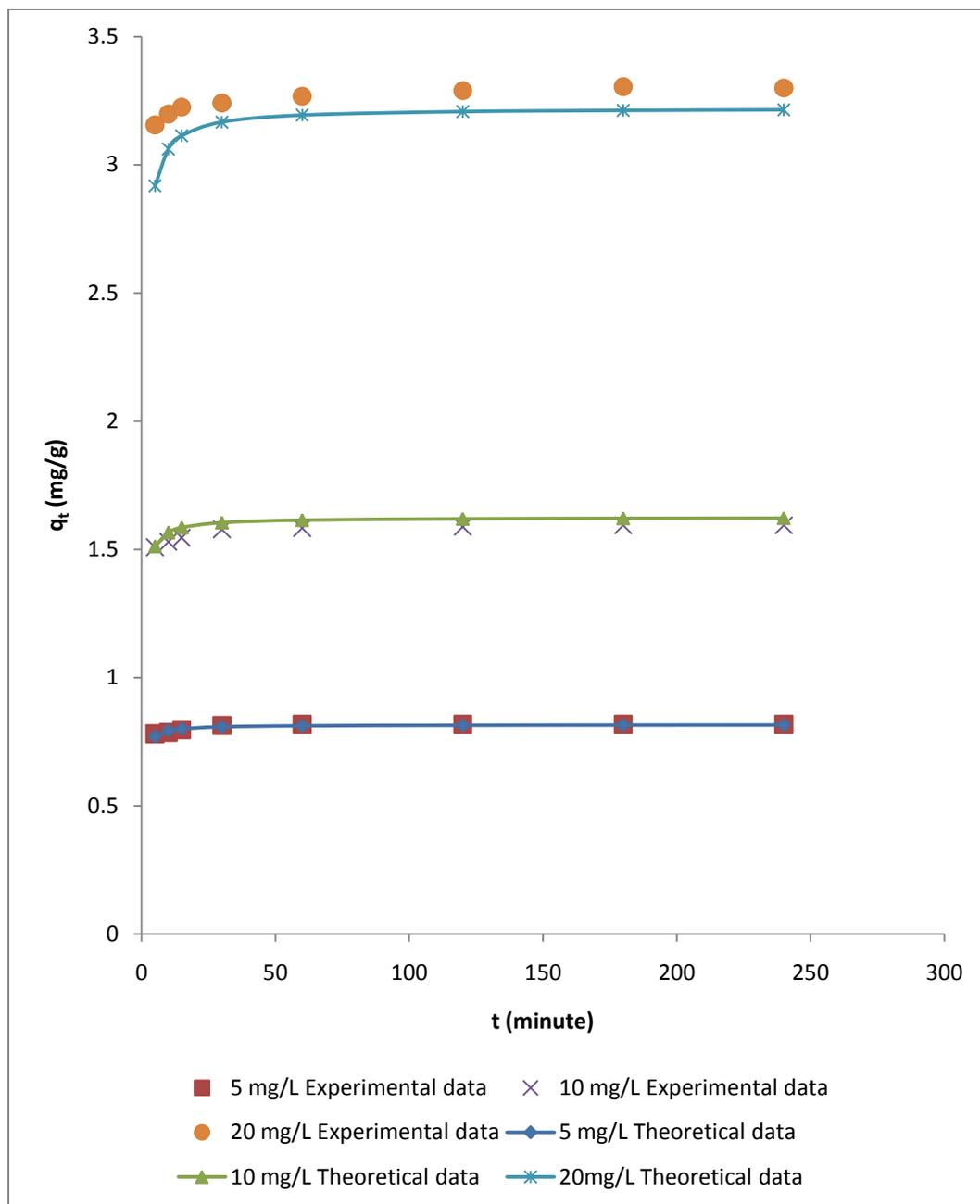
Figure 4.7: Comparison between the measured and pseudo-second order modeled time profiles for sorption of Cu(II) ions by mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 5 mg/L, 10 mg/L, and 20 mg/L of Cu(II)   solution   at   150   rpm   for   2   hours.

200 rpm at various sorption times. Figure 4.8 shows the variation of Cu(II) ions uptake with agitation rate.

It was observed that the percentage uptake increased when the agitation rate was increased. During the first 5 minutes, the uptake was 88.20%, 92.76% and 96.35% for the agitation rate of 50 rpm, 150 rpm and 200 rpm, respectively. This was because increasing the agitation rate reduced the boundary layer resistance to mass transfer surrounding the sorbent particles, resulting in higher sorption rate. In addition to that, higher agitation rate also spread the Cu(II) ions in the solution, providing better access to the active sites on adsorbent surface.

A similar trend was observed for varying agitation speeds for the adsorption of Cu(II) and Pb(II) ions onto tartaric acid modified rice husk in the study of Wong *et al*. (2002). They investigated the uptake of metal ions by varying the agitation rate at 50 rpm, 150 rpm and 250 rpm and reported an increase in the percentage uptake with increasing agitation rate due to reduction in film boundary layer of sorbent particles, which increased the external mass transfer coefficient.

4.5   Effect of particle size

Particle size of adsorbents is an important factor affecting the adsorption capacity as it influences the surface area of adsorbent. The effect of particle size on the adsorption of Cu(II) ions was investigated in the range of 106 μm-1 mm.
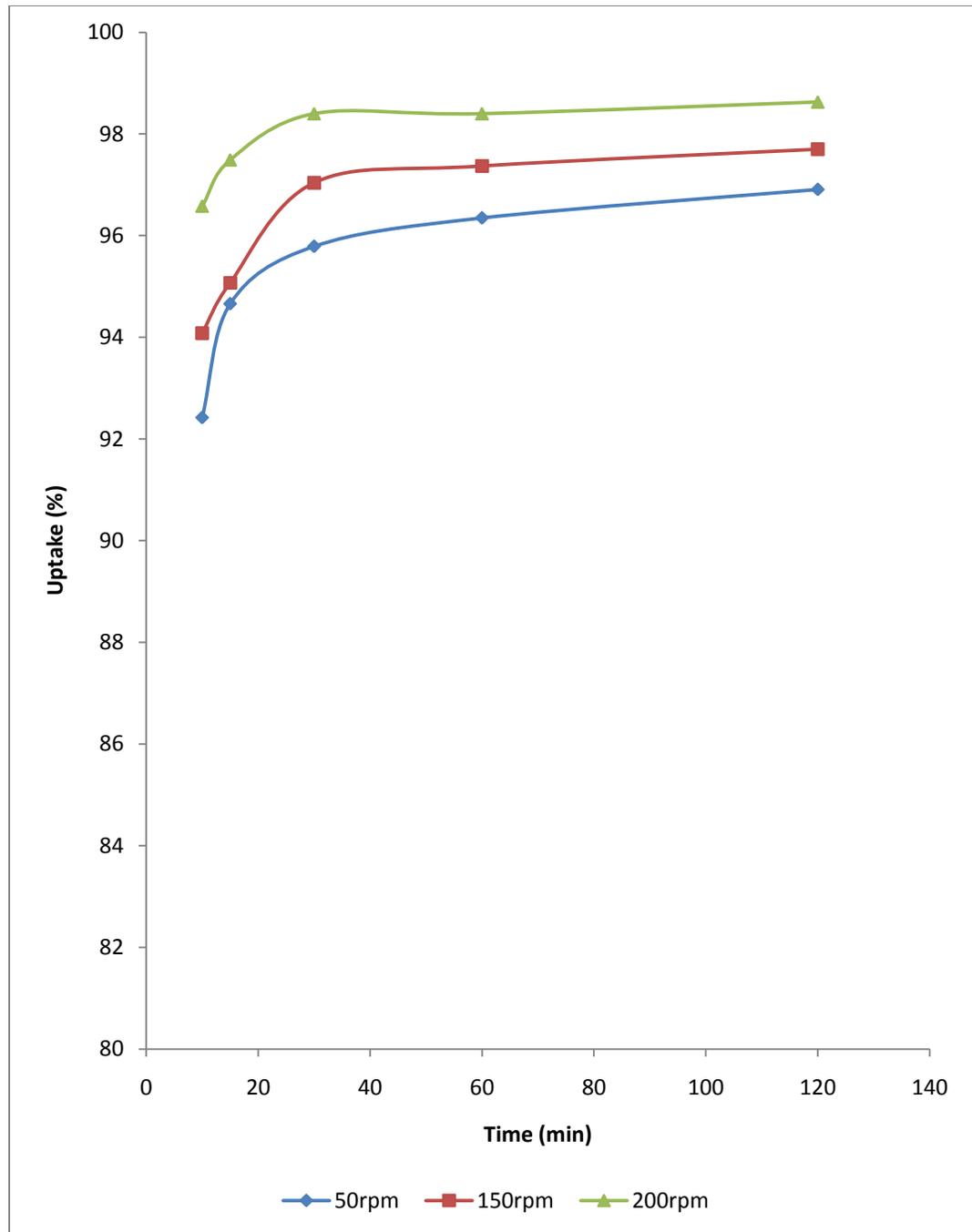
Figure 4.8: Effect of agitation rate on uptake of Cu(II) ions by mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 10 mg/L Cu(II) solution at 50, 100,

and   150   rpm   for   2   hours.

Figure 4.9 shows the variation of Cu(II) ions uptake with time for adsorbent of different particle size. The results indicated that the metal ions uptake increased with decreasing particle size. As can be seen, for the first 5 minutes of contact, the uptake increased from 91.34% to 96.71% when the particle size decreased from 425 μm-1 mm to <106 μm.

The higher uptake with decreasing particle size was attributed to the fact that smaller particles had larger external surface area compared to larger particles, hence more binding sites were exposed on the surface and thus, leading to higher adsorption capacity since adsorption is a surface process. Apart from that, particles with smaller size also moved faster in the solution compared to larger particles, consequently, the adsorption rate was faster.

Sekar *et al*. (2004) utilized activated carbon prepared from coconut shell for the removal of Pb(II) ions and investigated the uptake of ions at different sizes of particles from 75 μm to 850 μm. The authors found that the percent removal of Pb(II) ions increased from 42% to 99% as the particle size decreased from 850 μm to 75 μm for an initial concentration of 20 mg/L Pb(II) solution. According to Sekar *et al*. (2004), for larger particles the diffusional resistance to mass transport was higher and most of the internal surface of the particle might not be utilized for adsorption, hence, the amount of Pb(II) ions adsorbed was small.
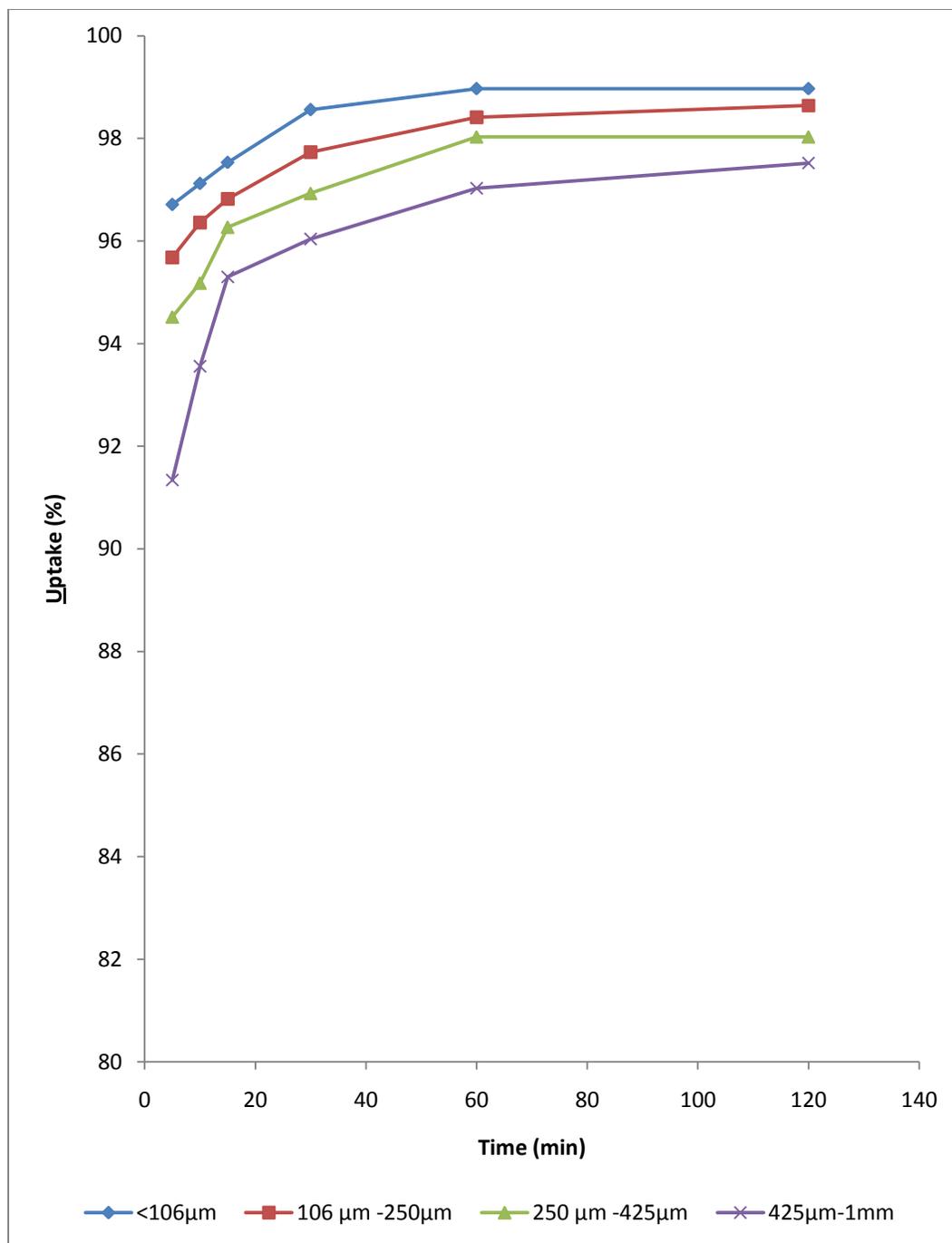
Figure 4.9: Effect of particle size on uptake of Cu(II) ions by mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 10 mg/L of Cu(II) solution at 150
rpm for 2 hours

Similar result was also reported in removal of Cu(II) ions by *Tectona grandis* leaves (Kumar *et al*., 2006), removal of Pb(II) and Cu(II) ions by tartaric acid modified rice husk (Wong *et al*., 2002) and removal of Cr(VI) ions by almond shell (Demirbas *et al*., 2004).

4.6   Effect of chelating agent

Chelating agents are organic compounds capable of coordinating with metals through two or more atoms of the organic compounds, forming a chelate. Chelating agents are widely used in industrial applications such as metal finishing and plating industry, detergent media, cosmetics industry, paper and pulp industry, polymerization, and photographic industry. Hence, wastewater generated from these industries contain significant amount of chelating agents. Chelating agents most widely used in industrial application are ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) (Amer, 2004). Figures 4.10 and 4.11 showed the structure of EDTA and NTA molecules, respectively.
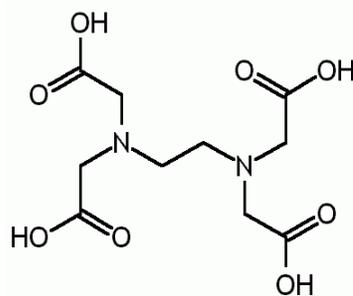
Figure 4.10: Structure of EDTA
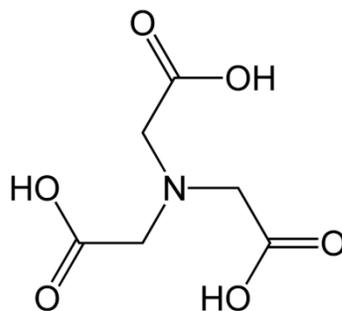
Figure 4.11: Structure of NTA

EDTA and NTA were selected in this study to test how the presence of chelating agent affect Cu(II) ions uptake by mango leaves. Figure 4.12 shows the uptake of Cu(II) ions in the presence of different concentration of chelators. It was evident that the percentage uptake was significantly reduced in the presence of chelators. The uptake of Cu(II) ions reduced from 97.62% to 69.95% when 10 mg/L of EDTA was added, and further decreased to 20.57% when the concentration of EDTA added was increased to 30 mg/L. The same trend was observed for NTA addition. When 10 mg/L of NTA was added to Cu(II) solution, the uptake reduced to 58.91% and further decreased to 26.27% when the NTA concentration was increased to 30 mg/L.

The reduction in uptake of Cu(II) ions in the presence of chelators occurred because Cu(II) ions combined strongly with both EDTA and NTA rather than mango leaves, forming a stable complex and hence, inhibited the uptake of Cu(II) ions by mango leaves. The sorbent adsorbed Cu(II) via free cations form and was not able to bind EDTA-Cu and NTA-Cu complexes, thus leaving behind unadsorbed Cu(II) in the solution.
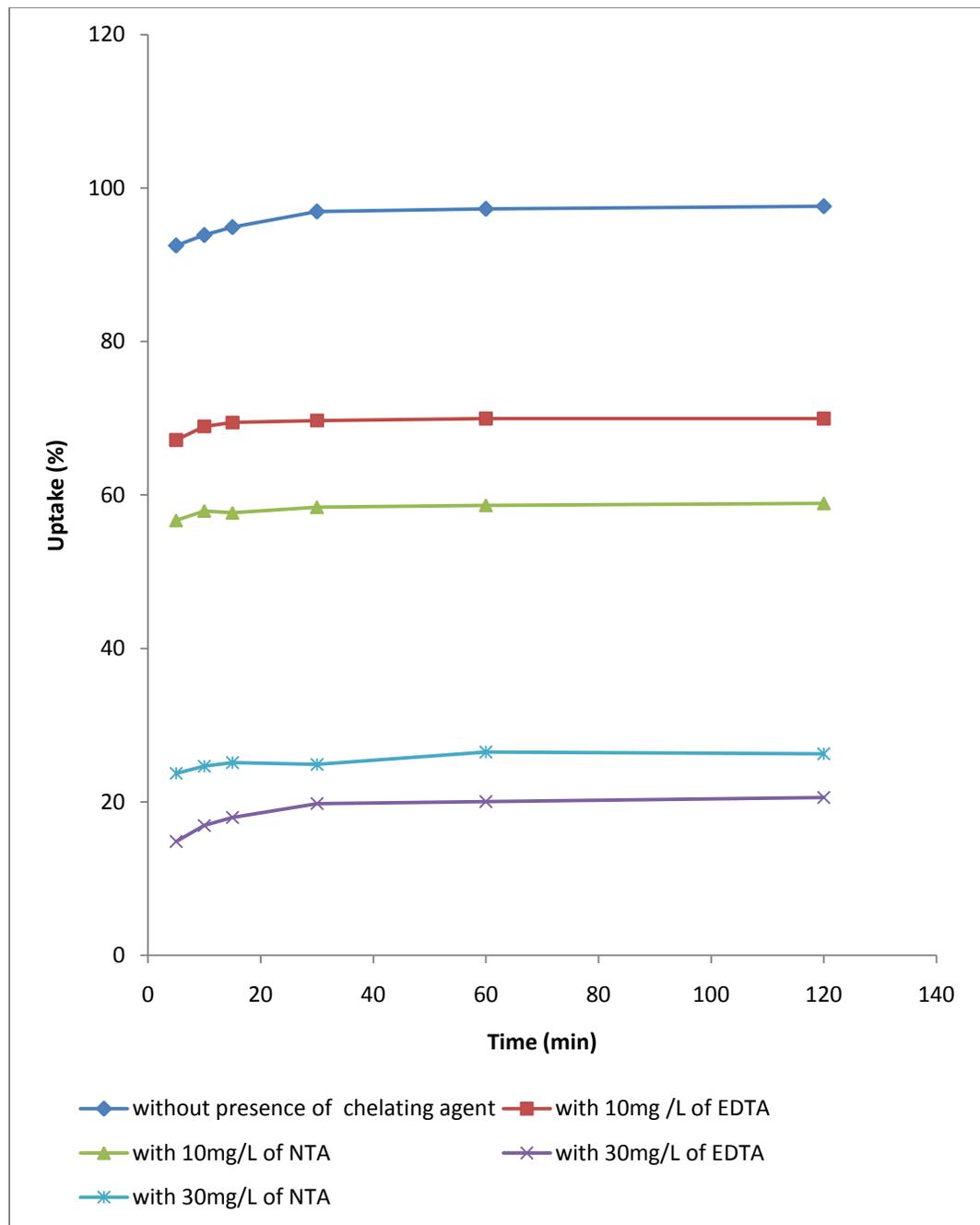
Figure 4.12: Effect of presence of chelating agent on uptake of Cu(II) ions by mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 10 mg/L of Cu(II) solution at 150 rpm for 2 hours

Wong *et al*. (2002) investigated the removal of Cu(II) and Pb(II) ions by tartaric acid modified rice husk. They investigated the effect of EDTA, NTA, salicyclic acid (SA) on the metal ions sorption by using various copper to chelator metal ratios. The results revealed that higher molar ratios of EDTA and NTA caused significant suppressing effect on the uptake of both Cu(II) and Pb(II) ions. Meanwhile, SA had little effect on the sorption of both ions onto rice husk as the reduction in percentage uptake in the presence of SA was minimal.

The suppressing effect in the uptake of ions by chelators was also confirmed in the study by Lu and Gibb (2007) on the removal of Cu(II) ions using spent-grain as biosorbent. The authors reported that in the presence of 1 mmol/L of EDTA, the efficiency of Cu removal dropped by 78% and when the concentration of EDTA was increased to 10 mmol/L, the efficiency of removal reduced to less than 10%. They concluded that EDTA could be used as an effective agent for recovering Cu(II) ions from loaded biosorbent.

4.7   Equilibrium sorption study

Biosorption studies describe how adsorbate interacts with biosorbent and equilibrium is established between adsorbed metal ions and the residual metal ions in solution during the surface biosorption (Feng *et al*., 2010). The interaction between adsorbate and adsorbent is characterized using adsorption isotherm models. Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of

assumptions that are mainly related to the heterogeneity or homogeneity of adsorbents, the type of coverage and possibility of interaction between adsorbate species (Kumar and Kirthika, 2009).

The sorption equilibrium data collected in this study were fitted into three well-known adsorption isotherms, namely Langmuir, Freundlich, and Brunauer-Emmett-Teller (BET) models.

4.7.1   Langmuir isotherm model

The Langmuir isotherm is based on assumptions that: (Langmuir, 1916)

(i)   Maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface

(ii)   The energy of adsorption is constant

(iii)   There is no transmigration of adsorbate in the plane of the surface

The Langmuir model was expressed in equation 4.12:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$
[4.12]

where

C_e = Concentration of Cu(II) ions at equilibrium (mg/L)

q_e = Amount of Cu(II) ions adsorbed at equilibrium (mg/g)

K_L = Langmuir isotherm constant related to free energy of adsorption (L/mg)

q_m = Maximum adsorption capacity (mg/g)

Equation 4.12 could be linearised into:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad [4.13]$$

The plot of C_e/q_e against C_e gave a straight line with slope of $\frac{1}{q_m}$ and intercept of $\frac{1}{q_m K_L}$. Figure 4.13 showed the Langmuir plot of Cu(II) ions adsorption by mango leaves with a correlation coefficient of 0.9918, which was close to unity, thus indicating that the data conform well to the Langmuir isotherm model. According to the Langmuir equation, the maximum uptake capacity for Cu(II) ions was 15.77 mg/g.

The Langmuir parameters were also used to predict the affinity of the leaf powder surfaces towards the Cu(II) ions by using dimensionless separation factor, R_L, which was expressed in equation 4.14.

$$R_L = \frac{1}{1 + K_L C_o} \qquad [4.14]$$

According to R_L, the isotherm shape may be interpreted as in Table 4.3:

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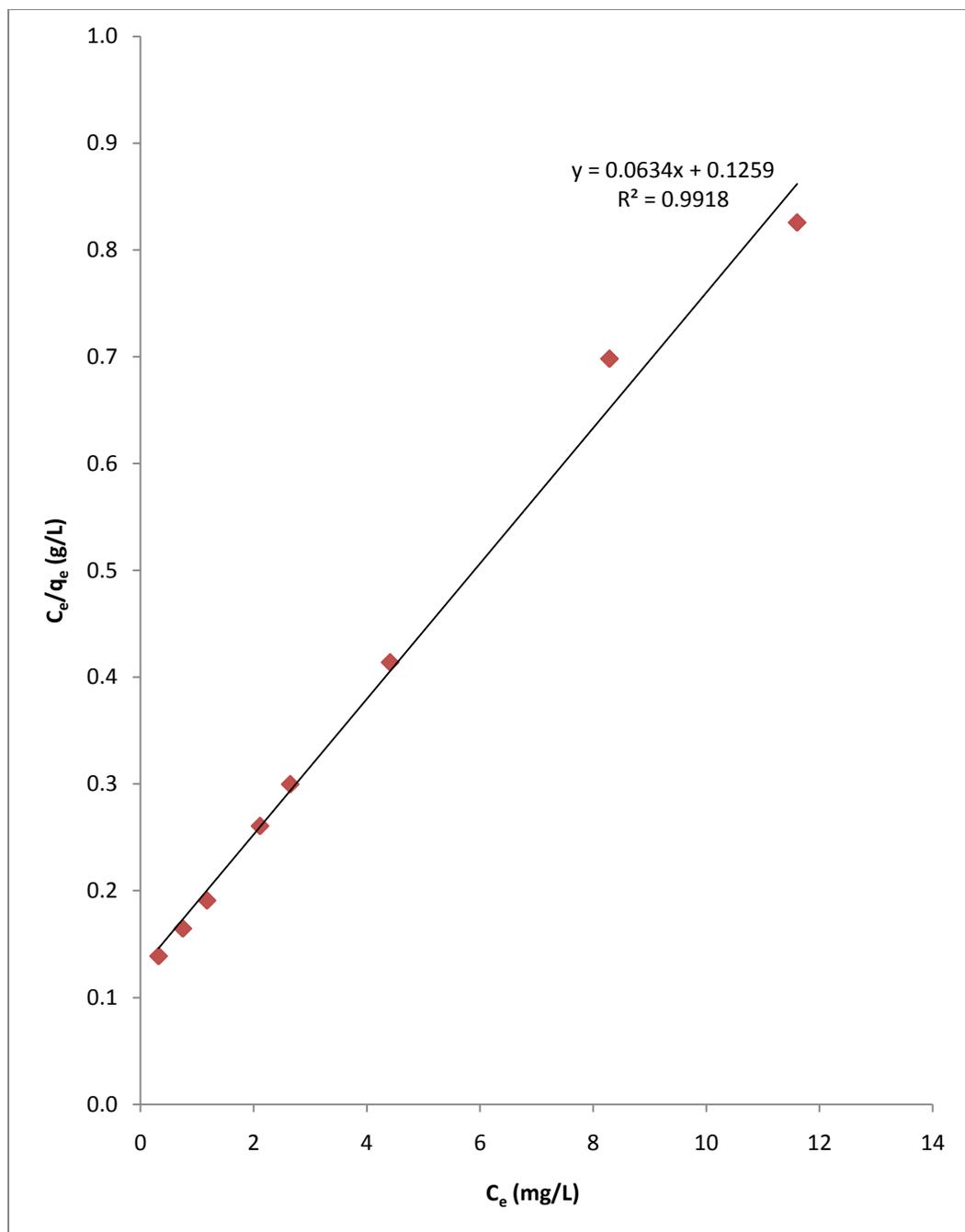
Figure 4.13: Langmuir isotherm plot for the sorption of Cu(II) ions onto mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 10, 20, 30, 40, 50, 60, 70, 80 mg/L

of Cu(II) solution at 150 rpm for 2 hours.

Table 4.3: Shape of isotherm

Value of R_L	Type of adsorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

(Amuda *et al*., 2007)

The R_L values obtained, as listed in Table 4.4, were in the range of 0 and 1, which indicated a favourable isotherm shape for adsorption of Cu(II) ions onto mango leaves in the concentration range studied.

Table 4.4: Values of R_L for the Cu(II) ions concentration range studied

C_o (mg/L)	R_L
11.8717	0.1433
23.4759	0.0780
31.9786	0.0585
42.6203	0.0445
46.7914	0.0407
57.7005	0.0333
67.6471	0.0285
81.8717	0.0237

4.7.2 Freundlich isotherm model

The Freundlich isotherm assumes a heterogeneous surface with a non-uniform distribution of heat of biosorption over the surface and a multilayer biosorption can be expressed (Freundlich, 1906). The Freundlich model was expressed as:

$$q_e = K_F C_e^n \qquad\qquad [4.15]$$

where

K_F = Freundlich indicative of relative adsorption capacity of adsorbent

n = Freundlich indicative of the intensity of adsorption

Equation 4.15 could be linearised by taking logarithms as followed:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad\qquad [4.16]$$

The plot of log q_e against log C_e gave a straight line with slope of $\frac{1}{n}$ and intercept of K_F. Figure 4.14 showed the Freundlich isotherm plot of Cu(II) ions adsorption onto mango leaves, with a correlation coefficient of 0.9426. The value of K_F and n obtained from the plot were 4.9854 and 2.1195 respectively. The n value of Freundlich equation could give an indication on the favourability of sorption. It is generally stated that values of n in the range of 2 to 10 is good, 1 to 2 as moderately difficult and less than 1 as poor sorption characteristic (Chen *et al*., 2010).
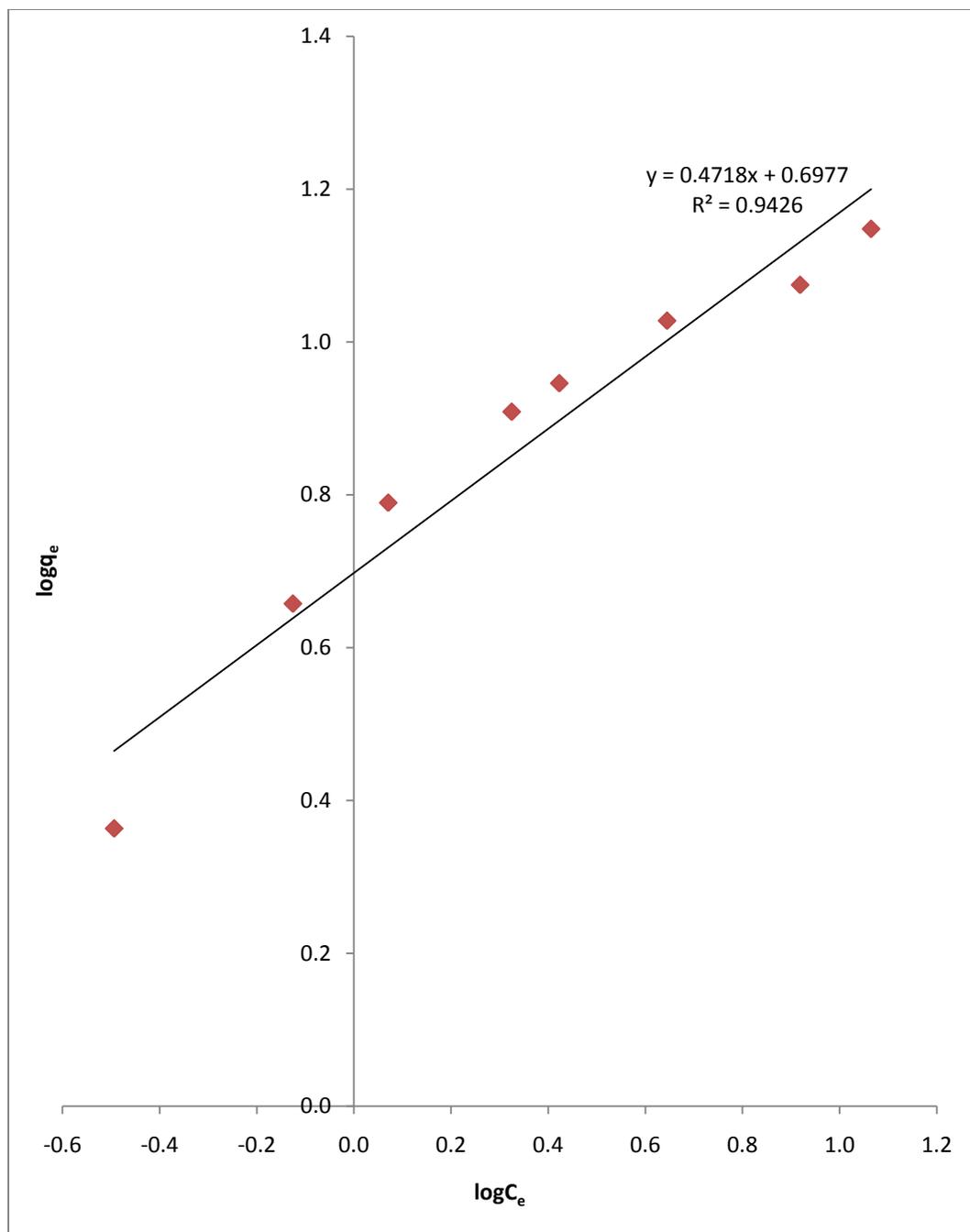
Figure 4.14: Freundlich isotherm plot for the sorption of Cu(II) ions onto mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 10, 20, 30, 40, 50, 60, 70, 80 mg/L of Cu(II) solution at 150 rpm for 2 hours.

4.7.3 BET model

The BET derived an adsorption isotherm based on assumption that the adsorbate molecules could be adsorbed in more than one layer thickness on the surface of adsorbent. It assumes that: (Brunauer, 1938)

(i)   The adsorbent surface is composed of uniform, localized sites

(ii)   The adsorption at one site does not affect adsorption at neighboring sites

(iii)   The energy of adsorption holds the first monolayer but the condensation energy of the adsorbate is responsible for adsorption of successive layers

The BET model was expressed as:

$$q_e = \frac{K_B.C_e.q_m}{(C_s-C_e).[1+(K_B-1).(\frac{C_e}{C_S})]} \qquad [4.17]$$

where

K_B = BET constant

Cs = solute concentration at the saturation of all layers (mg/L)

Equation 4.17 could be linearised into:

$$\frac{C_e}{(C_s-C_e)q_e} = \frac{1}{K_b q_m} + \left(\frac{K_b-1}{K_b q_m}\right)\left(\frac{C_e}{C_s}\right) \qquad [4.18]$$

A plot of $\dfrac{C_e}{(C_s - C_e)q_e}$ against $\dfrac{C_e}{C_s}$ gave a straight line with slope of $\dfrac{K_b - 1}{K_b q_m}$ and

intercept of $\dfrac{1}{K_b q_m}$. Figure 4.15 illustrateed the BET plot for biosorption of Cu(II)

ions onto mango leaves, with coefficient correlation of 0.8212. From the plot, the

value of q_m and K_b obtained were 2.3283 and -9.3167, respectively.

The parameters and correlation coefficients obtained from the plots of

Langmuir, Freundlich, and BET models are listed in Table 4.5. By comparing the

correlation coefficients obtained from the three isotherm models, the Langmuir

isotherm gave the best correlation for the sorption process and this indicated that

Cu(II) ions are adsorbed onto mango leaves surface in a monolayer pattern.

Table 4.5: Langmuir, Freundlich, and BET isotherm parameters

Langmuir			Freundlich			BET		
R^2	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2	q_m (mg/g)	K_B
0.992	15.77	0.50	0.943	4.99	2.12	0.82	2.33	-9.32

Upon linearising the non-linear isotherm equation, the error distribution

was varied; either being better or worse depending on the way the equation was

linearised (Kumar & Sivanesan, 2005). Non-linear method had an advantage that
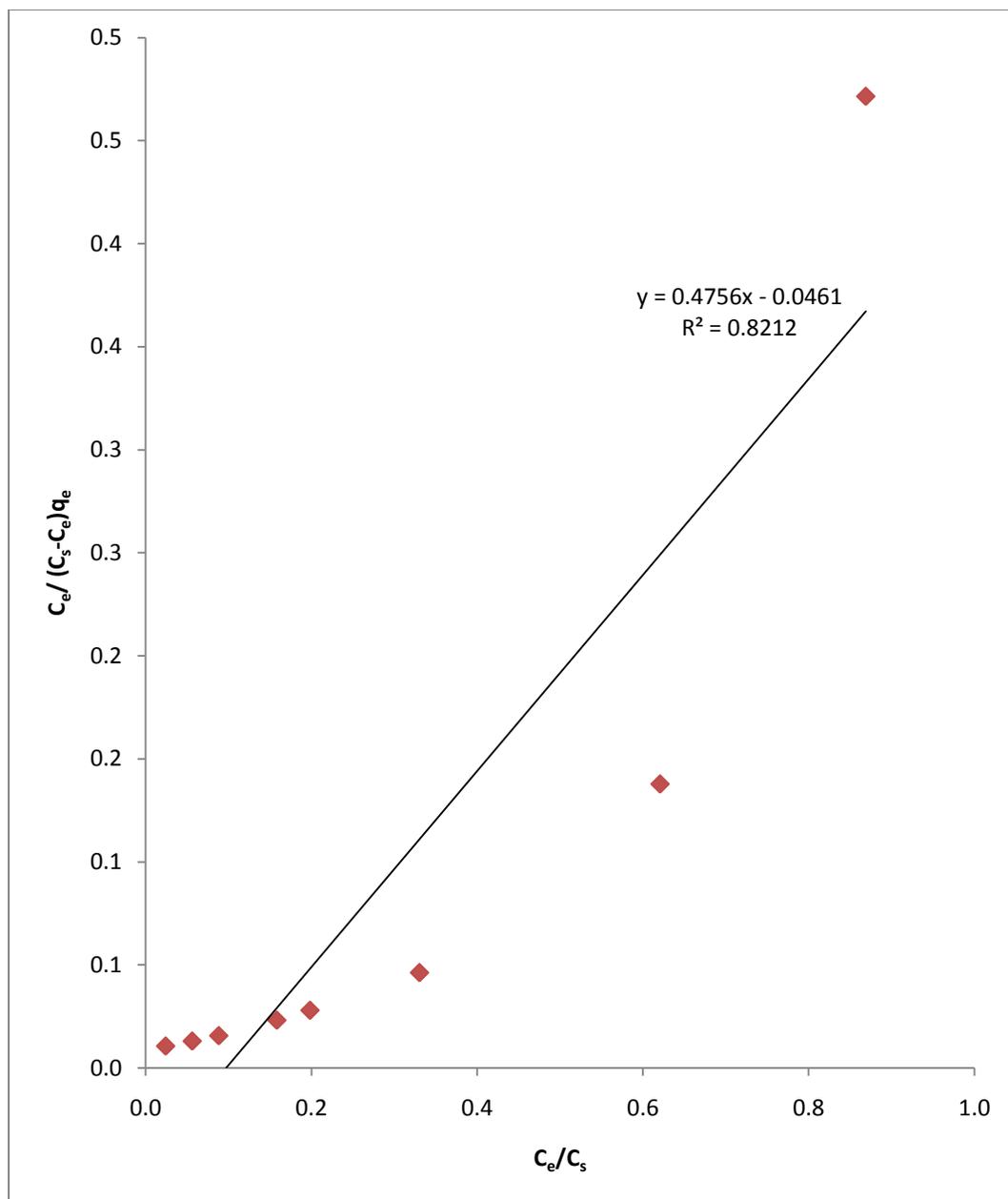
Figure 4.15: BET isotherm plot for the sorption of Cu(II) ions onto mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 10, 20, 30, 40, 50, 60, 70, 80 mg/L

of Cu(II) solution at 150 rpm for 2 hours.

the error distribution did not get altered as in linear technique, as all the isotherm parameters were fixed in the same axis. Figure 4.16 showed the non-linear plot of Langmuir isotherm. A high correlation coefficient of 0.9927 was obtained and this confirmed the applicability of Langmuir equation to the experimental data.

Similar result was obtained in the study of Chakravarty $et\ al$, (2009) using bael leaves for removal of Pb(II) ions. It was found that the adsorption of Pb(II) ions onto bael leaves fitted better to the Langmuir model ($R^2 = 0.97$) as compared to Freundlich model ($R^2 = 0.8$) under the concentration range studied. Amuda $et\ al$. (2007) investigated the removal of Zn(II) ions using activated coconut shell carbon modified with chitosan. They found out that Langmuir isotherm ($R^2 = 0.997$) had a better fitting model than Freundlich isotherm ($R^2 = 0.975$) due to the fact that activated carbon has a small surface area for metal adsorption, therefore, monolayer adsorption occurred on its surface in spite of any surface modification.

In order to investigate the effectiveness of mango leaves as a potential adsorbent in removal of Cu(II) ions, the value of the maximum adsorption capacity obtained in this study was compared with that from other reported adsorbents. As shown in Table 4.6, the Cu(II) ions adsorption capacity of mango leaves was comparable to other reported adsorbents.
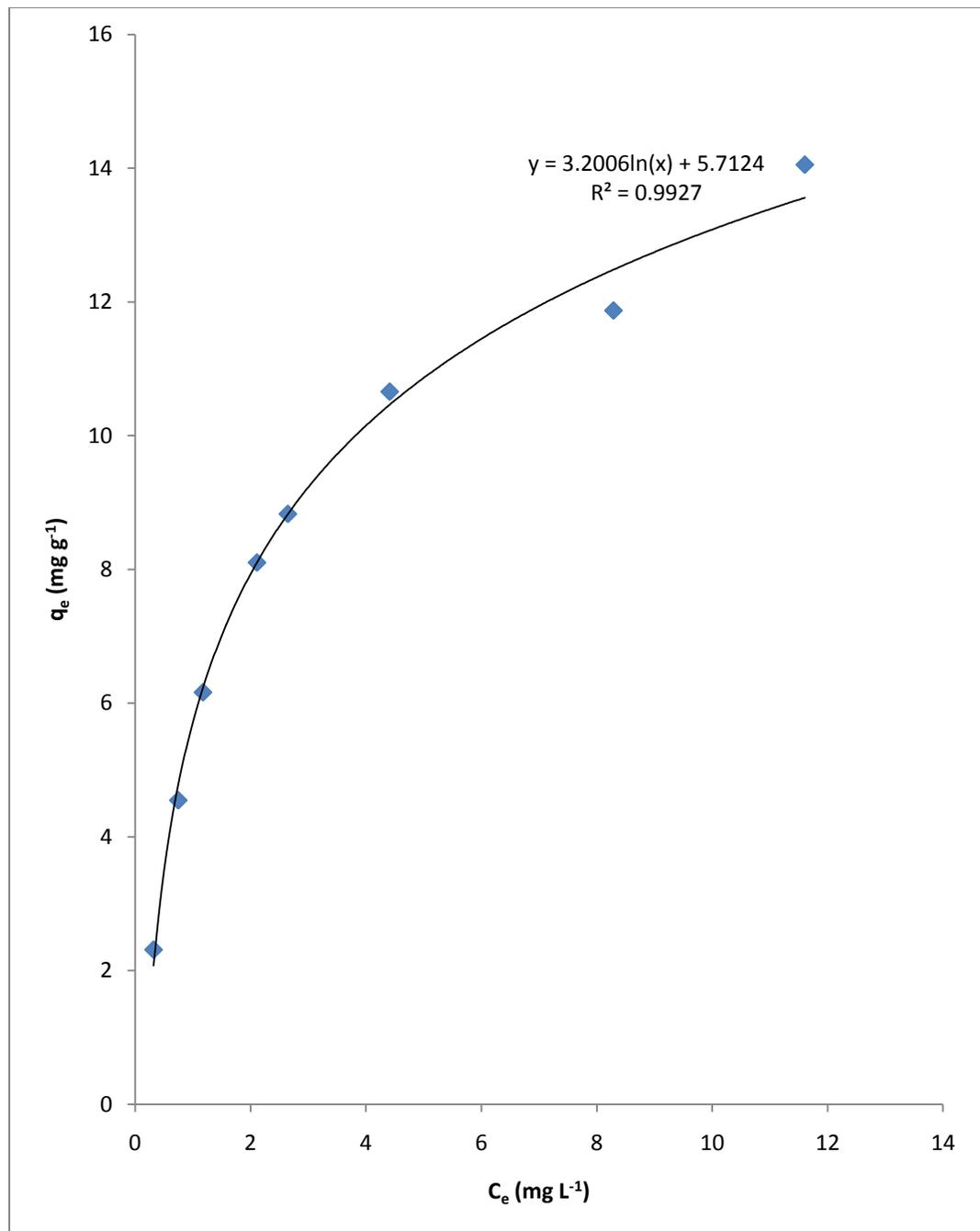
Figure 4.16: Non-linear Langmuir isotherm plot for the sorption of Cu(II) ions onto mango leaves

Condition: 0.1 g of mango leaves in 20 mL of 10, 20, 30, 40, 50, 60, 70, 80 mg/L of Cu(II) solution at 150 rpm for 2 hours.

Table 4.6: **Comparison of Cu(II) ions uptake of selected similar nature adsorbents**

Adsorbent	q_m (mg/g)	References
Peanut shell	25.39	Witek-Krowiak *et al*., 2010
Cinnamomum Camphora leaves	16.76	Chen *et al*., 2009
Tectona Grandis leaves	15.43	Kumar *et al*., 2006
Spent grain	10.47	Lu & Gibb, 2007
Rubber (Hevea Brasiliensis) leaves	8.92	Ngah & Hanafiah, 2007
Cashew nut shell	20.00	Kumar *et al*., 2010
Mango leaves	15.78	This study

CHAPTER 5

CONCLUSION

5.1   Conclusion

FTIR spectra of mango leaves revealed the presence of O-H, C-H, C=C and C-O stretching in the adsorbent. The results of this study indicated that the uptake of Cu(II) ions by mango leaves was affected by pH, contact time, initial Cu(II) ions concentration, agitation rate, particle size and the presence of chelating agent. The optimum pH for adsorption of Cu(II) ions was found to be at pH 5. The uptake of Cu(II) ions increased with increasing contact time and decreasing ions concentration and equilibrium was attained in 60 minutes of contact.

The kinetic data obtained from this study fitted well with the pseudo-second order model and the sorption profiles derived based on the pseudo-second order kinetic model showed good agreement with the experimental curves. The uptake of Cu(II) ions also increased with higher agitation rate, smaller size of adsorbents and in the absence of chelating agent. The equilibrium data conformed well to the Langmuir isotherm with a high correlation coefficient of 0.9918, indicating that the adsorption of Cu(II) ions onto surface of mango leaves followed a monolayer pattern. The maximum adsorption capacity determined from the Langmuir isotherm model was 15.77 mg/g. It can be concluded that mango leave can be considered as an alternative biomass for the removal of Cu(II) ions since it is effective, low cost, abundant and can be obtained locally.

5.2 Further Studies

Mango leave had been shown to have the potential in removing Cu(II) ions from aqueous solution. Thus in order to further investigate its effectiveness, the following study could be carried out:

- Application of mango leave to remove other heavy metal ions such as Cd(II), Cr(II), Ni(II), Pb(II) and Zn(II) ions as well as dyes present in commercial industries wastewater such as Methylene Blue, Congo Red and Reactive Yellow.

- Chemical modification of mango leave to enhance its adsorption capacity.

- Investigate in detail the morphological characteristics of mango leave by using Scanning Electron Microscope (SEM), X-ray diffractometer (XRD), and energy-dispersive X-ray spectroscopy (EDX).

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APPENDICES

APPENDIX A

Calibration curve of Cu(II) ions
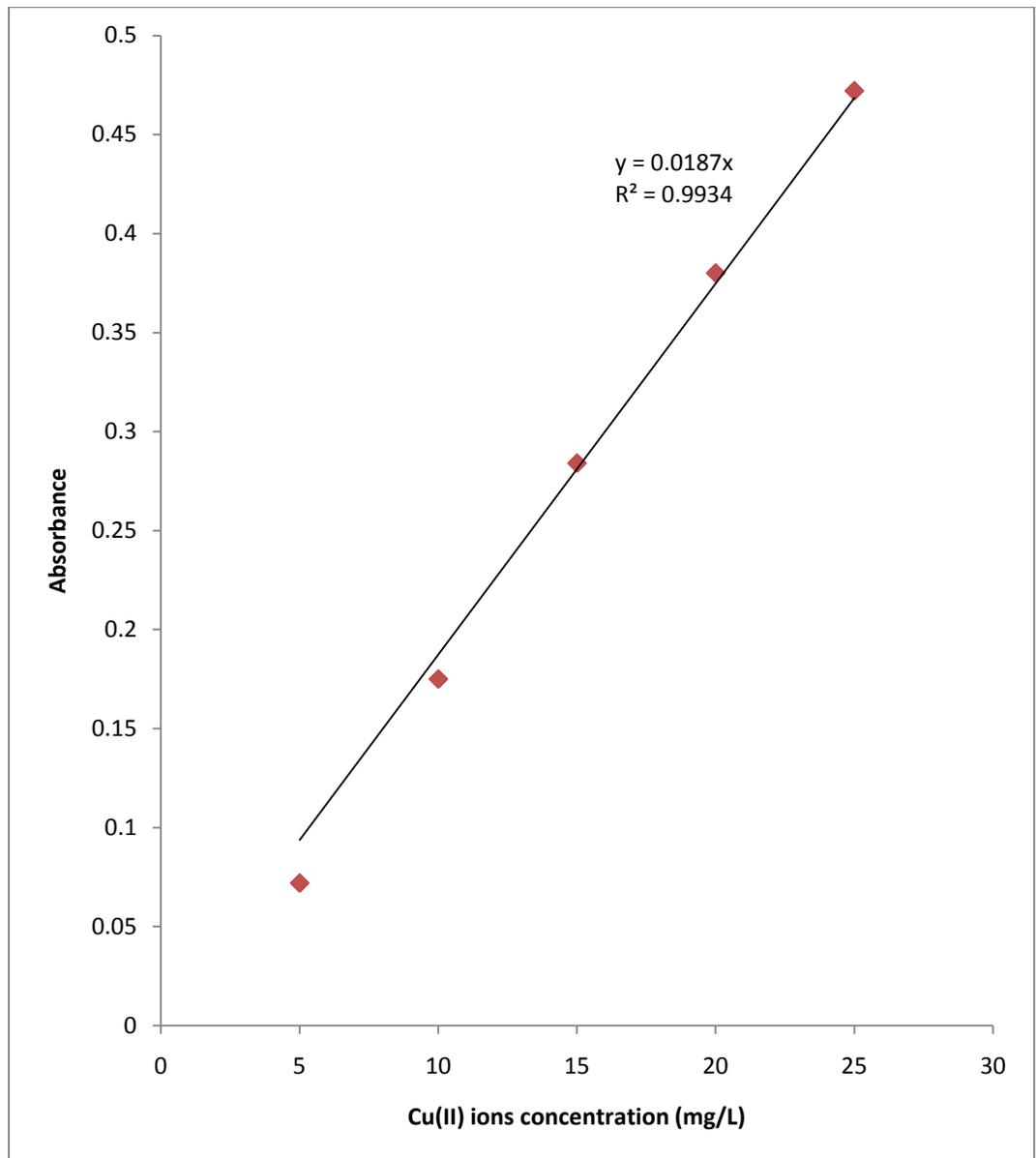
APPENDIX B

Effect of pH on uptake of Cu(II) ions by mango leaves

pH	Uptake (%)
2	15.19
3	89.77
4	95.83
5	97.75
6	96.56
7	96.37
8	96.43
9	95.14
10	95.25

APPENDIX C

Effect of initial metal ions concentration and contact time on uptake of Cu(II)

ions by mango leaves

Time (min)	Uptake (%)		
	5 mg/L	**10 mg/L**	**20 mg/L**
5	93.59	92.76	92.48
10	94.23	94.08	93.73
15	95.51	95.07	94.51
30	97.44	97.04	94.98
60	98.08	97.37	95.77
120	98.08	97.70	96.39
180	98.08	98.03	96.87
240	98.08	98.03	96.71

APPENDIX D

Pseudo-first order and pseudo second-order parameters for Cu(II) ions

removal by mango leaves

Time,t (min)	5 mg/L				
	q_t (mg/g)	q_e (mg/g)	q_e-q_t (mg/g)	$\log(q_e-q_t)$	t/q_t (min g/mg)
5	0.7807	0.8182	0.0374	-1.4267	6.4041
10	0.7861	0.8182	0.0321	-1.4937	12.7211
15	0.7968	0.8182	0.0214	-1.6698	18.8255
30	0.8128	0.8182	0.0053	-2.2718	36.9079
60	0.8182	0.8182	-	-	73.3333
120	0.8182	0.8182	-	-	146.6667
180	0.8182	0.8182	-	-	220.0000
240	0.8182	0.8182	-	-	293.3333

Time, t	10 mg/L				
(min)	q_t (mg/g)	q_e (mg/g)	q_e-q_t (mg/g)	log(q_e-q_t)	t/q_t (min g/mg)
5	1.5080	1.5936	0.0856	-1.0677	3.3156
10	1.5294	1.5936	0.0642	-1.1927	6.5385
15	1.5455	1.5936	0.0481	-1.3176	9.7059
30	1.5775	1.5936	0.0160	-1.7947	19.0169
60	1.5829	1.5936	0.0107	-1.9708	37.9054
120	1.5882	1.5936	0.0053	-2.2718	75.5556
180	1.5936	1.5936	-	-	112.9530
240	1.5936	1.5936	-	-	150.6040

Time, t	20 mg/L				
(min)	q_t (mg/g)	q_e (mg/g)	q_e-q_t (mg/g)	log(q_e-q_t)	t/q_t (min g/mg)
5	3.1551	3.3048	0.1497	-0.8247	1.5847
10	3.1979	3.3048	0.1070	-0.9708	3.1271
15	3.2246	3.3048	0.0802	-1.0957	4.6517
30	3.2406	3.3048	0.0642	-1.1927	9.2574
60	3.2674	3.3048	0.0374	-1.4267	18.3633
120	3.2888	3.3048	0.0160	-1.7947	36.4878
180	3.3048	3.3048	-	-	54.4660

| 240 | 3.2995 | 3.3048 | - | - | 72.7391 |

Graph of $1/q_e$ against $1/C_o$ for sorption of Cu(II) ions by mango leaves

$y = 6.1044x + 0.0052$
$R^2 = 0.9995$

(x-axis: $1/C_o$ (L/mg); y-axis: $1/q_e$ (g/mg))

Graph of $1/k_2$ against $1/C_o$ for sorption of Cu(II) ions by mango leaves

y = -7.7506x + 1.7014
R^2 = 0.8818

x-axis: $1/C_o$ (L/mg)
y-axis: $1/k^2$ (mg min/g)

Graph of 1/h against 1/C_o for sorption of Cu(II) ions by mango leaves
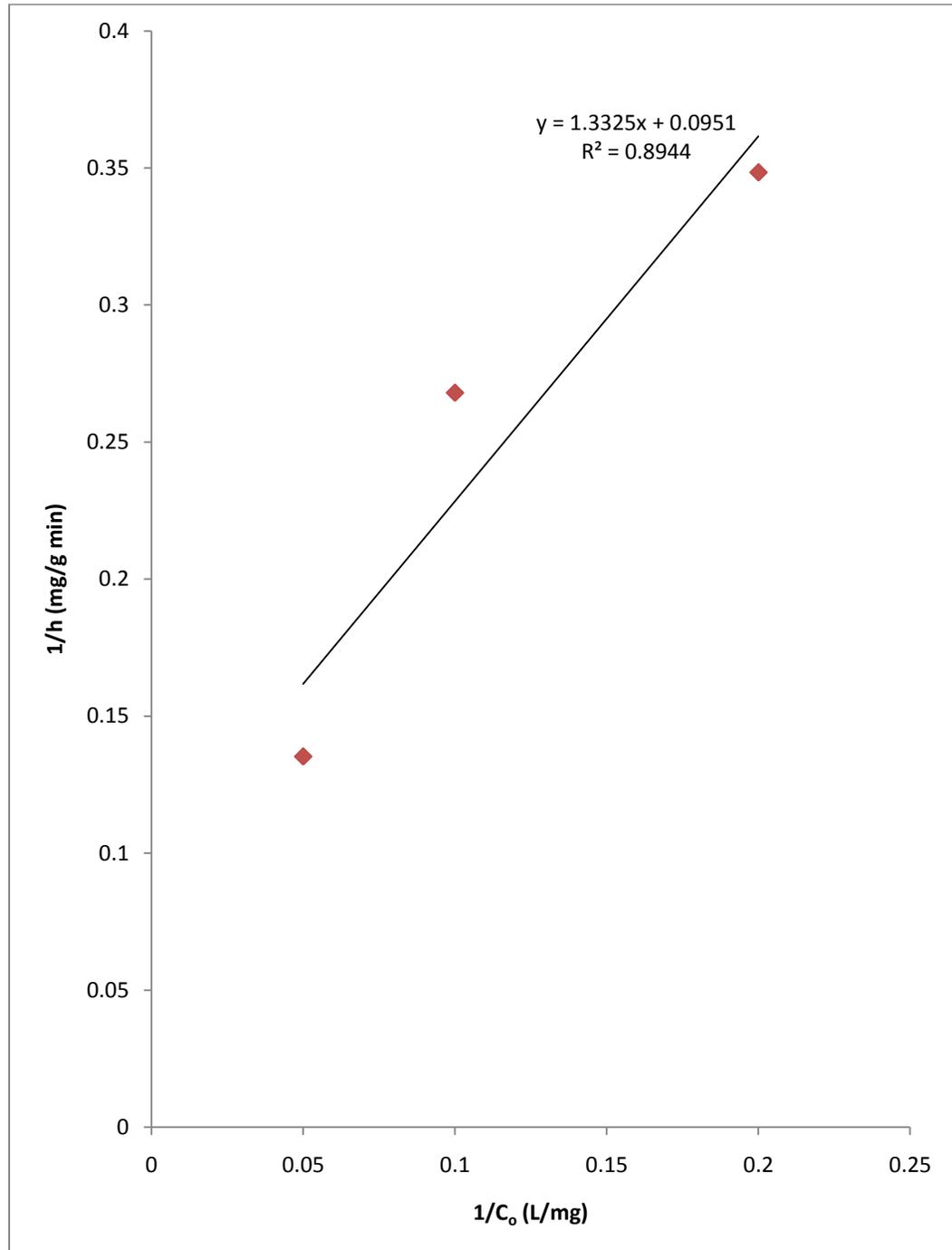
APPENDIX H

Parameters for theoretical model of pseudo-second order of Cu(II) ions

removal by mango leaves

Time (min)	$q_{t,cal}$ (mg/g)		
	5 mg/L	10 mg/L	20 mg/L
5	0.7702	1.5122	2.9175
10	0.7922	1.5662	3.0619
15	0.7999	1.5851	3.1133
30	0.8077	1.6045	3.1665
60	0.8116	1.6143	3.1937
120	0.8136	1.6193	3.2075
180	0.8143	1.6210	3.2121
240	0.8146	1.6218	3.2145

APPENDIX I

Effect of agitation rate on uptake of Cu(II) ions by mango leaves

Time (min)	Uptake (%)		
	50 rpm	**150 rpm**	**200 rpm**
5	88.20	92.76	96.35
10	92.42	94.08	96.58
15	94.66	95.07	97.49
30	95.79	97.04	98.40
60	96.35	97.37	98.40
120	96.91	97.70	98.63

APPENDIX J

Effect of particle size on uptake of Cu(II) ions by mango leaves

Time	Uptake (%)			
(min)	<106 μm	106 μm -250 μm	250 μm -425 μm	425 μm-1 mm
5	96.71	95.68	94.52	91.34
10	97.12	96.36	95.18	93.56
15	97.53	96.82	96.27	95.30
30	98.56	97.73	96.93	96.04
60	98.97	98.41	98.03	97.03
120	98.97	98.64	98.03	97.52

APPENDIX K

Effect of presence of chelating agent on uptake of Cu(II) ions by mango leaves

Time (min)	Uptake (%)			
	10 mg/L of EDTA	30 mg/L of EDTA	10 mg/L of NTA	30 mg/L of NTA
5	67.17	14.84	56.68	23.73
10	68.94	17.97	57.92	24.65
15	69.44	16.93	57.67	25.12
30	69.70	19.79	58.42	24.88
60	69.95	20.05	58.66	26.50
120	69.95	20.57	58.91	26.27

APPENDIX L

Langmuir, Freundlich, and BET isotherm parameters for Cu(II) ions removal by mango leaves

C_o (mg/L)	C_e (mg/L)	q_e (mg/g)	C_e/q_e (g/L)	log C_e	log q_e	$C_e/(C_s-C_e)q_e$	C_e/C_s
11.8717	0.3209	2.3102	0.1389	-0.4937	0.3636	0.0107	0.0240
23.4759	0.7487	4.5455	0.1647	-0.1257	0.6576	0.0131	0.0561
31.9786	1.1765	6.1604	0.1910	0.0706	0.7896	0.0157	0.0881
42.6203	2.1123	8.1016	0.2607	0.3248	0.9086	0.0232	0.1582
46.7914	2.6471	8.8289	0.2998	0.4228	0.9459	0.0280	0.1982
57.7005	4.4118	10.6578	0.4139	0.6446	1.0277	0.0463	0.3303
67.6471	8.2888	11.8717	0.6982	0.9185	1.0745	0.1378	0.6206
81.8717	11.6043	14.0535	0.8257	1.0646	1.1478	0.4715	0.8689