CHAPTER 1

INTRODUCTION

1.1 Background

The release of heavy metals in large quantities into the natural environment is one of the factors which result in environmental catastrophic. Cadmium, zinc, copper, nickel, lead, mercury, chromium and arsenic are commonly detected in the environment. Besides already existing in nature, main sources of heavy metals contamination include urban industrial aerosols, solid wastes from animals, mining activities, agricultural chemicals and industrial wastewater. These sources of heavy metals become major environmental problems and bring harm to the human health due to the high tendency for accumulation in the organism especially towards the human body. Guanyu and Viraraghavan (2003) stated that heavy metal ions are reported as priority pollutant according to their toxicity and mobility in the natural water ecosystem. Furthermore, they are stable and persistent as environmental contaminants since they cannot be degraded and destroyed. These metal ions can be harmful to aquatic life. Water contamination by toxic metal ions can cause serious health problem for human (Demirbas, 2008).

Among the heavy metals described above, copper is largely generated from various industries such as metal plating, pigment, automotive, battery and fertilizer (Wan Ngah and Hanafiah, 2009). As a trace element and micronutrient, copper is essential to maintain human body metabolism. However, excessive intake of copper may cause serious health problems such as damages to the

heart, kidney, liver, pancreas, muscular irritation, central nervous system irritation, gastrointestinal irritation and anemia (Abu Al-Rub *et al*., 2006).

Environmental regulations require the treatment of wastewater to remove heavy metals. A number of technologies have been developed over the years to remove toxic metals from water. However the technology used like chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction are expensive and non- environmental friendly (Anwar *et al*., 2010). In addition, numerous conventional techniques used in wastewater treatment are suitable for high concentration metals. They become inefficient and expensive when the heavy metals concentration is less than 100 $mg.L^{-1}$. Therefore, there is a need to search for low cost and high efficiency techniques of heavy metals removal from aqueous solutions (Benaïssa and Elouchdi, 2011; Dermirbas, 2008; Sud *et al*., 2008; Nourbakhsh *et al*., 1994).

Biosorption approach which is more environmental friendly has been evaluated since the past few decades (Wan Ngah and Hanafiah, 2008a). It has been considered as a potential alternative approach to remove pollutants from industrial effluents (Wang, 2002). Furthermore, this technique has major advantages which include low cost, high efficiency, minimization of chemical or biological sludge and possible of regeneration of biosorbent (Volesky, 1990; Aksu, 2005; Feng *et al*., 2011).

Biosorption needs a biomass as an adsorbent which is naturally abundant, easily feasible and very selective. In Malaysia, weed or *Imperata cylindrica* L. is a good example of biomass which complies with the character of potential

biosorbent. Bryson and Carter (1993) explained that this species is considered as a pernicious pest plant due to its ability to colonize, spread and subsequently displace vegetation. It can disperse easily by seed and by its extensive rhizome system, making it difficult to control (Hanafiah *et al*., 2010a). Furthermore MacDonald (2004) indicates that *Imperata cylindrica* L. is now considered to be one of the ten most troublesome weeds in the world. Introducing *Imperata cylindrica* L. as a new potential biosorbent will be an interesting effort since they are highly abundant and have no economic value. Thus it is most welcome for them to be turned into an alternative product for removing harmful pollutants such as toxic heavy metal ions from aqueous solutions.

1.2 Problem statement

The increase in heavy metals concentration in aquatic ecosystem caused by rapid industrialisation has created a major global concern. Heavy metals can be accumulated in food chain and are persistent in nature. These characters pose major threat to the environment and public health. In the aspect of regulation, the Environmental Quality Act 1974, Environmental Quality (Industrial Effluent) Regulation 2009, has clearly provided guidelines regarding pemissible limits of heavy metals concentration in industiral effluents to be complied with. Therefore, there is an insistent demand for related parties to provide the proper mechanism for heavy metals removal.

Conventional treatment methods have been used in heavy metals removal from wastewaters which have several disadvantages such as incomplete removal, expensive maintenance , only effective in high strength wastewater (more than

100 $mg.L^{-1}$) , need additional reagent, generation of other waste product which require disposal and etc. Therefore, new technology approaches are required so that heavy metals concentration in wastewater treatment plants can be reduced to the environmentally acceptable level. For this purpose, biosorption process using natural adsorbents or biosorbents is becoming the new alternative for the wastewater treatment. Recently, plant leaves have been used widely as a biosorbent for the removal of heavy metals especially Cu(II). Modification of biosorbent is required so that the potential of biosorbent can be maximized. Early studies have shown that untreated biosorbent shows low biosorption capacity in removing heavy metals (Zhou *et al.*, 2011; Wan Ngah and Hanafiah, 2008c). This study was carried on how to improve the biosorption capacity in the removal of Cu(II).

1.3 Significance of study

This study used modified *Imperata cylindrica* L. to increase biosorption capacity and in the same time to introduce a cheaper biosorbent in the removal of Cu(II). It was expected to be economically competitive due to several considerations such as it involves low cost of preparation, highly abundant in nature and environmental friendly. This may contribute to the emergence of cost-effective and efficient alternatives for the removal of heavy metals in Malaysia. Therefore, a new biosorbent material synthesized from weed (*Imperata cylindrica* L.) leaf powder was introduced to remove Cu(II) in the synthetic wastewater solution.

1.4 Aim and objectives of study

The aim of this study was to evaluate the potential of Cellulose Xanthogenate of *Imperata cylindica* L. (CXIC) to be used as biosorbent.

The objectives of the study were as follows:

- To characterize the CXIC by using spectroscopic analyses which consist of identification of functional group using Fourier Transform Infra-red (FTIR) and morphological analysis using Scanning Electron Microscope (SEM) coupled with Energy Dispersive Spectroscopy (EDS).
- To study the effects of varying various physicochemical parameters on biosorption efficiency of Cu(II), particularly biosorbent dosage, pH, initial concentrations, contact time and kinetics.
- To achieve the maximum biosorption capacity of CXIC by using biosorption isotherm of Cu(II).

1.5 Scope of work

This study focused on a single metal (copper) study using batch system experiments and was carried out in the laboratory. Cellulose xanthogenate derived from weed (*Imperata cylindrica* L.) leaf powder (CXIC) was selected as a biosorbent for the biosorption of Cu(II). The biosorbent was tested through the influence of selected parameters such as initial concentration of Cu(II) solution, contact time, pH and biosorbent dosage. The experimental work was conducted under room condition temperature and the analysis of Cu(II) concentration was conducted using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) Optima 5300 DV.

The flow diagram of the biosorption studies of Cu(II) on the chemically modified of biosorbent (*Imperata cylindirica* L.) leaf powder is shows in Figure 1.1 below.

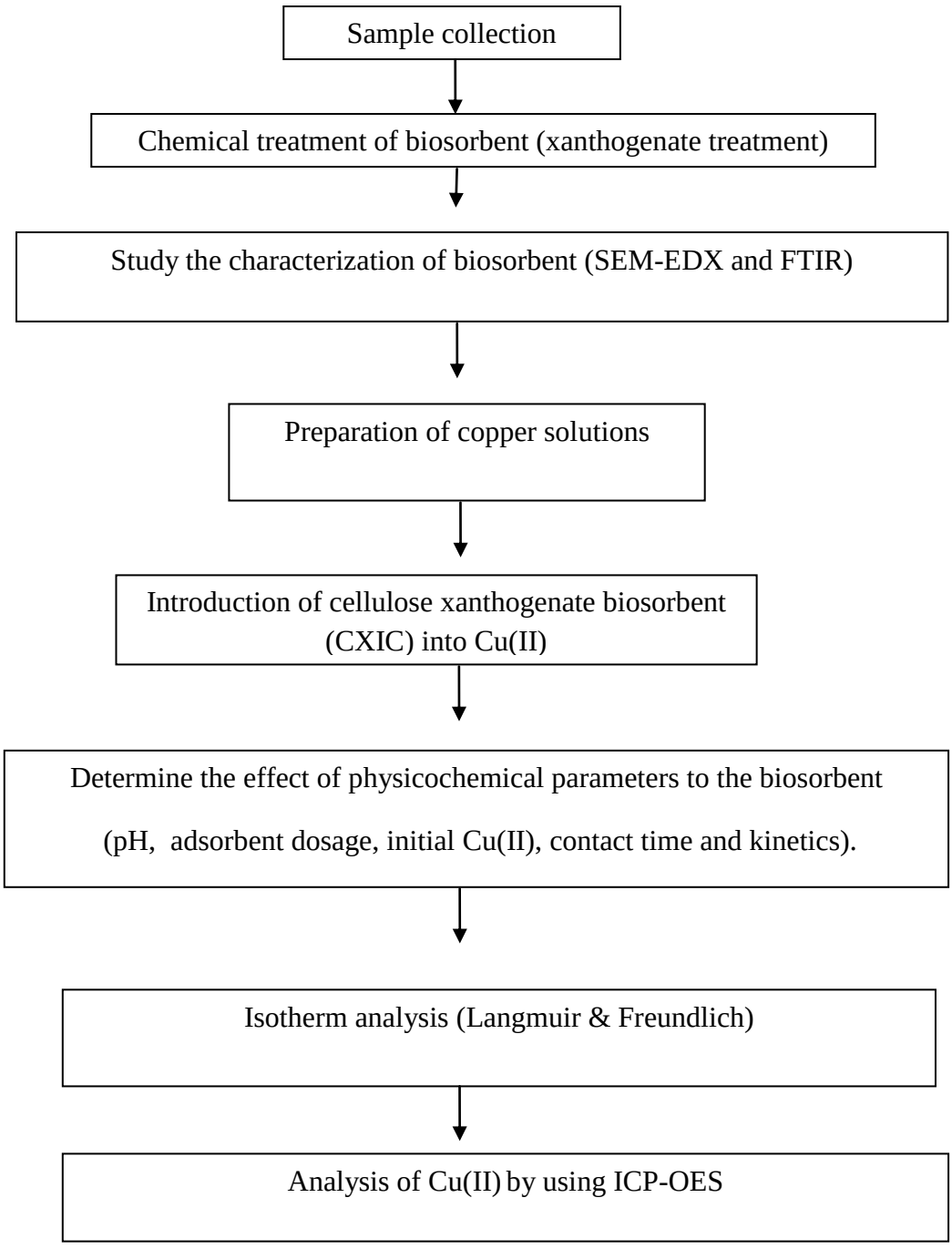


Figure 1.1: Flow chart of the batch biosorption study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The discharge of heavy metals in the waste stream by various industrial activities and processes has been a great concern. In order to combat the toxicity of heavy metals, the industry sectors are looking forward on the wide range of wastewater treatment strategies for effective removal in order to gain benefit in the environmental conservation and also to reduce the cost involved for the treatment of effluents. Furthermore, the awareness on heavy metals removal in the aquatic environment is also inspired by the implementation of strict regulations for its disposal by legal authorities (Gurgel *et al*., 2009).

2.2 Heavy metal pollution

In general, heavy metals are considered as a group of metals with an atomic density higher than 6.0 g cm^{-3} (O'Connell *et al*., 2008), having atomic weights between 63.5 and 200.6, specific gravity greater than 5.0 and also poisonous in low concentrations (Srivasta and Majumder, 2008). Malaysia legislation applied the term of heavy metals to the elements such as, Aluminium (Al), Arsenic (As), Barium (Ba), Boron (B), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Mercury (Hg), Nickel (Ni), Lead (Pb), Selenium (Se), Silver (Ag), Tin (Sn) and Zinc (Zn) which are directly linked with toxicity problems and they are included in the list of acceptable conditions of sewage

discharge which determine the permitted level of Standard A and B effluents (EQA 1974).

Heavy metals are considered as one of the contributors to the environmental pollution. The existence of heavy metals in aquatic streams lead to potentially damaging effects on human physiology and other biological systems particularly whenever the tolerance level is exceeded (Babarinde *et al*., 2006). Several past disasters due to the pollution of heavy metals in aquatic streams are the Minimata tragedy in Japan caused by contamination of methyl mercury and Itai-itai in Jintsy river of Japan which occured due to the contamination of cadmium (Friberg and Elinder, 1985).

Nowadays, heavy metals are reported as priority pollutants due to their high toxicity, tendency of bio-accumulation, cannot be destroyed and highly persistent in nature (Garg *et al*., 2007). Fu and Wang (2011) stated that the trend of heavy metals pollution in the environment is increasing consistent throughout the world especially among developing countries with the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries, pesticides and etc.

Reports from other researchers in Table 2.1 regarding the outlines of industrial sources and pollution arising for several metals discharged disclose the anthropogenic sources of metals in the environment. As a consequence of this issue, various regulatory bodies have set the maximum prescribed limits as

measures to reduce for the discharge of toxic in heavy metals in the aquatic systems. However it is hard to control the discharging of metals due to continuously ongoing industrial activities related to heavy metals, thus leading to health hazards and environmental degradation as shown in Table 2.2 (Sud *et al*., 2008).

Table 2.1 : Anthropogenic sources of heavy metals in the environment

Industry	**Metals**	**Pollution arising**	**References**
Agricultural materials Fertilisers	Cd, Cr, Mo, Pb, U, V, Zn	Run-off, surface and groundwater contamination, plant bioaccumulation	Nicholson *et al*. (2003) Otero *et al*.(2005)
Manures sewage sludge	Zn, Cu, Ni, Pb, Cd, Cr, As, Hg	Land spreading threat to ground and surface water	Nicholson *et al*. (2003) Cheung and Wong (1983) Walter *et al*.(2006)
Metallurgical industries Specialist alloys and steels	Pb, Mo, Ni, Cu, Cd, As, Te, U, Zn	Manufacture, disposal and recycling of metals. Tailings and slag heaps	Rule *et al*. (2006) Cheng (2003)
Waste disposal Landfill leachate	Zn, Cu, Cd, Pb, Ni, Cr, Hg	Landfill leachate, contamination of ground surface water	Fernandez *et al*. (2005)
Electronics	Pb, Cd, Hg, Pt, Au, Cr, As, Ni, Mn	Aqueous and solid metallic waste from manufacturing and recycling process	Veglio *et al*. (2003)
Metal finishing industry Electroplating	Cr, Ni, Zn, Cu	Liquid effluents from plating processes	Zhao *et al*. (1999) Alvarez-Ayuso *et al*. (2003)
Paints and pigments	Pb, Cr, As, Ti, Ba, Zn	Aqueous waste from manufacture, old paint deterioration and soil pollution	Davis and Burns (1999)

Table 2.2 : Permissible limit and health effects of various toxic heavy metals

Metal Contaminants	**Concentration limits of wastewater components for wastewater introduced in the water catchment areas (Standard A) or in other area inland water (Standard B) is shown below[a]**		**Permissible limits by international bodies ($\mu g.l^{-1}$)[b]**		**Health hazards[b]**
	Standard A ($mg.L^{-1}$)	**Standard B ($mg.L^{-1}$)**	**WHO**	**USEPA**	
Arsenic	0.05	0.10	10	50	Carcinogenic, producing liver tumors, skin and gastrointestinal effects
Cadmium	0.01	0.02	03	05	Carcinogenic, cause lung fibrosis, dyspnea and weight loss
Copper	**0.20**	**1.0**	**-**	**1300**	**Long term exposure causes irritation of nose, mouth, eyes, headache, stomachache, dizziness, diarrhea**
Chromium	0.05	0.05	50	100	Suspected human carcinogen, producing lung tumors, allergic dermatitis
Lead	0.10	0.5	10	05	Suspected carcinogen, loss of appetite, anemia, muscle and joint pains, diminishing IQ, cause sterility, kidney problem and high blood pressure

Table 2.2, continued

Mercury	0.005	0.05	01	02	Corrosive to skin, eyes and muscle membrane, dermatitis, anorexia, kidney damage and severe muscle pain
Nickel	0.20	1.0	-	-	Causes chronic bronchitis, reduced lung function, cancer of lungs and nasal sinus
Zinc	2.0	2.0	-	-	Causes short-term illness called "metal fume fever" and restlessness

Source: [a]Environmental Quality Act (1974) Environmental Quality (Industrial Effluent) Regulation 2009
[b]Sud *et al*., 2008

2.3 Copper pollution

Copper is one of the heavy metals which is largely generated from various industries and also considered as an essential element. It is required by living tissues in a very small amount. Nevertheless, excessive intake and even a short period of exposure can cause serious damage to human health (Mohan and Sreelakshmi, 2008).

As an essential trace metal, copper has been found in all living organisms in the oxidized Cu(II) and reduced Cu(I) states which allows this metal to play a vital role in cell physiology (Tapiero *et al*., 2003). This metal is a biological poison

which requires control of exposure and can be harmful to human if exposed to large doses (Hoissain *et al*., 2012). USEPA (2002) stated that, copper is considered as phyto-toxic and any dissemination of copper to land must be prevented in order to avoid plant damage.

The source of copper discharge as industrial effluents are from paper and pulp industry, petroleum refining, wood preserving, metal plating, metal cleaning, corrosion, mining and electronic device manufacturer (Wan Ngah and Hanafiah, 2009; Wan Ngah and Fathinathan, 2006). Those activities may release considerable amount of toxic and polluting heavy metals especially copper. Wan Ngah and Fathinathan (2006) stated that at lower pH values, excess copper can accumulate in the liver and can be toxic to fish. Furthermore, an excessive amount of copper in the marine system has been found to damage the gills, liver, kidneys, nervous system and change the sexual life of fishes (Flemming and Trevors, 1989).

According to Ho *et al*. (2002), copper plays a primary carcinogenic role among coppersmiths and the presence of Zn: Cu ratio in the soil at exceeded limit can lead to stomach cancer. According to Meena *et al*. (2005), Copper has been reported to cause neurotoxicity commonly known as "Wilson's disease" due to deposition of copper in the lenticular nucleus of the brain. Bhattacharyya and Gupta (2006) stated that, a higher exposure of copper (>5 $mg.L^{-1}$) in the body has been the linkage of many health problems such as kidney damage, high fever, haemolysis and vomiting. Since heavy metals can cause many problems,

therefore there is a necessary to remove them. Next section will discuss on the removal of heavy metal with various treatment method which available nowadays.

2.4 Removal of heavy metal

Heavy metals are the most common contaminants which contributed by anthropogenic activities. Efforts to minimize the production of heavy metals have become one of the most important environmental challenges that the world faces today (Obuseng *et al*., 2012). Therefore, various treatment methods which are effective and efficient for the removal of heavy metals are needed in order to solve the problem. The commonly used procedures or conventional techniques for removing heavy metals from wastewater include chemical precipitation, ion exchange, membrane filtration, coagulation and flocculation, floatation and electrochemical treatment (Fu and Wang, 2011).

Although all the conventional techniques can be employed, they still have difficulties in treating heavy metals in wastewater. There are several challenges to overcome so that the treatment used can fit to the characteristics of heavy metals in effluent and are highly effective to remove them. Singh *et al*. (2008) stated that the selection of the most suitable treatment depends on initial concentration of heavy metals, level of pH, temperature, flow volume, component of wastewater, biological oxygen demand, capital investment, operational cost, plant flexibility and environmental impact, etc. Table 2.3 below

shows the advantages and disadvantages of conventional treatment technologies for the removal of heavy metals from the wastewaters.

Table 2.3 : Conventional treatment technologies for the removal of heavy metals from the wastewaters and associated advantages and disadvantages

Method	**Disadvantages**	**Advantages**
Chemical precipitation and filtration	For higher concentration	Simplicity process
	Produce large amount of sludge	Inexpensive capital cost
	Ineffective for low metal concentration	
Membrane filtration	High cost	High efficiency
	Process complexity	
Coagulation-flocculation	Involve chemical consumption	Good sludge settling and dewatering characteristics
	Increased sludge volume generation	
Floatation	High initial capital cost	High metal selectivity
	High maintenance	High removal efficiency
		Low detention periods
Electrochemical treatment	Involve high initial capital investment	Require less chemicals
	Expensive electricity supply	Provide good reduction yields
		Produce less sludge
Ion Exchange	Regenerated by chemical reagents	Effective
	Cause secondary pollution	Possible recovery metals for pure effluent.
	Expensive	
	Cannot be used at large scale	

Source: Fu and Wang, 2011

2.5 Removal of copper

Copper can be found in various sources of industrial activities such as manufacturing of printed circuit board, electrical mining, electronics plating, wire drawing, copper polishing, manufacturing of paint, wood preservatives and printing operations (Aksu and Isoglu, 2005; Zhu *et al*., 2009; Al-Rashidi *et al*., 2012). Methods which are available in the treatment of copper by various processes include chemical precipitation, electrochemical, ionic exchange, solvent extraction, etc (Fu *et al*., 2006; Kakitani *et al*., 2009).

Chemical precipitation is the most common method used for copper removal in a wastewater treatment plant (Sheikholeslami and Bright, 2002). It requires precipitation agents such as sodium hydroxide, sodium carbonate, calcium hydroxide, etc (Grimshaw *et al*., 2011). During the process, these agents are combined with copper in the wastewaters before being transformed into another compound such as insoluble hydroxide or basic salt whereby the copper contents of wastewaters can be effectively removed to acceptable levels by precipitating the metal in an insoluble form (Fu and Wang, 2011). However, the degree of copper removal from wastewater is highly depend on the pH of solution, the initial concentration of copper ions in the wastewater, the nature of precipitation agent and the nature of other compounds which are present in the solution (Negrea *et al*., 2008). Other than chemical precipitation, electrochemical method can also be utilised for copper removal.

Electrochemical method requires electrochemical reactor such as tank cells, plate and frame cells, rotating cells, packed bed cell, porous carbon packing cells, etc to perform electrochemical process for copper ion removal (Chen, 2004). Although electrochemical technology has been available for a period of time, research on refining this method still continues to meet the challenges of more complex and variety of effluent compositions (Basha *et al*., 2011).

Another option which offers solution for copper removal is ion exchange. This method involves the exchange of ions between liquid phase and a porous solid phase (Vuorio *et al*., 2003). The porous solid used in this process can be either synthetic or natural (Anand *et al*., 2001). Normally the weak base cation resin in the sodium form which functioning as a porous solid is effective for this treatment (Inglezakis and Grigoropoulou, 2003). This method is useful in selectively removing copper in the presence of other metals. The equipment normally used for this process is a batch treatment system for high concentration of copper. In the case of ion exchange with resin, this process has problems due to the complexity to regenerate the resins after desorption of the metals from the loaded resins (Valenzuela *et al*., 2005).

Solvent extraction is also one of the effective method has been used in copper removal (Agrawal *et al*., 2008). Usually copper is extracted from effluent into an organic solvent. The organic solvents used are usually composed of extractant which acts as an active component to extract copper (Chang *et al*., 2010). This process become possible with chelating agents or ligands which bind to the

copper and selectively extract the copper from effluent into the organic solvent since the ligands is dissolved in the solvent. Once the copper has been extracted into the solvent, the solvent is contacted with acidic solution where the protons are higher concentration than copper. As a result, the H^+ produce complexes with the ligand and stripping copper from the ligand. The ligand can be reused and at the end of the process, copper is concentrated in the acidic solution or aqueous solution. The principle of this process could be clarified by the following equation (Fillipi *et al*., 1998):

$$[2R\text{-}H]_{org} + [M^{2+}]_{aq} \overset{\text{Extraction}}{\Longleftrightarrow} [R_2M]_{org} + [2H^+]_{aq} \overset{\text{Stripping}}{\Longleftrightarrow} [2R\text{-}H]_{org} + [M^{2+}]_{aq}$$

However, this method is suitable for higher concentration of copper and the cost become high for very dilute copper solution (Aggarwal *et al*., 1986).

Most of the methods used for the purpose of copper removal have some disadvantages such as ineffective in the low concentration of copper, time consuming, high investment and operating cost, very sensitive to operational condition, continuous chemical requirements and incomplete copper removal (Ferrah *et al*., 2011). This situation has introduced a growing interest among researchers by on alternative method which involves a low cost, robust technology with minimum manpower and limited energy consumption for the removal of copper from wastewater (Da'na and Sayari, 2011). For this purpose, copper removal by using biosorption can be a promising method especially when it involves low cost of biosorbents.

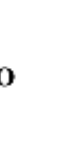
2.6 Biosorption study on heavy metal removal

The discovery and development of biosorption is one of the most promising technologies involved in the removal of heavy metals from wastewater (Kumar *et al*., 2006). Biosorption requires materials from any biological origin such as plant-derived materials, algae, fungi, bacteria, etc. as adsorbents (Han *et al*., 2006). This approach is becoming a potential alternative to replace conventional techniques for the removal of heavy metals due to the low cost, easily feasible, minimum volume of chemical or biolological sludge to be disposed, high efficiency in detoxifying very dilute effluent (1-100 $mg.L^{-1}$) and no nutrient requirements (Feng *et al*., 2011). Kratochvil and Volesky (1998) stated that this process utilizes inexpensive biomass to remove heavy metals therefore beneficial for the sequestration of contaminants from industrial effluents.

Biosorption is the term given to describe the removal of heavy metals by passive binding to non-living biomass (Mack *et al*., 2007). Certain types of biomaterials or biosorbents used during biosorption are able to bind heavy metals from even very dilute aqueous solutions (Witek-Krowiak *et al.,* 2011). The mechanism of biosorption is a complicated process which is influenced by several factors such as status of biosorbents (living or non living), types of biomaterials, chemical properties of heavy metals solution, ambient conditions, etc. (Das, 2010). It is metabolism independent processes which are generally based on physico-chemical interaction between metals ions and the functional groups present on the cell surface such as electrostatic interaction, ion exchange, complexation, metal ion chelation and microprecipitation that take place in the cell wall (Mao *et al*., 2009). The most common functional groups involved in such interactions

include carboxylate, hydroxyl, amine and phosphoryl groups which exist within the cell wall of biosorbents (Dziwulska *et al*., 2004). The other major functional groups which contribute to the effectiveness of biosorption also has been summarized by Volesky (2007) in the Table 2.4.

Table 2.4 : Major functional groups for biosorption

Functional group	**Structural formula**
Amide	
Amine	**$-NH_2$**
Carbonyl (ketone)	**>C=O**
Carboxyl	
Hydroxyl	**-OH**
Imine	**=NH**
Phosphodiester	
Phosphonate	
Sulfhydryl (thiol)	**-SH**
Sulphonate	

Source: Volesky, 2007

2.6.1 Kinetic of biosorption

There are many models that can be utilized in order to describe the process of biosorption. It can be explained by empirical equations with the constant being determined in an experimental manner by focusing on both the equilibrium and the kinetic of biosorption. Models most commonly used in the literature are the pseudo-first order and pseudo-second order model which are useful in describing the process of kinetic whereas the Langmuir and Freudlich models have been used in describing the process of equilibrium. The simplest method for determination of constant in the model is through transformation of the equation describing the equilibrium to a linear equation form (Witek-Krowiak *et al*., 2011). In addition, linear regression is commonly used to determine the model parameters, however non-linear regression is used to allow for better accuracy and correlation of the model with the experimental results (Tsai, 2000; Lin and Wang, 2009). Table 2.5 shows several models proposed by other researchers to help in describing both kinetic and equilibrium in the study of biosorption.

Table 2.5 : Proposed models used in the study of biosorption

Categories of model	Types of models	Functions
Kinetic models	Fractional power, Zero order, First order, Pseudo-first order, Elovich, Second order, Pseudo-second order, Intra-particle diffusion	To correlate the experimental (contact time & concentration) data and to determine the biosorption kinetic
Two- parameters isotherm models	Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Halsey	To correlate the experimental (equilibrium) data and to determine the biosorption isotherm
Three- parameter isotherm models	Redlich-Peterson, Slips, Khan, Toth, Radke-Prausnitz, Jossens, Langmuir-Freundlich	

Source: Das *et al*., 2012

2.7 Inexpensive and effective biosorbents

A large number of materials have been widely investigated as potential biosorbents for heavy metals removal especially copper. According to Saha and Orvig (2010), the tested biosorbents can be derived from several sources which include non-living biomass such as bark, lignin, crab shell and etc. Futhermore, other examples are algal biomass and microbial biomass such as bacteria, fungi and yeast. Kratochvil and Volesky (1998) stated that highly preferable biosorbents are determined based on their availability in nature, requires little processing and by-product of waste material from industrial waste. These factors are useful to categorise that particular biosorbent as a low-cost adsorbent because they have no or very minimum economic value.

Another consideration needed when choosing an appropriate biosorbent is the effectiveness of the biosorbent. According to Witek-Krowiak *et. al* (2011), the effectiveness of biosorbent is recognised by maximum biosorption capacity. It is a very important parameter that allows for estimation of process costs, since the determined value allow researchers to predict the amount of biosorbent required for effective biosorption. Typically the value is determined experimentally at constant temperature and the results gained are presented as isotherms. It technically calculates the maximum amount of the adsorbed heavy metals which are available for the uptake during biosorption per unit mass or unit volume of biosorbent and the unit is usually represented in $mg.g^{-1}$.

2.7.1 The use of non living plant materials as biosorbent

Different forms of inexpensive biosorbents among non-living plant materials have been widely studied as they have very low economic value. Most of them have been focused on untreated plant waste such as lalang (*Imperata cylindrica* L.) leaf powder (Hanfiah *et al*., 2007), rubber (*Hevea brasiliensis*) leaf powder (Hanfiah *et al*., 2010b), neem leaves (Bhattacharyya and Sharma, 2004), banana skin, green tea waste, oak leaf, walnut shell, peanut shell and rice husk (Park *et al*., 2008), black gram husk (Saeed *et al*., 2005), fern (Ho et al., 2004), maize leaf (Babarinde *et al*., 2006), teak leaf powder (King *et al*., 2006), peanut hull pellets (Johnson *et al*., 2002) and sago waste (Quek *et al*., 1998).

Even though the application of untreated non-living plant materials as biosorbents poses several potential, there are still weaknesses which cause some

problems. Zhou *et al.* (2011) stated that plant fibre which consists in the biosorbent generally has low biosorption capacity for heavy metal ions in aqueous solution. Apart from that, it can also lead to several environmental problems such as high chemical oxygen demand (COD), high biological oxygen demand (BOD) and high total organic carbon (TOC) due to the release of soluble organic compounds contained in the plant materials as biosorbents (Gaballah *et al*., 1997; Nakajama and Sakaguchi, 1990). The increase of those problems can cause depletion of oxygen content in water thus threaten the aquatic life. In order to enhance the biosorption capacity and to avoid the side effect (high BOD, COD and TOC), the biosorbents need to be modified or treated first before being applied to the process of removing heavy metals (Wan Ngah and Hanafiah, 2008b).

There is still lack of studies regarding the use of *Imperata cylindrica* L. as biosorbent to remove heavy metal from aqueous solution. Studies on effectiveness of biosorption by *Imperata cylindrica* L. have been carried out by Hanafiah *et al*. (2006), Hanafiah *et al*. (2007) and Hanafiah *et al*. (2010a). In general, these studies revealed that the value of maximum biosorption capacity obtained by treated *Imperata cylindrica* L. are much higher than untreated. Apart from that, a faster equilibrium time was also achieved by treated *Imperata cylindrica* L. compared to untreated biosorbent (Hanafiah *et al*., 2006 and Hanafiah *et al*., 2007)

2.7.2 Modification of biosorbent

There are a large number of research works on the modification of biosorbents to upgrade the effectiveness of the biosorption process. The biosorbents usually undergo chemical modification or pretreatment process using various types of modifying agents such as mineral acids, organic acids, bases, organic compounds, metal salts, oxidizing agent and dye (Wan Ngah and Hanafiah, 2009). According to Gaballah *et. al* (1997), pretreatment of biosorbents can extract soluble organic compounds and increase chelating efficiency. Many researchers have used various types of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic solutions (hydrochloric acid, nitric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agents (hydrogen peroxide) and dye (Reactive Orange 13) for the purpose of removing soluble organic compounds, eliminating colouration of the aqueous solutions and enhancing the efficiency of metal adsorption (Wan Ngah and Hanafiah, 2008c). However, among all of the modifying agents, acids and bases are the most common chemicals used for the pretreatment or chemical modification of biosorbent (Sun, 2009). Table 2.6 shows several findings of previous studies on the types of chemicals used for modifying biosorbents and their maximum biosorption capacities.

Table 2.6 : Summary of modified biosorbents for the removal of copper from aqueous solution

Biosorbent	Modifying agent	Maximum biosorption capacity, q_{max} ($mg.g^{-1}$)	Reference
Eichhornia crassipes (water hyacinth)	Sodium hydroxide, Carbon disulphide and Magnesium sulphate	262.66	Tan *et al.* (2008)
Sugarcane bagasse	Ethylenediamine	139.00	Junior *et al*. (2006)
Nipah palm shoot biomass	Mercaptoacetic acid	66.71	Wankasi *et al*. (2006)
Azolla filiculoides (aquatic fern)	Hydrogen peroxide-Magnesium chloride	62.00	Ganji *et al*. (2005)
India barks	Hydrochloric acid	51.40	Reddy *et al*. (1997)
Coirpith	Sulphuric acid and ammonium persulphate	39.70	Namasivayam and Kadirvelu (1997)
Rice husk	Tartaric acid	29.00	Wong *et al*. (2003a)
Imperata cylindrica L. (leaf powder)	Sodium hydroxide	11.64	Hanafiah *et al*. (2009)
Jute fibres	Reactive orange 13	8.40	Shukla and Pai (2005a)

2.7.3 Cellulose Xanthogenate as a modified biosorbent

In general, the chemical modification of biosorbent is capable to increase biosorption capacity and also improve the stability of biosorbent (Kamel *et al*., 2006; O'Connell *et al*., 2008). Cellulose xanthogenate is produced by introducing inorganic substances including carbon disulphide, sodium hydroxide and magnesium sulphate into the cellulose backbone of biosorbent (Tan *et al*.,

2008). The introduction of carbon disulphide and sodium hydroxide might alter other functional group such as -CS-S and carboxyl on modified biosorbent which is useful in enhancing the binding capacities due to the attraction of different charges between various functional groups of modified biosorbent and the metal ions of aqueous solution (Zhou *et al*., 2011). The principle of preparation of cellulose xanthogenate could be clarified by the following equation (Tan *et al*., 2008):

$$\text{Cell-OH} + \text{NaOH} \longrightarrow \text{Cell-ONa} + H_2O$$

$$CS_2 + \text{Cell-ONa} \longrightarrow \text{Cell-OCS}_2\text{Na}$$

$$2\text{Cell-OCS}_2\text{Na} + Mg^{2+} \longrightarrow (\text{Cell-OCS}_2)_2\,Mg + 2Na^{+}$$

Previous studies using cellulose xanthogenate as modified biosorbent which derived from biomass resources are not easily available in literature except shown by Tan *et al*. (2008), Zhou *et al*. (2009) and Zhou *et al*. (2011). These studies have included their preparation, structural characterization, biosorption mechanism and biosorption capacity of cellulose xanthogenate derivatives of *Eichhornia crassipes*. In this study, the application is extended by focussing on the biosorption of copper by using *Imperata cylindrica* L. as a biosorbent. The modified biosorbent proposed in this study is known as Cellulose Xanthogenate *Imperata Cylindrica* L. (CXIC).

CHAPTER 3

METHODOLOGY

3.1 Characterisation of CXIC

Characterisation of CXIC was performed by spectroscopic analysis after sample collection and preparation of CXIC. The Fourier transform infrared (FTIR) spectra of untreated *Imperata cylindrica* L. (UIC) , CXIC before and CXIC after Cu(II) biosorption were recorded with Fourier Transform Infrared Spectrophotometer (Perkin Elmer, FTIR System 1600 Model, USA) in the range of 400-4000 cm^{-1} . The morphological characteristics of CXIC were evaluated using scanning electron microscope (SEM; Leo Supra 40VP, Carl-Zeiss SMT, Germany) couple with energy-dispersive spectroscopy (EDS).

3.1.1 Sample Collection

The fresh weed (*Imperata cylindrica* L.) leaves were collected during the dry season from the surrounding areas of Universiti Teknologi MARA, Shah Alam. The leaves were washed with distilled water to remove dirt and adhering particles, and were dried in the sun for three days followed by drying in an oven at 80°C overnight to remove all moisture.

3.1.2 Preparation of CXIC

The dried brownish leaves were cut into small pieces, ground and sieved to obtain an average particle size of 180-355 µm. Ten grams of *Imperata cylindrica* L. were mixed with 100 mL of 5 M NaOH and stirred at 500 rpm for 90 min at room temperature to obtain an alkali-treated leave. The alkali-treated leave is then esterified with 0.15 mL carbon disulfide and 50 mL 2.5 M of NaOH for another 90 min. The process was continued by treating it with 10 mL of 0.5 M $MgSO_4$ for 10 min to obtain cellulose xanthogenate. The mixture was then filtered using filter paper and cleaned extensively with deionised water. All of the samples were dried in an oven and grounded into fine powder. The powder was stored in a desicator at room temperature until ready to be used. The product is called cellulose xanthogenate *Imperata Cylindrica* L. (CXIC). All the reagents used were of analytical grade.

3.1.3 Fourier transform infrared (FTIR) analysis

A volume of 100 mL of 150 $mg.L^{-1}$ Cu(II) solutions was prepared by diluting 1000 $mg.L^{-1}$ Copper standard solution. A weight of 0.05 g of CXIC and 50 mL of 150 $mg.L^{-1}$ Cu(II) solutions was added into 150 mL conical flask and the initial pH of Cu(II) was fixed at pH 4 by addition of 1M HCl or NaOH solutions. The mixture was shaken on a rotary shaker at 250 rpm for 2 h and filtered using Whatman glass microfiber filter GF/C 90mm. The sample was dried overnight in the oven at $80^{o}C$. This procedure was only required for the preparation of CXIC after biosorption. For the preparation of sample disks, 0.002 g of UIC, CXIC before biosorption and CXIC after biosorption were weighed using analytical balance and each of the sample were mixed together with 0.2 g of KBr

by grinding it for 10 min before being analysed with FTIR. Analysis on the functional groups of UIC, CXIC before biosorption and CXIC after biosorption was performed using FTIR (Perkin Elmer, System 1600, USA) in the range of 400 – 4000 cm^{-1}

3.1.4 SEM and EDS analysis

The surface morphology of UIC, CXIC before biosorption and CXIC after biosorption were observed by Scanning Electron Microscope (SEM; LeoSupra VP50, Carl-Zeiss SMT, Germany) coupled with Energy Dispersive Spectroscopy (EDS). All samples were required to follow the coating procedure before being applied to SEM. The tweezers were used to insert all samples into the sample holder before being properly fixed and placed in the small chamber of sputter coater. After coated with gold, all of the samples were placed under SEM and bombarded with electrons by 15 keV power supply. In order to avoid contamination, all of the samples were kept dried by storing them in a dessicator.

3.2 Experimental design to determine the effects of various physicochemical parameters on biosorption of Cu(II)

The CXIC biosorbent was introduced into Cu(II) aqueous solution in batch biosorption experiments to study the effect of biosorbent dose, the effect of pH, the effect of initial Cu(II) concentration and contact time. The experiments were conducted after the preparation of Cu(II) aqueous solution.

3.2.1 Cu(II) aqueous solution preparation

Copper standard solutions were prepared by diluting 1000 $mg.L^{-1}$ copper standard solution (Merck) into series of desired concentration of Cu(II). The calculated volume of copper solution was pipetted into volumetric flasks and diluted with deionised water to the mark.

3.2.2 Batch biosorption studies

All batch biosorption experiments were carried out in duplicates and the results were reported as average. All chemicals used were of analytical reagent grade.

3.2.3 Effect of biosorbent dose

The effect of biosorbent dose on biosorption of Cu(II) was performed at room temperature (24 ± 0.5 °C). The different amounts of CXIC (0.01 to 0.1 g) were used and 50 mL of 10 $mg.L^{-1}$ copper solutions were added into the conical flasks. The pH of copper solution was adjusted to pH 4 by addition of 1M HCl or NaOH solutions. The mixture was shaken on rotary shaker at 150 rpm for 180 min and then filtered through Whatman glass microfiber filter GF/C mm and the filtrates were analyzed for Cu(II) content using ICP-OES at the wavelength of 327.393 nm. The weight of biosorbent varied from 0.01 to 0.1 g at intervals of 0.01 g, 0.02 g, 0.03 g, 0.04 g, 0.1 g.

3.2.4 Effect of pH

The effect of pH was investigated over a pH range 2 to 5 to avoid precipitation of $Cu(OH)_2$ which starts to occur at pH above 5 (Reddy *et al*., 1997). This study was performed at room temperature by mixing 0.05 g of CXIC with 50 mL of 10 $mg.L^{-1}$ copper solutions into 150 mL conical flask. The initial pH of 10 mg L^{-1} was adjusted to 2, 3, 4 and 5 by addition of 1 M HCl or NaOH solutions. The mixture was shaken on a rotary shaker at 150 rpm for 180 min and then filtered through Whatman glass microfiber filter GF/C mm and the filtrates were analysed for Cu(II) content using ICP-OES at the wavelength of 327.39 nm.

3.2.5 Equations used

The equations used in the subtopics 3.2.3 and 3.2.4 were as follow:

Equation 1:

The amount of Cu(II) adsorbed by the biosorbent (CXIC) were calculated by using the following mass balance equation (Wan Ngah and Hanafiah, 2008d):

$$q_e = \frac{C_o - C_e}{m} V$$

Where C_o and C_e are Cu(II) concentrations ($mg.L^{-1}$) before and after biosorption, respectively, V is the volume of copper solution (L) and m is the weight of the biosorbent (g).

Equation 2:

The percentage removal of Cu(II) was calculated from the following equation (Wan Ngah and Hanafiah, 2008d):

$$\text{Removal (\%)} = \frac{C_o - C_e}{m} \times 100$$

Where C_o and C_e are Cu(II) concentrations ($mg.L^{-1}$) before and after biosorption, respectively and m is the weight of the biosorbent (g).

3.2.6 Effect of initial Cu(II) concentration, contact time and kinetics

To determine the contact time required for equilibrium state, kinetic studies were carried out by varying the contact time (2-240 min) using two different concentration of copper solution (10 and 20 $mg.L^{-1}$) in the 150 mL conical flasks at room temperature. The time intervals chosen for this study varied at 2, 5, 10, 20, 30, 60, 90, 120, 180 and 240 min. The initial pH was fixed at 4 and 0.05 g of CXIC was used. The mixtures were shaken at 150 rpm and then filtered through Whatman glass microfiber filter GF/C 90 mm and the filtrates were analyzed for Cu content using ICP-OES at a wavelength of 327.39 nm.

3.2.7 Equations used

The equations used in the subtopic 3.2.6 were as follow:

Equation 3:

The pseudo-first order kinetic equation (Ho and Mckay, 1998) is given as:

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

Where q_t and q_e are the amount of Cu(II) adsorbed ($mg.g^{-1}$) at time t(min) and at equilibrium, and k_1 is the constant rate of the pseudo-first order biosoption process (min^{-1}).

Equation 4:

The pseudo-second order equation (Ho and McKay, 2000) is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t$$

Where $h = k_2 q_e^2$ can be regarded as the initial sorption rate as $t \rightarrow 0$, and k_2 is the constant rate of pseudo-second order biosorption ($g.mg^{-1}.min^{-1}$). The plot t/q_t versus t should give a straight line if pseudo-second order kinetic is applicable and q_e , k_2 and h can be determined from the slope and intercept of the plot, respectively.

3.3 Experimental design to determine the maximum biosorption capacity of CXIC by isotherm of Cu(II)

For isotherm study, 0.05 g of CXIC was mixed with 50 mL of copper solutions at various Cu(II) concentrations (20-100 $mg.L^{-1}$) at room temperature in the 150 mL conical flasks. The initial pH of copper solutions was fixed at 4 by adding 1 M HCl and NaOH solutions. The mixture was shaken on the rotary shaker for 2 h to ensure the equilibrium time achieved. The copper concentrations varied from 20 to 100 $mg.L^{-1}$. The mixture was filtered through Whatman glass microfiber filter GF/C 90 mm and the filtrates were analyzed for copper content using ICP-OES at a wavelength of 327.39 nm.

3.3.1 Equations used

The equations used in the subtopic 3.3 were as follow:

Equation 5:

The linearized form of the Langmuir model is given as (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\, b} + \frac{C_e}{q_{max}}$$

Where C_e is the equilibrium Cu(II) concentration ($mg.L^{-1}$). q_e is the amount of Cu(II) adsorbed at equilibrium ($mg.g^{-1}$), q_{max} is the maximum biosorption capacity ($mg.g^{-1}$), and b is a constant ($L.mg^{-1}$) related to the energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate.

Equation 6:

The Freundlich model is given by (Freundlich, 1906):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

K_F is maximum biosorption capacities ($mg.g^{-1}$) and n is related to biosorption intensity.

3.4 Analysis of Cu(II)

All of the mixtures were filtered through a Whatman glass microfiber filter GF/C 90 mm after biosorption batch studies had been conducted. The concentration of Cu(II) in the solutions before and after equilibrium were analysed by ICP-OES. The setting parameters that had been used during the analysis of Cu(II) are shown in Table 3.1.

Table 3.1 : ICP-OES setting parameters for analysis of copper

Instrument : Spectrometer, Read Time, Replicates			
Purge Gas Flow :	Normal	Resolution :	Normal
Read Delay Time (sec) :	60	Replicates :	3
Minimum Time :	1.000sec	Maximum Time :	5.000sec
Survey and Auto Integration Spectral Windows			
Element :	Cu	Wavelength (nm) :	327.39
Survey Lower :	327.30	Auto Lower :	327.30
Survey Upper :	327.51	Auto Upper :	327.51
Sampler: Plasma Parameters			
Source Equilibrium Delay:	11 sec	Plasma View :	Radial
Plasma (L/min) :	15	Aux (L/min) :	0.2
Neb (L/min) :	0.65	Power Watts :	1300
Sampler : Peristaltic pump & Wash Parameters			
Sample Flow Rate:	1.5 mL/min	Sample Flush Time :	10 sec
Wash Frequency:	Between samples	Wash Time :	30 sec

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterisation of CXIC

4.1.1 Fourier transform infrared (FTIR) analysis

FTIR analysis was carried out in order to identify the functional groups in the CXIC that might be involved in the biosorption process. Figure 4.1 shows the comparison between results of FTIR spectra of UIC, CXIC before biosorption and CXIC after biosorption which loaded with Cu(II).

The FTIR spectrum of UIC displayed a number of peaks indicating the presence of different types of functional groups in the biosorbent. The broad and strong band ranging from 3000 to 3600 cm^{-1} represents the overlapping Si-OH (silanol), R-OH (hydroxyl) and $–NH_2$ (amine) stretching vibrations. The peaks observed at 2913.04 and 2847.82 cm^{-1} could be assigned to asymmetric and symmetric CH_2 groups. The strong peak located at 1591.72 cm^{-1} corresponds to the C=C stretching of aromatic rings of lignin (Ncibi *et al*., 2006). The sharp peak observed near 1382.16 and 1349.65 cm^{-1} indicates the presence of carboxylate (COO^-) groups. The region below 1000 cm^{-1} was called “finger print region” and the biosorption cannot be clearly assigned to any particular vibration because they correspond to complex interacting vibration systems (Hanafiah *et al*., 2010b). The highest percentage of transmittance for UIC shown in Figure 4.1 also means the lowest intensity of absorbance achieved. This indicates that UIC contained less active O-H and C=O groups compared to CXIC which

explain the reason of lower biosorption capacity among untreated biosorbent compared to the treated biosorbent (Zhou *et al*., 2011).

Meanwhile, the FTIR spectrum of CXIC displayed a bit of change indicating the existence of different types of functional groups due to the structural modification of the biosorbent. The broad and strong band ranging from 3000 to 3600 cm^{-1} still exists as in UIC spectra which represents the overlapping Si-OH (silanol), R-OH (hydroxyl) and $–NH_2$ (amine) stretching vibrations. Likewise to the peaks observed at 2920.28 and 2855.07 cm^{-1} could be assigned to asymmetric and symmetric CH_2 groups and the strong peak located at 1595.33 cm^{-1} corresponds to the the C=C stretching of aromatic rings of lignin (Ncibi *et al*., 2006) as well. The sharp peak observed near 1382.16 cm^{-1} and 1349.65 cm^{-1} indicates the presence of carboxylate (COO^-) groups similar as UIC. The presence of sulphur groups ($-CS_2$) due to the modification had been identified by the appearance of new peaks at 1154.54 and 1107.57 corresponding to S-C-S and C=S. In addition, the peak located at 1049.76 cm^{-1} could also be assigned to C-O-C of ether group (Hanafiah *et al*., 2010a). It was noticeably shown in Figure 4.1 that the intensity for CXIC was higher than UIC indicating that more O-H and C=O groups are available in CXIC which might account for the higher Cu(II) biosorption capacity of CXIC.

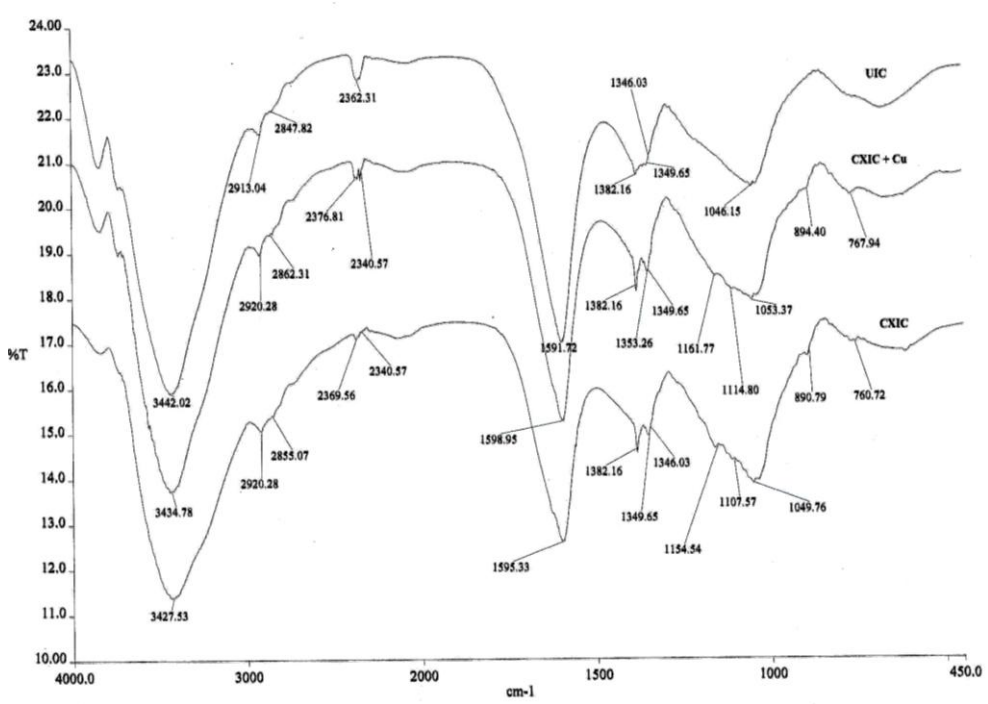


Figure 4.1 : FTIR spectra of UIC, CXIC before and after Cu(II) biosorption

As predicted, some distinct changes in the spectrum were noted after copper biosorption. For instance, the broad peak at 3427.53 cm^{-1} had shifted to 3434.78 cm^{-1}, suggesting chemical interaction between functional groups of hydroxyl, silanol and amine group with Cu(II). Hanfiah *et al,* (2010a) stated that, the shift of the wavenumber around this region could suggest the exchange of H^+ with light metal ions in the biosorbent. The C=C aromatic rings group also took part in the biosorption of Cu(II) as the wavenumber shifted from 1595.33 cm^{-1} to 1598.95 cm^{-1} . The shift in wavenumber from 1349.65 cm^{-1} to 1353.26 cm^{-1} suggested a chemical interaction between carboxylate (COO^-) groups and Cu(II). Furthermore, a sharp peak appeared at 1382.16 cm^{-1} after copper biosorption confirming the involvement of carboxylate (COO^-) groups during the process. The sulphur (S-C-S and C=S) groups, and ether (C-O-C) groups might also

form interactions with Cu(II) as there were a shift in wavenumber from 1154.54 cm^{-1} to 1161.77 cm^{-1} , 1107.57cm^{-1} to 1114.80 cm^{-1} and 1049.76 cm^{-1} to 1053.37 cm^{-1} respectively .

Overall, the main functional groups that might be involved in the binding of Cu(II) are -OH, -NH, C=C, COO-, -CS_2 and C-O-C. The FTIR analysis clearly revealed the major functional groups which are responsible during biosorption of Cu(II). All of the major functional groups in CXIC carried negative charges whereby play an important role in the electrostatic interaction of Cu(II) from aqueous solution to the binding site of the biosorbent (Mao *et al*., 2009).

4.1.2 SEM and EDS analysis

SEM and EDS are powerful tools for examining the structure of surface morphology and elemental features of the biosorbents which have been widely used in study of heavy metals adsorption particularly in evaluating the biosorption mechanism (Akar and Tunali, 2005; Tunali *et al*., 2006; Panda *et al*., 2007; Pino *et al*., 2006). The SEM images and EDS spectra for UIC without Cu(II) biosorption, CXIC before Cu(II) biosorption and CXIC after Cu(II) biosorption are shown in Figure 4.2, 4.3 and 4.4 respectively.

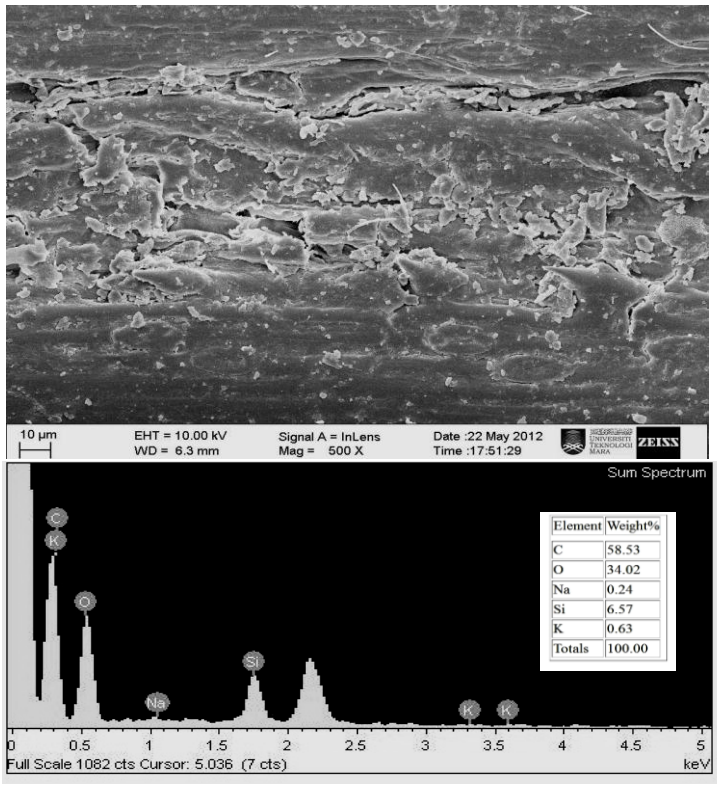


Figure 4.2 : SEM images at 500X magnification and the EDS spectra of UIC

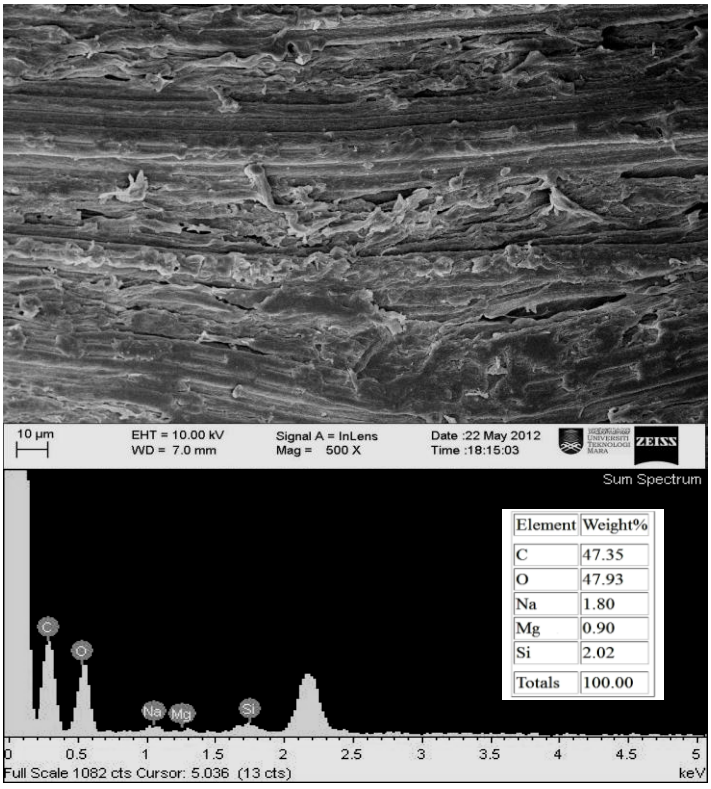


Figure 4.3 : SEM images at 500X magnification and the EDS spectra of CXIC before biosorption

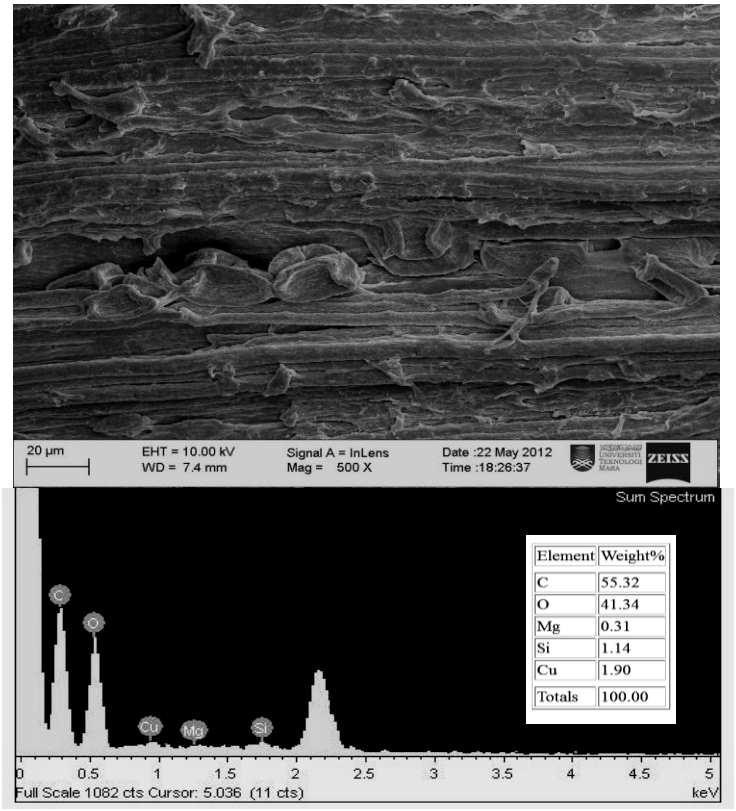


Figure 4.4 : SEM images at 500X magnification and the EDS spectra of CXIC after biosorption

In general, the SEM images with 500X magnification showed non-porosity and has rough irregular surface for all biosorbents. These characters allow Cu(II) to be adsorbed to the surface of CXIC. Although SEM images of UIC, CXIC before and CXIC after biosorption appeared quite similar, the EDS spectra revealed an interesting finding. EDS is a very useful tool for identifying elements on the biosorbent surface and help to confirm the binding of Cu(II) onto the binding site of CXIC.

The EDS spectrum for UIC showed some peaks for light metal elements such as sodium (Na) and Potassium (K) with the weight percentage of 0.24% and 0.63%

respectively (Figure 4.2). Silica (Si) which existed in the SEM spectrum was also confirmed by the peak at 1.7keV in the EDS spectrum and the existence of Si was consistent in both CXIC before and CXIC after biosorption. There were several changes observed on the EDS spectrum for CXIC before biosorption. The consumption of $MgSO_4$ and NaOH solution during biosorbent preparation led to the presence of Magnesium (Mg) on the CXIC surface and increase in weight percentage of Na to 1.8%. Meanwhile, after biosorption, a new peak was observed at 0.9keV with 1.9% of weight percentage which represented Cu(II). However, the peak that represented Na totally disappeared and the weight percentage of Mg had decreased to 0.31%.

The disappearance of light metal peak (Na) and the appearance of copper peak as revealed by the EDS spectra indicated that besides complexation as showed by the FTIR spectra, the removal of Cu(II) could also take place by ion exchange between light metal ions and Cu(II) during the biosorption process. This kind of removal mechanism was also observed in other studies (Akar and Tunali, 2005; Wan Ngah and Hanfiah, 2009).

4.2 The effect of various physicochemical parameters on biosorption of Cu(II)

4.2.1 Effect of biosorbent dose

In this study, six different biosorbent dosage were selected ranging from 0.01 to 0.1g while the Cu(II) concentration was constantly fixed at 50ml of 10 $mg.L^{-1}$ .The results are shown in Figure 4.5. In general, it can be seen that the percentage removal of Cu(II) increased as the biosorbent dose increased but

remain constant beyond 0.04g dose. The lowest percentage of Cu(II) removal was 39.6% (0.01g) and reached the maximum at a dose of 0.1g (92.6%). There was an increase in the percentage removal of Cu(II) from the solution as the biosorbent dosage increase which was due to an increase in the availability of active sites for copper binding. Therefore, more surface area of biosorbent were being exposed which eventually facilitated Cu(II) to be adsorbed (Cabuk *et al*., 2007)

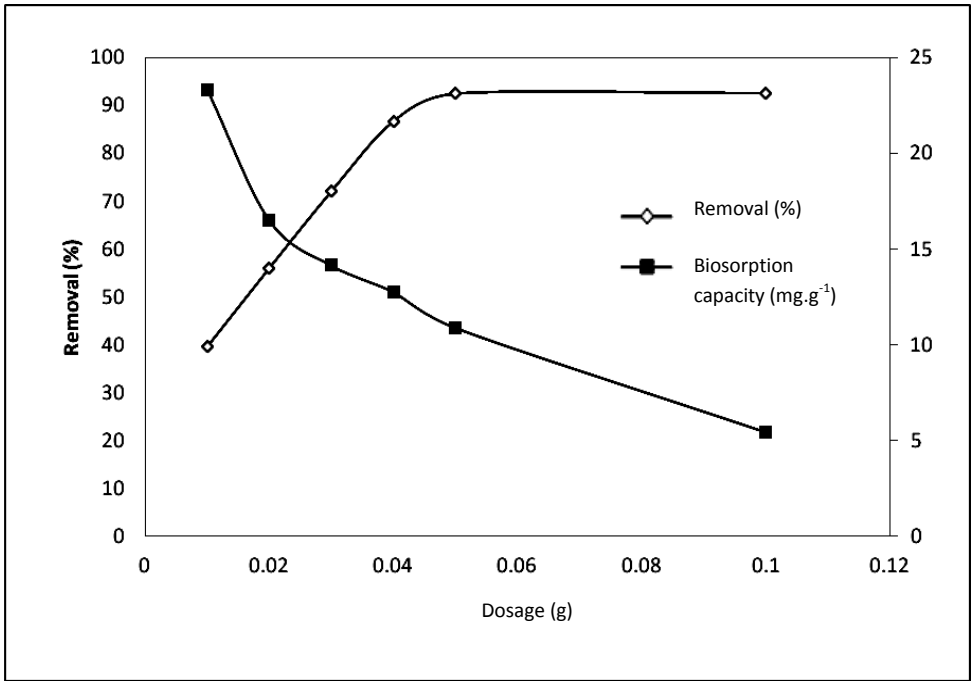


Figure 4.5 : Effect of biosorbent dose on Cu(II) biosorption onto CXIC (initial Cu(II) concentration = 10mg.L^{-1}; shaking rate = 150rpm; pH = 4)

Conversely, an increase in biosorbent dose was linked with the decrease in biosorption capacities (mg.g^{-1}). The biosorption capacities of Cu(II) decreased from 23.3 mg.g^{-1} until reaching the minimum value of 5.5 mg.g^{-1} with an increasing biosorbent dose from 0.01 to 0.1g as shown in Table 4.1. Similar effects were reported by other researches during biosorption studies (Sahin *et al*.,

2005; Han *et al.,* 2007; Ofomaja *et al*., 2009). In this study, the concentration of Cu(II) was kept constant while the biosorbent dosage was increased. Therefore the amount of Cu(II) adsorbed ($mg.g^{-1}$) showed the opposite trend. This behaviour was mainly caused by the large number of biosorption sites which remain unadsorbed as the biosorbent dosage increased (Hanafiah *et al*., 2010). Wong *et al.* (2007) stated that the presence of a high number of biosorbent in the solution at a fixed concentration of adsorbate produces a process called the 'shielding effect' in which some biosorption sites were protected and this leads to a drop in the level of heavy metal adsorbed. In addition, Shukla *et al*. (2002) mentioned that particle aggregation could be another reason to explain this condition whereby it is a result from the high dosage of biosorbent which would lead to a decrease in the total surface area of the biosorbent.

Table 4.1 : Amount of Cu(II) removed (%) and adsorbed ($mg.g^{-1}$) at different biosorbent dosage

Biosorbent dose (g) ($mg.g^{-1}$)	**Removal (%)**	**Cu(II) adsorbed**
0.01	39.63	23.32
0.02	56.06	16.49
0.03	72.12	14.15
0.04	86.74	12.76
0.05	92.53	10.89
0.1	92.63	5.45

Both biosorption capacity and percentage removal were equally important in biosoption experiments since the data gained were useful especially in deciding the biosorption performance at particular biosorbent dosage (Balasubramaniam *et al.*, 2009). The biosorbent dosage of 0.05g was selected for further biosorption studies because it showed both relatively high percentage of removal and high biosorption capacity.

4.2.2 Effect of pH

The experiments were performed in the pH range of 2-5 while the Cu(II) concentration was constantly fixed at 50ml of 10 $mg.L^{-1}$. As can be seen in Figure 4.6, the biosorption of Cu(II) from aqueous solution was mainly influenced by pH. The graph indicated no biosorption of Cu(II) in a strongly acidic condition (pH < 1). However, it was noticed that the biosorption trend increased continuously with a decrease in acidity until it reached maximum biosorption capacity at pH 4. The same trend has also been reported in the removal of Cu(II) by other biosorbents such as base treated rubber (*Hevea brasiliensis*) leaves powder (Wan Ngah and Hanafiah, 2008), brewery biomass (Kim *et al*., 2005), pretreated biomass of *Neurospora crassa* (Kiran *et al*., 2005), and wood sawdust (Šćiban and Klašnja, 2004). The lowest amount of Cu(II) adsorbed occurred at pH 2 with 1.59 $mg.g^{-1}$ representing 13.6% removal followed by pH 3 with 3.57 mg/g representing 29.9% removal. The adsorbed amount continued with a sharp increase to 10.84 $mg.g^{-1}$ representing 92.5% removal at pH 4 which was considered the highest amount.

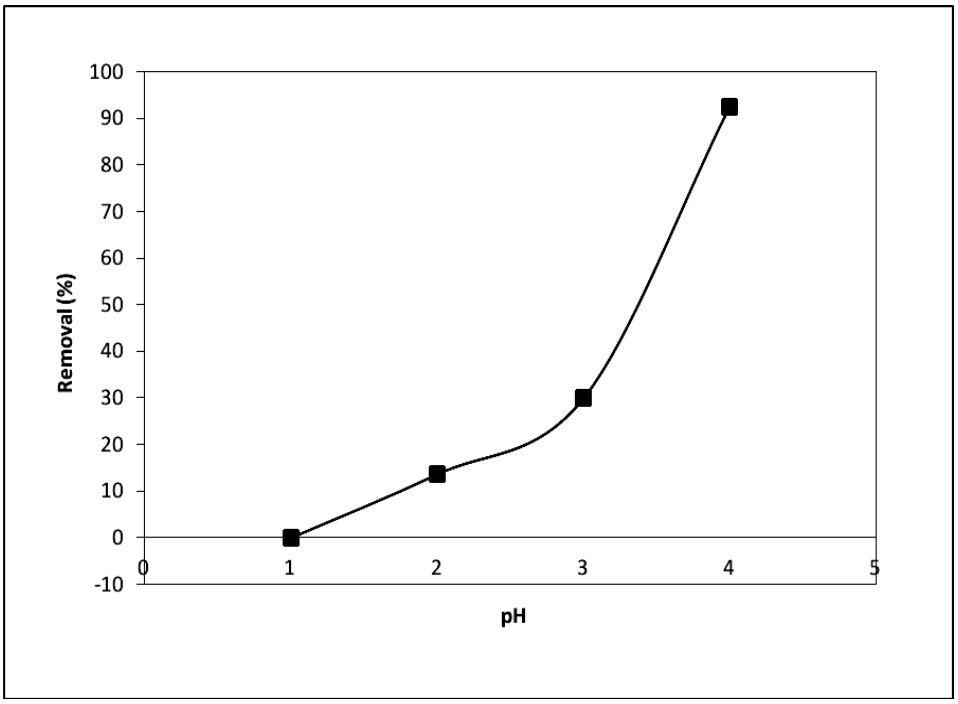


Figure 4.6 : Effect of pH on the Cu(II) biosorption by CXIC (initial Cu(II) concentration = 10mg.L^{-1}; shaking rate = 150rpm; biosorbent weight = 0.05g)

The low amount of Cu(II) adsorbed at low pH can be explained in terms of competition for biosorption sites between Cu(II) and H^+. At a pH lower than 2 (pH < 2), the concentration of H^+ is much higher than Cu(II). As more H^+ were attached to the biosorbent surface, the biosorption sites would carry a positive charge and Cu(II) could not be adsorbed due to the repulsive force. As the pH increased, there would be fewer H^+ in solution and CXIC surface would carry more negative charge, thus the repulsive force would be lowered which led to the condition that favour copper biosorption (Hanafiah *et al.*, 2010). The experiments were conducted at pH below 5 to avoid possible precipitation of $Cu(OH)_2$ and to ensure that only Cu(II) species were dominant in the biosorption process (Reddy *et al.*, 1997). Therefore, pH is an important parameter that needs

to be optimized first. Due to the fact that maximum biosorption occurred at pH 4, subsequent analyses were performed at this pH value.

4.2.3 Effect of initial Cu(II)concentration and contact time

The data gained from the experiment revealed the time required for the transport of adsorbate to the binding sites of CXIC. The effect of Cu(II) concentration on the rate of biosoption was clearly shown in Figure 4.7. From the Figure 4.7, it can be noticed that the biosorption capacity and equilibrium time were dependent on Cu(II) biosorption. The biosorption capacity increased with contact time for both Cu(II) concentration.

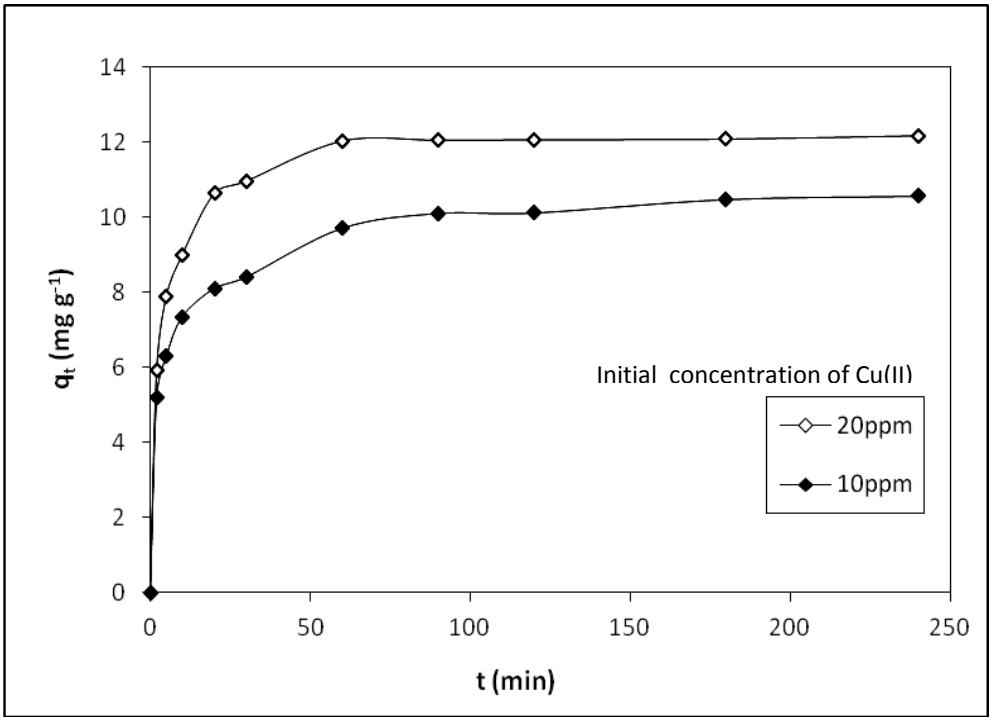


Figure 4.7 : Effect of initial Cu(II) ions concentration and contact time of Cu(II) biosorption by CXIC (biosorbent weight = 0.05g; pH = 4; volume = 50ml; shaking rate = 150rpm).

In general, all of the plots at both curves which are shown in Figure 4.4 explained that there are 2 phases which exist in determining the behavioural rate of biosorption. The first phase was an initial rapid phase (within 30min) where the rate of biosorption occurred fast. This condition was related to external surface biosorption which occurs instantaneously. Hanafiah *et al*. (2010a) stated that the rapid phase of biosorption was probably due to participation of the functional groups of the biosorbent. As these functional groups were progressively covered by Cu(II), the rate of biosorption would be reduced before finally reaching equilibrium, whereas the second phase was a slower phase (more than 30min) where equilibrium biosorption was achieved. This stage was the gradual adsorption stage before the biosorption of Cu(II) achieved equilibrium. According to all the data, it indicated that after 60 min there was no further change in the amount of Cu(II) adsorbed on CXIC. For both concentrations, the required time taken to reach equilibrium was 60 min and therefore this period was selected as the equilibrium time for isotherm studies.

Apart from that, the biosorption capacities also had increased as the concentration and contact time increased. The initial concentration of Cu(II) provided an important driving force to overcome the mass transfer resistance between the aqueous and solid phases (Malkoc and Nuhoglu, 2005). Furthermore, Ozsoy and Kumbar (2006) explained that the higher the concentration, the better the driving force achieved and therefore increased the higher probability of collision between Cu(II) and CXIC surface. Hence, more heavy metal could be transferred to the biosorbent surface.

The maximum biosorption capacities recorded at 10 and 20 $mg.L^{-1}$ were 10.6 and 12.1 $mg.g^{-1}$ respectively. However, the percent removal of Cu(II) were 94.67 and 54.80% for Cu(II) concentration of 10 and 20 $mg.L^{-1}$ respectively. On changing the concentration of copper from 10 to 20 $mg.L^{-1}$ the amount of Cu(II) adsorbed had been increased. This was a clear evidence that CXIC has numerous biosorption sites which therefore allow more Cu(II) to be adsorbed. Besides, the value of percentage removal being slightly higher at lower concentration (10 $mg.L^{-1}$) can be explained as when the concentration was lower, the ratio of Cu(II) to the available biosorption sites was relatively low, hence increased the tendency for available Cu(II) to be taken up due to less competition among Cu(II) for biosorption sites (Gupta and Bhattacharyya, 2008). Overall, it is interesting to note that the equilibrium showed by CXIC was achieved at a relatively short period of time (less than 100min) which is a very important criteria to be considered for economical wastewater treatment plant application (Kadirvelu and Namasivayam, 2003).

4.2.4 Biosorption kinetic studies

Determining the rate of biosorption of adsorbate and the rate of the determining step is important especially in designing a biosorption system of a full scale batch process. Previous studies reported that adsorption processes were controlled by several factors such as the transport of adsorbate from bulk liquid to adsorbent surface, diffusion across the liquid film surrounding the adsorbent, intraparticle diffusion and adsorption via surface complextion or ion exchange (Ofomaja, 2008; Ornek *et al*., 2007; Djeribi and Hamdaoui, 2008). In order to analyse the rate of biosorption and possible adsorption mechanism of copper

onto CXIC, the pseudo- first order and pseudo-second order were applied to the biosorption data.

The pseudo-first order kinetic equation (Ho and Mckay, 1998) is given as:

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

Where q_t and q_e are the amount of Cu(II) adsorbed ($mg.g^{-1}$) at time t(min) and at equilibrium, and k_1 is the constant of the pseudo-first order biosoption process (min^{-1}). Straight line plots of log (q_e-q_t) against t were used to determine the rate constant, k_1 and correlation coefficients, R^2 for different Cu(II) concentrations (Figure 4.8). The constants (k_1) obtained from the slopes of the plots are in the range of 0.0269- 0.0626 min^{-1} as shown in Table 4.2. Although these plots show good linearity (Figure 4.6), the values of calculated biosorption capacities ($q_{e,cal}$) are different from the experimental ones ($q_{e,exp}$) as shown in Table 4.2, suggesting that biosorption reaction is not of pseudo-first order.

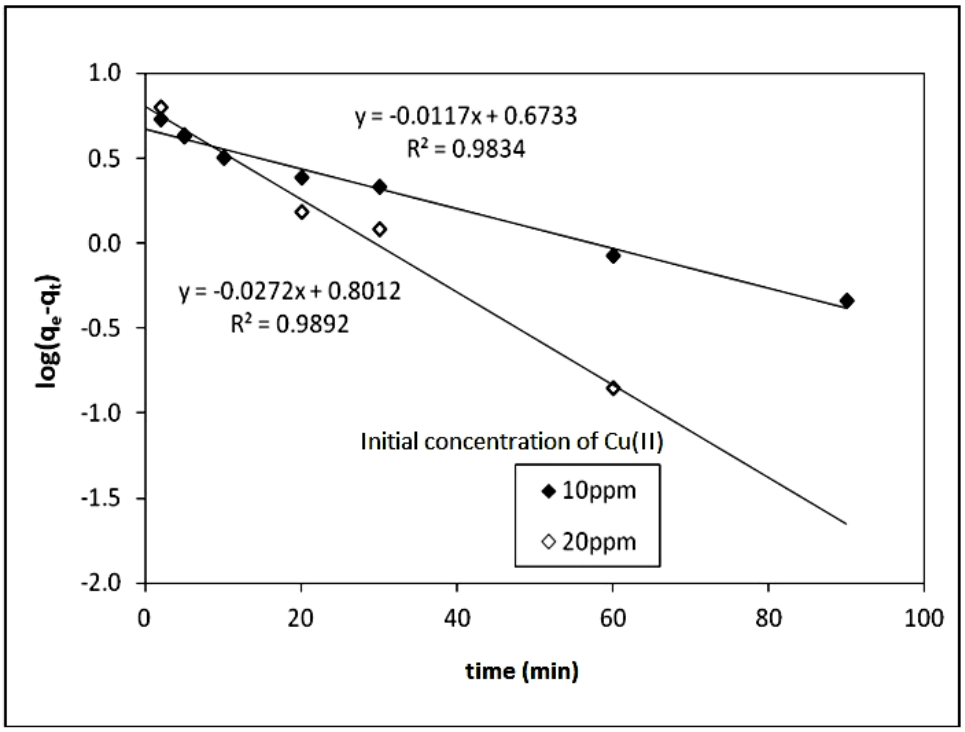


Figure 4.8 : Pseudo-first order plots of Cu(II) biosorption by CXIC (biosorbent weight = 0.05g; pH = 4; volume = 50ml; shaking rate = 150rpm).

The pseudo-second order equation (Ho and McKay, 2000) is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t$$

Where $h = k_2 q_e^2$ can be regarded as the initial sorption rate as $t \rightarrow 0$, and k_2 is the constant of pseudo-second order biosorption ($g.mg^{-1}.min^{-1}$). The plot t/q_t versus t should give a straight line if pseudo-second order kinetic is applicable and q_e, k_2 and h can be determined from the slope and intercept of the plot, respectively. Better linearity was obtained for these plots as shown in Figure 4.9 with regression coefficient (R^2) greater than 0.99 and the pseudo-second order rate

constants, k_2 having values from 0.022 to 0.035 $g.mg^{-1}.min^{-1}$. The values are given in Table 4.2. The calculated values of biosorption capacities ($q_{e,cal}$) also agree well with the experimental ones ($q_{e,exp}$). Both facts suggest that the biosorption of Cu(II) by CXIC follows the pseudo-second order kinetic model.

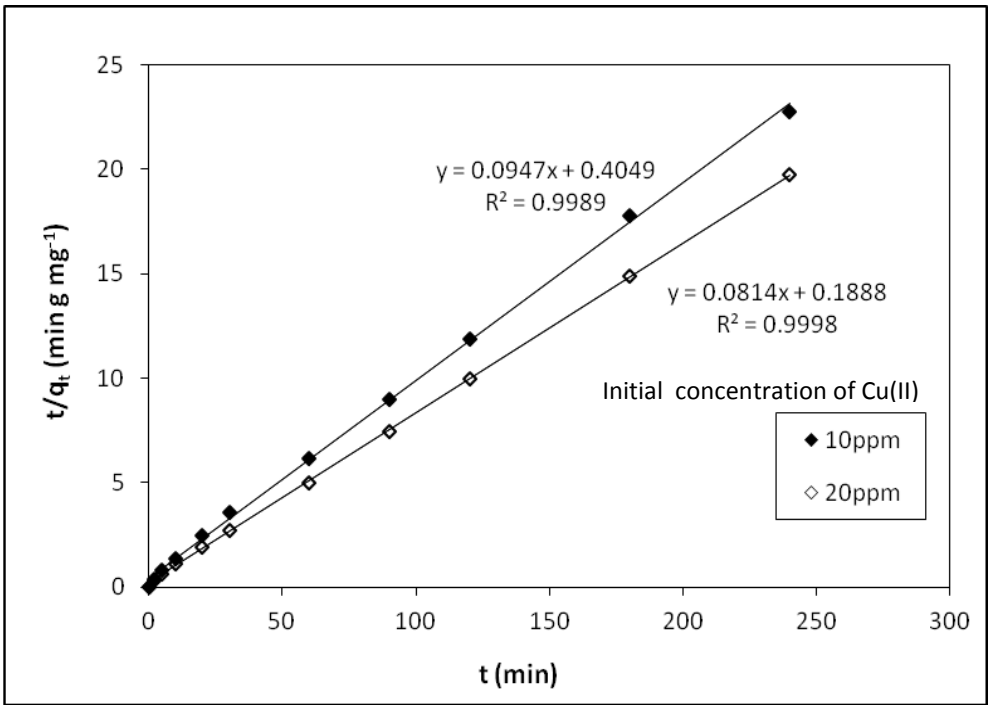


Figure 4.9 : Pseudo-second order plots of Cu(II) biosorption by CXIC (biosorbent weight = 0.05g; pH = 4; volume = 50ml; shaking rate = 150rpm)

Table 4.2 : The pseudo-first order and pseudo-second order at different concentration of Cu(II)

[Cu]	$q_{e,exp}$	**Pseudo-first order**			**Pseudo-second order**			
($mg.L^{-1}$)	**($mg.g^{-1}$)**	**$q_{e,cal}$**	**k_1**	**R^2**	**h**	**k_2**	**$q_{e,cal}$**	**R^2**
		($mg.g^{-1}$)	**(min^{-1})**		**(mg/(g.min))**	**(mg/(min.g))**	**($mg.g^{-1}$)**	
10	10.6	4.7	0.0269	0.9834	2.4697	0.022	10.6	0.9989
20	12.2	6.3	0.0626	0.9892	5.2966	0.035	12.3	0.9998

The failure of the pseudo-first order model to fit the kinetics data could possibly due to the limitations of boundary layer that control the biosorption process. The experimental data were observed to fit well to the pseudo-second order equation. The correlation coefficients (R^2) for the linear plots of t/q_t against t for the pseudo-second order equation were observed to be close to 1 for Cu(II). The calculated q_e values for Cu(II) were also very close to the experimental q_e values. These observations suggest that Cu(II) sorption by CXIC followed the second-order reaction, which suggest that the process controlling the rate may involve valence forces through sharing or exchanging of electrons between CXIC and Cu(II) ion (Ho *et al*., 1998).

4.3 Maximum biosorption capacity of CXIC by isotherm of Cu(II)

Biosorption isotherms are very useful in determining the maximum biosorption capacity of biosorbent. It helps in giving information on biosorption mechanisms, the properties of biosorbent surface and the affinity of a biosorbent towards heavy metal ions. In other words, it describes the relationship between the amount of adsorbate that is adsorbed per unit weight of adsorbent (q_e $mg.g^{-1}$) and the concentration of adsorbate in the bulk solution (C_e, $mg.L^{-1}$) at given temperature under equilibrium conditions. Adsorption equilibrium is established when the amount of adsorbate being adsorbed is equal to the amount being desorbed from the adsorbent (Ho, *et al*., 2002).

Figure 4.10 shows the experimental biosorption isotherm data of Cu(II) on CXIC. In general, the plots clearly indicate that the adsorption capacities

increase as the initial concentrations of Cu(II) increased. There was a steeper slope of the curve at lower concentrations of Cu(II) (< 20 $mg.L^{-1}$) before reaching plateau at higher concentrations (> 40 $mg.L^{-1}$). The result showed that at lower concentrations, CXIC had a sufficient number of biosorption sites to adsorb Cu(II). Meanwhile, at higher concentrations, the quantity of Cu(II) increased, hence introducing the saturation of the biosorption sites. It is interesting to note that the shape of the isotherm from the graph can provide some information on adsorbate- adsorbent interaction. According to Giles *et al.* (1974) the plot gained is a 'H' type isotherm in Giles classification system. Usually, the H type isotherm indicates chemical adsorption (chemisorption) and reflects relatively high affinity or strong interaction between adsorbate and the adsorbent.

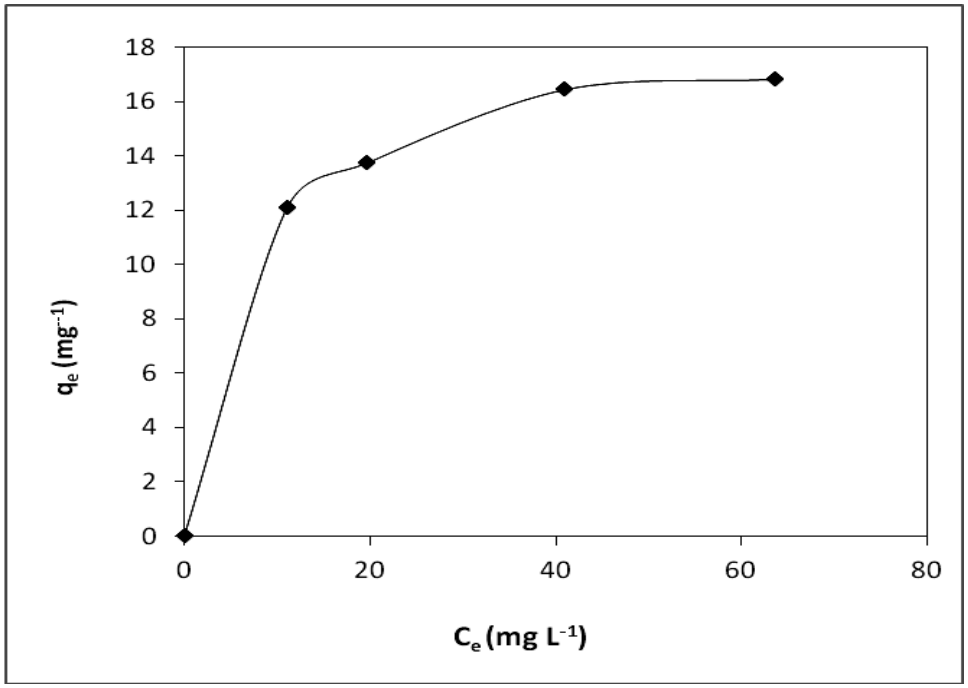


Figure 4.10 : General biosorption isotherm plot of Cu(II) by CXIC (biosorbent weight = 0.05g; pH = 4; volume = 50ml; shaking rate = 150rpm)

In this study, the isotherm data were examined by employing two models: the Langmuir and Freundlich. Both models were used to describe the nature of biosorption on CXIC. The results obtained for both isotherm models gave a correlation coefficient with $R^2 > 0.95$. Langmuir which is probably the most widely applied isotherm model in many adsorption studies was developed based on assumptions that adsorption occurs at specific homogenous sites on the adsorbent and was used successfully in many monolayer adsorption processes (Langmuir, 1916). This model assumes uniform energies of biosorption onto the biosorbent surface and no transmigration of adsorbate in the plane of the surface. The linearized form of the Langmuir model is given as (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\, b} + \frac{C_e}{q_{max}}$$

Where C_e is the equilibrium Cu(II) concentration ($mg.L^{-1}$). q_e is the amount of Cu(II) adsorbed at equilibrium ($mg.g^{-1}$), q_{max} is the maximum biosorption capacity ($mg.g^{-1}$), and b is a constant ($L.mg^{-1}$) related to the energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate. The values of maximum adsorption capacity can be obtained from the slope of the plot of C_e/ q_e versus C_e (Figure 4.11). The maximum biosorption capacity of Cu(II) by CXIC was 18.59 $mg.g^{-1}$, which is almost similar to the experimental value (16.84 $mg.g^{-1}$) as shown in Table 4.3.

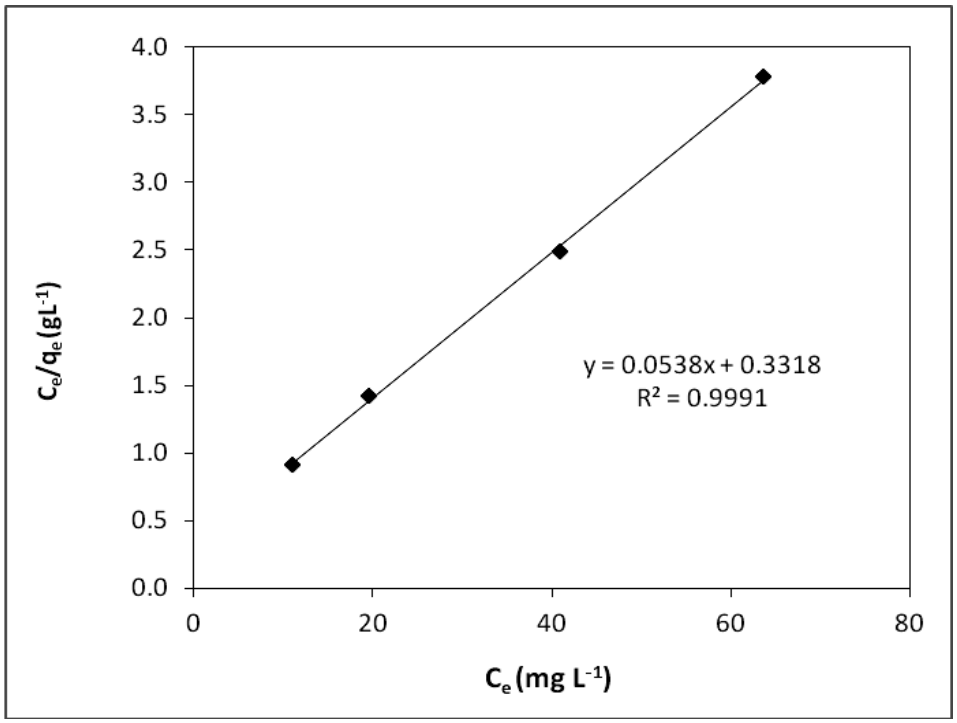


Figure 4.11 : Linearized Langmuir isotherm plot of Cu(II) biosorption by CXIC (biosorbent weight = 0.05g; pH = 4; volume = 50ml; shaking rate = 150rpm)

Differing from Langmuir isotherm, Freundlich isotherm is applicable to highly heterogeneous surface with interactions between adsorbed molecules (Freundlich, 1906). It gives a relationship between equilibrium liquid and solid phase capacity based on multilayer adsorption and not only restricted to the monolayer adsorption (Wan Ngah and Hanafiah, 2008). The Freundlich model is given by (Freundlich, 1906):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where K_F is maximum biosorption capacities (mg.g^{-1}) and n is related to biosorption intensity. The Freundlich plots are shown in Figure 4.12. If the value

of n is greater than unity, this in an indication of a favourable biosorption (Hanafiah *et al*., 2010a). The values of n determined from the Freundlich isotherm were greater than 1 as shown in Table 4.3, indicating that Cu(II) are favourably adsorbed by CXIC. Although the value of n is greater than 1, the K_F value (7.57 $mg.g^{-1}$) is far much lower than the experimental biosorption capacity while the R^2 value of 0.9695 indicates that biosorption of Cu(II) did not fit well towards the Freundlich model.

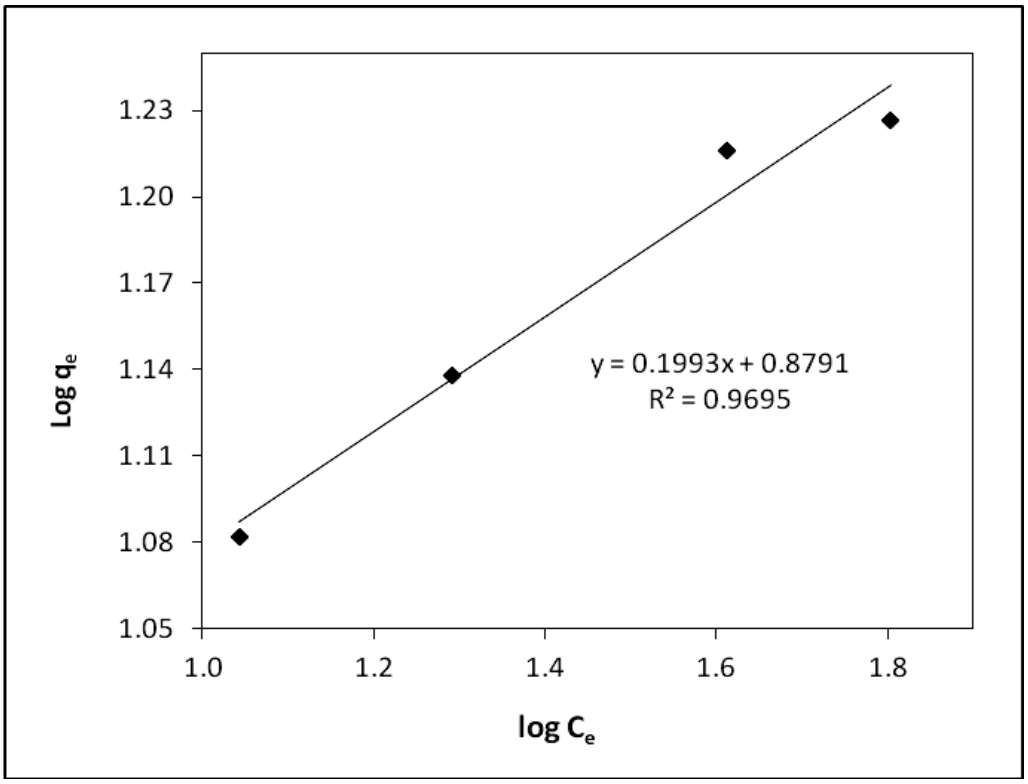


Figure 4.12 : Linearized Freundlich isotherm plot of Cu(II) biosorption by CXIC (biosorbent weight = 0.05g; pH = 4; volume = 50ml; shaking rate = 150rpm)

Table 4.3 : Langmuir and Freundlich isotherm constants and correlation coefficients

Langmuir				Freundlich			
$q_{e,exp}$ ($mg.g^{-1}$)	q_{max} ($mg.g^{-1}$)	b ($L.mg^{-1}$)	R^2	$q_{e,exp}$ ($mg.g^{-1}$)	K_F ($mg.g^{-1}$)	n	R^2
16.84	18.59	0.16	0.9991	16.84	7.57	5.02	0.9695

It is also important to compare the value of maximum biosorption capacity (q_{max}) obtained from this study with values from other reported biosorbents, since this will suggest the effectiveness of CXIC as a potential biosorbent for treatment of water containing Cu(II). For that purpose, the maximum biosorption capacities (q_{max}) for Cu(II) using CXIC is comparable with other biosorbents as shown in Table 4.4. Even though the value of q_{max} for CXIC does not show the highest value compared to the other biosorbent, it is interesting to note that the maximum bisorption value (q_{max}) of CXIC is still considered high and can be another promising biosorbent for treating wastewater containing Cu(II) since *Imperata cylindrica* L. is relatively abundant in Malaysia and highly accessible as well as economically feasible

Table 4.4 : Comparison of biosorption capacity of CXIC for Cu(II) with other biosorbents

Biosorbent	**Maximum biosorption capacity, q_{max} ($mg.g^{-1}$)**	**Reference**
Carrot residues	32.74	Nasernejad *et al*. (2005)
Rice husk	31.85	Wong *et al*. (2003b)
CXIC	18.59	*This study*
Cork powder	15.60	Chubar *et al*. (2004)
Poplar tree sawdust	13.95	Acar and Eren (2006)
Banana pith	13.46	Low *et al*. (1995)
Peanut pellets	12.00	Johnson *et al*. (2002)
SoHIC	11.64	Hanafiah *et al*. (2009)
Peanut husk	10.15	Li *et al*. (2006)
Cercis siliquastrum leaves	9.35	Salehi *et al*. (2008)
Rubber leaf powder	8.92	Wan Ngah and Hanafiah (2008)
Modified carrot residues	8.74	Güzel *et al*. (2008)
Groundnut shells	7.60	Shukla and Pai (2005b)
Rubber wood sawdust	5.73	Kalavathy *et al*. (2005)
Unmodified Juta fibres	4.23	Shukla and Pai (2005a)
Modified oak sawdust	3.60	Argun *et al*. (2007)
Potato peels	0.38	Aman *et al*. (2008)
Sugar beet pulp	0.15	Pehlivan *et al*. (2006)
Mangifera indica sawdust	0.005	Ajmal *et al*. (1998)

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

Based on the study, it can be concluded that Cellulose Xanthogenate *Imperata cylindrica* L. (CXIC) has potential to be used as biosorbent in removing of Cu(II) from aqueous solution.

The characterisation of CXIC showed that complexation and ion exchange could be the main biosorption mechanisms involved as indicated by FTIR and SEM-EDS spectra respectively. The FTIR analysis clearly revealed that -OH,-NH, C=C, $-COO^-$, $-CS_2$ and C-O-C as the major functional groups that act as biosorption sites for Cu(II). At the same time, ion exchange between light metals ions and Cu(II) could occurred during the biosorption process which contribute to the effectiveness of CXIC on removal of Cu(II).

The biosorption capacity decreased at a high dosage of biosorbent and low pH. However the biosorption capacity increased with increasing pH whereby maximum biosorption occurred at pH 4. In addition, the biosorption capacity increased with a rise in concentration and contact time. The equilibrium of CXIC was achieved at a relatively short period of time (less than 100 min) which is a very important criteria for economical wastewater treatment plant application. The biosorption kinetic of Cu(II) on CXIC followed the pseudo-

second order kinetic model which is based on the assumption chemisorption which is the rate limiting step.

The maximum biosorption capacity of Cu(II) by CXIC was 18.59 $mg.g^{-1}$. The equilibrium data presented fits better towards the Langmuir isotherm model which is based on assumptions that biosorption occurs at specific homogenous sites on the biosorbent and was used successfully in many monolayer biosorption processes.

For future study, it is highly recommended that the following aspects be carried out in order to have better understanding on biosorption mechanisms:

i. Conducting further confirmation on ion exchange quantitatively by measuring the amount of cations released from blanks to the amount of cations measured in the effluent after biosorption.

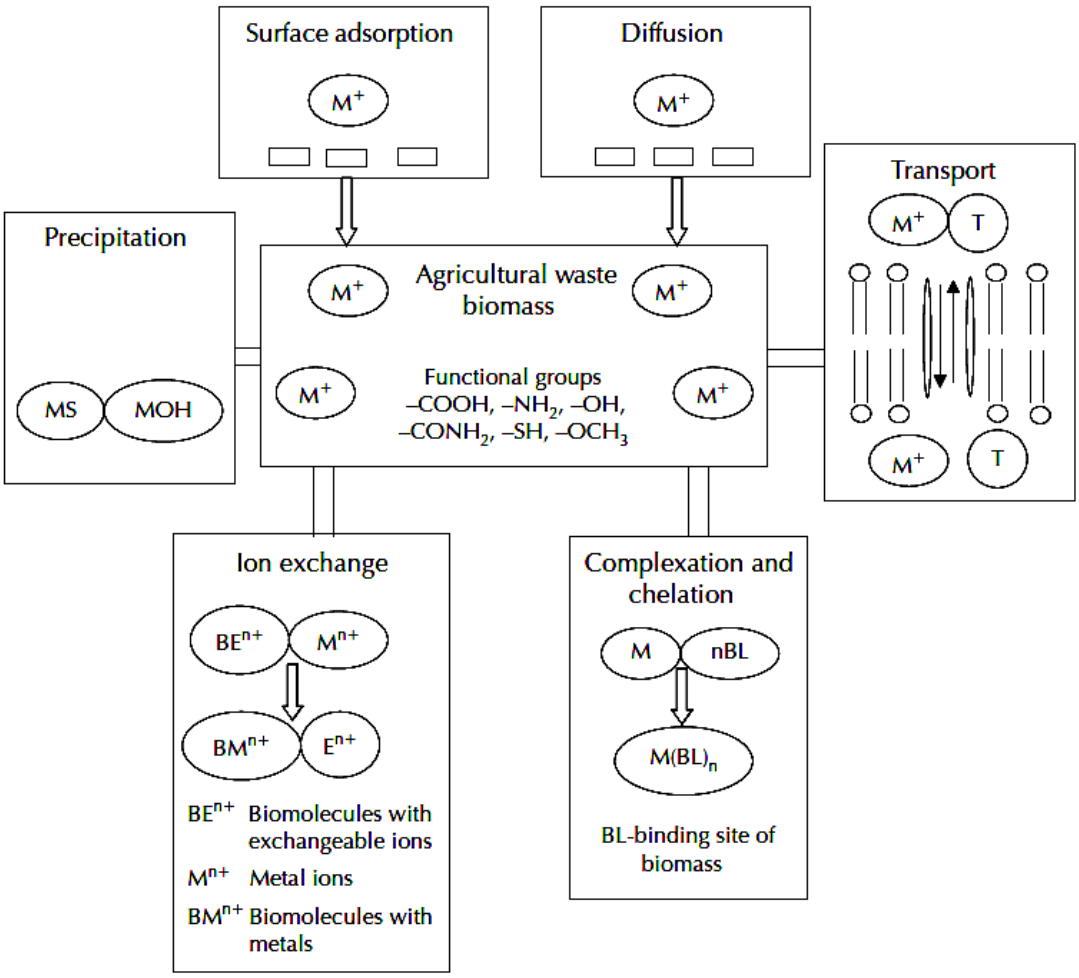
ii. Adding several effects of important physicochemical parameters which can affect copper biosorption such as shaking rate, temperature and size of particles.

iii. Performing desorption and regeneration studies as an enhancement on the explanation of biosorption removal behaviour.

iv. Performing COD analysis to investigate the leaching of organic matter from CXIC into solution during the biosorption process.

APPENDIX

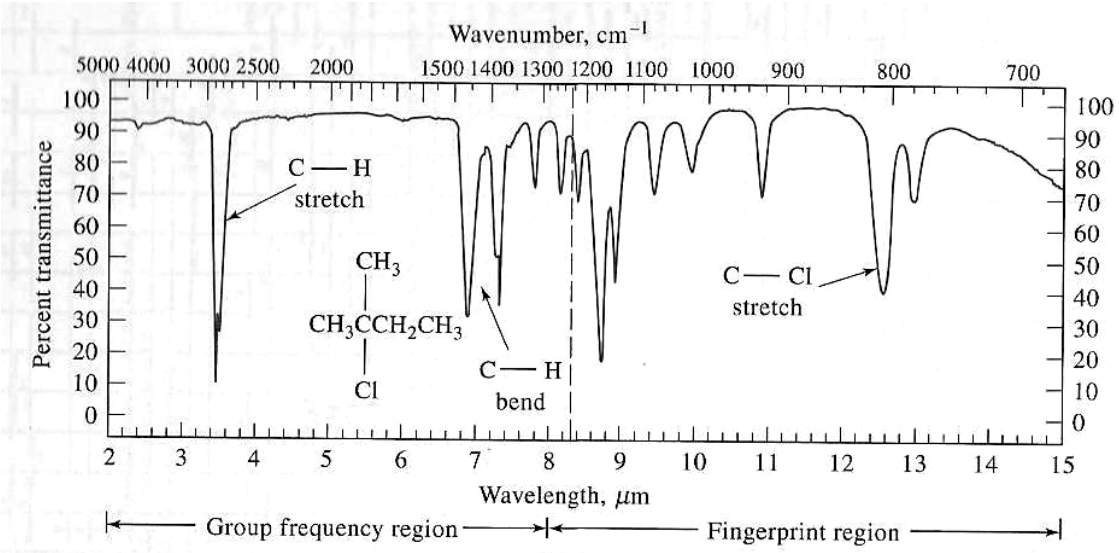
APPENDIX A : Plausible mechanism of biosorption



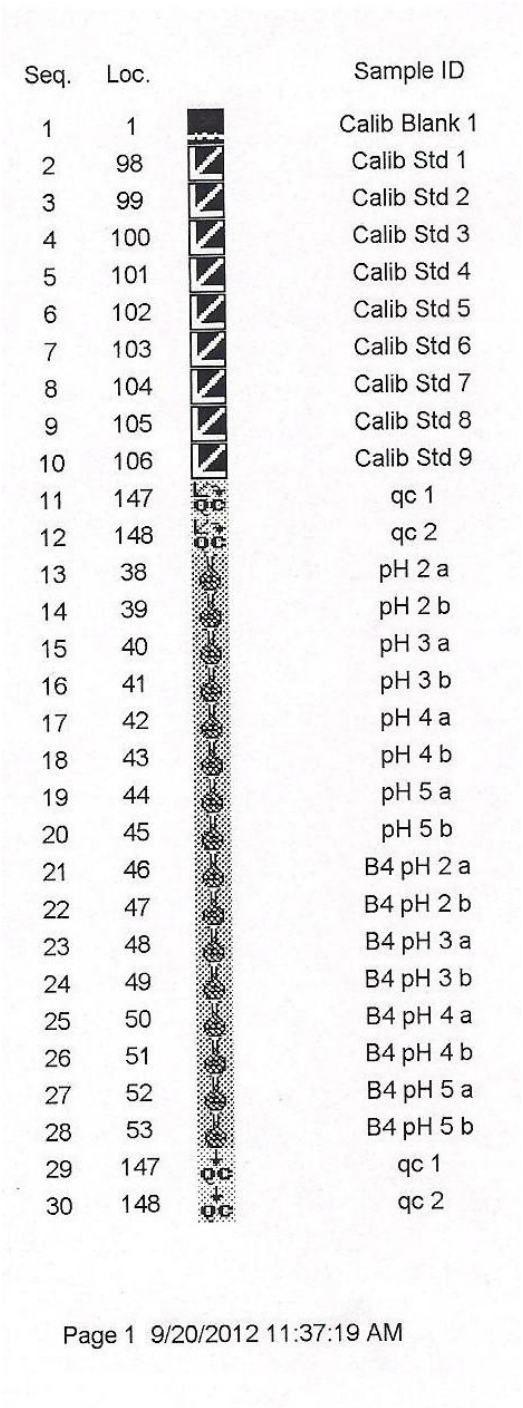
APPENDIX B : Abbreviated table of group frequencies for organic functional groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes ($>C=C<^{H}$)	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡C—H)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO_2	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

APPENDIX C : Group frequency region and fingerprint region



APPENDIX D : Analytical sequence of ICP-OES



Seq.	Loc.	Sample ID
1	1	Calib Blank 1
2	98	Calib Std 1
3	99	Calib Std 2
4	100	Calib Std 3
5	101	Calib Std 4
6	102	Calib Std 5
7	103	Calib Std 6
8	104	Calib Std 7
9	105	Calib Std 8
10	106	Calib Std 9
11	147	qc 1
12	148	qc 2
13	38	pH 2 a
14	39	pH 2 b
15	40	pH 3 a
16	41	pH 3 b
17	42	pH 4 a
18	43	pH 4 b
19	44	pH 5 a
20	45	pH 5 b
21	46	B4 pH 2 a
22	47	B4 pH 2 b
23	48	B4 pH 3 a
24	49	B4 pH 3 b
25	50	B4 pH 4 a
26	51	B4 pH 4 b
27	52	B4 pH 5 a
28	53	B4 pH 5 b
29	147	qc 1
30	148	qc 2

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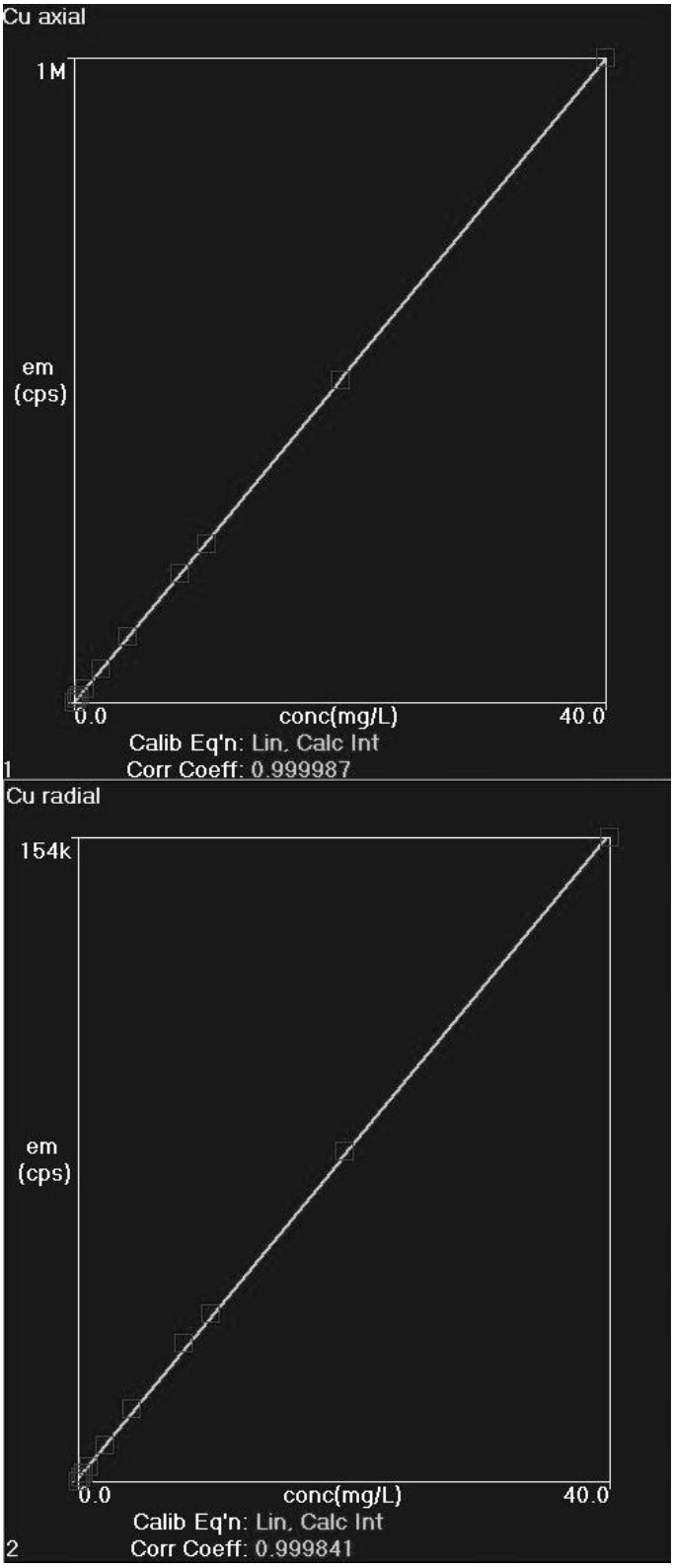
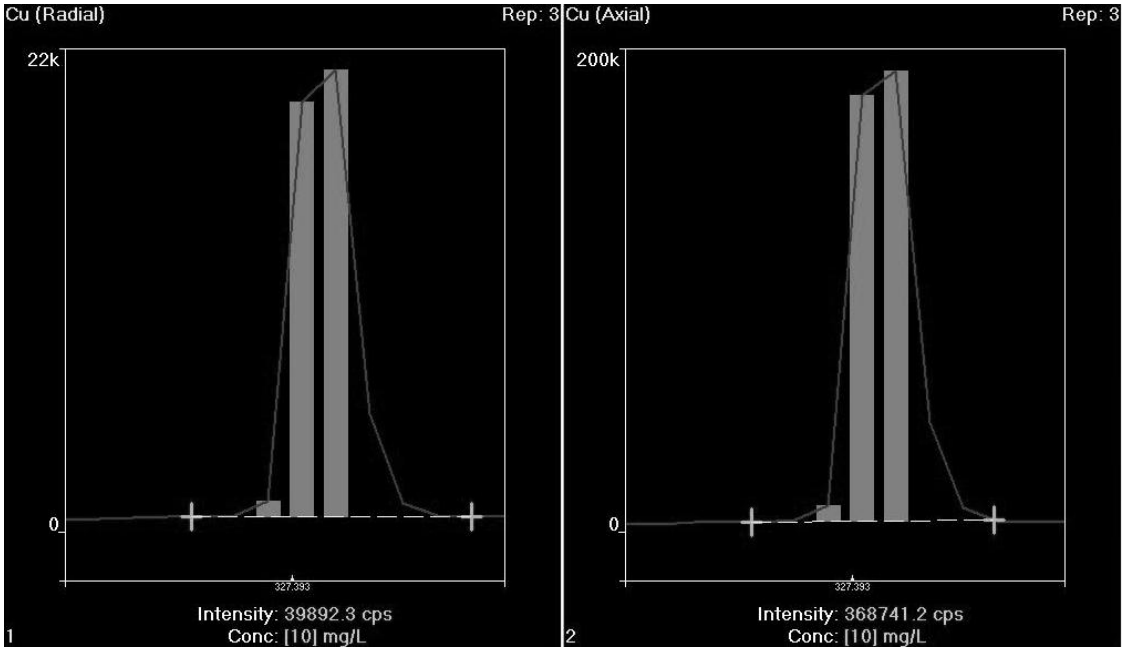
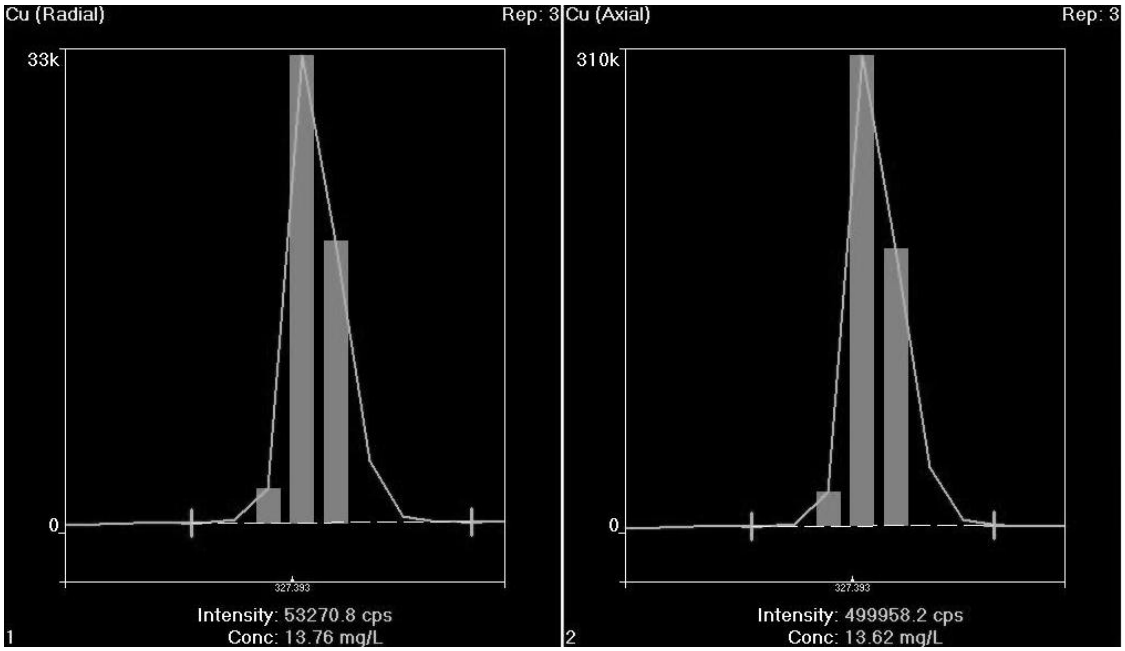
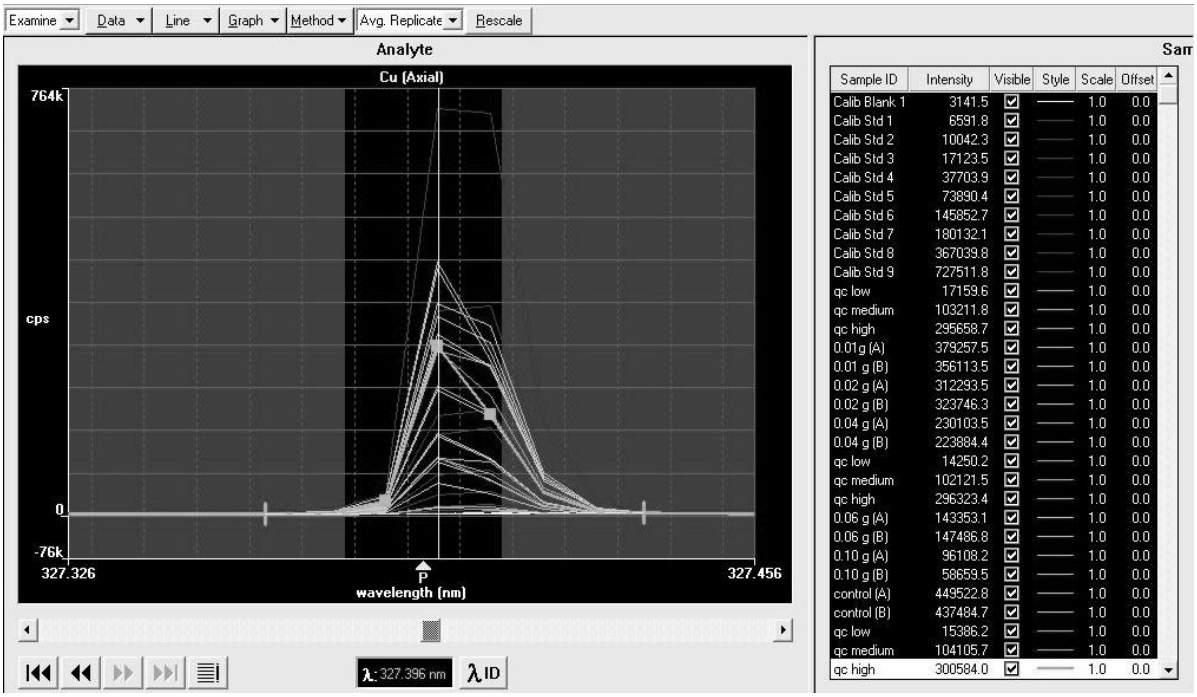
APPENDIX E : Calibration graph

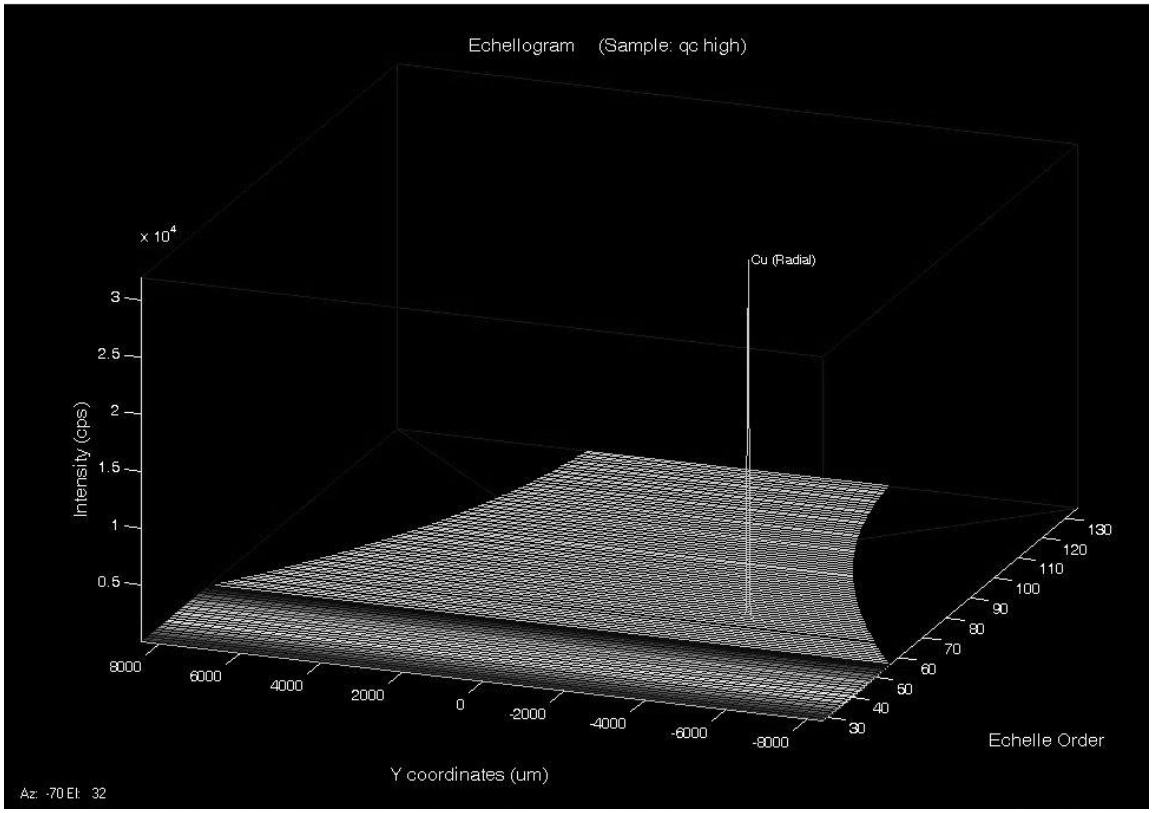


APPENDIX F : Example of ICP spectra

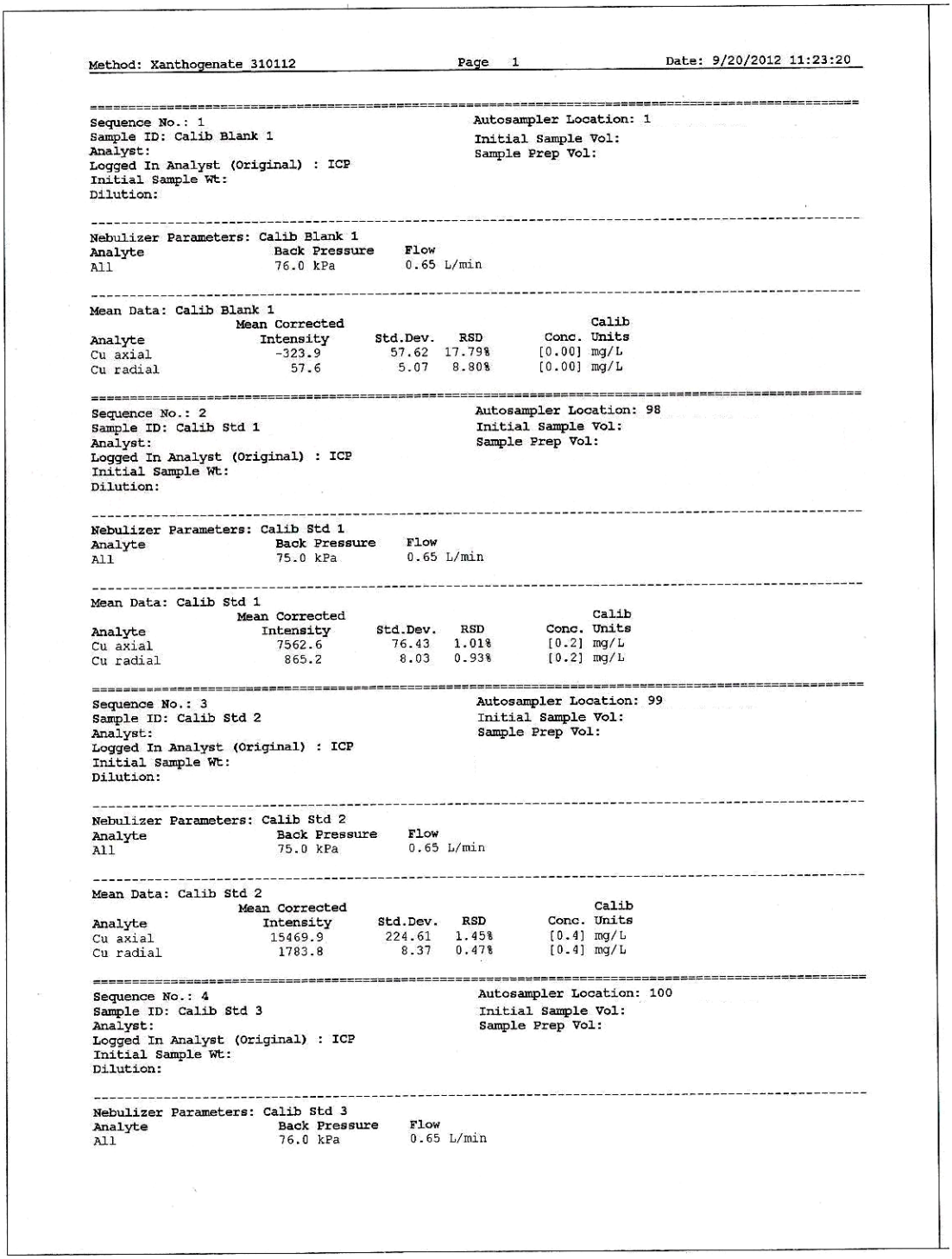





Examine
Data
Line
Graph
Method
Avg. Replicate
Rescale
Analyte
Cu (Axial)
764k
cps
0
-76k
327.326
327.456
wavelength (nm)
λ: 327.396 nm
λ ID
Sam
Sample ID
Intensity
Visible
Style
Scale
Offset
Calib Blank 1 3141.5 1.0 0.0
Calib Std 1 6591.8 1.0 0.0
Calib Std 2 10042.3 1.0 0.0
Calib Std 3 17123.5 1.0 0.0
Calib Std 4 37703.9 1.0 0.0
Calib Std 5 73890.4 1.0 0.0
Calib Std 6 145852.7 1.0 0.0
Calib Std 7 180132.1 1.0 0.0
Calib Std 8 367039.8 1.0 0.0
Calib Std 9 727511.8 1.0 0.0
qc low 17159.6 1.0 0.0
qc medium 103211.8 1.0 0.0
qc high 295658.7 1.0 0.0
0.01g (A) 379257.5 1.0 0.0
0.01 g (B) 356113.5 1.0 0.0
0.02 g (A) 312293.5 1.0 0.0
0.02 g (B) 323746.3 1.0 0.0
0.04 g (A) 230103.5 1.0 0.0
0.04 g (B) 223884.4 1.0 0.0
qc low 14250.2 1.0 0.0
qc medium 102121.5 1.0 0.0
qc high 296323.4 1.0 0.0
0.06 g (A) 143353.1 1.0 0.0
0.06 g (B) 147486.8 1.0 0.0
0.10 g (A) 96108.2 1.0 0.0
0.10 g (B) 58659.5 1.0 0.0
control (A) 449522.8 1.0 0.0
control (B) 437484.7 1.0 0.0
qc low 15386.2 1.0 0.0
qc medium 104105.7 1.0 0.0
qc high 300584.0 1.0 0.0


Echellogram (Sample: qc high)
x 10^4
Cu (Radial)
Intensity (cps)
3
2.5
2
1.5
1
0.5
8000
6000
4000
2000
0
-2000
-4000
-6000
-8000
Y coordinates (um)
130
120
110
100
90
80
70
60
50
40
30
Echelle Order
Az: -70 El: 32

APPENDIX G : Examples of ICP data



Method: Xanthogenate 310112 Page 1 Date: 9/20/2012 11:23:20

Sequence No.: 1
Sample ID: Calib Blank 1
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 1
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Blank 1

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: Calib Blank 1

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	-323.9	57.62	17.79%	[0.00]	mg/L
Cu radial	57.6	5.07	8.80%	[0.00]	mg/L

Sequence No.: 2
Sample ID: Calib Std 1
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 98
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Std 1

Analyte	Back Pressure	Flow
All	75.0 kPa	0.65 L/min

Mean Data: Calib Std 1

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	7562.6	76.43	1.01%	[0.2]	mg/L
Cu radial	865.2	8.03	0.93%	[0.2]	mg/L

Sequence No.: 3
Sample ID: Calib Std 2
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 99
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Std 2

Analyte	Back Pressure	Flow
All	75.0 kPa	0.65 L/min

Mean Data: Calib Std 2

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	15469.9	224.61	1.45%	[0.4]	mg/L
Cu radial	1783.8	8.37	0.47%	[0.4]	mg/L

Sequence No.: 4
Sample ID: Calib Std 3
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 100
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Std 3

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: Calib Std 3

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	31423.2	292.75	0.93%	[0.8]	mg/L
Cu radial	3554.4	36.63	1.03%	[0.8]	mg/L

Sequence No.: 5
Sample ID: Calib Std 4
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 101
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Std 4

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: Calib Std 4

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	75376.7	1239.02	1.64%	[2.0]	mg/L
Cu radial	8643.7	83.45	0.97%	[2.0]	mg/L

Sequence No.: 6
Sample ID: Calib Std 5
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 102
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Std 5

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: Calib Std 5

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	148985.8	2013.61	1.35%	[4.0]	mg/L
Cu radial	17132.0	86.87	0.51%	[4.0]	mg/L

Sequence No.: 7
Sample ID: Calib Std 6
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 103
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Std 6

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: Calib Std 6

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	289793.2	2327.78	0.80%	[8.0]	mg/L
Cu radial	32798.4	643.81	1.96%	[8.0]	mg/L

Sequence No.: 8
Sample ID: Calib Std 7
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 104
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Std 7

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: Calib Std 7

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	356803.1	4248.84	1.19%	[10]	mg/L
Cu radial	40132.1	176.14	0.44%	[10]	mg/L

Sequence No.: 9
Sample ID: Calib Std 8
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 105
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Std 8

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: Calib Std 8

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	723110.1	2744.02	0.38%	[20]	mg/L
Cu radial	78688.3	366.83	0.47%	[20]	mg/L

Sequence No.: 10
Sample ID: Calib Std 9
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 106
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: Calib Std 9

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: Calib Std 9

Analyte	Mean Corrected Intensity	Std.Dev.	RSD	Calib Conc.	Units
Cu axial	1446048.5	8758.14	0.61%	[40]	mg/L
Cu radial	153522.4	2007.28	1.31%	[40]	mg/L

Calibration Summary

Analyte	Stds.	Equation	Intercept	Slope	Curvature	Corr. Coef.	Reslope
Cu axial	9	Lin, Calc Int	1175.1	36100	0.00000	0.999987	
Cu radial	9	Lin, Calc Int	920.2	3840	0.00000	0.999841	

Sequence No.: 11
Sample ID: qc high
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 148
Date Collected: 1/31/2012 1:52:37 PM
Data Type: Reprocessed on 9/20/2012 11:20:39 AM

Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: qc high

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: qc high

Analyte	Mean Corrected Intensity	Calib Conc.	Units	Std.Dev.	Sample Conc.	Units	Std.Dev.	RSD
Cu axial	561191.6	15.51	mg/L	0.115	15.51	mg/L	0.115	0.74%
QC value within limits for Cu axial Recovery = 103.42%								
Cu radial	61101.1	15.67	mg/L	0.149	15.67	mg/L	0.149	0.95%
QC value within limits for Cu radial Recovery = 104.49%								

All analyte(s) passed QC.

Sequence No.: 12
Sample ID: pH 2 a
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 38
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: pH 2 a

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: pH 2 a

Analyte	Mean Corrected Intensity	Calib Conc.	Units	Std.Dev.	Sample Conc.	Units	Std.Dev.	RSD
Cu axial	777385.4	21.50	mg/L	0.093	21.50	mg/L	0.093	0.43%
Cu radial	84764.7	21.84	mg/L	0.224	21.84	mg/L	0.224	1.03%

Sequence No.: 13
Sample ID: pH 2 b
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 39
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: pH 2 b

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: pH 2 b

Analyte	Mean Corrected Intensity	Calib Conc.	Units	Std.Dev.	Sample Conc.	Units	Std.Dev.	RSD
Cu axial	766166.7	21.19	mg/L	0.206	21.19	mg/L	0.206	0.97%
Cu radial	85121.8	21.93	mg/L	0.201	21.93	mg/L	0.201	0.92%

Sequence No.: 14
Sample ID: pH 3 a
Analyst:
Logged In Analyst (Original) : ICP
Initial Sample Wt:
Dilution:

Autosampler Location: 40
Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: pH 3 a

Analyte	Back Pressure	Flow
All	76.0 kPa	0.65 L/min

Mean Data: pH 3 a

Analyte	Mean Corrected Intensity	Calib Conc.	Units	Std.Dev.	Sample Conc.	Units	Std.Dev.	RSD
Cu axial	352334.3	9.728	mg/L	0.0690	9.728	mg/L	0.0690	0.71%
Cu radial	37849.6	9.618	mg/L	0.0684	9.618	mg/L	0.0684	0.71%

Sequence No.: 15
Sample ID: pH 3 b
Analyst:
Logged In Analyst (Original) : ICP

Autosampler Location: 41

APPENDIX H : Result for effect of biosorbent dose

Bisorbent dose (g)	**C_o (mg L^{-1})**	**C_e (mg L^{-1})**	**$C_o - C_e$ (mg L^{-1})**	**V (L)**	**q_e (mg g^{-1})**	**Removal (%)**
0.01	11.77	7.11	4.66	0.05	23.32	39.63
0.02	11.77	5.17	6.60	0.05	16.50	56.06
0.03	11.77	3.28	8.49	0.05	14.15	72.12
0.04	11.77	1.56	10.21	0.05	12.76	86.74
0.05	11.77	0.88	10.89	0.05	10.89	92.53
0.1	11.77	0.87	10.90	0.05	5.45	92.63

APPENDIX I : Result for effect of pH

pH	**C_o (mg L^{-1})**	**C_e (mg L^{-1})**	**$C_o - C_e$ (mg L^{-1})**	**V (L)**	**weight (g)**	**q_e (mg g^{-1})**	**Removal (%)**
pH 2	22.59	21.50	1.09	0.05	0.10	0.55	4.83
pH 3	22.81	9.73	13.08	0.05	0.10	6.54	57.35
pH 4	22.52	2.25	20.27	0.05	0.10	10.14	90.09
pH 5	20.94	3.41	17.54	0.05	0.10	8.77	83.74

pH	**C_o (mg L^{-1})**	**C_e (mg L^{-1})**	**$C_o - C_e$ (mg L^{-1})**	**V (L)**	**weight (g)**	**q_e (mg g^{-1})**	**Removal (%)**
pH 2	11.65	10.06	1.59	0.05	0.05	1.59	13.65
pH 3	11.94	8.37	3.57	0.05	0.05	3.57	29.92
pH 4	11.72	0.88	10.84	0.05	0.05	10.84	92.50

APPENDIX J : Kinetic study (Concentration & Contact Time)

	C_o (mg L^{-1})		**C_e (mg L^{-1})**		**C_o-C_e (mg L^{-1})**		**V (L)**
Time (min)	10 mg/L	20 mg/L	10 mg/L	20 mg/L	10 mg/L	20 mg/L	0.05
0	0.00	0.00	0.000	0.000	0.000	0.000	0.05
2	11.46	22.28	6.250	16.360	5.210	5.920	0.05
5	11.49	22.35	5.201	14.480	6.289	7.870	0.05
10	11.38	22.31	4.035	13.320	7.345	8.990	0.05
20	11.37	22.32	3.269	11.690	8.101	10.630	0.05
30	11.30	22.18	2.997	11.220	8.303	10.960	0.05
60	11.23	22.17	1.526	10.140	9.704	12.030	0.05
90	11.54	22.36	1.543	10.310	9.997	12.050	0.05
120	11.21	22.26	1.100	10.200	10.110	12.060	0.05
180	11.32	22.37	0.853	10.290	10.467	12.080	0.05
240	11.15	22.21	0.594	10.040	10.556	12.170	0.05

Bisorbent dose (g)	**q_e (mg g^{-1})**		**t/q_t (pseudo-second order)**		**$\log(q_e-q_t)$ (pseudo-first order)**	
0.05	10 mg/L	20 mg/L	10 mg/L	20 mg/L	10 mg/L	20 mg/L
0.05	0.000	0.000	0.000	0.000	1.023	1.085
0.05	5.210	5.920	0.384	0.338	0.728	0.796
0.05	6.289	7.870	0.795	0.635	0.630	0.633
0.05	7.345	8.990	1.361	1.112	0.507	0.502
0.05	8.101	10.630	2.469	1.881	0.390	0.188
0.05	8.303	10.960	3.613	2.737	0.353	0.083
0.05	9.704	12.030	6.183	4.988	-0.070	-0.854
0.05	9.997	12.050	9.003	7.469	-0.253	-0.921
0.05	10.110	12.060	11.869	9.950	-0.351	-0.959
0.05	10.467	12.080	17.197	14.901	-1.051	-1.046
0.05	10.556	12.170	22.736	19.721	ND	ND

APPENDIX K : Isotherm Study

ppm	C_o (mg L^{-1})	C_e (mg L^{-1})	C_o-C_e (mg L^{-1})	V (L)
20	23.12	11.04	12.08	0.05
30	33.34	19.60	13.74	0.05
50	57.37	40.92	16.45	0.05
70	80.50	63.66	16.84	0.05
100	114.00	99.38	14.62	0.05

Bisorbent dose (g)	q_e (mg g^{-1})	C_e/q_e	log C_e	log q_e
0.05	12.08	0.914	1.042969	1.082067
0.05	13.74	1.426	1.292256	1.137987
0.05	16.45	2.488	1.611936	1.216166
0.05	16.84	3.780	1.803867	1.226342
0.05	14.62	6.798	1.997299	1.164947

APPENDIX L : Example of calculation

a) Biosorption capacity for the effect of biosorbent dose.

V = 0.05 L

$$q_e = \frac{C_o - C_e}{m} V$$

$$q_e = \frac{11.77 - 0.88 \text{ X } 0.05}{0.05}$$

= **10.89 mg g^{-1}**

Calculation for percentage removal (%)

$$\text{Removal (\%)} = \frac{C_o - C_e}{m} \text{ X } 100$$

$$\text{Removal (\%)} = \frac{11.77 - 0.879 \text{ X } 100}{11.77}$$

= **92.53%**

*Same calculation applied for other dosage.

b) Biosorption capacity for the effect of pH

V = 0.05 L

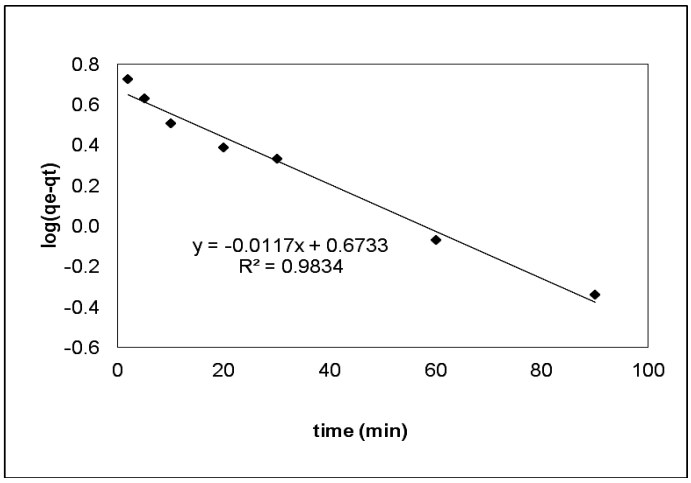
$$q_e = \frac{C_o - C_e}{m} V$$

$$q_e = \frac{11.720 - 0.879 \text{ X } 0.05}{0.05}$$

= **10.841 mg g^{-1}**

*Same calculation applied for other pH.

c) Pseudo-first-order kinetic



C_t = 10 mg L^{-1}

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

$$y = -0.0117x + 0.6733$$

$$-\frac{k_1}{2.303} = -0.0117$$

$$k_1 = 0.0269$$

$$\log q_e = 0.6733$$

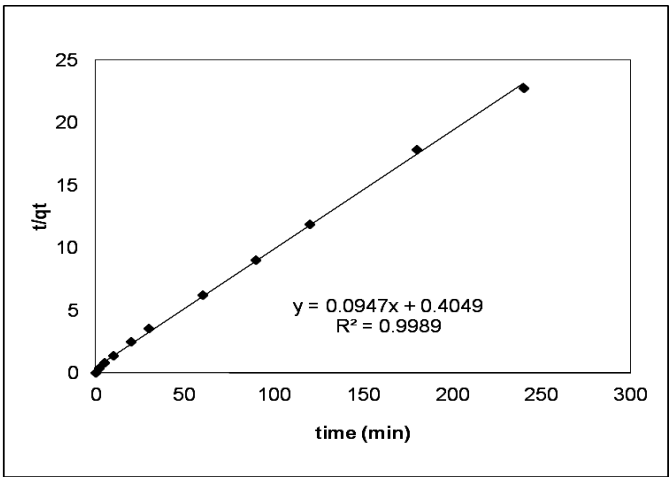
$$q_e = \text{antilog } 0.6733$$

$$q_e = 4.71 \text{ mg } g^{-1}$$

$$R^2 = 0.9834$$

* Same calculation applied for C_t = 20 mg L^{-1}

d) Pseudo-second-order kinetic



$C_t = 10 \text{ mg } L^{-1}$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad h = k_2 q_e^2$$

$y = 0.0947x + 0.4049$

$\frac{1}{h} = 0.4049 \qquad h = 2.4697$

$\frac{1}{q_e} = 0.0947 \qquad q_e = 10.5596$

$R^2 = 0.9989$

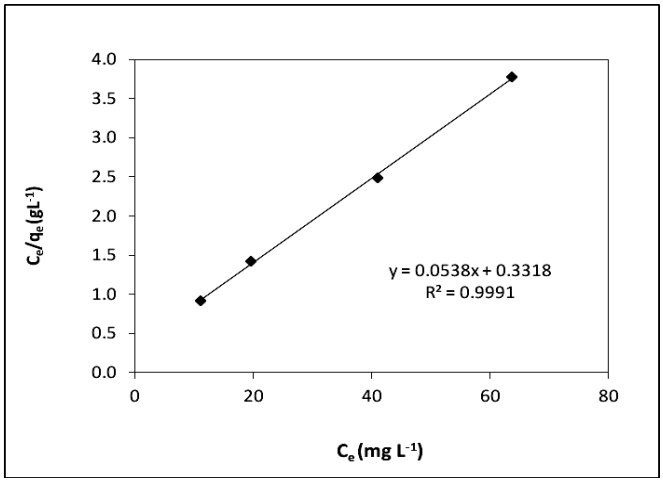
$h = k_2 q_e^2$

$k_2 = \frac{h}{q_e^2}$

$k_2 = \frac{2.46}{(10.5596)^2} \qquad k_2 = 0.0221$

* Same calculation applied for $C_t = 20 \text{ mg } L^{-1}$

e) Langmuir isotherm



$$\frac{\mathbf{C}}{\mathbf{q_e}} = \frac{\mathbf{1}}{\mathbf{q_{max}\, b}} + \frac{\mathbf{C}}{\mathbf{q_{max}}}$$

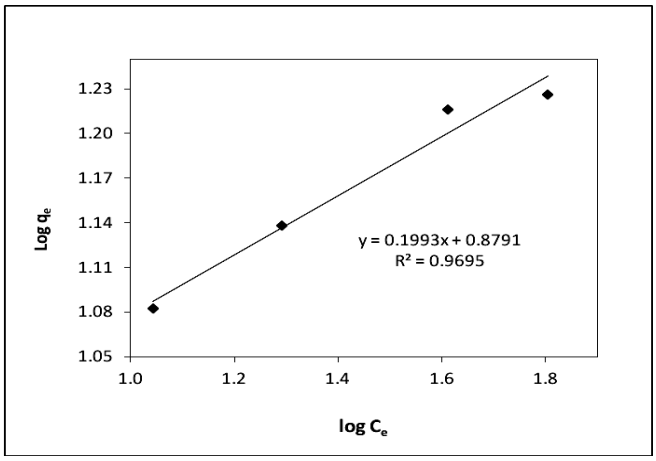
$$y = 0.0538x + 0.3318$$

$$\frac{1}{q_{max}} = 0.0538 \qquad \mathbf{q_{max} = 18.5893\ mg\ g^{-1}}$$

$$\frac{1}{q_{max}b} = 0.3318 \qquad b = \frac{3.0139}{18.5893} = 0.1621$$

$$R^2 = 0.9991$$

f) Freundlich isotherm



$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

$y = 0.1993x + 0.8791$

$\log K_F = 0.8791$

K_F = antilog 0.8791

K_F = 7.57 mg g^{-1}

$\frac{1}{n} = 0.1993$

n = 5.0176

R^2 = 0.9695

REFERENCES

Abu Al-Rub, F.A., El-Naas, M.H., Ashour, I., Al-Marzouqi, M., 2006. Biosorption of copper (II) from aqueous solution by pre-treated biomass of marine algae *Padina sp*. *Biochemistry*, 41: 457-464.

Abia, A.A., Horsfall, M., Didi, O., 2003. The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. *Bioresource Technology*, 90: 345-348.

Acemioğlu, B., Alma, M.H., 2004. Sorption of copper (II) ions by pine sawdust. *Holz Roh Werkst*, 62: 268-272.

Acar, F.N., Eren, Z., 2006. Removal of Cu(II) ions by activated poplar sawdust (*Samsun Clone*) from aqueous solutions. *Journal of Hazardous Materials*. 137: 909-914.

Aggarwal, A.J., Sebba, F., Rodarte, A., 1986. Copper extraction using predispersed solvent extraction. *Journal of Seperation Process Technology*, 7: 29.

Agrawal, A., Manoj, M.K., Kumari, S., Bagchi, D., Kumar, V., Pandey, B.D., 2008. Extractive separation of copper and nickel extraction route. *Mineral Engineering*, 21: 1126-1130.

Aharoni, C., Sparks, D.L., Levinson, S., Ravina, I., 1991. Kinetics of soil chemical reactions: relationships between empirical equations and diffusion models. *Soil Science Society of American Journal*, 55: 1307-1312.

Ajmal, M., Khan, A.H., Ahmad, S., 1998. Role of sawdust in the removal of copper(II) from industrial waste. *Water Resource*, 32: 3085-3091.

Akar, T., Tunali, S., 2005. Biosorption performance of *Botrytis cinerea* fungal by-products for removal of Cd(II) and Cu(II) ions from aqueous solutions. *Minerals Engineering*, 18: 1099-1109.

Aksu, Z., 2001. Equilibrium and kinetic modeling of cadmium(II) biosorption by *C. vulgaris* in a batch system. *Seperation and Purification Technology*, 21: 285–294.

Aksu, Z., 2005. Application of biosorption for the removal of organic pollutants: a review. *Process Biochemistry*, 40: 997-1026.

Aksu, Z., Isoglu, I.A., 2005. Removal of copper (II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp. *Process Biochemistry*, 40: 3031-3044.

Al-Rashidi, B., Tizaoui, C., Hilal, N., 2012. Copper removal from aqueous solution using nano-scale diboron trioxide/ titanium dioxide (B_2O_3/ TiO_2) adsorbent. *Chemical Engineering Journal*, 183: 294-302

Alvarea-Ayuso, E., Garcia-Sanchez, A., Querol, X., 2003. Purification of metal electroplating waste waters using zeolites. *Water Research*, 37: 4855-4862.

Aman, T., Kazi, A.A., Sabri, M.U., Bano, Q., 2008. Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/ industrial effluent. *Colloid and Surfaces B: Biointerfaces*, 63: 116-121.

Anand, V., Kandarapu, R., Garg, Sanjay., 2001. Ion-exchange resins: carrying drug delivery forward. *Drug Discovery Today*, 6: 905-914.

Annadurai, G., Juang, H.S., Lee, D.J., 2002. Adsorption of heavy metal from water using banana and orange peels. *Water Science and Technology*, 47: 185-190.

Anwar, J., Shafique, U., Zaman, U., Salman, M., Dar, A., Anwar, S., 2010. Removal of Pb (II) and Cd (II) from water by adsorption on peels of banana. *Bioresource Technology*, 101: 1752-1755.

Argun, M.E., Dursun, S., Ozdemir, C., Karatas, M., 2007. Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of Hazardous Materials*, 141: 77-85.

Babarinde, N.A.A., Oyebamiji, B.J., Adebowale, S.R., 2006. Biosorption of lead ions from aqueous solution by maize leaf. *International Journal of Physical Science*, 1: 23-26.

Basha, C.A., Somasundaram, M., Kannadasan, T., Lee, C.W., 2011. Heavy metal removal from copper smelting effluent using electrochemical filter press cells. *Chemical Engineering Journal*, 171: 563-571.

Balasubramianiam, R., Perumal, S.V., Vijayaraghavan, K., 2009. Equilibrium isotherm studies for the multicomponent adsorption of lead, zinc and cadmium onto Indonesian peat. *Industrial & Engineering Chemistry Research*, 48: 2093-2099.

Benaïssa, H., Elouchdi, M.A., 2011. Biosorption of copper(II) ions from synthetic aqueous solutions by drying bed activated sludge. *Journal of Hazardous Materials*, 194: 69-78.

Bhattacharyya, K.G., Gupta, S.S., 2006. Kaolinite, montmorillonite and their modified derivatives as adsorbents for removal of Cu(II) from aqueous solution. *Separation and Purification Technology*, 50: 388-397.

Bhattacharyya, K.G., Sharma, A., 2004. Adsorption of Pb(II) from aqueous solution by *Azadirachta indica* (Neem) leaf powder. *Journal of Hazardous Materials*, 113: 97-109.

Bryson, C.T., Carter, R., 1993. Cogon grass (*Imperata cylindrica*) in the United States. *Weed Technology*, 7: 1005-1009.

Cabuk, A., Akar, T., Tunali, S., Gedikli, S., 2007. Biosorption of Pb(II) by industrial of *Saccharomyces cerevisiae* immobilized on the biometric of cone biomass of *Pinus nigra*; equilibrium and mechanism analysis. *Chemical Engineering Journal*, 131: 293-300.

Chang, S.H., Teng, T.T., Ismail, N., 2010. Extraction of Cu(II) from aqueous solution by vegetable-oil based organic solvents. *Journal of Hazardous Materials*, 181: 868-872.

Chen, G., 2004. Electrochemical technologies in wastewater treatment. *Separation and Purification Technology*, 38: 11-41.

Cheng, S.P., 2003. Heavy metal pollution in China: origin, pattern and control. *Environmental Sciences and Pollution Research*, 10: 192-198.

Cheung, Y.H., Wong, M.H., 1983. Utilisation of animal manures and sewage sludges for growing vegetables. *Agricultural Wastes*, 5: 63-81.

Chuah, T.G., Jumasiah, A., Katayon, S., Thomas, C.S.Y., 2005. Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: An overview. *Desalination*. 175: 305-316.

Chubar, N., Calvalho, J.R., Correia, M.J.N., 2004. Heavy metals biosorption on cork biomass: Effect of the pre-treatment. *Colloid and Surfaces A: Physicochemical and Engineering Aspects*, 238: 51-58.

Da'na, E., Sayari, A., 2011. Optimization of copper removal efficiency by adsorption on amine-modified SBA-15; Experimental design methodology. *Chemical Engineering Journal*, 167: 91-98.

Das, D., Basak, G., Lakshmi, V., Das, N., 2012. Kinetic and equilibrium studies on removal of zinc(II) by untreated and anionic surfactant treated dead biomass of yeast: Batch and column mode. *Biochemical Engineering Journal*, 64: 30-47.

Das, N., 2010. Recovery of precious metals through biosorption: A review. *Hydrometallurgy*. 103: 180-189.

Davis, A.P., Burns, M., 1999. Evaluation of lead concentration in runoff from painted structures. *Water Resource*, 33: 2949-2958

Demirbas, A., 2008. A review of heavy metal adsorption onto agro-based waste materials. *Journal of Hazardous Materials*, 157: 220-220.

Djeribi, R., Hamdaoui, O., 2008. Sorption of Copper (II) from aqueous solution by cedar sawdust and crushed brick. *Desalination*, 225: 95-112.

Dziwulska, U., Bajguz, A., Godlewska, B., 2004. The use of algae *Chlorella vulgaris* immobilized on Cellex-T support for separation / preconcentration of trace amounts of platinum and palladium before GFAAS determination. *Analytical Letters*, 37: 2189-2203.

Environmental Quality Act (1974) Environmental Quality (Industrial Effluent) Regulation 2009.

Feng, N., Guo, X., Liang, S., Zhu, Y., Liu, J., 2011. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. *Journal of Hazardous Materials*, 185: 49-54.

Fernandez, Y., Maranon, E., Castrillon, L., Vazquez, I., 2005. Removal of Cd and Zn from inorganic industrial waste leachate by ion exchange. *Journal of Hazardous Materials*, 126: 169-175.

Fillipi, B. R., Scamehorn, J.F., Christian, S.D., Taylor, R.W., 1998. A comparative economic analysis of copper removal from water by ligand-modified micellar-enhanced ultrafiltration and by conventional solvent extraction. *Journal of Membrane Science*, 145: 24-44.

Fleming , C.A., Trevors, J.T., 1989. Copper toxicity and chemistry in the environment: a review. *Water, Air and Soil Pollution*, 44: 143-158.

Freundlich, H.M.F., 1906. Over the adsorption in solution. *Journal of Physical Chemistry*, 57: 385-470.

Friberg, L., Elinder, C.G., 1985. Encyclopedia of occupational health. International Labor Organisation 3rd edition, Geneva.

Fu, F., Chen, R., Xiong, Y., 2006. Application of a novel strategy- coordination polymerisation precipitation to the treatment of Cu^{2+}- containing wastewaters. *Seperation and Purification Technology*, 52: 388-393

Fu, F., Wang, Q., 2011. Removal of heavy metals ions from wastewaters : A review. *Journal of Environmental Mangement*, 92: 407-418.

Gaballah, I., Goy, D., Allain, E., Kilbertus, G., Thauront, J., 1997. Recovery of copper through decontamination of synthetic solutions using modified barks. *Metallurgical and Materials Transactions*, 28: 13-23.

Ganji, M.T., Khosravi, M., Rakhsaee, R., 2005. Biosorption of Pb, Cd, Cu and Zn from wastewater by treated *Azolla filiculoides* with H_2O_2/ $MgCl_2$. *International Journal of Environmental Science and Technology*, 1: 265-271.

Garg, U.K., Kaur, M.P., Garg, V.K., Sud, D., 2007. Removal of hexavalent Cr from aqueous solutions by agriculturalwaste biomass. *Journal of Hazardous Materials*, 140: 60-68.

Giles, C.H., Smith, D., Huitson, A., 1974. A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *Journal of Colloid and Interface Science*, 47: 755-765.

Grimshaw, P., Calo, J.M., Hradil, G., 2011. Cyclic electrowinning/ precipitation (CEP) system for the removal of heavy metal mixtures form aqueous solutions. *Chemical Engineering Journal*. 175: 103-109.

Guanyu, Y., Viraraghavan, T., 2003. Heavy metal removal from aqueous solution by fungus *Mucor rouxii*. *Water Research*, 39: 4486-4496.

Gulnaz, O., Saygideger, S., Kusvuran, E., 2005. Study of Cu(II) biosorption by dried activated sludge: effect of physic-chemical environment and kinetics study. *Journal of Hazardous Materials*, 120: 193-200.

Gupta, S.S., Bhattacharyya, K.G., 2008. Immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium. *Journal of Environmental Management*, 87: 46-58.

Gurgel, L.V.A., Gil, L.F., 2009. Adsorption of Cu(II), Cd(II) and Pb(II) ions from aqueous single metal solutions by succinylated mercerized cellulose modified with triethylenetetramine. *Journal of Carbohydrate polymer*, 77: 142-149.

Güzel, F., Yakut, H., Topal, G., 2008. Determination of kinetic and equilibrium parameters of the batch adsorption of Mn(II), Co(II), Ni(II) and Cu(II) form aqueous solution by black carrot (*Daucus carota*) residue. *Journal of Hazardous Materials*, 153: 1275-1287.

Han, R., Li, H., Li, Y., Zhang, J., Xiao, H., Shi, J., 2006. Biosorption of copper and lead ions by waste beer yeast. *Journal of Hazardous Materials*, 137: 1569-1576.

Han, R., Zou, W., Yu, W., Cheng, S., Wang, Y., Shi, J., 2007. Biosorption of methylene blue from aqueous solution by fallen phoenix tree's leaves. *Journal of Hazardous Materials*, 141: 156-162.

Hanafiah, M.A.K.M., Ibrahim, S.C., Yahya, M.Z.A., 2006. Equilibrium, adsorption ion study of lead ions onto sodium hydroxide modified lalang (*Imperata cylindrica*) leaf powder. *Journal of Applied Sciences Research*, 2: 1169-1174.

Hanafiah, M.A.K.M., Wan Ngah, W.S., Zakaria, H., Ibrahim, S.C., 2007. Batch study of liquid-phase adsorption of lead using lalang (*Imperata cylindrica*) leaf powder. *Journal of Biological Sciences*, 7(2): 222-230.

Hanafiah, M.A.K.M., Zakaria, H., Wan Ngah, W.S., 2009. Preparation, characterisation, and adsorption behaviour of Cu(II) ions onto alkali-treated weed (*Imperata cylindrica*) leaf powder. *Water, Air & Soil Pollution*, 201: 43-53.

Hanafiah, M.A.K.M., Zakaria, H., Wan Ngah, W.S., 2010a. Base treated cogon grass (*Imperata cylindrica*) as an adsorbent for the removal of Ni(II) : Kinetic, isothermal and fixed-bed column studies. *Clean- Soil, Air, Water*, 38: 248-256.

Hanafiah, M.A.K.M., Khalir, W.K.A.W.M., Mohamed, K., Zakaria, H., Wan Ngah, W.S., 2010b. Sequestration of toxic Pb(II) ions by chemically treated rubber (*Hevea brasiliensis)* leaf powder. *Journal of Environmental Sciences*, 22: 248-256.

Ho, Y.S., Huang C.T., Huang, H.W., 2002. Equilibrium sorption isotherm for metal ions on tree fern. *Process Biochemistry*, 37: 1421.

Ho, Y.S., McKay, G., 1998. A comparison of chemisorptions kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environmental Protection*, 76: 332-340.

Ho, Y.S., McKay, G., 2000. The kinetic of sorption of divalent metal ions onto sphagnum moss peat. *Water Research*, 34: 735-742.

Ho, Y.S., Porter, J.S., McKay, G., 2002. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. *Water, Air and Soil Pollution*, 142: 1-33.

Ho, Y.S., Chiu, W.T., Hsu, C-S., Huang, C-T., 2004. Sorption of lead ions from aqueous solution using tree fern as a sorbent. *Hydrometallurgy*, 73: 55-61.

Hossain, M.A., Ngo, H.H., Guo, W.S., Setiadi, T., 2012. Adorption and desorption of copper (II) ions onto garden grass. *Bioresource Technology*, 121: 386-395.

Inglezakis, V.J., Grigoropoulou, H.P., 2003. Modeling of ion exchange of Pb^{2+} in fixed beds of clinoptilolite. *Microporous and Mesoporous Materials*, 61: 273-282.

Johnson, P.D., Watson, M.A., Brown, J., Jefcoat, I.A., 2002. Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater. *Waste Management*, 22: 471-480.

Junior, O.K., Gurgel, L.V.A., de Melo, J.C.P., Botaro, V.R., Melo, T.M.S., de Freitas Gil, R.P., Gil, L.F., 2006. Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugar bagasse. *Bioresource Technology*, 98: 1291-1297.

Kadirvelu, K., Namasivayam, C., 2003. Activated carbon from coconut coir pith as metal adsorbent: Adsorption of Cd(II) from aqueous solution. *Advances in Environmental Research*, 7: 471-478.

Kakitani, T., Hata, T., Kajimoto, T., Koyanaka, H., Imamura, Y., 2009. Characteristic of a bioxalate chelating extractin process for removal of chromium, copper and arsenic from treated wood. *Journal of Environmental Management*, 90: 1918-1923.

Kalavathy, M.H., Karthikeyan, T., Rajgopal, S., Miranda, L.R., 2004. Kinetic and isotherm studies of Cu(II) adsorption onto H_3PO_4 activated rubber wood sawdust. *Journal of Colloid and Interface Science*, 292: 354-362.

Kamel, S., Hassan, E.M., El-Sakhawy, M., 2006. Preparation and application of acrylonitrile-grafted cyanoethyl cellulose for the removal of copper (II) ions. *Journal of Applied Polymer Science*, 100: 329-334.

Khan, M.N., Wahab, M.F., 2006. Characterisation of chemically modified corncobs and its application in the removal of metal ions from aqueous solution. *Journal of Hazardous Materials*, 141: 237-244.

Khoo, K.H., Ting, Y.P., 2001. Biosorption of gold by immobilized fungal biomass. *Biotechnology and Bioengineering Journal*, 8: 51-59.

Kim, T.Y., Park, S.K., Cho, S.Y., Kim, H.B., Kang, Y., Kim, S.D., Kim, S.J., 2005. Adsorption of heavy metals by brewery biomass. *Korean Journal Chemical Engineering*, 22: 91-98.

King, P., Srivinas, P., Prasanna, K., Y., Prasad, V.S.R.K., 2006. Sorption of copper (II) ion from aqueous solution by *Tectona grandis* (teak leaves powder). *Journal of Hazardous Materials*, 136: 560-566.

Kiran, I., Akar, T., Tunali, S., 2005. Biosorption of Pb(II) and Cu(II) from aqueous solution by pretreated biomass of *Neurospora crassa*. *Process Biochemistry*, 40: 3550-3558.

Kratochvil, D., Volesky, B., 1998. Advances in the biosorption of heavy metals. *Trends in Biotechnology*, 16: 291-300.

Kumar, U., Bandyopadhyay, M., 2006. Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource Technology*, 97: 104–109.

Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids, *Journal of the American Chemical Society*, 38: 2221-2295.

Li, Q., Zhai, J., Zhang, W., Wang, M., Zhou, J., 2006. Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk. *Journal of Hazardous Materials*. 141: 163-167.

Li, W., Zhang, L., Peng, J., Li, N., Zhang, S., Guo, S., 2008. Tobacco stems as a low cost adsorbent for the removal of Pb(II) from wastewater: Equilibrum and kinetic studies. *Industrial Crops and Products*, 28: 294-302.

Lin, J., Wang, L., 2009. Comparison between linear and non-linear forms of pseudo-first-order and pseudo-second-order adsorption kinetic models for the removal of methylene blue by activated carbon. *Frontiers of Environmental Science and Engineering in China*, 3: 320-324.

Low, K.S., Lee, C.K., Leo, A.C., 1995. Removal of metals from electroplating wastes using banana pith. *Bioresource Technology*, 51: 227-231.

MacDonald G.E., 2004. Cogograss (*Imperata cylindrica*)- Biology, Ecology and Management. *Critical Review in Plant Science*, 23: 367-380.

Mack, C., Wilhelmi, B., Duncan, J.R., Burgess, J.E., 2007. Biosorption of precious metals. *Biotechnology Advances*, 25: 264-271.

Malkoc, E., Nuhoglu, Y., 2005. Investigations of nickel (II) removal from aqueous solutions using tea factory waste. *Journal of Hazardous Materials*, 127: 120-128.

Mao, J., Won, S.W., Vijayaraghavan, K., Yun, Y.S., 2009. Surface modification of Corynebacterium glutamicum for enhanced reactive red 4 biosorption. *Bioresource Technology*, 100: 1463-1466.

Mohan, S., Sreelakshimi G., 2008. Fixed bed column study for metal removal using phosphate treated rick husk. *Journal of Hazardous Materials*, 153: 75-82.

Namasivayam, C., Kadirvelu, K., 1997. Agricultural and solid wastes for the removal of heavy metals: adsorption of Cu(II) by coirpith carbon. *Chemosphere*, 34: 377-399.

Ncibi, M. C., Mahjoub, B., Seffen, M., 2006. Studies on the biosorption of textile dyes from aqueous solutions using *Posidonia oceanica* (L.) leaf sheath fibres. *Adsorption Science and Technology*, 24: 461–473.

Negrea, A., Ciopec, M., Lupa,L., Muntean, C., Negrea, P., 2008. Studies regarding the copper ions removal from waste waters. *Chemistry Bulletin*, 53; 93-97.

Nicholson, F.A., Smith, S.R., Alloway, B.J., Carlton-Smith, C., Chambers, B.J., 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. *The Science of the Total Environment*, 311: 205-219.

Nourbakhsh, M., Sag, Y., Ozer, D., Aksu, Z., Katsal, T., Calgar, A., 1994. A comparative study of various biosorbents for removal of chromium (VI) ions from industrial wastewater. *Process Biochemistry*, 29: 1-5.

Obuseng, V., Nareetsile, F., Kwaambwa, H.M., 2012. A study of the removal of heavy metals from aqueous solutions by *Moringa oleifera* seeds and amine-based ligand 1,4-bis[N,N-bis(2-picoyl)amino]butane. *Analytica Chimica Acta*, 730: 87-92.

O'Connell, D.W., Birkinshaw, C., O'Dwyer, T.F., 2008. Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource Technology*, 99: 6709-6724.

Ofomaja, A.E., 2008. Sorption removal of methylene blue from aqueous solution using palm kernel fibre: Effect of fibre dose. *Biochemical Engineering Journal*, 40: 8-18.

Ofomaja, A.E., Naidoo, E.B., Modise, S.J., 2009. Removal of copper(II) from aqueous solution by pine and base modified pine cone powder as biosorbent. *Journal of Hazardous Materials*, 168: 909-917.

Ornek, A., Ozacar, M., Sengil, I.A., 2007. Adsorption of lead onto formaldehyde or sulphuric acid treated acorn waste: Equilibrium and kinetic studies. *Biochemical Engineering Journal*, 37: 192-200.

Otero, N., Vitoria, L., Soler, A., Canals, A., 2005. Fertiliser characterisation: major, trace and rare earth elements. *Applied Geochemistry*. 20: 1473-1488.

Özer, A., Özer, D., Özer, A., 2004. The adsorption of copper(II) ions onto dehydrated wheat bran (DWB): Determination of equilibrium and thermodynamic parameters. *Process Biochemistry*, 39: 2183- 2191.

Ozsoy, H.D., Kumbur, H., 2006. Adsorption of Cu(II) ions on cotton ball. *Journal of Hazardous Materials*, 136: 911-916.

Panda, G.C., Das, S.K., Bandopadhyay, T.S., Guha, A.K., 2007. Adsorption of nickel on husk of *Lathyrus sativus*: Behaviour and binding mechanism. *Colloids and Surfaces B: Biointerfaces*, 57: 135-142.

Park, D., Seong, R.L., Yeoung, S.Y., Park, J.M., 2008. Development of a new Cr(VI) biosorbent form agricultural biowaste. *Bioresource Technology*, 99: 8810-8818.

Pehlivan, E., Cetin, S., Yanık, B.H., 2006. Equilibrium studies for the sorption of zinc and copper from aqueous solution using sugar beet pulp and fly ash. *Journal of Hazardous Materials*, 135: 193-199.

Pino, G.H., de Mesquita, L.M.S., Torem, M.L., Pinto, G.A.S., 2006. Biosorption of cadmium by green coconut shell powder. *Minerals Engineering*, 19: 380-387.

Quek, S.Y., Wase, D.A.J., Forster, C.F., 1998. The use of sago waste for the sorption of lead and copper. *Water Research*, 24: 251-256.

Reddad, Z., Gerente, C., Cloirec, P.L., 2002. Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies. *Environmental Science Technology*, 36: 2067-2073.

Reddy, B.B., Mighaffari, N., Gaballah, I., 1997. Removal and recycling of copper from aqueous solution using treated indian barks. *Resources Conservation Recycling*, 21: 227-245.

Rule, K.L., Comber, S.D.W., Ross, D., Thornton, A., Makropoulus, C.K., Rautiu, R., 2006. Diffuse sources of heavy metals entering an urban wastewater catchment. *Chemosphere*, 63: 64-72.

Saeed, A., Iqbal, M., Akhtar, M.W., 2005. Removal and recovery of lead (II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). *Journal of Hazardous Materials*, 117: 65-73.

Saha, B., Orvig, C., 2010. Biosorbents for hexavalent chromium elimination from industrial and municipal effluents. *Coordination Chemistry Reviews*. 254: 2959-2972.

Sahin, O., Demirel, S., Dilekoglu, M.F., 2005. Removal of Pb(II) from aqueous solution by antep pistachio shells. *Fresenius Environmental Bulletin*, 14: 986-992.

Salam, M.A., Al-Zhrani, G., Kosa, S.A., 2012. Simultaneous removal of copper (II), lead (II), zinc (II) and cadmium (II) from aqueous solutions by multi-walled carbon nanotubes. *Comptes Rendus Chimie*.15: 398-408.

Salehi, P., Asghari, B., Mohammadi, F., 2008. Removal of heavy metals from aqeous solution by *Cercis siliquatrum* leaves. *Journal of the Iranian Cehmical Society*, 5: 80-86.

Šćiban, M. and Klašnja, M., 2004. Wood sawdust and wood originate materials as adsorbents for heavy metal ions. *Holz Roh Werkst*, 62: 69-73.

Šćiban, M., Klašnja, M., Skrbić, B., 2006. Modified softwood sawdust as adsorbent of heavy metal ions from water. *Journal of Hazardous Materials*, 136: 266-271.

Sert, S., Kutahyali, C., Inan, S., Talip, Z., Cetinkaya, B., Eral, M., 2008. Biosoption of lanthanum and cerium from aqueous solution by *Platanus orientalis* leaf powder, *Hydrometallurgy*, 90: 13-18.

Sheikholeslami, R., Bright, J., 2002. Silica and metals removal by pretreatment to prevent fouling of reverse osmosis membranes. *Desalination*, 143: 255-267.

Shinde, N.R., Bankar, A.S., Kumar, A.R., Zinjarde, S.S., 2012. Removal of Ni(II) ions from aqueous solutions by biosorption onto two strains of *Yarrowia lipolytica*. *Journal of Environmental Manangement*, 102: 115-124.

Shukla, A., Zhang, Y.H., Dubey, P., Margrave, J.L., Shukla, S.S., 2002. The role of sawdust in the removal of unwanted materials from water. *Journal of Hazardous Materials*, 95: 137-152.

Shukla, S.R., Pai, R.S., 2005a. Adsorption of Cu(II), Ni(II) and Zn(II) on modified jute fiebres. *Bioresource Technology*, 96: 1430-1438.

Shukla, S.R., Pai, R.S., 2005b. Adsorption Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust. *Separation and Purification Technology*, 43: 1-8.

Singh, C.K., Meikap, B.C., Sahu, J.N., Mahalik, K.K., Mohanty, C.R., Mohan, B.R., 2008. Studies on the removal of Pb(II) from wastewater by activated carbon developed from Tamarind wood activated with sulphuric acid. *Journal of Hazardous Materials*, 153: 221-228.

Srivastava, N. K., Majumder, C.B., 2008. Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *Journal of Hazardous Materials*, 151: 1–8.

Sud., Mahajan, G., Kaur, M.P., 2008. A review of agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions. *Bioresource Technology*, 99: 6017-6027.

Sun, R.C., 2009. Cereal straw as a resource for sustainable biomaterials and biofuels. China. *Elsevier*, 227-234.

Tan, L., Zhu, D., Zhou, W., Mi, W., Ma, L., He, W., 2008. Preferring cellulose of *Eichhornia crassipes* to prepare xanthogenate to other plant materials and its adsorption properties on copper. *Bioresource Technology*, 99: 4460-4466.

Tapiero, H., Towsend, D.M., Tew, K.D., 2003. Trace elements in human physiology and pathology. Copper. *Biomedicine and Pharmacotheraphy*, 57: 386—398.

Tsai, K.W., 2000. Comparison of linear and non-linear forms of isotherm models for strontium sorption on a sodium bentonite. *Journal of Radioanalytical and nuclear chemistry*, 243: 741-746.

Tunali, S., Cabuk, A., Akar, T., 2006. Removal of lead and copper ions from aqueous solution by bacterial stain isolated from soil. *Chemical Engineering Journal*, 115: 203-211.

USEPA, 2002. Lead and copper monitoring and reporting guidance for public water systems. *Ground Water and Drinking Water Division, US Environmental Protection Agency*.

Vaghetti, J.C.P., Lima, E.C., Royer, B., Dacunha B.M., Cardoso, N.F., Brasil, J.L., Dias, S.L.P., 2008. Pecan nutshell as biosorbent to remove Cu(II), Mn(II) and Pb(II) from aqueous solutions. *Journal of Hazardous Materials*, 162: 270-280.

Valenzuela, F., Fonseca, C., Basualto, C., Correa, O., Tapia, C., Sapag, J.,2005. Removal of copper from a waste mine water by a liquid emulsion membrane method. *Mineral Engineering*, 18: 33-40.

Veglio, F., Quaresima, R., Fornari, P., Ubaldini, S., 2003. Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning. *Waste management*, 23: 245-252.

Volesky, B., 1990. Biosorption of heavy metals, United States of America. *CRC Press*, 3–5.

Volesky, B., 2007. Biosorption and me. *Water Research*, 41: 4017-4029.

Vuorio, M., Manzanares, J.A., Murtomäki, L., Hirvonen, J., Kankkunen, T., Kontturi, K., 2003. Ion-exchange fibres and drugs: a transient study. *Journal of Controlled Release*, 91: 439-448.

Walter, I., Martinez, F., Cala, V., 2006. Heavy metal speciation and phytotoxic effects of three representative sewage sludges for agricultural uses. *Environmental pollution*, 139: 507-514.

Wang, J.L., 2002. Biosorption of copper (II) by chemically modified biomass of *Saccharomyces cerevisiae*. *Process Biochemistry*, 37: 847-850.

Wankasi, D.,Horsfall., M., Spiff, A.I., 2006. Sorption kinetic of Pb^{2+} and Cu^{2+} ions from aqueous solution by Nipah palm shoot biomass. *Electronic Journal of Biotechnology*, 9: 587-592.

Wan Ngah, W.S., Endud, C. S., Mayanar, R., 2002. Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads. *Reactive and Functional Polymers*, 50: 181–190.

Wan Ngah, W.S., Fathinathan, S., 2006. Adsorption of Cu(II) ions in aqueous solutions using chitosan beads, chitosan-GLA beads and chitosan-alginate beads. *Chemical Engineering Journal*, 143: 62-72.

Wan Ngah, W.S., Hanafiah, M.A.K.M., 2008a. Biosorption of copper ions from dilute aqeous solutions on base treated rubber (*Hevea brasiliensis*) leaves powder: kinetics, isotherm, and biosorption mechanisms. *Journal of Environmental Sciences*, 20: 1-9.

Wan Ngah, W.S., Hanafiah, M.A.K.M., 2008b. Kinetic, equilibrium and thermodynamic studies of copper adsorption onto rubber tree (*Hevea brassiliensis*) leaf powder. *Journal of Biochemical Engineering*, 39: 521-530.

Wan Ngah, W.S., Hanafiah, M.A.K.M., 2008c. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents : A review. *Bioresource Tecnology*, 99: 3935-3948.

Wan Ngah, W.S., Hanafiah, M.A.K.M., 2009. Surface modification of rubber (*Hevea brasiliensis*) leaves powder for the adsorption of copper ions: kinetics, thermodynamic and binding mechanisms. *Journal of Chemical Technology and Biotechnology*, 84: 192-201.

Witek-Krowiak, A., Szafran, R.G., Modelski, S., 2011. Biosorption of heavy metals from aqueous solutions onto peanut shell as low-cost biosorbent. *Desalination*, 265: 126-134.

Wong, K.K., Lee, C.K., Low, K.S., Haron, M.J., 2003a. Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere*, 50: 23-28.

Wong, K.K., Lee, C.K., Low, K.S., Haron, M.J., 2003b. Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. *Process Biochemistry*, 39: 437-445.

Wong, K.S., Wong, K.H., Ng, S., Chung, W.K., Wong, P.K., 2007. Adsorption of copper ion on magnetite-immobilised chitin. *Water Science and Technology*, 56: 135-143.

Zhao, M., Duncan, J.R., Van Hille, R.P., 1999. Removal and recovery of zinc from solution and electroplating effluent using *Azolla filiculoides*. *Water Research*, 33: 1516-1522.

Zhou, W., Zhu, D., Langdon, A., Li, L., Liao, S., Tan, L., 2009. The structure characterization of cellulose xanthogenate derived from the straw of *Eichhornia crassipes*. *Bioresource Technology*, 100: 5366-5369.

Zhou, W., Ge. X., Zhu, D., Langdon, A., Deng, L., Deng, L., Hua, Y., Zhao, J., 2011. Metal adsorption by quasi cellulose xanthogenates derived from aquatic and terrestrial plant materials. *Bioresource Technology*, 102: 3629-3631.

Zhu, C.S., Wang, L.P., Chen, W.B., 2009. Removal of Cu (II) from aqueous solution by agricultural by – product; Peanut Hull. *Journal of Hazardous Materials*, 168: 739-746.