

**BIOSORPTION OF LEAD (II) IONS BY STEM OF
MANIHOT ESCULENTA (CASSAVA STEM)**

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2017

**BIOSORPTION OF LEAD (II) IONS BY STEM OF
MANIHOT ESCULENTA (CASSAVA STEM)**

by

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**Thesis submitted in partial fulfilment of the requirement for
the degree of Bachelor of Chemical Engineering**

June 2017

ACKNOWLEDGEMENT

Upon completion of this project, I would like to acknowledge School of Chemical Engineering, University of Science Malaysia, Engineering Campus for giving me the opportunity in doing and completing this final year project. First, I would like to express my gratitude my supervisor, Dr. Khairiah Abd. Karim for her support, valuable comments and advices throughout the period of this project.

I would also extend my gratitude towards my course coordinator, Associate Professor Dr. Mohd Azmier Ahmad who have given many information, advices and guidance in preparing this project paper. Besides, I also would like to thank all technicians that assisted me in carrying out my experiment.

Finally, I would like to express my deepest gratitude to my beloved family, friends and to all individuals who helped me in completing this work. Once again, I would like to thank all the people, who have helped me directly and indirectly, their contributions are very much appreciated. Thank you.

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LIST OF SYMBOLS

	Symbol	Unit
C_e	Equilibrium concentration of adsorbate	mg/L
C_o	Initial adsorbate concentration	mg/L
C_t	Concentration at time, t	mg/L
k_1	Adsorption rate constant for the pseudo-first-order kinetic	1/hr
k_2	Adsorption rate constant for the pseudo-second-order	g/mg.hr
K_F	Freundlich isotherm constant	mg/g (L/mg) ^{1/n}
K_L	Langmuir adsorption constant	L/mg
W	Mass of adsorbent	g
n_f	Constant for Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Adsorption capacity of Langmuir isotherm	mg/g
q_t	Amount of adsorbate adsorbed at time, t	mg/g
R^2	Correlation coefficient	-
t	Time	Min
V	Solution volume	L

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
FTIR	Fourier Transform Infrared
IR	Infrared
RPM	Rotation per minute

**BIOPENJERAPAN ION PLUMBUM (II) DI ATAS BATANG *MANIHOT*
ESCULENTA (BATANG UBI KAYU)**

ABSTRAK

Logam berat menjadi bahan pencemar kerana ciri-ciri ketidakbolehan biodegradasi, keracunan dan ketekunan dalam persekitaran di mana plumbum adalah salah satu daripadanya. Dalam kajian ini, biojisim batang *Manihot esculenta* telah digunakan dalam proses penjerapan plumbum (II) ion dalam kelompok. Kesan rawatan awal (mentah, asid dan alkali), kawalan pH (2-6), muatan biojisim (0.25 g - 1.25 g), masa sentuhan (20 minit – 100 minit) dan kepekatan logam awal (50 mg / L - 250mg / L). Pemerhatian menyatakan bahawa persekitaran yang sesuai untuk kapasiti penjerapan yang tinggi, iaitu penyingkiran sebanyak 99.60% oleh batang *M. esculenta* ialah seperti penjerap yang telah dirawat awal menggunakan alkali, pada pH 6, muatan biojisim sebanyak 0.75 g, kepekatan logam sebanyak 100 mg/L, dalam 60 minit masa sentuhan. Ia juga mendapati bahawa model isoterma Langmuir ($R^2 = 0.9783$) bersesuaian untuk proses biopenjerapan ini sebagai isoterma penjerapan, bukannya model isoterma Freundlich ($R^2 = 0.7581$). Pemodelan data kinetik menunjukkan penyesuaian yang lebih baik bagi model baik dengan model kinetik ‘pseudo-second-order’ ($R^2 = 1.000$) berbanding model ‘pseudo-first-order’ ($R^2 = 0.6244$). Keputusan keseluruhan menunjukkan bahawa batang *M. esculenta* adalah biopenjerap yang baik, dan boleh digunakan sebagai biopenjerap kos rendah alternatif untuk penyingkiran ion plumbum (II).

BIOSORPTION OF LEAD (II) IONS ONTO STEM OF *MANIHOT ESCULENTA*
(CASSAVA STEM)

ABSTRACT

Heavy metals becoming pollutants due to its non-biodegradable characteristics, toxicity and persistence in the environment where lead is one of it. In this study, *Manihot esculenta* stem biomass was used in the biosorption process of lead (II) ions in batch. The effects of pretreatment (raw, acid and alkali), pH control (2-6), biomass loading (0.25 g – 1.25 g), contact time (20 minutes – 100 minutes) and initial metal concentration (50 mg/L – 250mg/L) were studied on the removal of lead (II) ions from aqueous solution. Observations stated that the suitable conditions for high biosorption capacity, which is removal up to 99.60% by *M. esculenta* stem are alkali pretreated biosorbent, at pH 6, biomass loading of 0.75 g, metal concentration of 100 mg/L, in 60 minutes contact time. It is also found that Langmuir isotherm model ($R^2= 0.9783$) fits well for this biosorption process as adsorption isotherm, rather than Freundlich isotherm model ($R^2= 0.7581$). Kinetic data modelling resulted in good fit with the pseudo-second-order model ($R^2= 1.000$) compared to pseudo-first-order model ($R^2= 0.6244$). Overall result shows that *M. esculenta* stem is a good biosorbent, and can be used as an alternative low-cost biosorbent for removal of lead (II) ions.

CHAPTER ONE

INTRODUCTION

1.1 Research background

The term 'heavy metal' are commonly heard nowadays, which is considered very polluting elements with the ability to accumulate in living tissues along the food chain. Heavy metal usually exists in water, but in a lower amount. It is essential for human life and health. When they are present in excess, it will lead to several health problems for animals, plants and human beings. Lead is one of the heavy metals found in the water. Since lead is widely used material, there are many actual or potential sources of lead pollution. The origin of heavy metal normally from many industries, as some shown in Table 1.1. In outcome, the treatment of effluents accused of these contaminants is drawing in developing interest on account of ecological and sterile issues, and progressively prohibitive enactments (Castro et al, 2017).

The recovery of these metals can likewise be monetarily intriguing due to its higher costs (Barakat, 2011). Such effluents posture significant issues for the industry because of the high cost of metal removal utilizing traditional technologies. One of the commonly well-known processes for metal removal from industrial effluent is chemical precipitation of metals by which the procedure is by using lime and followed by settling of metal precipitates in a clarifier (Chareerntanyarak, 1999). Eventually, this conventional method poses disadvantages of low proficiency at low concentration of heavy metals and the high cost in safe disposal of toxic sludge. Besides filtration and chemical precipitation, there are also other methods being implemented such as electrochemical treatment, reverse osmosis, ion exchange, adsorption and evaporation (Zhao et al, 2016).

Biological methods also have been implemented. Biosorption is a financially low cost alternative that can be used for treating effluents with low metal focuses and can likewise be utilized to remove different contaminants, for example, dyes and organic compounds. It is a property of specific type of organic matter or biomass to latently tie metals on chemically active sites or functional groups. The kind of biomass utilized decides the metal take-up and the selectivity of the recovery procedure. Most biosorption studies have been completed on microbial, microorganisms, microalgae and fungi, and with poisonous metals and radionuclides. In any case, the utilization of dead biomass makes the procedure supplement-independent, faster and increases the metal take-up (Castro et al, 2017).

Table 1.1 Level of Pb²⁺ ions in wastewater of various industries (Verma et al, 2016).

Industry	Pb ²⁺ ions concentration on wastewater (mg/L)
Chemical manufacturing plant, Glubczyce (Poland)	326.4
Oil	125-150
Battery manufacturing plant	5-15
Electroplating	116.42
Industrial plant	19.1

1.2 Problem statement

Lead is significantly toxic heavy metal and inorganic forms are absorbed through medium such as water. Lead poisoning can cause severe disorders such as anaemia, kidney disease and mental retardation if contain in high level for a long term (Yap et al, 2017). Therefore, heavy metals should be removed from water stream to avoid

consequences. Biosorption is a promising process, which is highly effective in removing heavy metals from wastewater. Other methods are available, such as physiochemical methods, but they have high operating cost, low selectivity and high production of waste, which act as disadvantages.

The removal of heavy metal through biosorption process shown that is one of the most potential, economical and efficient method to be implemented compared to other conventional methods available out there. Biosorbent can be obtained from agricultural or industrial wastes such as wastes that produced by food industries. Researches have been done for the removal of lead (II) ions using biosorbents such as banana peels, palm fibres, coconut shell, coffee ground and rice husk (Gomez-Gonzalez et al, 2016). Eventually not all biosorbents can be an efficient metal removal, since different biosorbents have different functional group on the surface. Functional group plays a main role in binding metals to the surface of biosorbent.

Therefore, in this research, stem of *M. esculenta* (cassava stem) will be used to adsorb lead or specifically biosorption of lead (II) ions onto the stem of *M. esculenta* (cassava stem). As an advantage, it can reduce the operational cost and reduce generation of toxic materials. Parameters that being studied are pH, biomass loading, contact time and initial heavy metal concentration. The kinetics of biosorption were examined by using pseudo-first-order method and pseudo-second-order-method, and adsorption isotherms were chosen to describe the biosorption equilibrium, which is Langmuir and Freundlich.

1.3 Objectives

The objectives of this project are:

- i. To characterize the functional groups of the biosorbent (stem of *M. esculenta*) using Fourier Transform Infrared Spectroscopy (FTIR)
- ii. To investigate the effects of parameters (pH, biomass loading, contact time and initial adsorbate concentration) on the biosorption of lead (II) ions.
- iii. To study the adsorption isotherms and adsorption kinetics of lead (II) ions.

1.4 Scope of study

In this study, stem of *M. esculenta*, as treated and untreated are used as a biosorbent for heavy metal ions removal, which is lead (II) ions. Lead is chosen in this study since it is widely used in many industries and exist in the effluent from the industries. Parameters that are chosen are pH, biomass loading, contact time and initial adsorbate concentration. The equilibrium data for biosorbents were analysed using Langmuir and Freundlich isotherms. The kinetic models were also proposed. The characterization of the functional group will be investigated by using Fourier transform infrared spectroscopy (FTIR) and atomic adsorption spectrophotometer (AAS) is used to quantify the remaining metal ions in the aqueous solution after biosorption process.

1.5 Organization of thesis

The following are the contents for each chapter in this study:

CHAPTER ONE introduces the usage of heavy metal in industries, problem statement, research objectives and organization of thesis.

CHAPTER TWO discusses the literature review of this study, which includes the adsorption process, biosorbent, isotherm models and kinetic models.

CHAPTER THREE covers the materials and details of methodology. It discusses on the description of equipment and materials used, batch adsorption experiment, experimental procedure and description of factors affecting the adsorption process.

CHAPTER FOUR refers to the experimental results and discussions of the data obtained. Further elaboration on the effect of different factors on batch system adsorption, the results on equilibrium, kinetic and characterization are provided in this chapter.

CHAPTER FIVE concludes all the findings obtained in this study and recommendations are included as well.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy metal in wastewater

In developing countries, acceleration of consumption of commodities and increase in waste generation occur due to population growth and economic development in the urban areas (Islam et al, 2015a). Wastewater contains heavy metals, organic compounds, macronutrients, organic micro pollutants, microorganisms and eggs of parasitic organisms (Yuan et al, 2011). Accumulation of heavy metals in the industrial wastewater poses a growing environment problem and the disposal of these wastewaters with toxic metals may result in secondary environmental pollution. Contamination of aquatic environment by toxic metals from untreated wastewater considered a worldwide environmental problem (Islam et al, 2016). Main source of heavy metals in the environment are from mining, electroplating, textile, tanneries, metal processing, battery manufacturing, paint manufacturing, petroleum refining, pigment manufacturing, pesticides, printing and photographic industries (Ahmaruzzaman, 2011). Metals such as chromium, nickel, copper, arsenic, cadmium and lead categorized as hazardous metals (Ahmaruzzaman, 2011; Islam et al, 2015b). Heavy metals are non-biodegradable and have tendency to be adsorbed, accumulated and biomagnified in the body that leads to various diseases (Herojeet et al, 2015; Islam et al, 2016). The metals have different effects on human body based on the nature of particular metal. They can potentially affect the neurological system, kidney function, ossification process and various other organs (Lohani et al, 2008). The maximum contaminant level (MCL) standards, for heavy metals, are summarized in Table 2.1.

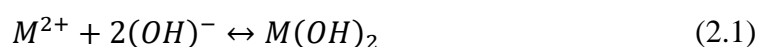
Table 2.1 The MCL standards for the most hazardous heavy metals (Barakat, 2011).

Heavy metal	Toxicities	MCL (mg/l)
Arsenic	Skin manifestation. Visceral cancers, vascular disease	0.05
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

2.2 Heavy metal wastewater treatment techniques

2.2.1 Chemical precipitation

One of the most widely used processes for removal of heavy metal from inorganic effluent is chemical precipitation. The conceptual mechanism of heavy metal removal by chemical precipitation is shown in Equation (2.1)



where M^{2+} and OH^{-} represent the dissolved metal ions and the precipitant, respectively. $M(OH)_2$ is the insoluble metal hydroxide that formed. Adjustment of pH to the basic

conditions, with pH range between 9 to 11 is the common parameter that significantly improves heavy metal removal by chemical precipitation (Barakat, 2011). Variety of precipitant has been used to precipitate metal from wastewater. Lime and limestone are commonly used precipitant agents due to their availability and low-cost (Aziz et al, 2008). Inorganic effluent with a metal concentration of higher than 1000 mg/L can be treated using lime precipitation (Barakat, 2011). Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations. However, this process does have some disadvantages, such as chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge, its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Aziz et al, 2008). The processes of a conventional metal precipitation treatment plant is as given in Figure 2.1.

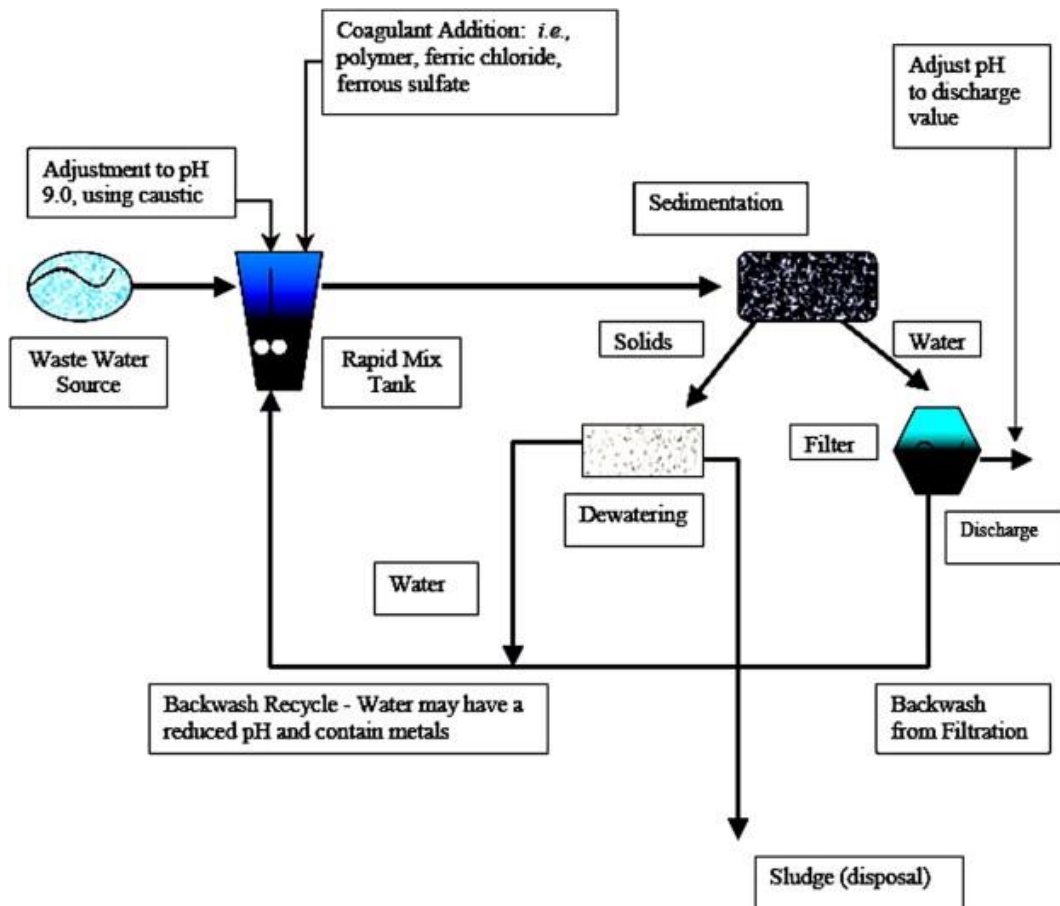
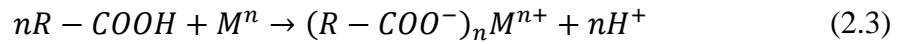
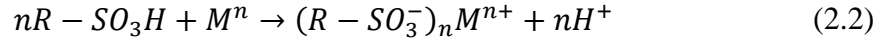


Figure 2.1 Processes of a conventional metal precipitation treatment plant (Barakat, 2011)

2.2.2 Ion exchange

Ion exchange is also another widely used method of heavy metal removal from effluent. Ion exchange resin, which is either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Synthetic resin are effective in removing the heavy metals from the wastewater, thus it is commonly preferred (Alyüz and Veli, 2009). The most common cation exchangers are strongly acidic resins with sulfonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups ($-COOH$). Hydrogen ions in the sulfonic group or carboxylic group of the

resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the ion-exchange process shown in Equation (2.2) and Equation (2.3) (Fu and Wang, 2011).



Variables such as pH, temperature, initial metal concentration and contact time are certain variables that affects the uptake of heavy metal ions by ion exchange resin (Gode and Pehlivan, 2006). Ion exchange has many advantages, such as high treatment capacity, high removal efficiency, and fast kinetics (Kang et al, 2004). At the same time, it also cannot handle concentrated metal solution as organics and other solid in the wastewater easily foul the matrix. Moreover, ion exchange is non-selective (Barakat, 2011).

2.2.3 Membrane filtration

Membrane filtration is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Various type of membrane filtration can be employed for heavy metal removal such as ultrafiltration, nanofiltration and reverse osmosis depending on size of particle that can be retained (Barakat, 2011).

2.2.3.1 Ultrafiltration

Ultrafiltration utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution. The pore size range from 5 nm to 20 nm and molecular weight of the separating compound range from 1000 Da to 100000 Da. This enables water and low-molecular weight solutes to pass through, while retaining macromolecules, which have a size of larger than the membrane's pore size (Vigneswaran et al, 2005). Studies on removal of Cu(II) and Zn(II) ions from synthetic wastewater has been done using chitosan-enhanced membrane filtration. The outcome shows that about 100% and 95% rejection were achieved at pH ranging from 8.5 to 9.5 for Cu(II) and Zn(II) ions respectively. This indicates that chitosan significantly enhanced metal removal by 6 to 10 times compared to using membrane alone (Juang and Shiau, 2000).

2.2.3.2 Nanofiltration

Nanofiltration is the intermediate process between ultrafiltration and reverse osmosis. Through the researches that have been conducted, nanofiltration seems to be a promising technology for removal of heavy metal ions such as nickel, chromium, copper and arsenic from wastewater (Fu and Wang, 2011). Advantages of nanofiltration are it can be easily operated, reliable, low energy consumption and high efficiency of pollutant removal. A research to study on the removal of pentavalent arsenic from synthetic water has been done using two commercial nanofiltration membrane, NF90 and N30F. The outcome shows that an increase of pH and a decrease of operating temperature and As feed concentration leads to higher As removal for both membrane. Feed concentration played a key role for the production of permeate stream (Figoli et al, 2010). Besides,

another study has been done which was the application of a thin-film composite polyamide nanofiltration membrane for the rejection of nickel ions from aqueous wastewater. The maximum observed rejection of nickel is found to be 98% and 92% for an initial feed concentration of 5 and 250 mg/L, respectively (Murthy and Chaudhari, 2008). They also studied on the binary heavy metals, cadmium and nickel separation capability of commercial nanofiltration membrane from aqueous solution and found that for initial feed concentration of 5 mg/L, solute rejection of nickel and cadmium ions is 98.94% and 82.69%, respectively (Murthy and Chaudhari, 2009).

2.2.3.3 Reverse osmosis

The reverse osmosis process uses a semi-permeable membrane, which separates purified membrane from the contaminants. Reverse osmosis able to remove large range of dissolved species from water (Fu and Wang, 2011). In a study, Cu^{2+} and Ni^{2+} ions were removed using reverse osmosis and by using Na_2EDTA , the rejection efficiency increased up to 99.5% (Mohsen-Nia et al, 2007). Another study is done by applying a pilot-scale membrane bioreactor system in combination with reverse osmosis and the outcome, which is heavy metal removal efficiencies were very high. High power consumption due to pumping pressure and the restoration of the membrane became the major disadvantages (Dialynas and Diamadopoulos, 2009).

2.2.4 Adsorption

Adsorption is a mass transfer process by which a substance is transferred from a liquid phase to the surface of a solid, bounded by physical or chemical interaction (Barakat, 2011). Adsorption is considered effective and economic method for heavy

metal wastewater treatment. Its design is flexible and produces high-quality treated effluent. It also a reversible process, where adsorbents can be regenerated by using suitable desorption method. Adsorption involves three steps, the transport of the pollutant from the bulk solution to sorbent surface, adsorption on the particle surface and transport within the sorbent particle. Technical applicability and cost-effectiveness plays a large role in choosing the suitable adsorbent to treat inorganic effluent.

2.2.4.1 Activated carbon adsorbents

It is widely used in removal of heavy metal contaminant. It has a large micropore and mesopore volume and results in high surface area. A lot of studies are being done on activated carbon to be used as adsorbent to remove heavy metals (Jusoh et al, 2007). The increase in price occurs due to depletion source of commercial coal-based activated carbon and to make progress in heavy metals adsorption to activated carbon without expences, options like additives and activated carbon composite introduced, such as additives of alginate, tannic acid, magnesium and surfactants (Fu and Wang, 2011). There also been studies on alternative activated carbon to be produced from abundant and inexpensive sources. Activated carbon from eucalyptus bark used in the binary component sorption of Cu^{2+} and Pb^{2+} . The maximum sorption capacities for Cu^{2+} and Pb^{2+} were 0.45 and 0.53 mmol/g, respectively (Patnukao et al, 2008).

2.2.4.2 Low-cost adsorbent

Researches now focus mainly on finding low-cost adsorbent and easily available adsorbents to remove heavy metal ions. Studies has been done on agricultural waste, industrial by-product and wastes and natural substances as adsorbents for heavy metal

removal from effluent. Some of the researches that been done including adsorption of few heavy metals on natural and modified kaolinite and montmorillonite (Bhattacharyya and Gupta, 2008), removal of heavy metal ions from aqueous solutions using agricultural waste material as adsorbent (Sud et al, 2008) and usage of chemically modified plant wastes as adsorbents (Wan Ngah and Hanafiah, 2008). Besides, industrial by-products such as lignin (Betancur et al, 2009), diatomite (Sheng et al, 2009), clino-phyrrhotite (Lu et al, 2006), lignite (Mohan and Chander, 2006), aragonite shells (Köhler et al, 2007), etc have been investigated. Kaoline clay has been used to remove heavy metal ions from wastewater, the uptake is rapid with maximum adsorption being observed within 30 minutes. Then the kaoline clay was used to remove metal ions from real wastewater containing Pb^{2+} , where the concentration was reduced from 160.00 mg/L to 8.00 mg/L (Jiang et al, 2010).

2.2.4.3 Biosorbent

Biosorbent's major advantages are its high effectiveness in reducing heavy metal ions and the use of inexpensive biosorbents. Biosorption process is suitable to treat dilute heavy metal wastewater. Biosorbent can be obtained from three sources, non-living biomass (bark, lignin, shrimp, krill, squid, crab shell, etc), algal biomass and microbial biomass (bacteria, fungi and yeast) (Apiratikul and Pavasant, 2008). Sawdust, black oak bark, nut shell, peanut skin, redwood bark, walnut shell and waste tea have been investigated as potential biosorbent for heavy metal (Bailey et al, 1999). Algae, a renewable natural biomass found abundantly in the littoral zones of world has attracted the attention of many researchers. These organisms have been tested and used as new adsorbents to adsorb metal ions. Several advantages in applying algae as biosorbent

include the wide availability, low cost, high metal sorption capacity and reasonably regular quality (Apiratikul and Pavasant, 2008). Some of the researches that been done on algae are biosorption of Cu^{2+} and Zn^{2+} using dried marine green macroalga *Chaetomorpha linum* (Ajjabi and Chouba, 2009), biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera* (Pavasant et al, 2006), and biosorption of Pb^{2+} using green algae *Cladophora fascicularis* (Deng et al, 2007). Biosorption of Cu^{2+} and Zn^{2+} using dried marine green macroalga (*C. linum*) was done and found that at optimum particle size which is 100 – 315 mm, with biosorbent dosage of 20 g/L and initial solution pH of 5, the algae produced maximum Cu^{2+} and Zn^{2+} uptake value of 1.46 and 1.97 mmol/g, respectively (Ajjabi and Chouba, 2009). Biosorbents have the characteristic of broad source, low cost and rapid adsorption but the researches are still theoretic and in experimental phase. Besides, separation of biosorbent will be difficult after adsorption (Fu and Wang, 2011). Table 2.2 shows the uptake capacities of Pb (II) of various adsorbents.

Table 2.2 Uptake capacities of Pb (II) of various adsorbents (Tabaraki et al, 2014)

Adsorbents	pH	T (°C)	q (mg/g)
Crab shell and arca shell	5.5	25	19.83, 18.33
Chaff	5.5	25	12.4
Powder activated carbon	-	25	20.7
<i>Bacillus sp.</i>	3	25	92.27
<i>Phizopus arrhizus</i>	4.5	25	2.65
Waste baker's yeast in ethanol	5	25	17.49
<i>Caulerpa lentillifera</i>	5	25	28.7
<i>Gelidium algae</i>	5	25	64
<i>Chlamydomonas reinhardtii</i>	5	25	96.3
<i>Padina sp.</i>	5	22	122.6
<i>Sargassum sp.</i>	5	22	139.1
<i>Cladonia furcate</i>	5	20	12.5
<i>Parmelina tiliaceae</i>	5	20	75.8

2.3 Adsorption parameters

2.3.1 pH

In determining the suitable medium condition for efficient adsorption to occur, pH control plays a vital role. pH can affect the protonation of the functional group such as phosphate, carboxyl and amino group in the biomass and also the chemistry of the metal. Uptake of anion is favored at low pH with range of 1-3 whereas action at higher pH at range of 5-8 (Ma and Tobin, 2004). For Pb²⁺ removal, optimized value are found to be around 5 and 6, where in this range, adsorption activity will be optimum and higher

metal ions can be removed from the prepared heavy metal solution (Witek-Krowiak et al, 2011).

2.3.2 Biomass loading

Different percentage of heavy metal ion removal can be observed through the manipulation of biomass loading. Amount of biomass resembles the amount of binding sites that available for adsorption of heavy metal ions (Saeed et al, 2005). From a study, it is shown that effect of biosorption can be seen through various biosorbent dosages ranging from 0.6-4.0 g/L. When the biosorbent dosage increases, the biosorption yield is increased until certain value. The optimum biosorption observed was at 1.8 g/L (Tunali Akar et al, 2012).

2.3.3 Contact time

Contact time is the elapsed time required the liquid medium to have contact with the adsorbent. Typical biosorption kinetics exhibits a rapid initial uptake, followed by slower process. This might be due to higher availability of active sites on the adsorbent which is gradually being occupied and slows the process. After optimum reached, the amount of bound metal ions did not change during the course of the process (Saeed et al, 2005; Witek-Krowiak et al, 2011).

2.3.4 Initial concentration of heavy metal

The initial concentration of adsorbate or heavy metal ion concentration in liquid influences the removal efficiency through a combination factor such as availability of

specific surface functional groups and ability of it to bind heavy metal ions. The effect of initial concentration of adsorbate is that it can act as a driving force to overcome mass transfer resistance for heavy metal ions transport between the solution and the surface of biomass (Arief et al, 2008). In a study using *Cucumis melo*, the equilibrium data for Pb²⁺ biosorption fits well to Langmuir model when the initial concentration are ranged from 100-500 mg/L (Tunali Akar et al, 2012).

2.4 Mechanism of biosorption

This process involves the presence of solid phase, which is the adsorbent itself and liquid phase, which is the adsorbate. Due to high affinity of sorbent towards the metal ions species, the latter is attracted and bound rather complex process affected by several mechanisms (Sud et al, 2008). Specific ion mechanism is observed on the sorption of heavy metal ions onto algae, bacteria and higher plants, which involves replacement of protons, alkaline earth, alkali or other cations, by heavy metals. It is proven through Langmuir isotherm that sorption stops at monolayer, consistent with specific and strong sorption onto specific site (Schneider et al, 2001). Other alternative is the surface precipitation of condensation of heavy metal hydroxides on the biosurface. The precipitation is caused by accumulation of heavy metals within the diffuse part of electrical double layer. The concentration of heavy metal ions within the layer can be calculated using the Boltzmann equation, as shown in equation (2.4):

$$C_i(\text{surface}) = C_i(\text{bulk}) \exp\left(\frac{-zF\varphi}{RT}\right) \quad (2.4)$$

Where $C_i(\text{surface})$ is the concentration of species i on the surface, $C_i(\text{bulk})$ is the concentration of species i in the bulk solution, z represent the formal charge on the cation, F is Faraday constant, φ is delta Faraday number, R is gas constant and T is the absolute

temperature (Schneider et al, 2001). For process of biosorption of heavy metal ions by microorganism, there are two mechanism involved, which are the initial metal ion uptake due to surface binding on the cell walls and subsequent slow active uptake due to membrane transport of metal ion into the cell. The actual attachment of the metal ion on the cellular surface includes complexation, physical and chemical adsorption. Considering the complexation, the polysaccharides that form matrix around the cell maintains extensive complexing capacity for heavy metal and ion exchange properties. This characteristic contributes to the initiation of adsorption process (Sağ and Kutsal, 1995).

2.5 Adsorption isotherms

Isotherms describe the interaction of solutes with adsorbent and are critical in optimizing the use of the adsorbent. The analysis of equilibrium adsorption isotherm data were carried out by fitting them to different isotherm models to find a suitable model to describe the experimental data.

2.5.1 Langmuir isotherm model

Langmuir isotherm was derived originally from the biosorption on solid surface of gas molecules or metal ions. This model developed based on two assumptions. First, the adsorption occurs on a homogeneous surface which each molecule possess constant enthalpies and sorption activation energy without any interaction between adsorbed molecules (Wibowo et al, 2017). Second, the adsorption is considered as monolayer adsorption, in which the adsorption layer is one molecule in thickness with no relocation

of the adsorbate in the surface of adsorbent, even on adjacent sites (Vijayaraghavan et al, 2006).

Langmuir isotherm model is given by equation (2.5) and can be expressed in linear form as shown in equation (2.6).

$$q_e = \frac{k_L C_e q_{\max}}{1 + k_L C_e} \quad (2.5)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} k_L} + \frac{C_e}{q_{\max}} \quad (2.6)$$

where

k_L = equilibrium constant of Langmuir model

q_{\max} = maximum adsorption capacity

q_e = amount of adsorbate in the adsorbent at equilibrium

C_e = metal concentration in the solution at equilibrium

2.5.2 Freundlich isotherm model

The Freundlich isotherm model made of the assumption that the adsorption occurs on a heterogeneous surface with interaction between adsorbed molecules (Günay et al, 2007). The adsorption isotherm model can be applied for multilayer model and not restricted to the formation of monolayer adsorption (Foo and Hameed, 2010). There is a suggestion for this isotherm model where adsorption energy is not constant but exponentially decrease upon the completion of adsorption process (Wibowo et al, 2017).

Freundlich isotherm model is given by equation (2.7) and can be expressed in linear form as shown in equation (2.8).

$$q_e = K_f C_e^{1/n} \quad (2.7)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2.8)$$

where

K_f = Freundlich isotherm constant

n = adsorption intensity

q_e = amount of adsorbate in the adsorbent at equilibrium

C_e = metal concentration in the solution at equilibrium

2.6 Kinetic models

2.6.1 Pseudo-first-order kinetic model

Reaction rate is expressed in terms of first order reaction for unimolecular and multi-molecular reaction, which means that the reaction rate is proportional to the concentration of a single reactant raised to the first power. The general equation for pseudo-first-order kinetic model is expressed in equation (2.9).

$$\ln(Q_e + Q_t) = \ln Q_e - k_1 t \quad (2.9)$$

Where Q_e and Q_t are the adsorption capacities at the equilibrium and at given time (t) respectively (mg/g), k_1 is the rate constant of pseudo-first-order adsorption. For analysis, a plot of $(Q_e + Q_t)$ against time (t) is used for k_1 and Q_e . The correlation coefficient (R^2)

obtained from the plot determines whether the kinetic model fits perfectly the adsorption data (Özer and Özer, 2003; Vegliò et al, 2003).

2.6.2 Pseudo-second-order kinetic model

Pseudo-second-order kinetic model can be expressed as in equation (2.10)

$$\frac{dq_t}{dt} = k_2(Q_e + Q_t)^2 \quad (2.10)$$

Where k_2 is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$), Q_e and Q_t are the adsorption capacities at the equilibrium and at given time respectively (mg/g). For boundary conditions $t = 0$ to $t = t$ and $Q_t = 0$ to $Q_t = Q_t$, the integrated form is shown in equation (2.11)

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + k_2 t \quad (2.11)$$

And by rearranging the equation, linear form can be obtained as in equation (2.12) (Özer and Özer, 2003; Vegliò et al, 2003)

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (2.12)$$

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

List of chemicals used for this study are summarized in the Table 3.1.

Table 3.1 List of chemicals used in this study.

No	Materials / Chemicals	Principle of use
1	Stem of <i>Manihot esculenta</i>	Biosorbent
2	Lead (II) nitrate	Adsorbate
3	Sodium hydroxide (NaOH) solution, 0.1 M	pH control
4	Hydrochloric acid (HCl) solution, 0.1 M	pH control
5	Deionized water	Preparation of solutions, adsorbates and biosorbents

3.2 Equipments

List of equipments used for this study are summarized in the Table 3.2.

Table 3.2 List of equipments used in this study.

No	Equipments	Principle of use
1	Fourier Transform Infrared Spectroscopy (FTIR)	Determine the availability of certain surface functional group as part of the structure of biosorbents.
2	Atomic Absorption Spectroscopy (AAS)	Determine the concentration of metal in the sample solution.
3	Oven	Biosorbent preparation.
4	Shaker	Batch adsorption process.
5	Glasswares	Used to conduct the experiment.