THERMODYNAMIC STUDIES ON BIOSORPTION OF LEAD BY PALM SHELL ACTIVATED CARBON

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A project report submitted in partial fulfilment of the
requirements for the award of the degree of
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DECLARATION

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

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APPROVAL FOR SUBMISSION

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Specially dedicated to
my beloved family and friends

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ABSTRACT

The toxicity of lead, Pb(II) on living mechanisms has led to severe ecological and health issues. Conventional methods including ion exchange and precipitation are commonly applied in treating heavy metal, however they are not eco-friendly and expensive. In contrast, biosorption technique, which is defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake, is found to be more efficient in mitigating heavy metal pollution issue. This paper reviews the capability of palm shell activated carbon as biosorbent in removing Pb (II) using dilute aqueous solution. The thermodynamic parameters of biosorption process were evaluated by examining the enthalpy and standard free energy. Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) was used in the lab work, at which the effects of temperature, initial metal concentrations and contact time towards biosorption were investigated. Results showed that the optimum temperature for biosorption process was 50 ℃ whereby active binding sites in the biosorbent would be damaged at high temperature (60 ℃). Also, the adsorption capacity was found to be higher at low concentration. Furthermore, it was observed the amount of lead ions uptake increased over a period of time because the high solute concentration gradient and the adsorption site were unoccupied. The exhibited Langmuir model fitted well to the adsorption data of biosorption of lead (II) ions onto the palm shell activated carbon at 30, 40, 50 and 60 ℃, whereas Freundlich model is more suitable for the experiment at 20 ℃. Also, the adsorption process was found to be spontanenous as the values of ΔH^o and ΔS^o were positive whereas the ΔG^o value was negative. The findings of this research have proved that biosorption process can be very useful in removing the heavy metals, thus more future work and researches should be done in order to improve the efficiency of biosorption process.

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LIST OF SYMBOLS / ABBREVIATIONS

As	Arsenic
Cd	Cadmium
Hg	Mercury
Pb	Lead
b	Adsorption equilibrium constant
C_i	Initial concentration of metal ion (mg/L)
C_e	Final concentration of metal ion (mg/L)
ICP – OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
K_F	Freundlich constant
n	Freundlich constant
m	Mass of biosorbent (g)
MW	Molecular weight
q	Metal uptake (mg/g)
qH	Function of metal accumulated
q_{max}	Fixed number of surface sites in the sorbent (mg/g)
R	Ideal gas constant (8.3145 J/mol·K)
R^2	Linear regression coefficients
T	Temperature (K)
ΔG^o	Gibbs free energy
ΔH^o	Enthalpy
ΔS^o	Entropy

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CHAPTER 1

INTRODUCTION

1.1 Heavy Metal Pollution

The increase of industrial activities has attracted the public attention to various environmental pollution problems that has caused the deterioration of ecosystems with the accumulation of many pollutants, such as toxic metals. For instance, heavy metals are discharged from different types of industries such as ceramic and glass manufacturing, storage batteries, textile and metallurgical processes. Basically, heavy metals are metallic elements which have higher atomic weight and greater density than water. There are more than 20 heavy metals, and four of them are of particular concern to human health, namely lead (Pb), cadmium (Cd), mercury (Hg) and inorganic arsenic (As). Heavy metals are not biodegradable and persistent in the environment (MacFarlene and Burchett, 2001).

Heavy metals enter into the environment mainly via three routes, which are through deposition of atmospheric particulates, disposal of metal enriched sewage sludges as well as sewage effluents and by-products from metal mining processes. Heavy metals can be emitted into the environment by both natural and anthropogenic sources. The major causes of emission are the anthropogenic sources, specifically mining operations (Hutton and Symon, 1986). The emitted metals are likely to persist in the environment even longer after mining activities have ceased. Through mining activities, water bodies are most emphatically polluted, as these metals may leach to sloppy areas and they are carried by acidic water downstream.

Heavy metal pollution represents a severe ecological and health problem due to the toxic effect of heavy metal ions on living organisms and their bioaccumulation throughout the food chain. For example, heavy metal pollution of surface and underground water sources will lead to considerable soil pollution. When agricultural soils and water are polluted, these metals are taken up by plants and animals and are consequently accumulated in their tissues (Trueby, 2003). As a result, humans are also exposed to heavy metals by consuming contaminated plants and animals, which result in a range of biochemical disorders. This proves that all living organisms within the same ecosystem are contaminated along their cycles of food chain.

Human exposure to heavy metals has risen dramatically in the last 50 years as a result of an exponential increase in the use of heavy metals in industrial processes and products (Fourest and Roux, 1992). According to Figure 1.1, the production of heavy metals increased nearly 10 times between year 1850 and 1990, with emissions rising in tandem. Nowadays, many occupations involve daily heavy metal exposure; it is observed that there are over 50 professions entail exposure to lead and mercury. For example, lead has been used in plumbing, and lead arsenate has been used to control insects in apple orchards.

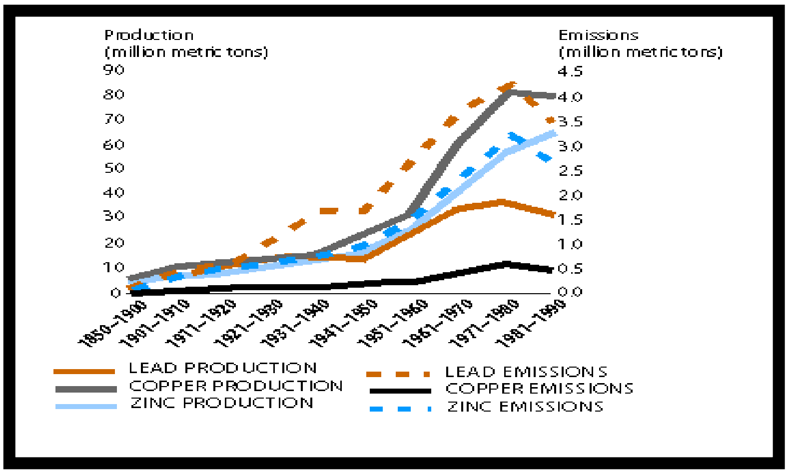

Figure 1.1: Productions and Emissions of Heavy Metals

Inhalation of heavy metal particles, even at levels well below those considered non-toxic, can have serious health effects. Virtually all aspects of human and animal immune system functions are compromised by the inhalation of heavy metal particulates. Toxic metals can enhance allergic reactions and even cause genetic mutation. Moreover, heavy metals can also increase the acidity of the blood. The body draws calcium from the bones to help restore the proper blood pH. Table 1.1 illustrates the major health effects towards human which appear as a result of heavy metal pollution.

Table 1.1: Heavy Metal Pollutant and its Negative Effects

Heavy Metal Pollutant	Major Sources	Effects on Human Health
Lead	Automobile, coal burning, paint, pesticide, smoking.	Liver, kidney, gastrointestinal damage, mental retardation in children
Mercury	Pesticide, paper industry, batteries	Damage to nervous system, protoplasm poisoning
Cadmium	Welding, nuclear fission plant, pesticide, electroplating	Bronchitis, cancer, kidney damage, gastrointestinal disorder
Arsenic	Fungicides, pesticides, metal smelters.	Bronchitis, dermatilis

Therefore, the removal and recovery of heavy metals is very important with respect to the environmental and economical considerations. There are conventional physicochemical techniques including ion exchange and precipitation processes for heavy metal removal from waste streams. However, these methods are expensive, not eco-friendly and inefficient for metal removal from dilute solutions containing from 1 to 100 mg/L of dissolved metal.

1.2 Biosorption Process

The search for new technology is strongly required as the conventional methods do not provide great solutions towards heavy metal pollution issue. In past decades, biosorption technique has emerged as a useful technique along with other conventional methods for metal removal.

In general, biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992). The term biosorption indicates a property of certain types of dead (inactive) or living (active) microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions. Biomass exhibits this property, acting just as a chemical substance, as an ion exchange of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria which is responsible for this phenomenon.

The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases (Fourest and Roux, 1992).

The use of biological materials, including living and non-living microorganisms, in the removal and possibly recovery of toxic or precious metals from industrial wastes has gained important credibility during recent years. This is because of the good performance, minimization of chemical/biological sludge volume and low cost of these materials. Some of the common examples of biosorbent include algae, fungi, activated carbon, bacteria and so forth.

Typically, strong biosorbent behaviour of certain micro-organisms towards metallic ions is a function of the chemical make-up of the microbial cells. This type of biosorbent consists of dead and metabolically inactive cells. Some types of biosorbents are capable of binding and collecting the majority of heavy metals with no specific activity, whereas others are specific for certain metals (Volesky and Holan, 1995).

Fungi are used as biosorbent as they have been proved to be economical and efficient for the removal of toxic metals from dilute aqueous solutions by biosorption. This is owing to the advantage of fungal biomass for having a high percentage of cell wall material, which provides good metal binding properties (Horikoshi et al., 1981). Besides, fungal biomass is also easily available from the food and antibiotic industries.

Algae are also largely used as biosorbents. Algae have low nutrient requirements and they produce a large biomass volume. One of the great advantages of algae is that they generally do not produce toxis substances. The binding of metal ions on algal surface usually depends on different conditions such as algal species, ionic charge of metal ion alongside chemical composition of the metal ion solution (Gupta et al., 2001).

Activated carbon is another type of materials that can be used in biosorption process. In general, activated carbon is highly porous with immense surface area. It is a highly effective filtering material. Activated carbon acts like a sponge, sucking contaminates from liquids and gasses. It can remove many organic and some inorganic substances from common industrial polluting streams.

1.3 Objectives of Study

Lead, Pb (II) is widely known as one of the most dangerous substances that cause long term effects on human health and the environment. Its toxicity affects microorganisms by retarding the heterotrophic breakdown of organic materials and damage to human nerve system. Although conventional methods for Pb (II) removal are well established, they are generally costly and use chemicals that would generate wastes which may be hazardous. Hence, green and low cost biosorption technique may be desirable for rapid lead removal from industrial effluent.

In this study, the capability of palm shell activated carbon as biosorbent in removing Pb (II) is evaluated using dilute aqueous solution. One of the major objectives of this study is to evaluate the thermodynamic parameters of biosorption process by determination the enthalpy and standard free energy. Furthermore, this project is also aimed to determine the biosorption potential of biosorbent mechanisms of adsorption by performing a batch experimental process. This experiment also targets to:

1. Evaluate effect of temperature (20 – 60 ℃).
2. Examine effect of initial metal ion concentrations.
3. Determine effect of contact time.
4. Characterise the biosorption process in terms of thermodynamic parameters.

CHAPTER 2

LITERATURE REVIEW

2.1 General

Water pollution is a major environmental problem faced by modern society that leads to ecological disequilibrium and health hazards. Heavy metal ions including lead, copper, nickel, cadmium and chromium are often found in industrial wastewater. Their presence results in acute toxicity to aquatic and terrestrial life, including humans. Thus, the discharge of effluents into the environment is a chief concern. Many conventional methods, such as chemical precipitation, ion exchange, membrane processes and so forth, have been used to remove heavy metal ions from various aqueous solutions. Nevertheless, the application of such processes is often restricted because of technical or economic constraints.

Biosorption is one of the many alternative methods that can be categorised as a green technology for heavy metals removal from industrial effluents. Biosorbent offers several advantages including low cost, easy available as by-products from enzymes fermentation industry or easily grown producing high yields of biomass. In addition, it can minimize the use of chemicals, has a high potential for regeneration and capable of removing substantial amount of heavy metals from diluted effluents.

Mechanisms involved in biosorption can be classified based on certain criteria, such as cell metabolism. A successful biosorption process requires preparation of good biosorbent. Although many biological materials can bind heavy metals, only those with sufficiently high metal-binding capacity and selectivity for heavy metals are suitable for use in a full-scale biosorption process. A large number of biomass types have been investigated for their metal binding capability under various conditions. Volesky and Holan (1995) have presented an exhaustive list of microbes and their metal-binding capacities. The published work on testing and evaluating the performance of biosorbents offered a good basis for looking for new and potentially feasible metal biosorbents. Another challenge is that the application of biosorption is facing up with great difficulty (Tsezos, 2001). Great efforts have to be made to improve biosorption process, including immobilization of biomaterials, improvement of regeneration and re-use, optimization of biosorption process and so forth.

2.2 Lead

Lead is naturally present in the earth crust in small concentrations. It is a soft, grayish or silvery-white metal in Group 14 of the periodic table. Lead is very malleable, ductile and considered as a poor conductor of electricity. Besides, it has no characteristic taste or smell. Metallic lead does not dissolve much in water and does not burn. Some natural and man-made substances contain lead, but do not look like lead in its metallic form. Lead (II) is a well known highly toxic substance and is a cumulative poison, exposure to which can produce a wide range of adverse health effects. Both adults and children can suffer from the effects of lead poisoning, but childhood lead poisoning is much more frequent.

2.2.1 Sources of Lead

There are many ways in which humans are exposed to lead, for example, through deteriorating paint, household dust, bare soil, air, drinking water, food, ceramics, home remedies, hair dyes and other cosmetics. Most of this lead is of microscopic size, invisible to the naked eye.

Drinking water is also a major source of lead exposure, estimated to be responsible for approximately 20 percent of the total daily exposure experienced by the majority of the U.S. population (Russell Jones, 1989). Drinking water can also sometimes contribute to elevated blood lead levels. Lead can leach into drinking water from certain types of plumbing materials (lead pipes, copper pipes with lead solder, and brass faucets). While water is usually not the primary source of exposure to lead for children with elevated blood lead levels, it is nevertheless important to note that formula-fed infants are at special risk of lead poisoning, if their formula is made with lead-contaminated water.

The 1986 amendments to the federal Safe Drinking Water Act banned the use of lead solder and leaded pipes from public water supply systems and plumbing, and limited faucets and other brass plumbing components to no more than eight-percent lead. Leaded plumbing components are still in used in schools and day care centres and this certainly pose a significant contribution to lead in drinking water in these buildings (Berkowitz, 1995). Normally, about 10% dietary lead intake comes from drinking water. However, the concentration of lead in water when comes out of tap, may be very different from when leaves the pumping station. The reason for the high lead content found in some water supplies is that many houses still have old lead pipes, which release lead into drinking water (Bryce-Smith and Waldron, 1974). In a retrospective study in Glasgow, Scotland, the water had been officially reported to contain abnormally high levels of lead. Beattie et al. (1975) found that mentally retarded children were significantly more likely than other echildren, not only to have high lead levels in their drinking water in their first year of life, but also to have mothers who had been exposed to such high concentration in pregnancy.

Lead can enter the body through ingestion. Nonetheless, the effective toxicity of lead entering orally is not considered as high as that of lead entering through the lungs (Stephens and Waldron, 1976). The highly unnatural lead levels in the modern diet result from the use of lead in food technology e.g. from the rims of food cans as well as to some extent from lead-glazed pottery, particularly if the glaze is chipped, cracked or improperly applied (Houk, 1985). Sometimes it is also used in flour mills as lubricants. Most lead pollution found in food is caused directly by the fall-out of air-borne lead particles. Nature has provided natural barriers in the roots of food crops and grass, which largely prevent the uptake of lead found in soil. However, air-borne lead fall-out is especially dangerous because it bypasses these natural barriers. As lead appears to have a particularly affinity for plant surface tissue and is only partially removed by rain or washing. Healy and Aslam (1981) reported that consuming such contaminated fruit or vegetables, as well as meat from farm animals grazed on polluted grass, can result in a considerable body burden of lead.

2.2.2 Health Effects of Lead

There are many different health effects associated with elevated blood lead levels. Young children under the age of six are especially vulnerable to lead's harmful health effects, because their brains and central nervous system are still being formed. For them, even very low levels of exposure can result in reduced IQ, learning disabilities, attention deficit disorders, behavioural problems, stunted growth, impaired hearing, and kidney damage. At high levels of exposure, a child may become mentally retarded, fall into a coma, and even die from lead poisoning. Within the last ten years, children have died from lead poisoning in New Hampshire and in Alabama (Kaewsarn and Yu, 2001). Lead poisoning has also been associated with juvenile delinquency and criminal behaviour.

In adults, lead can increase blood pressure and cause fertility problems, nerve disorders, muscle and joint pain, irritability, and memory or concentration problems. It takes a significantly greater level of exposure to lead for adults than it does for kids to sustain adverse health effects. Most adults who are lead poisoned get exposed to lead at work. Occupations related to house painting, welding, renovation and re-modelling activities, smelters, firing ranges, the manufacture and disposal of car batteries, and the maintenance and repair of bridges and water towers, are particularly at risk for lead exposure. Workers in these occupations must also take care not to leave their work site with potentially contaminated clothing, tools, and facial hair, or with unwashed hands.

Otherwise, they can spread the lead to their family vehicles and ultimately to other family members.

Moreover, when a pregnant woman has an elevated blood lead level, lead can easily be transferred to the fetus, as lead crosses the placenta. In fact, pregnancy itself can cause lead to be released from the bone, where lead is stored often for decades after it first enters the blood stream. Once the lead is released from the mother's bones, it re-enters the blood stream and can end up in the fetus. In other words, if a woman had been exposed to enough lead as a child for some of the lead to have been stored in her bones, the mere fact of pregnancy can trigger the release of that lead and can cause the fetus to be exposed. In such cases, the baby is born with an elevated blood lead level.

2.3 History of Biosorption

The ability of living microorganisms to take up metals from aqueous solution was investigated as early as 18th and 19th centuries, it is only during the last 3 decades that living or non-living microorganisms have been used as adsorbents for removal and recovery of substances from aqueous solutions. The earliest technological applications of biosorption techniques involved sewage and wastewater treatment. The first patent for a biosorption apparatus used for biological treatment of wastewater was registered by the Ames Crosta Mills & Company Ltd. in 1973.

Life science tests principally focus on the toxicological effects and accumulation of heavy metals in microorganisms. Meanwhile, environmental scientists and engineers use the capability of microorganisms as means of monitoring heavy metal pollution and for removal or recovery of metals from metal-bearing wastewaters. Some review papers have reported that the first quantitative study on metal biosorption was done by Hecke (1956), who described the copper uptake by fungal spores of *Tilletia tritici* and *Ustilago crameri* in year 1902. Similar studies were also completed by Pichler and Wobler (1922), in which uptake of Ag, Cu, Ce and Hg by corn smut were evaluated.

It was reported that activated sludge efficiently removed radioactive metals like plutonium-239 from contaminated domestic wastewater in year 1949 (Ruchoft, 1949). In year 1971, the practical use of biosorption technology for monitoring trace heavy metals in the environment was observed (Goodman and Roberts, 1971). Subsequently, Neufeld and Hermann (1975) studied the kinetics of biosorption by activated sludge and found rapid uptakes of Cd, Hg and Zn in the first few minutes, followed by a slow uptake over the next 3 hours. The first patent on the use of biosorption technology for removing uranium or thorium ions from aqueous suspension/solution was granted to Volesky and Tsezos in year 1982 (Volesky and Tsezoz, 1982).

2.4 Biosorbent Materials

The work of Adams and Holmes (1935) represented not only the threshold in ion-exchange chemistry but also an early attempt at biosorption. They described the removal of Ca and Mg ions by tannin resin, black wattle bark (*Acacia mollissima*), which were treated directly so that the condensation product was fixed on the woody fibers (Adams and Holmes, 1935). Strong biosorbent behavior of certain types of microbial toward metallic ions is a function of the chemical makeup of the microbial cells of which it consists. It is necessary to emphasize that this type of active biomass consists of dead and metabolically inactive cells. This aspect is particularly important when it comes to the process application, whereby new biosorbents represent “chemicals” capable of sequestering a relatively large amount of the metal (Volesky, 1990).

Some laboratories have used easily available biomass whereas others have isolated specific strains of microorganisms and some have also processed the existing raw biomass to a certain degree to improve biosorption properties (Volesky and Kuyucak, 1988). Biosorption experiments have focused attention on waste materials, which are by products or the waste materials from large scale industrial operations. For example, the waste mycelia available from fermentation processes and activated sludge from sewage treatment plants used dewatered waste activated sludge from a sewage treatment plant for the biosorption of zinc from aqueous solutions (Hammaini, 2003).

Activated carbon is a crude material from graphite. One of the applications of this substance is as pencil lead. Activated carbon differs from graphite by having the random imperfect structure, which is highly porous over a broad range of pore size from visible cracks and crevices to molecular dimensions. The graphite structure gives the carbon a very large surface area, which allows the carbon to adsorb a wide range of compounds. Activated carbon has the strongest physical adsorption forces of the highest volume of adsorbing porosity of any material known to mankind. It is a black, solid substance resembling granular or powdered charcoal and extremely porous with a very large surface area. Generally, activated carbon consists mainly of carbon (87 to 97%) and other elements such as hydrogen, oxygen, sulfur and nitrogen. It can also adsorb various substances both from gas and liquid phases. This ability justifies it as an adsorbent (Halena, Andrej & Jerzy, 1991).

In recent decades, activated carbon has been popular used by many scientists due to the effectiveness for the removal of heavy metal ion at trace quantities in biosorption process. Additionally, activated carbon has unquestionably been the most popular and widely used as adsorbent in wastewater treatment employed throughout the world. However, activated carbon remains a costly material since the higher the quality of activated carbon, the greater will be its cost (Babel and Kurmiawan, 2003). In that case, the search of low cost activated carbon for the wastewater treatment becomes essential. In Malaysia, the palm oil industry generates huge amounts of palm shell, a large portion of it is either burned in open air or dumped in area adjacent to the mill, which creates environmental and disposal problems. Therefore, application of palm shell activated carbon as an adsorbent offers highly effective technological means in dealing with pollution of heavy metals and solving palm shell disposal problems, with minimum investment required (Najua et al., 2008). Figure 2.1 shows the sample of activated carbon.

Figure 2.1: Activated Carbon

Aspergillus niger is a fungi which has already been used industrially in producing citric acid. Citric acid is used to be produced by extraction from lemons and other citrus fruits, but today microbial fermentation is a widely spread method and almost all citric acid is produced this way. In these fermentation industries *Aspergillus niger* also comes out as a waste product which makes it suitable for investigations of the biosorption capacity. It is a dark colored fungi which is known as black mold. Usually it could be seen at moldering food, as illustrated in Figure 2.2 and Figure 2.3 (Frida Skult, 2009). Fruits and vegetables are mostly affected by the mold, for example grape fruits, onions and peanuts.

Moreover, *Aspergillus niger* is a common saprophytic fungus in terrestrial environments and it has already been used in other studies to adsorb heavy metals and dyes. A study made by Khalaf (2008) focused on textile wastewater treatment by non-viable biomass of *Aspergillus niger* and the alga *Spirogyra*. The dye solution contained the commercial Synazol reactive dye, a mixture solution with one red and one yellow dye. The biosorption experiments were performed at different initial pH (1 – 8), different temperature (15 – 45℃) and different biomass loading (4 – 12g/L). The *Aspergillus niger* and *Spirogyra* biomass were inactivated by either gamma radiation or autoclaving. Autoclaving resulted in the highest biosorption values. If the cells of the fungi are active, they are easily affected by toxic compounds and chemicals in the waste water and they may then pollute the environment by releasing toxins or propagules.

Another problem when dealing with active biomass is that it could not be stored at room temperature for long time periods before it may decay. It is easier to store and transport the biomass when it is dead and is dried. The study made by Fu and Viraraghavan (2000 and 2002) showed that autoclaved biomass of *Aspergillus niger* even had higher biosorption capacity compared to living biomass (Khalaf, 2008). The surface characteristics of the biomass are changed in a way that improves the dye biosorption capacity. A possible explanation to that is that the autoclaving disrupts the biomass structure and then exposes the adsorption sites even more (Khalaf, 2008).

Figure 2.2: *Aspergillus niger* Growing on Czapek Dox Agar in a Petri Dish

Figure 2.3: Onion with Black Mold

Most bacteria can be divided into Gram-positive and Gram-negative groups based on their cell wall structure and response to the Gram staining. *Bacillus subtilis* has a well-studied gram-positive wall. If the bacterium is grown in the presence of phosphate, its wall has essentially two chemical components, namely peptidoglycan and teichoic acid. The use of microorganisms to treat aqueous streams for the removal, concentration and recovery of toxic and valuable heavy metals although receiving increased attention in the last decades, the removal of heavy metal from municipal and industrial wastes by biological treatment systems has continued to be of interest. Bacteria surfaces have great affinity to adsorb and precipitate metals resulting in metal concentration on bacterial surface. Bacteria reside in many geological settings from soil systems and groundwater aquifers to hydrothermal vents and deep sedimentary basins.

Bacteria are ubiquitous in low temperature surface environments. They have a high surface area per unit weight owing to its small size. Thus, bacteria are believed to play a significant role in the cycling of multivalent inorganic cations, such as lead or cadmium ions which can sorb onto their surfaces (Xavier Chatellier, 2004). In many of these systems, the cell walls of bacteria can represent a large percentage of the total surface area exposed to fluid. Bacteria cell wall surfaces exhibit a strong tendency to adsorb aqueous metal cations. Therefore, bacteria have the potential control major and trace metal geometry in water-rock systems through adsorption reactions (Fowle, 1999).

2.5 Biosorption Mechanism

Biomass acts as a chemical substance or ion exchange agent of biological origin. The bacterial cell wall is the first component that comes into contact with metal ions where the solutes can be deposited on the surface or within the cell wall structure (Beveridge and Murray, 1976). Since the mode of solute uptake by dead or inactive cells is extracellular, the chemical functional groups of the cell wall play vital roles in biosorption. Several functional groups, including amine, phosphonate, carboxyl and hydroxyl groups, are present on the bacterial cell wall because of the nature of the cellular components (Doyle et al., 1980). The functional groups are negatively charged and abundantly available, carboxyl groups actively participate in the binding of metal cations. Golab and Breitenbach (1995) indicated that the carboxyl groups of the cell wall peptidoglycan of Streptomyces pilosus were responsible for the binding of copper.

Also, amine groups are very effective at removing metal ions, as they not only chelate cationic metal ions, but also adsorb anionic metal species or dyes via electrostatic interaction or hydrogen bonding (Doyle et al., 1980). Meanwhile, Kang et al. (2007) observed that amine groups protonated at pH 3 and attracted negatively charged chromate ions via electrostatic interaction. In general, increasing the pH will raise the overall negative charge on the surface of cells until all the relevant functional groups are deprotonated, which favors the electrochemical attraction and adsorption of cations. Anions would be expected to interact more strongly with cells with increasing concentration of positive charges, due to the protonation of functional groups at lower pH values. The solution chemistry affects both bacterial surface chemistry and metal/dye speciation. Metal ions in solution undergo hydrolysis as the pH increases. The extent of it differs at different pH values and with each metal, but the usual sequence of hydrolysis is the formation of hydroxylated monomeric species, followed by the formation of polymeric species, and then the formation of crystalline oxide precipitates (Baes and Mesmer, 1976).

The complex structure of microorganisms implies that there are many ways for the metal to be taken up by the microbial cell. The biosorption mechanisms may be classified based on various criteria. According to the dependence on the cell's metabolism, biosorption mechanisms can be divided into:

1. *Metabolism dependent*: Transport of the metal across the cell membrane yields intracellular accumulation, which is dependent on the cell's metabolism. This means that this kind of biosorption may take place only with viable cells. It is often associated with an active defense system of the microorganism, which reacts in the presence of toxic metal.

2. *Non-metabolism dependent*: During non-metabolism dependent biosorption, metal uptake is by physico-chemical interaction between the metal and the functional groups present on the microbial cell surface. This is based on physical adsorption, ion exchange and chemical sorption, which is not dependent on the cells' metabolism. In the case of precipitation, the metal uptake may take place both in the solution and on the cell surface (Ercole et al., 1994). Cell walls of microbial biomass, mainly composed of polysaccharides, proteins and lipids have abundant metal binding groups such as carboxyl, sulphate, phosphate and amino groups. This process i.e., non-metabolism dependent is relatively rapid and can be reversible (Kuyucak and Volesky, 1988). Furthermore, it may be dependent on the cells' metabolism if the microorganism produces compounds that favor the precipitation process. Meanwhile, precipitation may not be dependent on the cells' metabolism, if it occurs after a chemical interaction between the metal and cell surface.

According to the location where the metal removed from solution is found, biosorption can be categorised as:

1. *Extra cellular accumulation/ precipitation*: Among these mechanisms, extracellular accumulation/ precipitation may be facilitated by using viable microorganisms and cell-surface sorption which can occur with alive or dead microorganisms.

2. *Cell surface sorption/ precipitation*: Biosorption to cell walls and other structural components can result in immobilisation; whereas precipitation can be due to metabolite release or reduction, intracellular deposition alongside adsorption and entrapment of colloids and particulates. The overall system is also affected by reciprocal interactions between biotic and abiotic components of the ecosystem. To illustrate, abiotic influence on microbial diversity, numbers and metabolic activity, ingestion of particulates and colloids by biotic modification of physico-chemical parameters can lead to changes in the entire system.

3. *Intracellular accumulation*: Intracellular accumulation requires microbial activity (Aksu et al., 1991). The relative balance between such processes depends on the environment and associated physico-chemical conditions and the microbes involved as well as relationships with plants, animals and anthropogenic activities. Usually chemical equilibria between soluble and insoluble phases are influenced by abiotic components, including dead biota and their decomposition products, as well as other physico-chemical components of the environmental matrix such as water, pH, inorganic and organic ions, molecules, compounds and so forth.

2.5.1 Transport Across Cell Membrane

Heavy metal transport across microbial cell membranes may be mediated by the same mechanism used to convey metabolically important ions such as potassium, magnesium and sodium. The metal transport systems may become confused by the presence of heavy metal ions of the same charge and ionic radius associated with essential ions. This kind of mechanism is not associated with metabolic activity. Basically, bioaccumulation by living organisms comprises of two steps. The metabolism independent binding takes place where the metals are bound to the cell walls comes first, and it is followed by metabolism dependent intracellular uptake, whereby metal ions are transported across the cell membrane (Huang et al., 1990). In metabolism-independent process, live biomass and nutrient is not required for growth which make this process cost effective. Besides, it can eliminate the problems that encountered with nutrient disposal.

Physical adsorption takes place due to van der Waals' forces. It is reported that biosorption of heavy metal by dead biomasses of algae, fungi and yeasts takes place through electrostatic interactions between the metal ions in solutions and cell walls of microbial cells (Kuyucak and Volesky, 1988). Electrostatic interactions have been demonstrated to be responsible for copper biosorption by bacterium *Zoogloea ramigera* and alga *Chiarella vulgaris* (Aksu et al., 1992), and also for chromium biosorption by fungi *Ganoderma lucidum* and *Aspergillus niger*.

Cell walls of microorganisms contain polysaccharides and bivalent metal ions exchange with the counter ions of the polysaccharides. For example, the alginates of marine algae occur as salts of K^+, Na^+, Ca^{2+}, and Mg^{2+}. These ions can exchange with counter ions such as CO^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} resulting in the uptake of heavy metals (Kuyucak and Volesky, 1988). The copper uptake by fungi *Ganoderma lucidium* (Muraleedharan and Venkobachr, 1990) and *Aspergillus niger* was also up taken by ion exchange mechanism.

The metal removal from solution may also take place by complex formation on the cell surface after the interaction between the metal and the active groups. Aksu

(1992) hypothesized that uptake of copper by *Chlorella vulgaris* and *Zoogloea ramigera* takes place through both adsorption and formation of coordination bonds between metals and amino and carboxyl groups of cell wall polysaccharides. Complexation was found to be the only mechanism responsible for calcium, magnesium, cadmium, zinc, copper and Mercury accumulation by Pseudomonas syringae. Microorganisms may also produce organic acids (e.g., citric, oxalic, gluonic, fumaric, lactic and malic acids), which may chelate toxic metals result in the formation of metallo-organic molecules. These organic acids help in the solubilisation of metal compounds and their leaching from their surfaces. Metals may be biosorbed or complexed by carboxyl groups found in microbial polysaccharides and other polymers.

Precipitation may be either dependent on the cellular metabolism or independent of it. In the former case, the metal removal from solution is often associated with active defense system of the microorganisms. They react in the presence of a toxic metal producing compound, which favors the precipitation process. In the case of precipitation not dependent on the cellular metabolism, it may be due to the chemical interaction between the metal and the cell surface.

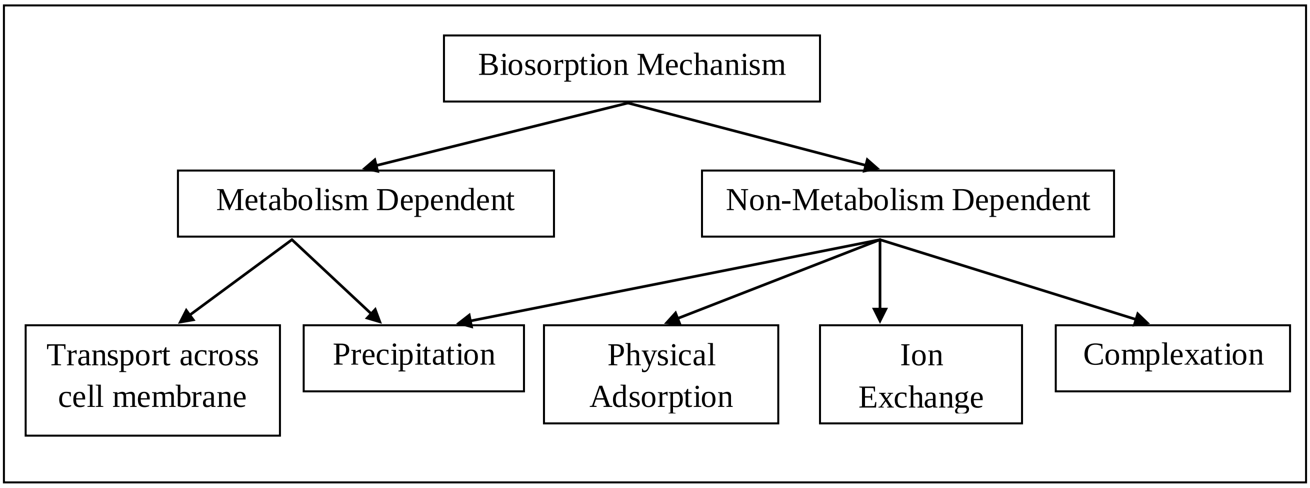

Figure 2.4 (a): Biosorption Mechanism Classified According to Dependence on the Cellular Metabolism.

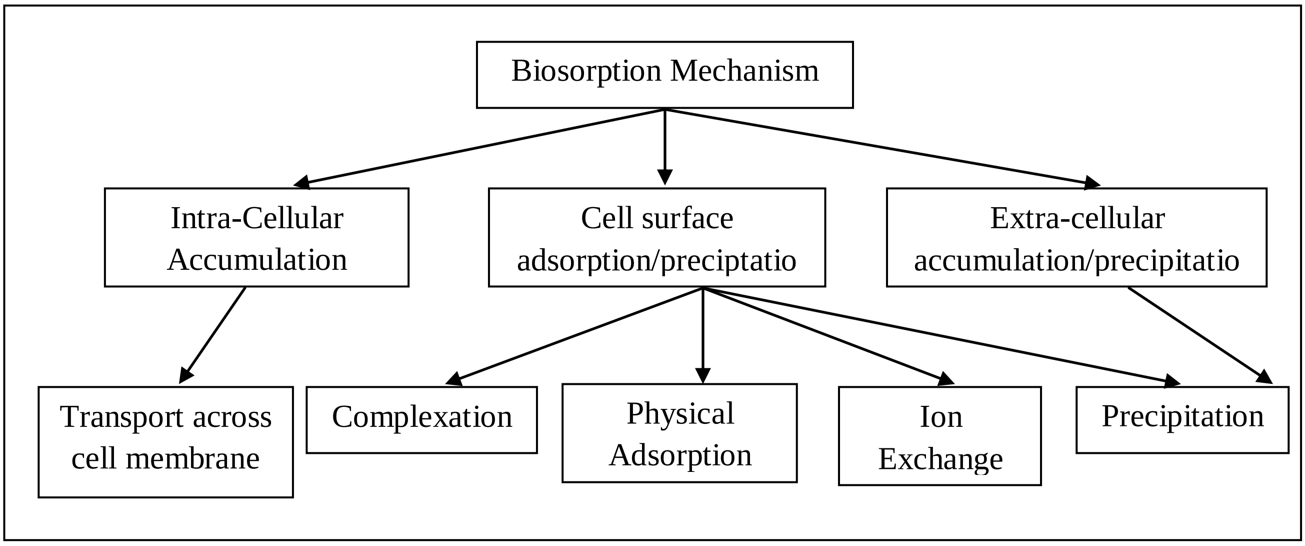

Figure 2.4 (b): Biosorption Mechanism Classified According to Location where Biosorption Occurs.

Figure 2.4 shows the biosorption mechanisms as classified by Veglio and Beolchini (1997), whereby Figure 2.4 (a) is classified according to the dependence on the cellular metabolism and Figure 2.4 (b) is categorised according to the location where biosorption occurs.

2.6 Factors Affecting Biosorption

The investigation of the efficacy of the metal uptake by the microbial biomass is essential for the industrial application of biosorption. It gives information about the equilibrium of the process which is necessary for the design of the equipment. The metal uptake is usually measured by the parameter 'q' which indicates the milligrams of metal accumulated per gram of biosorbent material. Meanwhile, parameter 'qH' is used as a function of metal accumulated, sorbent material used and operating conditions. There are several factors that can affect the biosorption process, namely pH, temperature, sorbent dose, contact time and metal ion concentration. These factors determine the overall biosorption performance of a given biosorbent, including its uptake rate, its specificity for the target, and the quantity of target removed. For this reason, the first step of almost all researches was to examine the individual or cooperative effects of various factors on biosorption (Modak, 1995 and Gupta, 2003).

2.6.1 Effect of pH

pH seems to be the most important parameter in the biosorption process. It affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Friis and Myers-Keith, 1986). Anirudvan and Krishnan (2004) observed that the pH of an adsorbent decreases with increase in acidic groups on the surface of the adsorbents. It is noticed that acid modification of the adsorbent gave a positive (acidic) surface charge for the adsorbent as the pH for the modified is lower than that of the unmodified surface. In general, as solution pH increases, the biosorption removal of cationic metals or basic dyes is enhanced, while that of anionic metals or acidic dyes is reduced. In some cases, a higher pH will cause precipitation of cationic metals, making neutral conditions essential in this case.

In this study, Hg (II), Cd (II) and Co (II) show high adsorption at basic pH values while Cr (VI) and Cu (II) and Pb (II) exhibit maximum adsorption under acidic conditions. Influence of pH on adsorption phenomena also related with the chemistry of the solution in which metal ions are present and on functional groups present on biosorbent. At very low and very high pH values the surface of the adsorbent would be surrounded mainly by hydrogen and hydroxyl ions. These positively and negatively charged ions may compete with the metal ions and as a result of which metal adsorption decreases that’s why metal ions show lesser adsorption at very high and very low pH value (Saeed and Iqbal, 2005). On the other hand, sometimes precipitation of metal ions as hydroxides also occurs at very high pH values which are not feasible for good adsorption. The potential binding sites in biosorbents are carbohydrates, amino groups, hydroxyl groups and carboxylic groups. These functional groups may be ionized or dissociated at different pH values.

2.6.2 Effect of Temperature

The metabolism of growing cells is strongly affected by temperature. However, biosorption by non-living biomass is metabolism independent, thus temperature is not expected to have a significant effect on the metal uptake (Modak and Natarajan, 1995). As temperature rises, the attractive forces between biomass surface and metal ions turn weak and the sorption decreases. In addition, the thickness of the boundary layer tends to decrease at higher temperature. This is because of the increased tendency of the metal ion to escape from the biomass surface to the solution phase (Aksu and Kutsal, 1991). Temperature seems to affect biosorption to a lesser extent within the range from 20 ℃ to 35 ℃ (Veglio and Beolchini, 1997). Biosorption removal of most adsorptive pollutants is endothermic, thus higher temperature usually enhances biosorption removal of the adsorbate through increases in its surface activity and kinetic energy (Vijayaraghavan and Yun, 2008). However, higher temperature can also cause physical damage to the biosorbent. Thus, room temperature is usually desirable for the biosorption processes.

2.6.3 Effect of Sorbent dose

The effect of adsorbent dosage on adsorption follows the same pattern where the rate of adsorption increases proportionally to the amount of adsorbent. Nevertheless, there is no significant increase in adsorption capacity beyond the optimal mass. In fact, it decreases slightly in some cases and it attains equilibria. Metal ion removal capacity of any adsorbent is directly related to the number of available binding sites. Therefore, greater available surface area and more binding sites can be attributed when the adsorbent dose increases (Radhika and Palanivelu, 2006). It is predicted that the interaction between adsorbent-adsorbent particles increases more compared to adsorbent-adsorbate particles at higher adsorbent dose (Akhtar et al., 2005). The interaction between particles of adsorbent may lead to aggregation of adsorbent and this aggregation can reduce the total available surface area resulting in decreased adsorption (Bhatti et al., 2007). Puranik suggested that at lower levels of adsorbent amount, higher adsorption is due to higher metal to adsorbent ratio, which decreases as adsorbent quantity increases (Puranik et al., 1999).

2.6.4 Effect of Metal Ion Concentration

Metal ion concentration is also one of the factors that affect the performance of biosorption process. Gadd et al. (1988) suggested that an increase in biomass concentration leads to interference between the binding sites. In the contrary, Fourest and Roux (1992) invalidated this hypothesis attributing the responsibility of the specific uptake decrease to metal concentration shortage in solution. Hence, this factor needs to be taken into consideration in any application of microbial biomass as biosorbent.

Biosorption is mainly used to treat wastewater where more than one type of metal ions would be present. Thus, the removal of one metal ion may or may not be influenced by the presence of other metal ions. To illustrate, the uranium uptake by biomass of bacteria, fungi and yeasts was not affected by the presence of manganese, cobalt, copper, cadmium, mercury and lead in solution (Sakaguchi and Nakajima, 1991). In contrast, the presence of Fe^{2+} and Zn^{2+} was found to influence uranium uptake by *Rhizopus arrhizus* (Tsezos and Volesky, 1982). Furthermore, cobalt uptake by different microorganisms seemed to be completely inhibited by the presence of uranium, lead, mercury and copper (Sakaguchi and Nakajima, 1991). It was observed that by increasing the adsorbate concentration in the solution, adsorption efficiency decreases. This may be explained by the fact that at very low concentrations of adsorbate, the ratio of available binding sites and adsorbate ions is high, so there is more chances to get adsorbed. Therefore, at low concentrations, adsorption capacity is high. On the other hand, when adsorbate concentration increases, binding sites become occupied more quickly because the amount of adsorbent is limited.

2.6.5 Effect of Contact Time

Contact time is an important parameter because this factor determines the adsorption kinetics of an adsorbate at a given initial concentration of the adsorbate. Initially adsorption increases when the contact time between two phases (adsorbent and solution containing adsorbate ions) is higher. Reaching the optimal value (specific in every case), maximum adsorption occurs, followed by an equilibrium state when there is no considerable increase or decrease in adsorption by increasing time span. The same pattern for different metal and adsorbent systems has also been reported by different researchers (Hanif and Akhtar, 2007). This may be justified by the fact that initially all the binding sites are available and adsorbate ions become easily bounded to these sites. As time passes more and more adsorbate ions get attached to these actives sites. When reaching to optimal time value, all the available adsorbent sites become saturated or occupied and after this a continuous process of adsorption and desorption starts and due to which no further or decrease in adsorption occurs.

CHAPTER 3

METHODOLOGY

The preparations of chemicals and materials involved in this project are discussed in this chapter. In batch adsorption experiments, 24 conical flasks were prepared to provide two sets of data, one set being the replicate control. The palm shell activated carbon used was purchased from a local manufacturer, namely Bravo Green Sdn. Bhd. Lead ions adsorption experiments onto palm shell activated carbon were carried out.

3.1 Preparation of Stock Solution

0.1M of lead (II) nitrate $Pb(NO_3)_2$ (R & M marketing Essex U.K. with MW=331.20g/mol.) was prepared for use throughout the experimental work. 16.56 g of lead (II) nitrate powder was dissolved in 500 mL of stock solution.

3.2 Preparation of Blank Solution

0.15M solution of Sodium Nitrate ($NaNO_3$) (Merck kGaA Darmstadt Germany with MW = 84.99g/mol.) was prepared by diluting sodium nitrate solids in deionised water. For the preparation of 5L Blank solution, 63.75g of sodium nitrate powder was dissolved in 5L of deionized water.

3.3 Preparation of Pb Solutions of Different Concentrations

In order to prepare 110 mL of Pb solutions with various concentrations, first of all we had to examine the 0.1M of Pb^{2+} concentration. Next, we calculated the volume of Pb^{2+} that is required to add into the blank solution. In this experiment, a total of 12 different concentrations of Pb solutions were prepared: 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L, 70 mg/L, 90 mg/L, 120 mg/L, 150 mg/L, 170 mg/L, 190 mg/L and 200 mg/L.

Subsequently, the blank solution with different concentrations of Pb and biosorbent materials were required to put into the orbital shaker (SSL1; Stuart®) at different temperatures (between 30 ℃ – 60 ℃). The rotational speed of shaker, in all the experiments, was kept constant at 220 rpm. This experiment was performed in duplicate and the best results were used. Lastly, the solution was filtered to prepare samples for the measurements of the metal ion concentration. Sample calculations for the preparation of Pb solutions are attached in Appendix H.

3.4 Estimation of Metal Uptake

The metal uptake, q_e, was determined using the following equation (Madhavi et al., 2011):

$$\boxed{q_e = \frac{V\,(C_i - C_e)}{m}} \qquad \text{(Eq 3.1)}$$

where q_e = metal ions per dry biosorbent (mg/g)

V = volume of solution (L)

C_i = initial concentration of metal in solution (mg/L)

C_e = final concentration of metal in solution (mg/L)

m= the mass of biosorbent (g)

The concentration of the metal ions was determined by using Inductively Coupled Plasma Optical Emission Spectrometer (Optima 7000DV; Perkin Elmer, Uberlingen, Germany). The instrument is shown in Figure 3.1. The complete procedures of determining the concentration are illustrated in the following subsections.

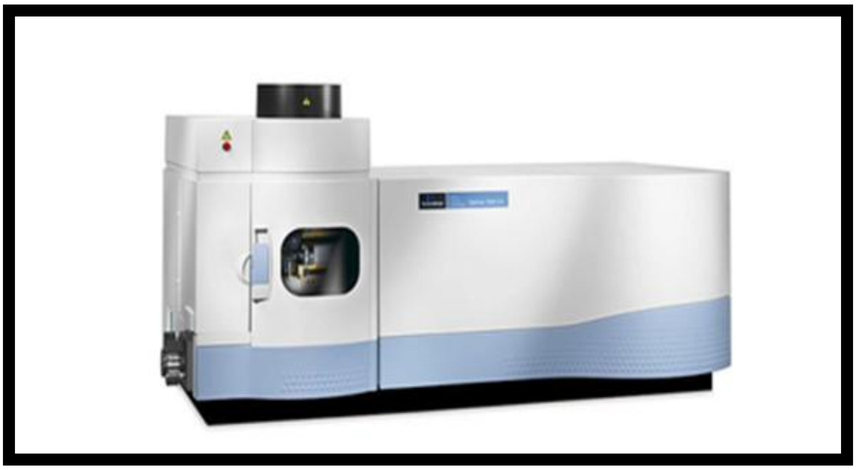

Figure 3.1: Inductively Coupled Plasma Optical Emission Spectrometer Equipment (Optima 7000DV; Perkin Elmer, Uberlingen, Germany)

Meanwhile, the efficiency of heavy metal removal was calculated from the amount of metal ions adsorbed on the biosorbent and the amount of metal ions available in the synthetic solution, as shown in Equation 3.2 (Madhavi et al., 2011).

$$\boxed{\text{Percentage removal} = \frac{mg\ heavy\ metal\ ions\ removed}{mg\ heavy\ metal\ available} \times 100\%} \quad \text{(Eq 3.2)}$$

3.5 Batch Adsorption Procedure at 20 ℃

In the adsorption experiment, 2000 mL of 0.15M blank solution was prepared. pH of blank solution was adjusted to pH 5 accurately using pH probe (refer Figure 3.2). Then, 200ppm of 0.1M of Pb^{2+} solution was added into 2000 mL of 0.15M blank solution. The 4.55g of activated carbon was weighed using analytical balance (ADAMS Model) and then added into the solution. Sample analytical balance is illustrated in Figure 3.3. The solution is placed on the orbital shaker (see Figure 3.4) under the rotational speed at 220rpm. After that, the samples were retaken using peristaltic pump for 4 hours.

For the first half an hour, the samples were retaken every 5 minutes; subsequently, it was retaken once in every 10 minutes for the next 60 minutes; then, it was retaken once in every 20 minutes for the next 60 minutes. For the final 90 minutes, the samples were retaken once in every 30 minutes. The peristaltic pump is shown in Figure 3.5 and its frequency is set at 220 rpm. All samples were filtered using filter paper (Filtres Fioroni) and then added into different samples tubes (15 mL). Prior to solution analysis on ICP-OES, calibration was made with different concentrations of $Pb(NO_3)_2$ (range 10-200 mg/L) solution to ensure sensitivity and optimization of the machine when test solutions were to be analysed. Finally, the concentrations of lead ions were determined through Optical Emission Spectrometer (ICP-OES) (Optima 7000DV; Perkin Elmer, Uberlingen, Germany).

Figure 3.2: pH Meter
(EUTECH pH510)

Figure 3.3: Analytical Balance
(ADAMS Model)

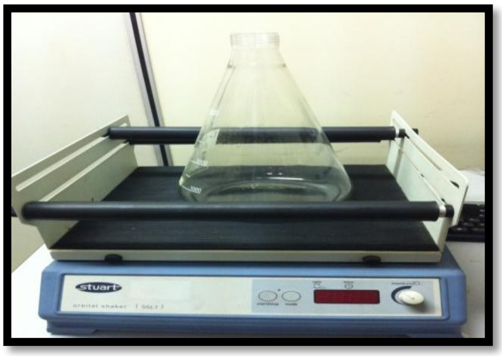

Figure 3.4: Orbital Shaker for 20 ℃
(Stuart, SSL1)

Figure 3.5: Peristaltic Pump
(Longer Pump, BT600-2J)

3.6 Batch Adsorption Procedure at 30 ℃, 40 ℃, 50 ℃ and 60 ℃

In the adsorption experiment, 0.15M blank solution was prepared. pH of blank solution was adjusted to pH 5 accurately. Next, 110 mL of blank solution was added into 24 conical flasks by using a 150mL of measuring cylinder. Different concentrations of 0.1M of Pb^{2+} solution were then added into all the conical flasks that contain 110 mL blank solution. After that, the mixture was inserted into 24 small tubes (with 10mL each) and they were labelled as initial concentrations. 24 sets of palm shell activated carbon (0.25g each) were weighed using analytical balance (ADAMS Model) before being inserted into 24 conical flasks. After adding in the palm shell activated carbon, the conical flasks were immediately placed into orbital shaker (refer Figure 3.6) which was set to operate at 30 ℃ and 220rpm for 24 hours.

Subsequently, the conical flasks were taken out after 24 hours and they were filtered through filter paper (Filtres Fioroni). The solution was poured into 24 small tubes (15mL) and they were labelled as final concentrations (see Figure 3.7). Similarly, before solution analysis on ICP-OES was done, calibration was made with different concentrations of $Pb(NO_3)_2$ (range 10-200 mg/L) solution to ensure sensitivity and optimization of the machine when test solutions were to be analysed. Finally, the initial and final concentrations of lead ions were determined through Optical Emission Spectrometer (ICP-OES) (Optima 7000DV; Perkin Elmer, Uberlingen, Germany). The above steps were repeated with all parameters remained constant, except that the temperature in the orbital shaker was controlled at 40 ℃, 50 ℃ and 60 ℃, respectively.

Figure 3.6: Orbital Shaker for 30, 40, 50 and 60 ℃ (DAIHAN LabTech CO., LTD)

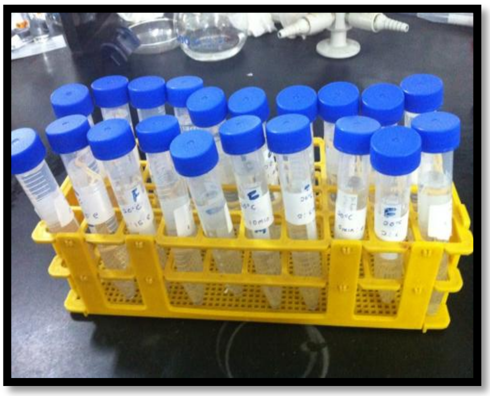

Figure 3.7: Samples prepared for ICP Analysis

There are several precaution steps to be taken into account during the experiments. First and foremost, we should ensure that the experiments are operated in an air-conditioned closed room to avoid any changes in the temperature. Next, we should allow more time in filtering out the solutions and the samples can be taken quickly using a clean beaker. The filtered solution should not be kept for more than three days to avoid inaccuracy in the results. Moreover, we must make sure that the calibration graph is equal to 0.99 prior to the operation of ICP equipment. Last but not least, we should switch off the fans and air-conditioner in the laboratory while weighing the biosorbent materials. All these steps are vital in order to acquire more accurate result.

In summary, two different methods were applied due to time constraint in running biosorption experiment using fungal and bacterial biomass. Moreover, the students had to take turns in using the lab equipments and apparatus and therefore it required longer time to complete one experiment. For the parameter of 20 ℃, we examined the metal ion concentration and time; meanwhile for 30, 40, 50 and 60 ℃, we focused on the determination of metal uptake at different concentrations and temperature.

3.7 Estimation of Thermodynamic Parameters

An adsorption isotherm is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of remaining adsorbate in a test medium at equilibrium. The Langmuir and Freundlich models are the most widely used models in the case of adsorption of metal ions by adsorbents even though the metal uptake may not always follow the monolayer adsorption mechanism.

The Langmuir isotherm has been used traditionally to quantify and contrast the performance of different biosorbents. The rate of attachment to the surface should be proportional to a driving force times an area. The driving force is the concentration in the fluid and the area is the amount of bare surface. The affinity between the biomass and the different metals is quantified by fitting the obtained sorption values to the Langmuir isotherm. Equation 3.3 represents Langmuir model (Li et al., 2005).

$$\boxed{\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}} \qquad \text{(Eq 3.3)}$$

where q_e = amount of solute adsorbed per unit weight of sorbent (mg/g)
C_e = solute equilibrium concentration (mg/L)
q_{max} = maximum uptake capacity of the sorbent (mg/g)
b = adsorption equilibrium constant.

On the other hand, the Freundlich model is perhaps the most popular adsorption model for a single solute system and is an empirical relation equation based on the distribution of solute between the solid phase and aqueous phase at equilibrium (Freundlich, 1928).

The equations of the Freundlich adsorption models are expressed as below (Li et al., 2005):

$$\boxed{\text{In } q_e = \text{In } K_F + \frac{1}{n} \text{ In } C_e} \qquad \text{(Eq 3.4)}$$

where K_F and $1/n$ = Freundlich constants

q_e = amount of solute adsorbed per unit weight of sorbent (mg/g)

C_e = solute equilibrium concentration (mg/L)

In order to determine the thermal effects of sorption, Gibbs free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) are calculated. The ΔG° is the fundamental criterion to examine if a process occurs spontaneously (Akar and Tunali, 2005).

$$\boxed{\Delta G^\circ = -RT \ln K^\circ} \qquad \text{(Eq 3.5)}$$

The ΔH° values are calculated from the slopes of the linear variation of ln K versus 1/T:

$$\boxed{\ln K^\circ = -\frac{\Delta H^\circ}{RT} + \text{constant}} \qquad \text{(Eq 3.6)}$$

Last but not least, the values of ΔS° are obtained from:

$$\boxed{\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}} \qquad \text{(Eq 3.7)}$$

where R = ideal gas constant (8.3145 $\text{Jmol}^{-1}\text{K}^{-1}$)

T = temperature (K)

CHAPTER 4

RESULTS AND DISCUSSION

The results of the experiments at different temperatures and concentrations of lead are discussed in this chapter. The thermodynamic parameters of biosorption process are evaluated and the effects of metal ion concentration, temperature, pH and contact time on the adsorption capacity are also discussed.

4.1 Effects of Temperature

Temperature plays a major role in the adsorption of heavy metals on activated carbon, regardless of the fact that the magnitude of the heat effect for the biosorption process is one of the most important criteria for the efficient removal of heavy metals from the wastewater. Temperature changes will affect a number of factors in heavy metal ion biosorption. These factors include: (i)) the stability of the metal ion species initially placed in solution; (ii) the stability of micro organism-metal complex depending on the biosorption sites; (iii) the effect of temperature on the micro organism cell wall configuration; (iv) the ionization of chemical moieties on the cell wall (Sag and Kutsal, 2000).

The temperature has two major effects on the adsorption process. One of them is that rising temperature will increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles. This is because liquid viscosity decreases as temperature increases. Also, the values of temperature affect the equilibrium capacity of the adsorbate depending on whether the process is exothermic or endothermic.

Figure 4.1 demonstrates the sorption capacity of Pb (II) ions as a function of temperature. Aforementioned, the adsorption experiments were conducted at 30 ℃, 40 ℃, 50 ℃ and 60 ℃, respectively, to investigate the effect of temperatures and different initial concentrations.

It was observed that the equilibrium uptake of lead ions was affected by temperature and rise with the increasing temperature up to 50 ℃. The quantities adsorbed reaching a maximum value up until 50 ℃ and then it became unstable as the temperature increased to 60 ℃. This situation could suggest that there is a predominance of physical sorption over chemical sorption. Instability at higher temperatures may be due to inhibit active binding sites in the biosorbent. The process involves the transfer of metal ions from the bulk liquid to the biosorbent and also sorption of metal ions onto the biosorbent surface.

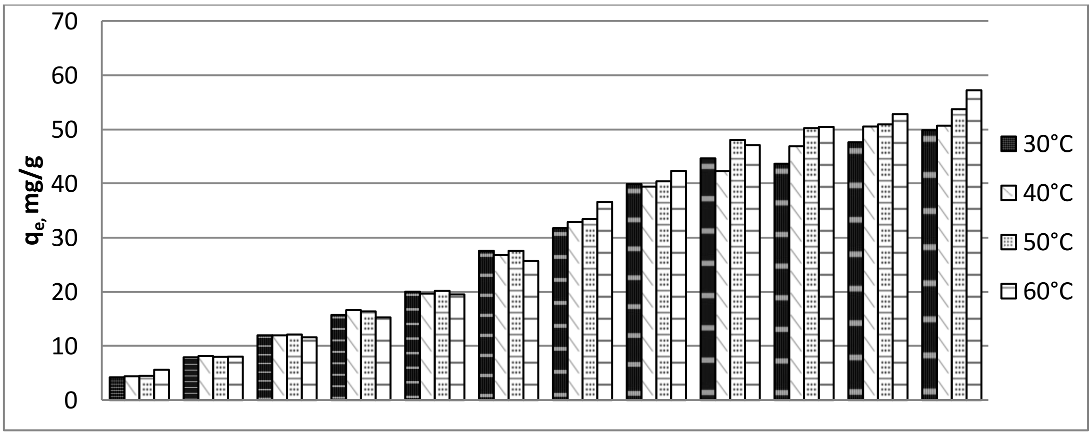

Figure 4.1: Comparisons of Sorption Capacity of Palm Shell Activated Carbon at 30, 40, 50 and 60 ℃

Generally speaking, the effect of temperature on the adsorption rate constants in liquid-solid sorption systems is likely a complicated issue. Literatures have reported many cases in which the increase in temperature caused a decrease in the rate constants of different adsorbate ions (Horsfall and Spiff, 2005). From a physicochemical perspective that is based on the behavior of gases, the rate constant is expected to usually increase as the temperature is increased (Rosene and Manes, 1977). This is usually caused by the fact that the increase in temperature, in a medium where the intermolecular forces are very weak, leads to an increase in the kinetic energy of gas molecules or atoms and thus enhances the rate of reactions. In liquid-solid sorption systems, however, the situation is much more complicated as the behavior of ions in solution or on the solid would be subject to factors like the inter-ionic forces, the hydration energy, the availability of sorption sites and the relative stability of sorbed ions at these sites (Shahwan et al., 2006).

4.2 Effects of Initial Metal Concentration

The feasibility and efficiency of a biosorption process depends not only on the properties of biosorbents but also on the concentration of the metal ion solution. The initial metal concentration provides an important driving force to overcome all mass transfer resistances of the metal between aqueous and solid phase (Aksu and Akpinar, 2000). The initial concentration of the metal (lead) in the solution remarkably influenced the equilibrium uptake of lead (II). It was noted that initial concentration level affected the sorption of lead (II) as generally expected owing to equilibrium process, as depicted in Figure 4.2.

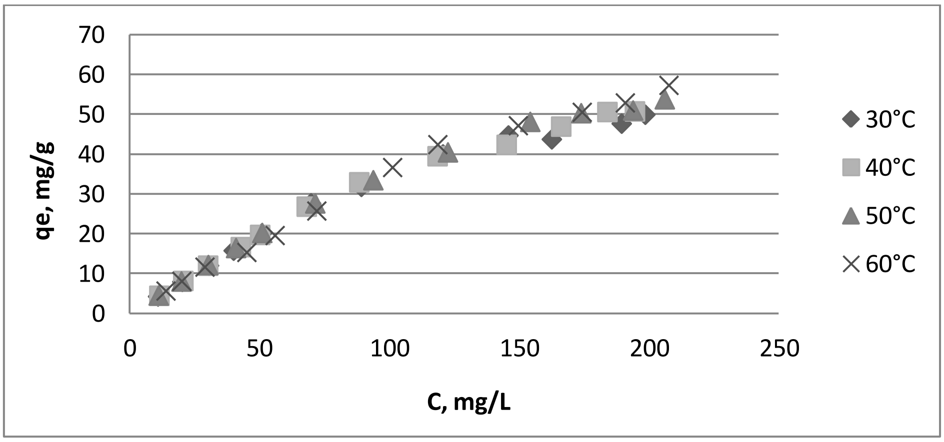

Figure 4.2: Metal Uptake against Initial Concentration at 30, 40, 50 and 60 ℃

The increase in uptake capacity of the biosorbent with the increase in initial metal concentrations is owing to higher availability of metal ions (lead) for the sorption.

Furthermore, higher initial concentration provides increased driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phase, resulting in higher probability of collision between metal ions and sorbents. As a consequence, this also led to higher metal uptake.

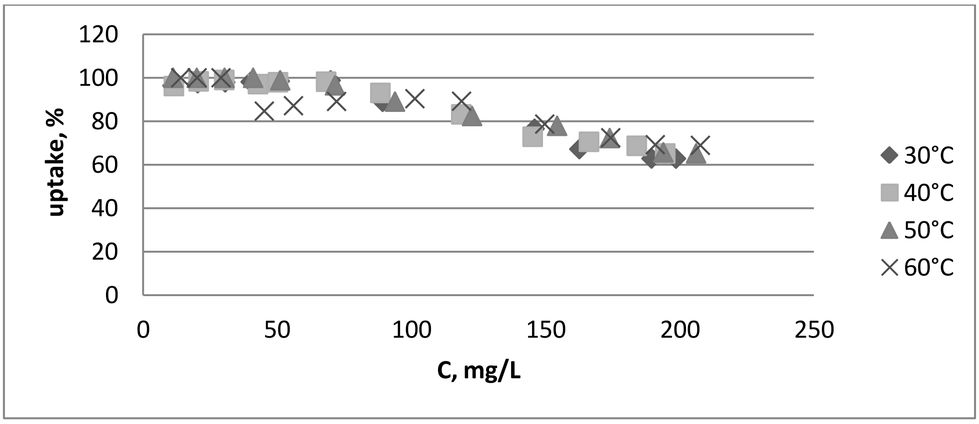

Figure 4.3: Uptake Efficiency over Initial Concentration of Lead Ions at 30, 40, 50 and 60 ℃

From Figure 4.3, it is observed that adsorption efficiency decreased as adsorbate concentration in the solution increased. This may be explained by the fact that the ratio of available binding sites and adsorbate ions is high at very low concentrations of adsorbate, thus the chances to get adsorbed are higher. Similarly, it was found that adsorption capacity was high at low concentrations in the experiments of this study. On the other hand, when adsorbate concentration increases, binding sites become occupied more quickly because the amount of adsorbent is limited. The other possible cause is the aggregation of adsorbent particles at higher concentrations. Such aggregation leads to a decrease in the total surface area of the adsorbent particles available for adsorption and an increase in the diffusional path length (Yasemin and Tez, 2007). The complete results of the batch experiments are described in detail in Appendices.

4.3 Effects of Contact Time

Contact time plays a vital role in the efficient removal of heavy metals using activated carbon. A series of contact time experiments for lead was carried out at initial concentration (200ppm) at temperature of 20 ℃ and the results are illustrated in Figure 4.4. The figure shows that the contact time required for lead with initial concentration of 200ppm to reach equilibrium was around 240 minutes. The amount of the adsorbed lead onto palm shell activated carbon increased with time. Removal efficiency increases from 11.4% to 59.5% as the contact time increased from 5 minutes to 240 minutes.

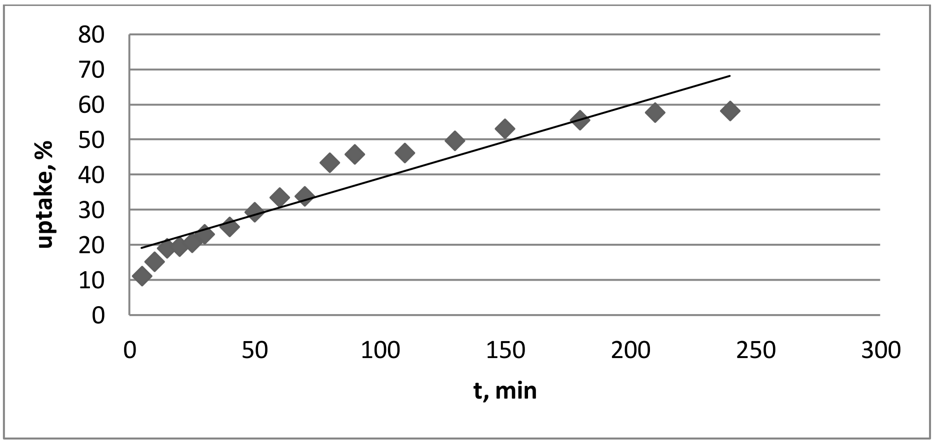

Figure 4.4: Uptake Efficiency of Pb versus Time at 20 ℃

The changes in the rate of Pb removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high, hence the rate of adsorption was also high. As these sites were exhausted, the uptake rate was controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles (Dorris et al., 2000). The lead uptake rate by adsorbent decreased significantly, due to the decrease in number of adsorption sites as well as lead concentration. The number of sites on the adsorbent filled up by the adsorbate also increased as time passed.

At equilibrium, when all the sites were occupied, the rate of adsorption was noticed to be equal to the rate of desorption. Therefore, after equilibrium, it was found that percentage of removal did not change with the increase in contact time. At this point, the amount of the lead desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the lead being adsorbed onto the activated carbon. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of lead adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. Decreased removal rate, particularly, towards the end of experiments, indicated the possible monolayer formation of lead ions. In the present work, a steady increase in percentage removal was observed up to a contact time of 210 minutes. After this period, equilibrium was achieved and percentage removal did not increase over time. The progressive increase in adsorption and consequently the attainment of equilibrium adsorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of activated carbon. It is evident that the palm shell activated carbon is efficient in adsorbing lead from aqueous solution, the process attaining equilibrium gradually.

4.4 Biosorption Isotherms

The equilibrium of the biosorption process, which is often described by fitting the experimental points into the models (Gadd et al., 1988), is frequently used for the representation of isotherm adsorption equilibrium. Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity or homogeneity of adsorbents, the type of coverage, and possibility of interaction between the adsorbate species.

The Langmuir model assumes that there is no interaction between the adsorbate molecules and the adsorption is localized in a monolayer. In addition, the model presumes uniform energies of sorption onto the surface and no transmigration of the sorbate. Moreover, it also assumes the adsorption is reversible and an equilibrium condition is achieved (Patel, 2008).

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface, and hypothesised that different sites with several adsorption energies are involved. Additionally, these models can be applied at a constant pH and used in literature for modeling of biosorption equilibrium in the presence of one metal. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2. The experimental data of Pb (II) adsorption were regressively analyzed with the Freundlich and Langmuir models. The results indicate that the Langmuir model fits the adsorption data better than Freundlich model.

The term q_{max} desorption is supposed to represent a fixed number of surface sites in the sorbent, and it should be constant and temperature-independent. It is determined solely by the nature of the sorbent. From this experiment, the initial concentration of Pb (II) was found to be in the range between 10 ppm and 200 ppm. The linearised Langmuir and Freundlich plots are given in Figure 4.5 and Figure 4.6, respectively.

Figure 4.5 indicates the relationship between the amounts of lead (II) ions sorbed per unit mass of palm shell activated carbon (mg) against the concentration of lead (II) ions remaining in solution (mg/l), as described in Langmuir model.

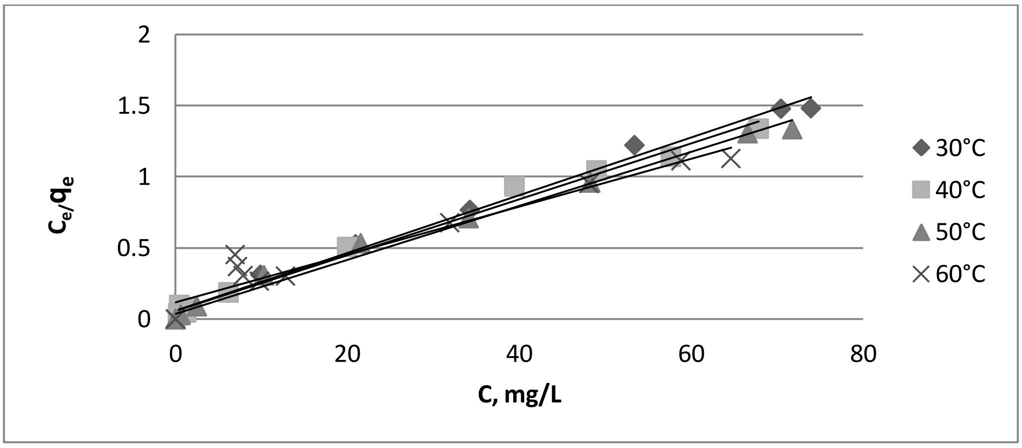

Figure 4.5: Langmuir Model Isotherms at 30, 40, 50 and 60 ℃

On the other hand, Figure 4.6 depicts the Freundlich adsorption isotherms obtained for biosorption of lead (II) ions onto the palm shell activated carbon at four different temperatures, i.e. 30, 40, 50 and 60 ℃.

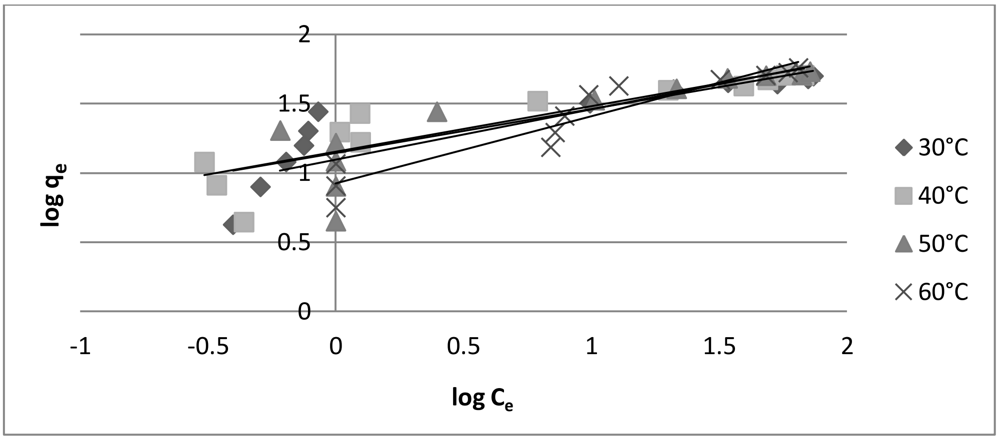

Figure 4.6: Freundlich Model Isotherms at 30, 40, 50 and 60 ℃

The slopes of the linearised Freundlich and Langmuir plots were used to calculate the adsorption constants tabulated in Table 4.1. According to the plots, in view of the values of linear regression coefficients (R^2), it is realised that the exhibited Langmuir model fitted well to the adsorption data compared to the Freundlich model. The value of correlation coefficient (R^2) is a measure of the goodness of fitting, which aims to verify that the equilibrium adsorption follows the Langmuir model. The R^2 values shown in Table 4.1 indicated that Freundlich model was not able to adequately describe the relationship between the amounts of lead (II) adsorbed by the palm shell activated carbon and its equilibrium concentration in the solution. In the contrary, the Langmuir model best fitted the equilibrium data as it presented higher R^2 values.

Table 4.1: The Langmuir and Freundlich Adsorption Models Parameters

Temperature (℃)	Langmuir parameters			Freundlich parameters		
	q_{max}	b	R^2	K_F	n	R^2
20	9.091	2.048	0.8147	227509.74	-0.5545	0.9139
30	49.2611	0.3322	0.9941	13.9669	3.1506	0.7482
40	51.0204	0.3339	0.9916	14.2069	3.0525	0.7957
50	52.6316	0.4855	0.992	15.0048	2.8736	0.6907
60	59.5238	0.1448	0.9378	8.4159	2.0636	0.895

Contradictorily, it was noted that the Freundlich model presented greater R^2 values than Langmuir model for the biosorption of lead (II) ions onto the palm shell activated carbon at 20 ℃. In this case, Freundlich model fitted better to the adsorption data and thus it is more suitable used to describe the relationship between the amounts of lead (II) adsorbed by the palm shell activated carbon and its equilibrium concentration in the solution at 20 ℃. The Langmuir adsorption isotherms obtained for biosorption of lead (II) ions onto the palm shell activated carbon at 20 ℃ is demonstrated in Figure 4.7.

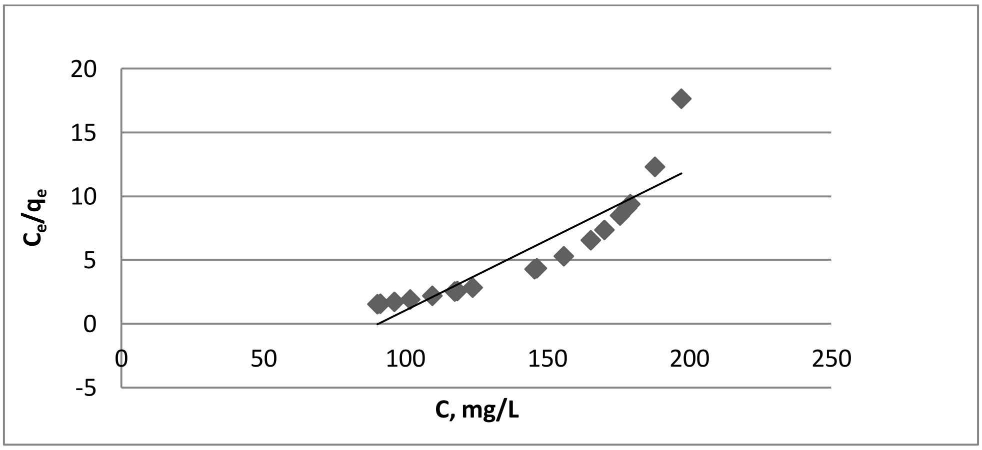

Figure 4.7: Langmuir Model Isotherms at 20 ℃

Meanwhile, Figure 4.8 shows the Freundlich adsorption isotherms obtained for biosorption of lead (II) ions onto the palm shell activated carbon at 20 ℃.

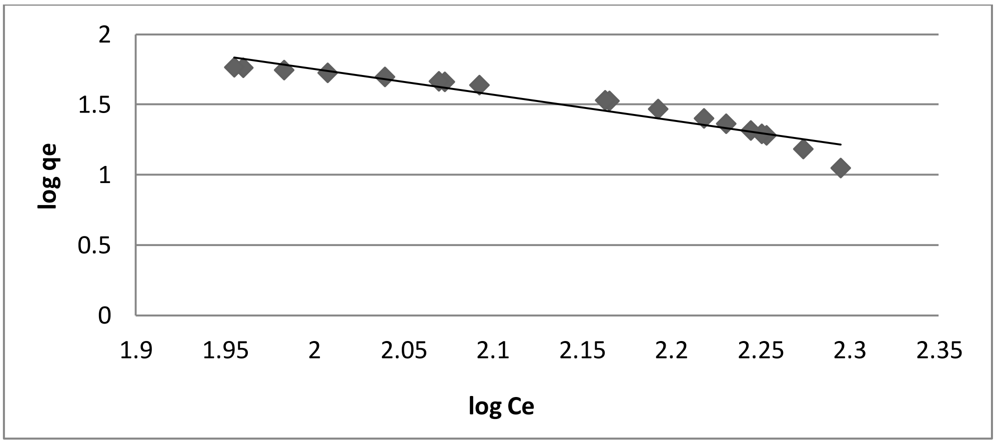

Figure 4.8: Freundlich Model Isotherms at 20 ℃

In this study, the Langmuir model was applied because it provides information on uptake capabilities and it is capable of reflecting the equilibrium sorption process behaviour. The values obtained from the Langmuir model (q_{max} and b) give information in the screening of the sorbent. The more favourable sorbent is indicated by the higher value of the slope of an adsorption isotherm. It means that potentially a “good’’ sorbent can be comparatively evaluated from values of q_{max} and b. However, the Langmuir model sheds no light on the mechanistic aspects of sorption. The nature of the binding processes in biosorption is largely unknown.

4.5 Thermodynamics Parameters of Lead Adsorption

The thermodynamic parameters, namely the values of enthalpy (ΔH^o), entropy (ΔS^o) and Gibbs free energy (ΔG^o) of the sorption are useful in defining whether the sorption reaction is either endothermic or exothermic, alongside the spontaneity of the adsorption process.

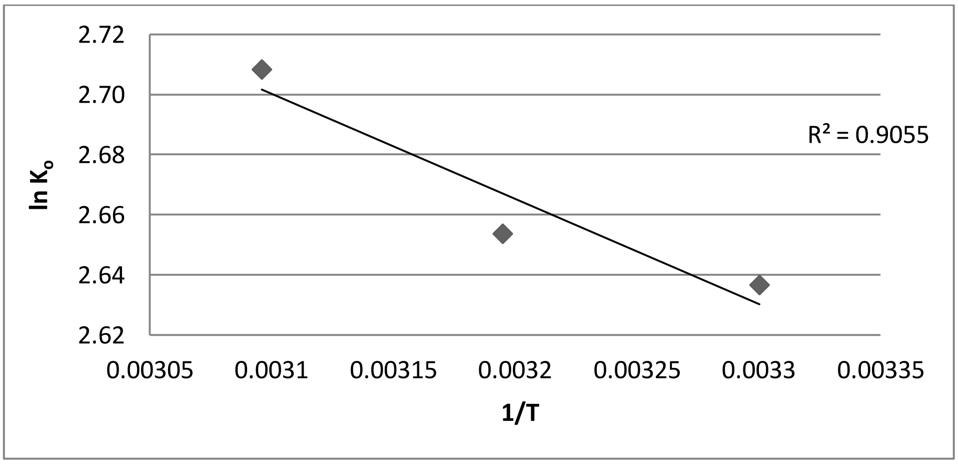

Figure 4.9: Delta G at 30, 40 and 50 ℃

Figure 4.9 is the illustration of the graph of ln k_o against 1/T whereas Table 4.2 tabulates the relevant data calculated from the above equations. It was observed that the adsorption of Pb (II) rose with increasing values of temperature. Also, the value of ΔH^o was found to be positive. The positive ΔH^o value confirmed that the adsorption process is endothermic for Pb(II), which is an indication of the existence of a strong interaction between palm shell activated carbon and Pb(II). For Pb (II) ions travel through solution and reach the sorption sites, it is necessary for the ions to be stripped out of their hydration shell first, whereby this process requires energy input. If the exothermic is associated with the adsorption of Pb (II) ions onto oxidised palm shell activated carbon does not exceed the dehydration enery of Pb (II) ions, the overall energy balance will lead to endothermic behavior. Similar results were obtained for the studies Langmuir isotherm model. This may be attributed to the enlargement of pore size or activation of the adsorbent surface. The complete data involved in the calculations of Delta G is shown in Appendix G.

Table 4.2: Thermodynamics Parameters of Lead Adsorption

ΔS^o= 0.031 kJ/mol	
ΔH^o= 2.899 kJ/mol	
Temperature (°C)	ΔG^o
30	-6.4940
40	-6.8040
50	-7.1140
60	-7.4240

Besides, the Gibbs free energy change (ΔG^o) was negative at different temperatures indicated the feasibility and spontaneity of the adsorption reaction. The decrease in ΔG^o with the increase of temperature indicated that efficient adsorption was higher at higher temperature. At higher temperature, ions are readily dehydrated, and therefore their adsorptions become more favourable. The ranges of ΔG^o values in this study were found to be between -6.68 and -7.30 kJ/mol, which were in the range of physical adsorption.

The positive values of entropy change, ΔS^o (31 $Jmol^{-1}K^{-1}$), reflected the affinity of oxidised palm shell activated carbon toward Pb (II) ions in aqueous solutions and may suggest some structure changes in adsorbents. The results indicated the higher randomness tendency at the adsorbents and adsorbates interface during the lead adsorption onto waste sludge.

The results for 60 ℃ were not included in Figure 4.9 as it would affect the shown trend. It was noticed that the equilibrium uptake of lead ions was affected by temperature and it increased with the increasing temperature up to 50 ℃. When the temperature was set to 60 ℃, the process became unstable. Therefore, it could be said that 30 ℃ to 50 ℃ was the suitable condition for biosorption process. Furthermore, increasing the adsorbate concentration would decrease the adsorption efficiency. Therefore, adsorption capacity was higher at low concentrations. For the experiment at 20 ℃, initially the metal uptake kept increasing. When the experiment was carried out continuously for approximately 200 minutes, it then reached equilibrium stage. This is due to limited mass transfer of the adsorbate molecules. From the results, it is suggested that the Langmuir model is more suitable in this study in comparison with the Freundlich model. Last but not least, positive ΔH^o value showed that the adsorption process is endothermic in nature for Pb (II) removal onto palm shell activated carbon.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This research was conducted to determine various thermodynamic parameters in removal of lead onto palm shell activated carbon. The relationship between time and lead ion concentrations at constant temperature (20 ℃) was investigated. Also, the removal efficiency of lead at different temperatures (30, 40, 50 and 60 ℃) and lead concentrations was studied.

Batch experiments for removal of lead (II) using initial concentrations between 10 mg/L and 200 mg/L were carried out by changing the variables including temperature, initial metal ion concentration and time. From the experiments, it was proven that the active binding sites in the biosorbent would be damaged at temperature 60 ℃. The optimum temperature for biosorption process was 50 ℃ as the maximum uptake capacity was higher at this temperature.

Furthermore, the adsorption capacity was found to be higher at low concentration, leading to higher efficiency in removing of lead ions. Besides, through the experiments it was observed that the initial concentration level would affect the sorption of lead (II). When the initial concentration of lead rises, the uptake efficiency would also increase. Higher concentrations leads to larger possibility of collision between metal ions and sorbents and eventually results in higher metal uptake. On the other hand, the adsorption efficiency decreases as adsorbate concentration in the solution increases. This might be due to the aggregation of adsorbent particles at higher concentrations, which causes diffusion path length to increase. The total surface area of the adsorbent particles available for adsorption reduces in this case.

Moreover, a series of contact time experiments for lead was carried out at initial concentration (200ppm) at temperature of 20 ℃. The amount of lead ions uptake was found to increase over time. This is because the high solute concentration gradient and the adsorption site were unoccupied. After 210 minutes, it started to reach equilibrium. This condition was caused by limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of activated carbon.

In addition, batch mode adsorption studies were carried out by varying the concentration of Pb (II) solution. Data obtained from the study on Pb (II) removal were evaluated using the Langmuir and Freundlich isotherm models. Correlation coefficients for Langmuir isotherm were observed to be higher adsorption of the isotherms for 30 to 60 ℃, whereas Freundlich isotherm was preferred for 20 ℃. Thermodynamic parameters ΔG^o, ΔH^o and ΔS^o were determined from the slope. The positive value of entropy (ΔS^o) indicated an increase in randomness of the ongoing process and hence a good affinity of lead with adsorbent. Next, negative value of Gibbs free energy change (ΔG^o) at each temperature illustrated the feasibility and spontaneity of ongoing adsorption. Meanwhile, positive value of enthalpy (ΔH^o) suggested that entropy is responsible for making (ΔG^o) value negative. Therefore, we can conclude that the adsorption process is spontaneous, since the entropy contribution is much larger than that of enthalpy.

5.2 Recommendations

From this project, it is recommended to operate biosorption process at 50 ℃. Additionally, low concentration, i.e. 50mg/L, is the ideal value for biosoption process. For the biosorption experiment of 20 ℃, contact time should be extended in order to reach the equilibrium phase and obtain a better result. In addition, the preparation methods of palm shell activated carbon should also be enhanced in future. For instance, chemical pre-treatment process could be applied. Also, the product yield and porous structure of activated carbons are found to be the functions of operating conditions. To illustrate, Azargohar (2009) reported that palm shell activated carbon with high reaction yield and larger surface area could increase the adsorption efficiency of lead in aqueous solutions. Thus, it is suggested that we could apply acid treatment which offers large surface area sites. It is able to increase the mesopore, micropore alongside total pore volume of adsorbate molecules.

Besides, biomass is another alternate biosorbent that could be used in biosorption process. We could compare the efficiency in removing heavy metals between biomass and palm shell activated carbon. On top of that, other variables such as different pH and adsorbent dose should be investigated to determine the optimum conditions in biosorption process.

Succinctly, biosorption process is proved to be a very useful technique in removing the heavy metals. It can be utilised in mitigating heavy metal pollution, which in turns protecting our environment. The applications of biosorption to heavy metals removal is expected to be economical and effective. More researches should be done in future to improve the efficiency of biosorption process by applying various types of biosorbent materials.

It is understood that the future application of biosorption is facing great challenges. Generally, the development of biosorption for metal removal is categorised into two trends. The first choice is to use hybrid technology for pollutants removal, especially using living cells. Another tendency would be to develop good commercial biosorbents just like a kind of ion exchange resin, and to exploit the market with great effort. The existing difficulties for biosorption application suggest that it is advisable to consider applying the hybrid technology which comprise of various processes to treat real effluents.

One of the factors that we need to consider in the application of biosorption is cost. The sources and type of biosorbent play a major role in determining the overall cost of the biosorbent material. If the biomass needs to be specifically cultured for this purpose, manufacturers would incorporate maintenance and production expenses in the total cost, as well as a commercial fee. The potential biosorbents can usually be obtained relatively free of charge from the respective producers. Thus, the only costs incurred should be those of drying (if required) and transport. These low-cost biosorbents will make the process highly economical and competitive particularly for environmental applications in detoxifying effluents.

To sum up, a variety of investigation demonstrated that biosorption is a useful alternative to the conventional systems for the removal of heavy metal ions from aqueous solution. The development of biosorption process requires further investigation in the direction of modeling, of regeneration and immobilization of biosorbents, and of treating the real industrial wastewater.

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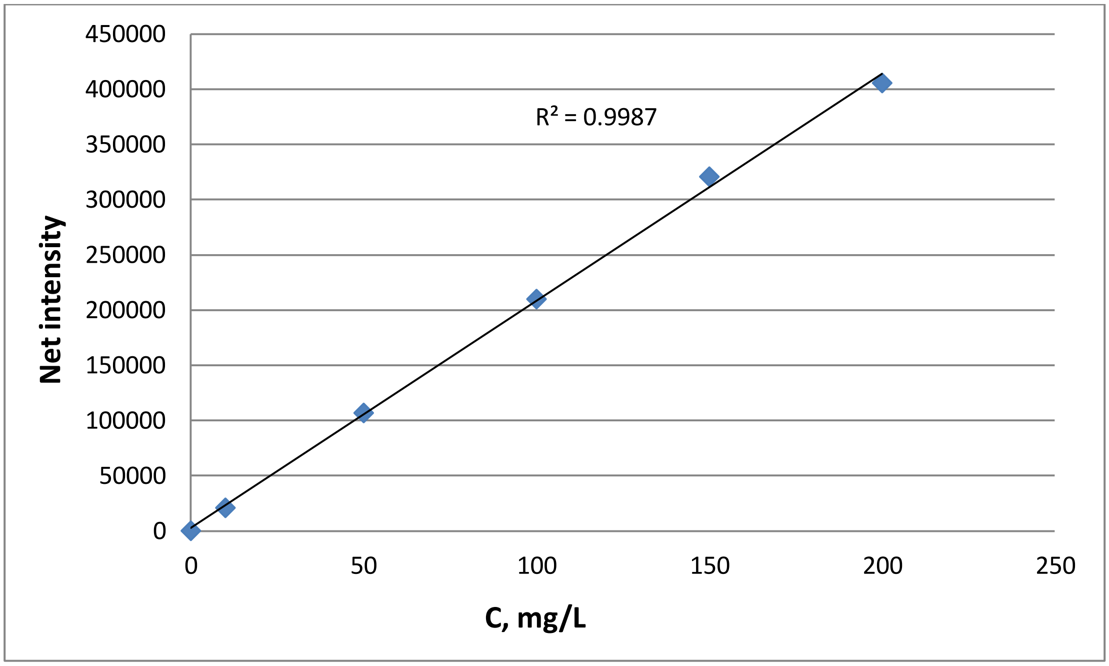
APPENDICES

APPENDIX A: Complete Results for the Experiment of Batch Adsorption at 20 ℃

Time (min)	C_e	C_i-C_f	$(C_i-C_f)/C_i$	Adsorption (%)	q_e	C_e/q_e	log q_e	log C_e
5	197.2	25.4	0.11410602	11.41060198	11.16483516	17.6625984	1.047852316	2.29490691
10	187.9	34.7	0.155884996	15.58849955	15.25274725	12.3190922	1.183348074	2.27392678
15	179.2	43.4	0.194968553	19.49685535	19.07692308	9.39354839	1.280508329	2.25333801
20	178.1	44.5	0.199910153	19.99101527	19.56043956	9.10511236	1.29137861	2.25066392
25	175.6	47	0.21114106	21.11410602	20.65934066	8.49978723	1.315116457	2.24452451
30	170.1	52.5	0.235849057	23.58490566	23.07692308	7.371	1.363177902	2.23070431
40	165.3	57.3	0.257412399	25.74123989	25.18681319	6.56295812	1.401173221	2.21827285
50	155.8	66.8	0.300089847	30.00898473	29.36263736	5.30606287	1.467795061	2.19256745
60	146.3	76.3	0.342767296	34.27672956	33.53846154	4.36215596	1.525543137	2.16524433
70	145.5	77.1	0.346361186	34.6361186	33.89010989	4.29328794	1.530072977	2.16286299
80	123.7	98.9	0.444294699	44.4294699	43.47252747	2.84547523	1.638214891	2.0923697
90	118.3	104.3	0.468553459	46.85534591	45.84615385	2.58036913	1.661302907	2.07298474
110	117.4	105.2	0.472596586	47.25965858	46.24175824	2.5388308	1.665034339	2.0696681
130	109.5	113.1	0.508086253	50.80862534	49.71428571	2.20258621	1.696481204	2.03941412
150	101.7	120.9	0.543126685	54.31266846	53.14285714	1.91370968	1.7254449	2.00732095
180	96.14	126.46	0.568104223	56.81042228	55.58681319	1.72954689	1.744971776	1.98290412
210	91.2	131.4	0.590296496	59.0296496	57.75824176	1.57899543	1.761613964	1.95999484
240	90.15	132.45	0.595013477	59.50134771	58.21978022	1.54844281	1.765070562	1.95496573

APPENDIX B: Calibration Graph



APPENDIX C: Complete Results for the Experiment of Batch Adsorption at 30 ℃

intercept :	-773.8
slope:	2559
R2 :	0.99983

Solution	Net intensity
Blank solution	-9
standard 1:10ppm	24354.5
standard 3:50ppm	80355.9
standard 3:100ppm	125321.5
standard 3:150ppm	378510.4
standard 3:200ppm	515897.2

C_i	%	q_e	C_e/q_e	C_e	log q_e	log C_e
10.96	96.38686	4.2256	0.093715	0.396	0.625888	-0.4023
20.31	97.50369	7.9212	0.064005	0.507	0.898791	-0.29499
30.59	97.91108	11.9804	0.053337	0.639	1.078471	-0.1945
40.08	98.12874	15.732	0.047674	0.75	1.196784	-0.12494
50.91	98.46788	20.052	0.038899	0.78	1.302158	-0.10791
69.88	98.77934	27.6108	0.030894	0.853	1.441079	-0.06905
89.27	88.94253	31.7596	0.310804	9.871	1.501875	0.994361
120.7	82.6512	39.904	0.524759	20.94	1.601016	1.320977
145.9	76.53187	44.664	0.766613	34.24	1.649958	1.534534
162.6	67.17097	43.688	1.221846	53.38	1.640362	1.727379
189.5	62.83905	47.632	1.478418	70.42	1.677899	1.847696
198.6	62.78953	49.88	1.481556	73.9	1.697926	1.868644

APPENDIX D: Complete Results for the Experiment of Batch Adsorption at 40 ℃

intercept :	-773.8
slope:	2559
R2 :	0.99983

Solution	Net intensity
Blank solution	-9
standard 1:10ppm	24354.5
standard 3:50ppm	80355.9
standard 3:100ppm	125321.5
standard 3:150ppm	378510.4
standard 3:200ppm	515897.2

C_i	%	q_e	C_e/q_e	C_e	log q_e	log C_e
11.47	96.19006	4.4132	0.099021	0.437	0.644754	-0.35952
20.69	98.34703	8.1392	0.042019	0.342	0.910582	-0.46597
30.24	98.9881	11.9736	0.025556	0.306	1.078225	-0.51428
42.82	97.08314	16.6284	0.075112	1.249	1.22085	0.096562
50.27	97.93913	19.6936	0.052606	1.036	1.294325	0.01536
68.22	98.17795	26.7908	0.046397	1.243	1.427986	0.094471
88.44	93.03822	32.9132	0.187068	6.157	1.51737	0.789369
118.6	83.16189	39.452	0.506185	19.97	1.596069	1.300378
145.2	72.85124	42.312	0.931651	39.42	1.626464	1.595717
166.2	70.5355	46.892	1.044315	48.97	1.671099	1.68993
184	68.68478	50.552	1.139816	57.62	1.703738	1.760573
194.6	65.14388	50.708	1.337659	67.83	1.705076	1.831422

APPENDIX E: Complete Results for the Experiment of Batch Adsorption at 50 ℃

intercept :	-773.8
slope:	2559
R2 :	0.999329

Solution	Net intensity
Blank solution	45.2
standard 1:10ppm	20840.8
standard 3:50ppm	106778.1
standard 3:100ppm	209856.1
standard 3:150ppm	320730.2
standard 3:200ppm	405586.6

C_i	%	q_e	C_e/q_e	C_e	log q_e	log C_e
11.2	100	4.48	0	0	0.651278	0
19.99	100	7.996	0	0	0.902873	0
30.34	100	12.136	0	0	1.084076	0
41	100	16.4	0	0	1.214844	0
51.1	98.81409	20.1976	0.030004	0.606	1.3053	-0.21753
71.5	96.52168	27.6052	0.090092	2.487	1.440991	0.168497
93.86	89.03686	33.428	0.307826	10.29	1.52411	0.912753
122.6	82.43067	40.424	0.532852	21.54	1.606639	1.333246
154.3	77.90668	48.084	0.708968	34.09	1.682001	1.532627
173.9	72.25417	50.26	0.960008	48.25	1.701222	1.745309
193.9	65.68334	50.944	1.30614	66.54	1.707093	1.823083
206.1	65.19651	53.748	1.334561	71.73	1.730362	1.855701

APPENDIX F: Complete Results for the Experiment of Batch Adsorption at 60 ℃

intercept :	-773.8
slope:	2559
R2 :	0.991511

Solution	Net intensity
Blank solution	-4.4
standard 1:10ppm	9505.1
standard 3:50ppm	28710.7
standard 3:100ppm	82458.5
standard 3:150ppm	120461.8
standard 3:200ppm	188524.5

C_i	%	q_e	C_e/q_e	C_e	log q_e	log C_e
14.02	100	5.608	0	0	0.748808	0
20.12	100	8.048	0	0	0.905688	0
29.03	100	11.612	0	0	1.064907	0
45.16	84.65678	15.2924	0.453101	6.929	1.184476	0.840671
56.05	87.14362	19.5376	0.368827	7.206	1.290871	0.857694
72.1	89.09986	25.6964	0.305841	7.859	1.409872	0.895367
101.3	90.37117	36.6184	0.266369	9.754	1.563699	0.989183
118.7	89.22494	42.364	0.301907	12.79	1.626997	1.106871
149.7	78.69071	47.12	0.676995	31.9	1.673205	1.503791
174.3	72.40964	50.484	0.952579	48.09	1.703154	1.682055
190.9	69.20901	52.848	1.112246	58.78	1.723029	1.76923
207.7	68.90226	57.244	1.128328	64.59	1.75773	1.810165

APPENDIX G: Table of Delta G

T (℃)	Temperature (K)	1/T	K_o	ln K_o
30	303	0.00330033	13.9668	2.63668
40	313	0.003194888	14.2069	2.65373
50	323	0.003095975	15.0048	2.70837

APPENDIX H: Sample Calculations

1. Mass of Sodium Nitrate ($NaNO_3$) for the preparation of blank solution.

0.15M ($NaNO_3$) × molecular weight of ($NaNO_3$), 85 g/mol × 5L = 63.75g of ($NaNO_3$)

2. Mass of lead (II) nitrate $Pb(NO_3)_2$ for the preparation of stock solution.

0.1M Pb × molecular weight of $Pb(NO_3)_2$, $(331.2 g/mol)$ × 0.5L deionized water
= 16.56g $Pb(NO_3)^2$

3. Determination of the 0.1M of Pb^{2+} concentration.

0.1M of Pb^{2+} concentration= 0.1 mol/L × atomic mass of Pb, 207.2 g/mol×1000mg/g
= 20720 mg/L

4. Volume of $Pb(NO_3)_2$ for the preparation of different concentrations of $Pb(NO_3)_2$.

$$\boxed{M_1V_1=M_2V_2}$$

To prepare concentration of 10 mg/L,

$10\ \text{mg/L}\ (0.11\text{L} + X) = 20720X\ \text{mg/L}$

$1.1 + 10X = 20720X$

$1.1 = 20710X$

$X = 1.1/20710 = 5.3112 \times 10^{-5}\ \text{L} = 0.0531\ \text{mL} = 53.1\ \mu\text{L}$

where X = volume of required Pb to be added into blank solution

M_1= Concentration of stock solution, mg/L

V_1= Volume of stock solution, L

M_2= Concentration of lead ions solution, mg/L

V_2= Volume of lead ions in solution, L

5. Determination of the heavy metal removal efficiency.

$$\text{Percentage removal} = \frac{mg\ heavy\ metal\ ions\ removed}{mg\ heavy\ metal\ available} \times 100\%$$

$$= \frac{C_i - C_e}{C_i} \times 100\%$$

By taking data at 50 ℃, C_i= 51.1 and C_e= 0.606,

Thus, Percentage removal $= \frac{C_i - C_e}{C_i} \times 100\%$

$$= \frac{51.1 - 0.606}{51.1} \times 100\%$$

$$= 98.81\%$$