DEVELOPMENT OF HYBRID POROUS HEAVY METAL ADSORBENTS BY MODIFICATION OF PALM SHELL ACTIVATED CARBON

By

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ABSTRACT

DEVELOPMENT OF HYBRID POROUS HEAVY METAL ADSORBENTS BY MODIFICATION OF PALM SHELL ACTIVATED CARBON

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Hybrid porous adsorbents were developed by biomodifying palm shell activated carbon (PSAC) with *Bacillus subtilis* (BS-PSAC) and *Aspergillus niger* (AN-PSAC) biomass, respectively. The obtained hybrid biosorbents were studied for their physico-chemical properties using different characterization techniques such as Boehm titration, BET surface area analysis, SEM, EDS and FTIR. The adsorption studies were carried out at various pHs (3 - 6), initial concentrations of adsorbates (30 - 300 mg/L), temperature (303 - 323 K) and contact time (20 mins - 24 hrs) using the original and developed PSACs in order to optimize the adsorption conditions. The results showed that the adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) is dependent on pH, initial metal ions concentration, contact time and temperature parameters.

The performance of the biosorbents was evaluated in terms of adsorption capacity for each heavy metal and extend of the maximum sorption capacity was estimated by the Langmuir isotherm model. The results showed that BS-PSAC had the highest removal efficiency for Pb(II) and Zn(II). Meanwhile, AN-PSAC showed highest capacity for Cu(II) removal, and original PSAC showed highest Cd(II) removal. Such difference between the biosorbents related to their physico-chemical properties. The results showed that the biomodification with *B. subtilis* and *A. niger* biomass improved the adsorption performance of PSAC.

The adsorption capacity of the original and biomodified PSCAs increased along the increase in temperature and the values of enthalpy change were positive confirming that the adsorption process was endothermic. The Langmuir isotherm model described the adsorption data better than the Freundlich isotherm model. The kinetics of adsorption of metal ions on the original and biomodified PSACs were described well by the pseudo-second-order kinetic model. Overall, the porous hybrid adsorbents showed good performance and potential to be used in environmental applications to remove heavy metal from wastewater.

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APPROVAL SHEET

This dissertation entitled **"DEVELOPMENT OF HYBRID POROUS HEAVY METAL ADSORBENTS BY MODIFICATION OF PALM SHELL ACTIVATED CARBON"** was prepared by CHEN SIEW KIM and submitted as partial fulfillment of the requirements for the degree of Master of Science at Universiti Tunku Abdul Rahman.

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DECLARATION

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

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TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

q_e	Amount of adsorbate adsorbed at equilibrium, mg/g
q_t	Adsorption capacity at time t, mg/g
K°	Equilibrium constant
q_{max}	Maximum of Langmuir monolayer adsorption capacity, mg/g
b	Langmuir constant, L/mg
K_f	Freundlich adsorption constant
n_f	Adsorption intensity constant
k_1	Rate constant of pseudo-first-order biosorption, min^{-1}
k_2	Rate constant pseudo-second-order, g/mg min
ΔH^o	Enthalpy change, kJ mol^{-1}
ΔS^o	Entropy change, kJ mol^{-1} K^{-1}
ΔG^o	Gibbs free energy, kJ mol^{-1}
T	Absolute temperature, K
m	Mass, g
V	Volume, L
T	Temperature, K
C_i	Initial heavy metal concentration, mg/L
C_e	Equilibrium heavy metal concentration, mg/L
L	Avogardros number (6.022 x 10^{23} mol^{-1})
R	Ideal gas constant
SSE	Sum of the squares of error

CHAPTER 1

INTRODUCTION

1.1 Rationale of the study

Water contamination by toxic organic chemicals and heavy metals from the miscellaneous industrial wastewater discharges has become a critical issue in the global context. According to the World Health Organization lead, zinc, cadmium and copper are the most toxic heavy metals present in wastewater (WHO, 2011). Heavy metals from sewage, especially from the wastewater discharged by factories, flows into the drainage systems and into the rivers without any filtering and cleaning resulting in hazardous levels of pollutants content in rivers. These dangerous concentration levels cause toxicity to human beings and even lethal effect. Nearly all heavy metals are highly toxic, non-biodegradable, non-thermodegradable and easily accumulated in the living organisms reaching toxic levels. Therefore, heavy metals are persistent and difficult to be removed naturally from the environment, especially at very low concentrations. Approaches to remove heavy metals from wastewater have significantly progressed and can now be applied for the protection of the environment and human health.

Heavy metal pollution has become a serious problem in the Malaysian aquatic environment. Thus, the researchers investigated heavy metal pollution status of the Johor Straits area located between Malaysia and Singapore. The concentration of lead and zinc in the sediments of the coastal environment~~s~~

were found to be 2 to 3 times higher than at the sampling sites closest to the causeway linking Malaysia and Singapore, which receives very high vehicle traffic (Shazili *et al.*, 2006). Also it was shown that the Langat River in Negeri Sembilan was seriously contaminated with zinc and cadmium while Juru River in Penang was heavily polluted by lead, zinc and copper (Shazili *et al.*, 2006). Lead, zinc, copper and cadmium present a primary concern for the present and future environmental monitoring.

Many methods of treatment for wastewater have been developed in the past decades. Amongst these methods are chemical precipitation, ion exchange, oxidation process, reverse osmosis and others. However, these methods are expensive and less efficient for streams with low heavy metal ions concentration.

Adsorption of environmental pollutants onto carbonaceous adsorbent materials is an intensive research area nowadays. Adsorption has been found to be superior to other techniques for water re-use in terms of the initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (Meshko *et al.*, 2001). Activated carbon is well known for high adsorption capacity but it also has high capital and regeneration cost. When the adsorption capacity of the carbon is exhausted, it can be reactivated by burning off the organics in a controlled manner.

Biomass raw material rich in carbonaceous elements are known today as alternative to replace the high production cost materials. Agricultural wastes such as oil palm shell, coconut shell, rice husk, corn hull and nutshell in Malaysia, are potential raw materials for the production of the activated carbon.

Palm shell is an abundant solid waste generated from the palm oil industry in Malaysia. The palm shell is an excellent raw material to produce good quality activated carbon. Utilization of palm shells for carbon production is important in terms of solid waste volume minimization. In turn, the produced palm shell activated carbon can be effectively used to remove pollutants from wastewater.

A number of methods on modification of activated carbon to enhance the adsorption capacity towards pollutants species have been studied. The common modification methods are physical, chemical and biological methods. Many studies have reported that the microbial biomass composition components such as polysaccharides, proteins and lipids offer abundant metal-binding functional groups. *Bacillus subtilis* and *Aspergillus niger* are recommended as the agents of biomodification for palm shell activated carbon as they are easily available in extensive quantities, easily grown in basic fermentation medium at low cost.

In this study, *Bacillus subtilis* and *Aspergillus niger* are used to biomodify palm shell activated carbon in order to study the possibility of enhancing the sorption process of selected heavy metals, namely Cu(II), Pb(II), Zn(II) and Cd(II) from aqueous solutions.

1.2 Significance of the study

The proposed research is important as it emphasizes on the utilization of the existing and abundant type of the solid wastes (palm shells) as an effective adsorbent material to remove metal ions from wastewaters. In recent years the interest to palm shell has increased mainly due to the fact that this material was shown to be an excellent source of high quality and low cost activated carbon. Biomodification of palm shell with another type of well known biosorbent, i.e. *Bacillus subtilis* and *Aspergilus niger* should have a positive effect on the uptake of heavy metals.

Both, palm shell and microorganism biomass are considered to be low cost materials, therefore the approach to combine their potential characteristics to achieve higher efficiency of the adsorption process presents more prospects for technology development and process optimization. Biosorption has the potential to find an industrial application in the separation technologies with renewable biosorbents complementing conventional methods in hybrid or integrated installations. Further research on bisorption mechanism and performance of biosorption models as well as more pilot scale demonstrations should bring convincing marketing arguments for large-scale applications.

1.3 Aim and objectives

Previously, it was shown that biosorbents such as palm shell activated carbon, bacterial and fungal biomass exhibit very good adsorption capacity to remove metals ions from aqueous solutions (Issabayeva *et al.*, 2006; Khambhaty *et al.*, 2009; Wang *et al.*, 2010a).

The present research is focused on the achieving higher metal adsorption capacity by developing porous hybrid biosorbents based on palm shell activated carbon and using bacterial and fungal biomass (separately) to modify it. It is highly anticipated that biomodification of palm shell activated carbon with bacterial or fungal biomass should increase efficiency of metal ions removal from wastewaters.

Therefore, the main objective of this research project was to examine the adsorption potential of the original palm shell activated carbon (PSAC), *Bacillus subtilis* biomodified PSAC and *Aspergillus niger* biomodified PSAC in removal of Pb(II), Cu(II), Cd(II) and Zn(II) ions from aqueous solutions.

The specific objectives of the study were:

1. To biomodify and surface characterise palm shell activated carbon with *Bacillus subtilis* and *Aspergillus niger* biomass, respectively, in comparison to the original palm shell activated carbon.

2. To evaluate adsorption capacity of the original and biomodified palm shell activated carbons in removal of metal ions in batch mode adsorption.

3. To determine optimal conditions for adsorption of metal ions by the original and biomodified palm shell activated carbons in terms of: initial concentration of metal ions, pH of solution, incubation temperature and contact time.

4. To evaluate the kinetics of the adsorption process for the original and hybrid biosorbents.

5. To determine the thermodynamic parameters (Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) of the adsorption process of metal ions onto original and biomodified PSACs.

1.4 Scope of the study

All together three different biosorbents were used in study: original palm shell activated carbon, palm shell activated carbon biomodified with *Bacillus subtilis*, and palm shell activated carbon biomodified with *Aspergillus niger*. Four metal ions were investigated: Pb(II), Zn(II), Cu(II) and Cd(II). The current research mainly focused on the determination of adsorption capacity of the biosorbents to remove metal ions at varying parameters such as initial metal ions concentration, initial pH, operational temperature and contact time in biosorption process.

The results were evaluated using the equilibrium adsorption isotherm models (Langmuir and Freundlich), kinetic models (pseudo-first-order and pseudo-second-order) and thermodynamic equations ($\Delta H°$, $\Delta G°$ and $\Delta S°$).

The surface characterization of the biosorbent materials was carried out by using several techniques such as the surface morphology analysis, surface area and pore size analysis, surface functional groups concentrations and pH of point of zero charge determination. Additionally, V. MINTEQ 3.0 software was used to determine metal ions speciation profiles in 1-14 pH range.

CHAPTER 2

LITERATURE REVIEW

This chapter presents a brief review of pollution problems and technological solutions to remove heavy metals from the effluents. Different types of technologies used to remove heavy metals from wastewater including conventional, non-conventional and novel adsorbents are summarized in this chapter. Production process of palm shell activated carbon (PSAC) and its adsorption characteristics are also presented. In addition, descriptions of various modification methods of activated carbon (physical, chemical and biological) are discussed.

2.1 Heavy metal pollution in Malaysia

There is an increasing concern about heavy metal pollution due to the rapid development of industries in Malaysia over the past decades. The major industrial wastewater generators in Malaysia are food and beverage processors, electrical and electronic industries, chemical-based industry, textiles, rubber and palm oil industries (DOE, 2002). The industries are required to treat effluent wastewater before discharging it as required by the Department of Environment Malaysia.

Heavy metals such as lead (Pb), copper (Cu), cadmium (Cd), chromium (Cr), arsenic (As), mercury (Hg), nickel (Ni), aluminum (Al), iron (Fe) and zinc (Zn) are commonly discharged into river, marine and groundwater. Water quality of almost all rivers in Malaysia is classified as Class III based on the Interim National Water Quality Standards (DOE, 2010) (Table 2.2, page 13). The water quality of rivers in Malaysia has deteriorated over the past few years due to the polluting effluents from palm oil mills, sewage treatment plants, animal farms, metal mining activities, construction industry, metal manufacturing and agricultural sector activities (DOE, 2010). Extensive water treatment is prescribed for heavy metal pollutants such as As, Hg, Cd, Cr, Pb and Zn.

For instance, wastewater discharged from animal farms (chicken, pig and fish) in Sarawak contains high concentrations of metals such as Cu. This is most likely due to the addition of these metals to animal feed as part of nutrition (Ling *et al.*, 2010). Besides, high Zn, Pb, Cd and Cu concentrations were also found in the drainage nearby the road side due to the high emissions from the vehicles. Nowadays, many people are still dependent on the river water for household activities. However, river water becomes increasingly polluted and causes harmful effect to human and animal health. Table 2.1 shows the guidelines for drinking water quality established in Malaysia and other countries.

Table 2.1 Guidelines for drinking water quality (Source: EPA, 2011; MOH, 2010; WHO, 2011)

Parameter (mg/L)	US EPA	WHO	Malaysia
Cd	0.005	0.003	0.003
Pb	0.015	0.010	0.010
Cu	1.300	2.000	1.000
Zn	5.000	3.000	3.000

Direct discharge of wastes containing heavy metals into the rivers and oceans causes metals bioaccumulation in fish and via marine food chain they are consumed by humans. High levels of contamination by Cu was found in the coastal areas of Perak and Johor, while high contamination by Pb was found in the estuaries of Sabah and Terengganu which is probably due to extensive anthropogenic and shipping activities in those areas (DOE, 2010).

Thanapalasingam (2005) investigated the concentration of heavy metals in water, plants and sediments of the Sungai Skudai river system in Johor, Malaysia. The average concentration of Cu in the Skudai river system was found to be 0.0275 mg/L; while concentrations of Cd, Pb and Zn were 0.0004, 0.0039 and 0.0492 mg/L, respectively. The results showed that Zn was present at the highest concentration and Cd at the lowest concentration. Such pollution is mainly due to many electroplating industries functioning there.

Alshaebi *et al.* (2009) reported that high concentrations of As, Pb, Cu, Zn, Cr and Ni were found in the abandoned tin mine of Lembing river in Pahang, Malaysia. Heavy metals present in the abandoned tin mine gradually migrated to the surroundings and caused severe widespread contamination of soil~~s~~, surface and ground water. The results showed that the sampes taken from the abandoned tin mine nearby Lembing river contained concentrations of metals ranging from 354.2 mg/kg to 25.03 g/kg for As, Pb, Cu, Zn and Ni; and from 96.04 to 205.52 mg/kg for Cr. The site urgently requires proper remediation treatment and other environmental protection measures.

Yap *et al.* (2006) analyzed the levels of Cd, Cu and Zn in Kelana Jaya lakes, Kuala Lumpur, Malaysia. These lakes were heavily polluted by Cd (0.027 - 0.122 mg/L) exceeding the limit of 0.01 mg/L, which is set by INWQS (Table 2.2) (DOE, 2010). High level of detected Cd in the lakes was associated with the electroplating industries and car repairing workshops located nearby the lakes. However, the concentration of Cu (0.060 - 0.133 mg/L) and Zn (0.019 - 0.045 mg/L) were below the INWQS threshold levels. In conclusion, water quality of Kelana Jaya lakes was classified as Class V, or in other words, water in the lakes is unhealthy and not suitable for recreational activities.

Table 2.2 Interim national water quality standards for Malaysia (INWQS, Source: DOE, 2010).

Parameters	Classes[1]				
	I (mg/L)	II (mg/L)	III (mg/L)	IV (mg/L)	V (mg/L)
Cd	Natural level	0.01	0.01	0.01	Levels above IV
Pb		0.05	0.02	5.00	
Cu		1.00	-	0.20	
Zn		5.00	0.40	2.00	

[1]Class I	Practically no treatment necessary
Class II	Conventional treatment required
Class III	Extensive treatment required
Class IV	Advanced treatment methods required
Class V	Must undergo wastewater treatment

2.2 Properties, application and sources of heavy metals

Heavy metals are usually defined as metals existing naturally in the environment with densities greater than 5 g/cm^3 (Naja and Volesky, 2009). They can be found in, for example, bed rocks and sediments. Besides, they

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[1] Classification of the water quality

mainly enter the water cycle through the industrial effluents and enter humans become exposed to them through ingestion and inhalation. Certain heavy metals (e.g., Zn, Cu, Fe and Mn) are considered to be nutritionally essential elements; the recommended daily intake ranges between 1-20 mg/day only (USDA, 2011). These metals become toxic to living organisms at higher concentrations. Furthermore, heavy metals are non-biodegradable and they show tendency to bioaccumulation. Some physical properties of the selected heavy metals which were also used as adsorbates in this study are shown in Table 2.3.

Table 2.3 Properties of heavy metals (Source: Usman, 2008).

Heavy Metal	Cu	Zn	Cd	Pb
Ionic Radius (Å)	0.70	0.74	0.97	1.21
Atomic Radius (Å)	1.28	1.53	1.54	1.80
Electronegativity	1.90	1.60	1.70	1.80
Density (g/mL)	8.94	7.14	8.64	11.34
First Hydrolysis Constant	8.00	9.00	10.10	7.80
Atomic Weight	63.54	65.38	112.41	207.20
Ionization Energy (First) (kJ/mol)	745.40	906.40	867.80	715.40

The following section presents a more detailed description of the above heavy metals in terms of their chemical properties, sources in the environment, toxicity and health effects.

2.2.1 Lead (Pb)

Pb exists naturally in the form of mineral deposits in three oxidation states: Pb(0), Pb(II) and Pb(IV), with Pb(II) being the most common. Pb is a soft, highly malleable, ductile, bluish-gray in colour metal that has excellent corrosion resistance property. These characteristics cause Pb to be widely used by humans since the ancient time. It is also the traditional metal used for organ pipes and as a lubricating agent in petrol. The consumption of Pb is in the order of three million tons annually, mostly used in the production of electrical accumulators and batteries, as gasoline alkyl additives, cable coatings, ammunition, etc. (Naja and Volesky, 2009).

Lead enters drinking water supply system primary through the plumbing system in buildings as earlier pipe metal alloys contained lead on regular basis (WHO, 2011). It is released even more rapidly into the environment due to its many industrial applications. Exposure to Pb is associated with a wide range of health effects including various neuro-developmental effects, cardiovascular diseases, impaired renal function, hypertension, impaired fertility and adverse pregnancy (WHO, 2011). Furthermore, Pb poisoning has been linked to lower intelligence quotient (IQ) especially in children (Canfield *et al.*, 2003). The EPA set the permissible level for Pb at 0.015 mg/L in drinking water.

2.2.2 Zinc (Zn)

Zn is bluish-white, shiny metal and it is an essential micronutrient for bio-oganisms. The common oxidation state of Zn in the environment is Zn(II). The world production of Zn reached 12 million tons in 2010 (USGS, 2011). Major applications of Zn include galvanization (anti-corrosion coatings on steel), zinc-based alloys, brass and bronze production (USGS, 2011). Other commercial and industrial uses include manufacturing of dyes, paints, rubber, wood preservatives, dry cell batteries, ointments, glass, ceramics and protective coating of other metals such as iron and steel to prevent corrosion. Zn is also widely used for many years as an additive in the cosmetics, pharmaceuticals, paint and plastic industries.

Three important sources of water contamination by Zn are metal manufacturing (33,000 - 178,000 metric tons/year), domestic waste water (21,000 - 58,000 metric tons/year), and atmospheric precipitation (2,600 - 31,000 metric tons/year) (Nriagu and Pacyna, 1988). The Recommended Dietary Allowance (RDA) for Zn is 11 mg/day for men and 8 mg/day for women (USDA, 2011). If high doses of Zn (10 - 15 times higher than the RDA) are taken through ingestion, even for a short time, stomach cramps, nausea, and vomiting may occur. The EPA has set drinking water standard of Zn to 5 mg/L, which is the highest allowable level among other heavy metals.

2.2.3 Cadmium (Cd)

It is a soft, silvery-white, ductile, lustrous but tarnishable metal. Cd can be found in the natural ore deposits and is commonly associated with presence of Zn, Pb and Cu. The world’s annual production of cadmium is around 20,000 tons (USGS, 2011). Discharge of Cd into water partly derives from electroplating industry (Naja and Volesky, 2009). Other sources of Cd exposure are cigarette smoking, nickel-cadmium batteries, smelter operation and industrial exposure in battery, paint pigment and plastic manufacturing industries. Recent trend of the increasing consumption of Cd in the industrial applications increases the risk of Cd release into the environment. For instance, rice and wheat from Cd-polluted areas of Japan showed concentration of Cd near 1 mg/kg, at least by a factor of 10 higher as compared to other parts of the world (Naja and Volesky, 2009).

The EPA has set the maximum acceptable concentration of Cd in drinking water at 0.005 mg/L. The tolerable daily intake of Cd established by the WHO is 0.06 and 0.07 mg/day for man and woman, respectively. Symptoms of acute Cd poisoning include pulmonary edema, headache, nausea, vomiting, chills and diarrhea. Long-term exposure to lower levels of Cd leads to the formation of kidney stones and kidney disease. At sufficiently prolong exposure, the human bones are severly affected resulting in *Itai Itai* disease, which is associated with ingestion of Cd-contaminated rice in Japan since 1950s by the aging women with low Fe and Zn levels in the blood (Naja and Volesky, 2009).

2.2.4 Copper (Cu)

Cu is a transition metal element with an average mass of 63.54 g/mol. Many Cu compounds can be recognized by their characteristic blue-green color. The worldwide mine production of Cu in 2010 reached 16,200 tons. It is widely used in electric and electronic products manufacturing, transportation vehicles, power generation and transmission, industrial machinery and equipment in building construction (USGS, 2011).

Cu is one of the first metals used by humans since 10,000 years ago. Cu has the best electrical and thermal conductivity among other metals which made it so useful in nearly all electrical contact applications including wiring, motors, radiators and various connectors. Other attractive properties of Cu include excellent alloying properties, corrosion resistance, ductility, anti-bacterial and recyclable properties (USGS, 2011).

About 5050 metric tons of Cu was discharged into the environment by various industries in the year of 2000 (ATSDR, 2004). Cu can be found in places near mines, smelters, industrial settings, landfills and waste disposal sites. The EPA has determined that drinking water should not contain more than 1.3 mg/L of Cu. The RDA of Cu is 0.9 mg/day for adults. Symptoms caused by Cu poisoning include nausea, vomiting and diarrhea (ATSDR, 2004). Intentionally high intakes of Cu can cause liver and kidney damage and even death.

2.3 Conventional technologies for metal removal

Conventional methods for heavy metals removal from wastewater include reverse osmosis, electrolysis, ion exchange, chemical precipitation, flocculation and coagulation. However, these conventional methods are quite expensive and not cost effective for metal concentrations lower than 100 mg/L (Zouboulis *et. al.*, 2010). Operational principle, key parameters, advantages and disadvantages of these treatment processes are discussed in the followed sections.

2.3.1 Reverse Osmosis

Operating principle of reverse osmosis involves a diffusive mechanism whereby metal ions are separated by a semi-permeable membrane at a pressure greater than osmotic pressure of the dissolved solids. The separation efficiency depends on the influent solute concentration, pressure, temperature and flow rate (Williams, 2003). The process is employed for the recovery of precious and common metals in the metal finishing industry. Reverse osmosis shows excellent performance in treating wastewaters containing a single metal or a mixture of metal ions. However, there are certain drawbacks limiting its wider applications in the industrial effluents treatment. In particular, the process requires high pressure (up to 100 atm) and thus is costly in terms of energy input. The delicacy of the membrane is also a restrictive factor depending on the solid content and pH of the treated wastewater (Cho *et al.*, 2010).

2.3.2 Electrodialysis

Electrodialysis is a membrane-based separation process in which electrically charged membranes and electrical potential difference are used to separate metal species from an aqueous solution. This process involves the migration of ions by electrical potential difference between two electrodes which causes separation of cations and anions making it suitable for separating non-ionized components from the ionized (Cho *et al.*, 2010). The key parameters of electrodialysis are concentration of feed solution, electric current density, flow velocities, stack resistance and the cell voltage. Advantage of this separation process is absence of flow phase changes and additional chemicals usage. One of the disadvantages of the process is the presence of other metal contaminants which may interfere by simultaneous or preferential plating on the membrane surface (Sameer, 1997). Another disadvantage is high operational cost due to the high energy consumption associated with electrolytic and membrane processes (Oliveira *et al.*, 2010). The process becomes less efficient for flows containing large particles such as metal hydroxides that cause fouling and clogging of the membranes.

2.3.3 Ion exchange

Ion-exchange is a physico-chemical process in which metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the ion-exchange resin. Resins used for the exchange of metal ions include zeolites, weak and strong anion and cation resins, chelating resins, microbial biomass and plant biomass (Tchobanoglous *et al.*, 2004). Several key parameters influence the efficiency of ion-exchange process: pH, presence of competing ions, the resin type, alkalinity and metal ions concentration. Heavy metals showed better removal in high pH medium because there is less competition with protons for the adsorption sites. The advantage of ion-exchange process is feasible regeneration of the saturated resin bed with acid or alkaline medium. However, the drawback of this treatment is its high cost associated with the required pretreatment process to reduce suspended solid concentration in influent and prevent fouling or channeling of the resins. Beside, resins tend to oxidize in the presence of magnesium or calcium ions and are prone to fouling by precipitates and organics (Cho *et al.*, 2010).

2.3.4 Chemical precipitation

Precipitation is a physico-chemical process in which soluble metals and inorganics are converted to relatively insoluble metal and inorganic salts (precipitates) by the addition of a precipitating agent. Most often, an alkaline reagent such as alum, lime and iron salts are used as precipitating agents to raise the solution' pH and lower the solubility of the metallic constituent initiating their precipitation. Thus, pH and concentration of metal ions in the influent are the key parameters influencing the efficiency of precipitation (Cho *et al.*, 2010).

The advantages of this process include relative simplicity of the treatment, low cost of chemical agents and automated pH control. However, this treatment has some drawbacks: it usually results in a net increase of the total dissolved solids and large volume of sludge that requires further treatment, which may be complicated due to the presence of toxic compounds (Cho *et al.*, 2010).

2.3.5 Adsorption

Adsorption is a process where a constituent in the liquid phase is accumulated on a surface of solid adsorbent by means of chemical, physical or electrostatic forces. Adsorption is an effective method for the removal of low concentration of metal ions and proven to be a simple technology to apply, operate and maintain (Hashem *et al.*, 2007). As we know, activated carbon is the most promising adsorbent for adsorption process because of its large surface area and high porosity. However, the cost of commercial activated carbon is quite high, roughly estimated at US$ 20 - 22/kg (Lin and Juang, 2009). In recent years, researchers have been looking for cheaper waste materials to produce low cost activated carbon to make application of activated carbon in adsorption process more attractive (Demirbas *et al.*, 2008).

2.4 Non-conventional adsorbents

In recent years, many non-conventional adsorbents including diverse agricultural waste, natural minerals, industrial by-products and microorganism biomass have been successfully used as alternative low cost and effective adsorbents for water purification purpose. Various precursors used for the preparation of the low cost adsorbents are naturally rich in a variety of functional groups and substances enabling their large scale applications.

Research showed that these adsorbents are inexpensive and readily available at various locations around the world. The natural biosorbents are biodegradable, generate zero waste and do not have long term negative impact on the environment as compared to other synthetic materials.

2.4.1 Agricultural wastes

Globally more than 140 billion metric tons of solid wastes are generated yearly only in agriculture sector alone (UNEP, 2009). Open burning of the waste generates CO_2 and other toxic substances which contribute to air, water pollutions and climate change. Besides, agricultural wastes are easily available in large quantities and in general show high efficiency in wastewater treatment. Thus, conversion of excessive and unutilized agricultural wastes into useful and high value adsorbent material has economic and environmental potentials.

A number of research studies evaluated the removal of heavy metals from wastewater onto a variety of agricultural wastes such as rice husk, orange peel, peanut shell, rice straw, mango peel, lemon peel, sugarcane baggase, nut shell and coffee husk (Daifullah *et al.*, 2003; Garg *et al.*, 2008; Oliveira *et al.*, 2008; Feng *et al.*, 2009; Iqbal *et al.*, 2009; Rocha *et al.*, 2009; Bhatnagar *et al.*, 2010; Hansen *et al.*, 2010).

In general, agricultural waste is a biomass, usually composed of cellulose and lignin as major constituents, and may also include hemicelluloses, pectin, extractives, lipids, proteins, simple sugars, water hydrocarbons and starch (Anwar *et al.*, 2010). Cellulose is a naturally occurring polysaccharide with a structure organized into fibrils surrounded by a matrix of lignin and hemicelluose with three hydroxyl groups. Hemicellulose is an amorphous polymer, usually consists of xylose, arabinose, galactose, glucose and mannose (Mandal and Chakrabarty, 2011). Lignin is a very complex molecule constructed of phenylpropane units containing many oxygen functional groups such as phenols and ketones which can serve as adsorption sites for binding heavy metals (Lalvani *et al.*, 1997).

Cellulose and lignin are rich in different kinds of functional groups, such as carboxyl, carbonyl, hydroxyl, phenolic and nitrogen-containing groups (Bailey *et al.*, 1999; Garcia-Reyes and Rangel-Mendez, 2009; Oliveira *et al.*, 2010). The oxygen in carbonyl and hydroxyl groups is considered as a strong Lewis base because of the presence of vacant double electrons, which could bind heavy metal ion by donation of an electron pair from these groups to form metal complexation for the sequencing of heavy metal ions (Pagnanelli *et al.*, 2003; Oliveira *et al.*, 2010). These components not only have excellent heavy metals sorption capability but they are also environmentally friendly due to their renewable, biocompatible, biodegradable and nontoxic nature (Iqbal *et al.*, 2009).

2.4.1.1 Sugar beet pulp and sugarcane bagasse

Removal of heavy metals by sugar beet pulp and sugarcane bagasse was reported by Aksu and Isoglu (2005) and Pereira *et al.* (2010). These natural adsorbents are able to strongly bind metal cations in aqueous solution due to the presence of pectic substances, hydroxyl and phenolic groups present in cellulose, polyoses and lignin (Wan Ngah and Hanafiah, 2008). Aksu and Isoglu (2005) reported adsorption capacity of raw sugar beet pulp of 28.5 mg Cu(II) /g. This material is a natural polysaccharide and composed of cellulosic and pectic substances. Another study by Isa *et al.* (2010) reported 5.32 mg(Cd)/g adsorption capacity of sugarcane bagasse.

2.4.1.2 Nut shells

Hansen *et al.* (2010) studied adsorption of copper by seven types of agriculture wastes at copper concentration of 764.6 mg/L, pH 5 and for 30 hours. It was observed that olive pips, peach stones and pine sawdust were the three best biosorbents, with desorption capacities of 18.4, 20.9 and 15.4 mg/g, respectively. Eucalyptus bark (12.3 mg/g), peanut shell (1.9 mg/g), nut shell (3.1 mg/g) and plum shell (6.6 mg/g) showed lower sorption capacities.

According to Pehlivan *et al.* (2009a), the maximum adsorption capacities of hazelnut shell (HNS) and almond shell (AS) were 28.18 and 8.08 mg Pb^{2+}/g, respectively. The results indicated that the optimum pH for the removal of Pb(II) by HNS and AS was around pH 6.0 - 7.0. Pehlivan and Altun (2008) also reported Cr(VI) ion adsorption capacities of 8.01, 8.28 and 3.40 mg/g for walnut (WNS), HNS and AS, respectively. The results indicated that optimum pH for the removal of Cr(VI) ion by the adsorbents was around pH 3.2 - 3.5 due to protonation leading to electrostatic attraction between Cr(VI) anion and surface functional group.

2.4.1.3 Rice husk

Rice husk is an agricultural waste of rice milling industry. Around 100 million metric tons of it is produced from every 500 million metric tons of harvested rice (Daifullah *et al.*, 2003). Rice husk contains large amounts of cellulose and lignin, which are important materials in adsorption process (Foo and Hameed, 2009). Daifullah *et al.* (2003) investigated efficiency of biosorbents made from rice husk in small scale wastewater treatment plant. Sorption experiments were carried out by taking 0.01 - 0.15 g of rice husk, mixed with 250 mL of wastewater samples with initial metals concentration ranging from 0.01 - 9.74 mg/L and agitated for 4 hours. The rice husk showed approximately 100% removal of Fe(II), Mn(II), Zn(II), Cu(II), Cd(II) and Pb(II).

2.4.1.4 Fruit peels

Orange peel was biomodified via hydrolysis of grafted copolymer which was synthesized by interaction of methyl acrylate with orange peel. The adsorption experiments were conducted at pH 5 with 0.05 g of sorbent in 25 mL of Cu(II) solution for 3 hours at 120 rpm and 30 ℃. Maximum adsorption capacity of chemically modified orange peel was 289 mg Cu^{2+}/g, about 6.5 times higher than that of the unmodified orange peel mainly due to the increase in carboxyl groups after the modification (Feng *et al.*, 2009).

High pectin content of pomelo peel was investigated for Cd(II) removal by Saikaew *et al.* (2009). The experiment was conducted by adding 0.1 g of sorbent into 100 mL of Cd(II) solution over a range of different initial concentrations from 25 to 100 mg/L for 24 hours, at 250 rpm and 25 ℃. Two pH 3.0 and pH 5.0 were investigated in the study. The results showed that the maximum adsorption capacity of pomelo peel reached 19.23 and 21.83 mg Cd^{2+} /g at pH 3.0 and pH 5.0, respectively.

Mango peel was evaluated as a new biosorbent for the removal of Cd(II) and Pb(II) from aqueous solutions (Iqbal *et al.*, 2009). Sorption capacity of mango peel was determined by placing 0.25 g of sorbent in 100 mL solutions of metal ions concentration (10 - 600 mg/L) at pH 5 and 100 rpm for 2 hours at room temperature. The maximum removal of Cd(II) and Pb(II) was found to be 68.92 and 99.05 mg/g, respectively. Anwar *et al.* (2010) conducted adsorption experiments with initial concentration of Pb(II) and Cd(II) varying from 30 to 80 mg/L. Two g for Pb(II) and 1.5 g for Cd(II) of dried banana peel was added into 50 mL of respective solution and agitated for 30 minutes. pH was adjusted to pH 5.0 for Pb(II); whereas for cadmium pH it was fixed at 3.0. Adsorption capacities of banana peel reached 2.18 mg Pb^{2+} /g and 5.71 mg Cd^{2+}/g, respectively. Table 2.4 shows a list of biosorbents prepared from the agricultural wastes which are arranged in the order of increasing adsorption capacity of various metal ions.

Table 2.4 Agricultural waste based biosorbents used for metal removal

Agricultural Waste	Metal Ion	Sorption Capacity (mg/g)	Reference
Maize corncon	Cd(II)	105.60	Garg *et al.*, 2008
Jatropha oil cake	Cd(II)	86.96	Garg *et al.*, 2008
Sugarcane bagasse	Cd(II)	69.06	Garg *et al.*, 2008
Mango peel	Cd(II)	68.92	Iqbal *et al.*, 2009
	Pb(II)	99.05	
Almond green hull	Co(II)	45.50	Ahmadpour *et al.*, 2009
Date pit	Cu(II)	35.90	Al-Ghouti *et al.*, 2010
	Cd(II)	39.50	
Ficus fruit	Cr(VI)	31.60	Rao and Rehman, 2010
Sugar beet pulp	Cu(II)	28.50	Aksu and Isoglu, 2005
Hazelnut shell	Pb(II)	28.18	Pehlivan *et al.*, 2009a
Lemon peel	Co(II)	22.00	Bhatnagar *et al.*, 2010
Pomelo peel	Cd(II)	21.83	Saikaew *et al.*, 2009
Peach stones	Cu(II)	20.90	Hansen *et al.*, 2010
Olive oil pomace	Cr(VI)	18.69	Malkoc *et al.*, 2006
Olive pips	Cu(II)	18.40	Hansen *et al.*, 2010
Coffee ground	Cd(II)	15.65	Azouaou *et al.*, 2010
Pine sawduct	Cu(II)	15.40	Hansen *et al.*, 2010
Eucalyptus bark	Cu(II)	12.30	Hansen *et al.*, 2010
Almond shell	Pb(II)	8.08	Pehlivan *et al.*, 2009a

Table 2.4 (continued) Agricultural waste based biosorbents used for metal removal

Agricultural Waste	Metal Ion	Sorption Capacity (mg/g)	Reference
Coffee husk	Cu(II)	7.50	Oliveira *et al.*, 2008
	Cd(II)	6.85	
	Zn(II)	5.57	
	Cr(II)	6.96	
Plum shell	Cu(II)	6.60	Hansen *et al.*, 2010
Cocoa shell	Pb(II)	6.23	Meunier *et al.*, 2003
Banana peel	Cd(II)	5.71	Anwar *et al.*, 2010
	Pb(II)	2.18	
Chestnut shell	Cd(II)	5.57	Vazquez *et al.*, 2009
Sugarcane bagasse	Cd(II)	5.32	Isa *et al.*, 2010
Nut shell	Cu(II)	3.10	Hansen *et al.*, 2010
Peanut shell	Cu(II)	1.90	Hansen *et al.*, 2010
Potato peel	Cu(II)	0.39	Aman *et al.*, 2008

2.4.2 Agriculture-based activated carbons

Activated carbon is the most preferred adsorbent with a relatively high cost which limits its widespread use. Biomass of agricultural wastes can be used to produce activated carbon. Conversion of agricultural waste materials into activated carbon increase the powerful adsorptive properties to the product because fine internal structure of activated carbon. Agricultural wastes have been successfully converted into activated carbon, for example, hazelnut shell, coconut coirpith, palm shell, apricot shell, pecan shell, almond shell and pine cone were converted into activated carbons which possess good performance in the removal of pollutants from the aqueous solutions (Bansode *et al.*, 2003; Kardirvelu and Namasivayam, 2003; Erdogan *et al.*, 2005; Demirbas *et al.*, 2008; Issabayeva *et al.*, 2010; Momcilovic *et al.*, 2011).

Conversion of agricultural wastes into activated carbon with highly developed porosity and correspondingly large surface area involves two main steps: 1) carbonization of carbonaceous agricultural wastes, and 2) physical or chemical activation, or sometimes both. During carbonization at temperatures below 700 ℃ in an inert atmosphere non-carbon elements are oxidized and removed leaving only carbon and inorganic ash. The physical activation occurs through introduction of activation agents such as steam or carbon dioxide at 700-1100 ℃ temperature to develop porosity within the carbonized material (Gua and Lua, 2000; Gua and Lua, 2003).

The chemical activation is normally a one-step method occurring at temperatures around 750 ℃. Chemical activation may involve different chemical activating agents, for example, zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4), potassium hydroxide (KOH), potassium carbonate (K_2CO_3), sodium hydroxide (NaOH) and sulphuric acid (H_2SO_4) which increase adsoptive properties of activated carbons (Rahman *et al.*, 2005; Adinata *et al.*, 2007; Demirbas *et al.*, 2008; Tay *et al.*, 2009; Zabihi *et al.*, 2010; Wang *et al.*, 2010b; Momcilovic *et al.*, 2011;)

The chemical agents help to develop the carbon porosity by dehydration and degradation of the carbonaceous material. Lower temperature range, lower energy cost, shorter activation time, higher adsorbent yields and high porosity are the advantages of chemical activation process (Geethakarthi and Phanikumar, 2011). However, the drawbacks of the method are the high costs of activating agents and the need to run additional washing procedures to remove chemical agents. Table 2.5 summarizes on metal ions adsorption by the agriculture-based activated carbons, based on the reported adsorption capacity starting with the highest uptake.

Table 2.5 Aqueous phase application of agricultural-based activated carbons

Agricultural-based Activated Carbon	Metal Ion	Adsorption Capacity (mg/g)	Surface Area (m^2/g)	Reference
Almond shell	Cr(VI)	190.30	412.00	Demirbas *et al.*, 2008
Hazelnut shell	Cr(VI)	170.00	-	Kobya, 2004
Walnut shell	Hg(II) Hg(II)	151.50 100.90	780.00 803.00	Zabihi *et al.*, 2010
Apricot shell	Ni(II)	101.01	1214.00	Erdogan *et al.*, 2005
Chestnut shell	Cu(II)	100.00	1319.00	Ozcimen and Ersoy-Mericboyu, 2009
Polygonum orientale Linn	Pb(II)	98.39	1398.00	Wang *et al.*, 2010b
Palm shell	Pb(II)	95.20	957.04	Issabayeva *et al.*, 2006
Coconut coirpith	Cd(II)	93.40	-	Kadirvelu and Namasivayam, 2003
Hazelnut shell	Cu(II)	58.27	441.00	Demirbas *et al.*, 2008
Bagasse	Cd(II) Zn(II)	49.07 54.00	960.00	Mohan and Singh, 2002
Grapeseed	Cu(II)	48.78	916.00	Ozcimen and Ersoy-Mericboyu, 2009
Coirpith	Cu(II)	39.70	-	Namasivayam and Kadirvelu, 1997
Palm shell	Cu(II)	30.80	-	Issabayeva *et al.*, 2010
Pine cone	Pb(II)	27.53	1094.10	Momcilovic *et al.*, 2011
Ceiba pentandra hull	Pb(II) Zn(II)	25.50 24.10	521.00	Rao *et al.*, 2008
Ceiba pentandra hull	Pb(II) Zn(II)	25.50 24.10	521.00	Rao *et al.*, 2008
Rice husk	As(II)	1.22	811.00	Kalderis *et al.*, 2008

Table 2.5 shows that the surface areas of agricultural-based activated carbons may range from 412 to 1398 m^2/g as well as the sorption capacity. The presented data in the reviewed literature clearly show that agricultural waste based activated carbons are promising materials for the removal of heavy metals from aqueous solutions.

2.4.3 Natural minerals

Natural minerals is naturally occurring inorganic solid chemical substances formed through biogeochemical processes with a unique chemical composition, highly ordered atomic structure and specific physical properties. Since mineral adsorbents are available in large quantities, they have good potential to be used for the removal of heavy metals from wastewater. The examples of the minerals commonly used as commercial adsorbents for wastewater treatment include activated alumina, dolomite, zeolite, kaolin, clay, bentonite and diatomine.

2.4.3.1 Activated alumina

Activated alumina comprised of a series of nonequilibrium forms of partially hydroxylated alumina oxide, Al_2O_3. In general, as a hydrous alumina precursor is heated, hydroxyl groups are driven off leaving a porous solid structure of activated alumina (Bhatnagar and Sillanpaa, 2010). It is commonly used as ion exchanger to remove inorganic compounds such as anions and cations in water treatment and it has surface area ranging from 50 to 300 m^2/g (Kasprzyk-Hordern, 2004). It is known to be an effective and inexpensive material for the removal of arsenic and selenium from drinking water and it was nominated by the EPA as the best available treatment for point-of-use applications (Su *et al.*, 2008).

Naiya *et al.* (2009) reported that the highest monolayer adsorption capacity of activated alumina was 35.06 mg/g for Cd(II) and 83.33 mg/g for Pb(II) at pH 5. The authors showed that the activated alumina is an effective adsorbent due to its high surface area, mechanical strength and amphoteric properties. However, one disadvantage of the adsorbent was noted: both acid and base are required for its regeneration and, the medium promotes dissolution of the mineral producing fine particles slowing the adsorption kinetics and the spent regenerant must be disposed of (Clifford, 1999).

2.4.3.2 Dolomite

Dolomite is a carbonate mineral consisting of alternating layers of calcium (Ca) and magnesium (Mg) separated by the layers of carbonate (CO_3) ions. It is typically represented by a stoichiometric chemical composition of $CaMg(CO_3)_2$ where Ca and Mg are present in equal proportions (Warren, 2000). It is a low-cost conventional adsorbent and has a widespread geological distribution; its deposits can be found in Turkey, China, India, Indonesia and Vietnam. Dolomite is a very cheap material and the total production cost is about 8 $/ton (Pehlivan *et al.*, 2009b). Ghaemi *et al.* (2011) investigated the adsorption efficiency of dolomite powder towards Sr(II) and Ba(II) removal from aqueous solution. The maximum adsorption capacities were found to be 1.17 and 3.96 mg/g at pH 5.5, respectively.

Pehlivan *et al.* (2009b) reported the adsorption capacity of 8.26 mg/g for Cu(II) and 21.74 mg/g for Pb(II) onto dolomite. The authors found that the metals adsorption occurs at low concentrations and precipitation starts dominating as the metal concentration increase, which is associated with the reactions of metal ions with CaO and MgO via surface complexation and ion exchange mechanisms. Salameh *et al.* (2010) reported successful removal of As(V) from aqueous solution onto dolomite. The capacity of dolomite toward As(V) was 0.652 mg/g. Dolomite showed very good results in the treatment of the groundwater in Bangladesh (Ayoub and Mehawej, 2007; Salameh *et al.*, 2010).

2.4.3.3 Zeolite

Zeolites are naturally occurring silicate minerals which can also be produced synthetically. There are 40 natural and over 100 synthetic zeolites. Common forms of natural zeolites such as clinoptilolite, mordenite, philipsite, chabazite, analcime and others are found in many parts of the world. Zeolite is a potential adsorbent mainly because its sorption properties provide a combination of ion exchange and molecular sieve properties (very regular pore structure of molecular dimensions) which can be easily modified (Cincotti *et al.*, 2006; Motsi *et al.*, 2009). Natural zeolites are also cost efficient, its price is around US$ 0.03 – 0.12/kg in the United States of America (Babel and Kurniawan, 2003).

Natural Bulgarian zeolite was tested for its ability to remove Cu(II) from wastewater (Panayotova, 2001). The uptake of Cu(II) by the natural zeolite was 6.74 mg/g. The study showed that the ion exchange sorption is the basic mechanism of Cu(II) uptake by the natural zeolite. Furthermore, zeolites have been reported as effective adsorbents for Cu(II), Pb(II), Fe(III), Mn(II) and Zn(II) removal (Wang and Ariyanto, 2007; Wang *et al.*, 2008; Motsi *et al.*, 2009).

2.4.4 Industrial and municipal solid wastes

Industrial and municipal solid wastes are often not properly utilized, abundantly available and can be obtained from industrial processing plants almost free of cost. From an environmental viewpoint, the elimination of industrial wastes represents a solution to pollution problems and thus deserves more attention. A number of different wastes generated by various industries have been investigated as adsorbents for heavy metal removal in recent years.

2.4.4.1 Fly ash

Fly ash is an abundant solid waste product mostly from power plants and construction sites. It consists of carbon, oxides of silica and alumina which play significant role in adsorption of pollutant species (Bhatnagar and Sillanpaa, 2010). Fly ash could easily be solidified after the metals are adsorbed because it contains pozzolanic particles that react with lime in the presence of water forming cementitious calcium-silicate hydrates. The main mechanisms involved in the removal of metal ions from solution are surface adsorption and precipitation (Bhatnagar and Sillanpaa, 2010). Bhattacharya *et al.* (2008) studied the sorption of Cr(VI) from aqueous solution using fly ash, the adsorption capacity reached 23.86 mg/g. It was reported that fly ash pellets can achieve adsorption of 20.92 mg Cu^{2+}/g and 18.98 mg Cd^{2+}/g (Papandreou *et al.*, 2007) showing that fly ash can be considered as a potential adsorbent for the removal of metal ions.

2.4.4.2 Blast furnace sludge and slag

A number of wastes are produced in large quantities by the steel industry such as blast furnace sludge and slag which have been tested as metal-adsorbents (Bhatnagar and Minocha, 2006). The dried sludge and slag have high content of iron oxides and coke making the materials effective metal adsorbents (Bailey *et al.*, 1999). According to Gupta *et al.* (1997), blast furnace slag showed good sorption property for Zn(II) and Cd(II) in batch adsorption experiments with the maximum uptakes of 17.66 mg Zn(II) /g at pH 6.0 and 18.72 mg Cd(II) /g at pH 5.0.

Kalmykova *et al.* (2010) also investigated the potential of blast furnace sludge for the removal of heavy metals. The maximum removal of Cu(II), Zn(II), Cr(VI), Pb(II) and Cd(II) at 80 ℃ were found to be 24, 9.7, 16, 80 and 10 mg/g, respectively. The capacity order was: Pb > Cu > Cr > Cd > Zn, correlating with the order of the metals' electronegativity and hydrated ionic radii.

2.4.4.3 Red mud

Red mud is a solid waste formed during bauxite processing in aluminium industry. A typical Bayer process plant (a facility for the process of refining bauxite to produce alumina) generates 1 to 2 tons of red mud per ton of produced alumina (Gupta and Ali, 2002). Red mud is composed of fine particles of silica, aluminum, iron, calcium, titanium oxides and hydroxides providing high surface reactivity of the material. Red mud was used for the removal of Cu(II) ions from aqueous solution by Nadaroglu *et al.* (2010). They found that the adsorption capacity of red mud was 5.35 mg Cu(II)/g at 30 ℃.

Besides, Lopez *et al.* (1998) investigated the use of red mud as metal adsorbent. The maximum adsorption capacities for Cu(II), Zn(II), Ni(II) and Cd(II) were found to be 19.72, 12.59, 10.95 and 10.57 mg/g, respectively. The research showed that red mud presents a promising application in wastewater treatment for the removal of heavy metals. Table 2.6 presents data on the application of the industrial and municipal solid wastes in wastewater treatment which are arranged in the order of the increasing metal uptake.

Table 2.6 Industrial and municipal solid wastes used for metal removal

Biosorbent	Metal ion	Sorption capacity (mg/g)	Reference
Blast furnace sludge	Pb(II) Cu(II) Cr(VI) Cd(II) Zn(II)	80.00 24.00 16.00 10.00 9.70	Kalmykova *et al.*, 2010
Blast furnace slag	Pb(II) Cr(VI)	40.00 7.50	Srivastava *et al.*, 1997
Fly ash	Cr(VI)	23.86	Bhattacharya *et al.*, 2008
Fly ash	Cu(II) Cd(II)	20.92 18.98	Papandreou *et al.*, 2007
Red mud	Cu(II) Zn(II) Ni(II) Cd(II)	19.72 12.59 10.95 10.57	Lopez *et al.*, 1998

Table 2.6 (continued) Industrial and municipal solid wastes used for metal removal

Biosorbent	Metal ion	Sorption capacity (mg/g)	Reference
Fly ash	As(V)	19.46	Li *et al.*, 2009
Blast furnace slag	Zn(II)	17.66	Gupta *et al.*, 1997
	Cd(II)	18.72	
Activated red mud	Zn(II)	14.92	Sahu *et al.*, 2011
Red mud	Cu(II)	5.35	Nadaroglu *et al.*, 2010

Besides, other various industrial and municipal wastes such as iron waste, iron slages, tires, sewage sludge and plastic wastes have been explored as materials to remove various pollutants including heavy metals (Bhatnagar and Sillanpaa, 2010).

2.4.5 Microorganism biomass

Numerous microorganisms' strains biomass have been investigated for metal ions adsorption. The biosorbents can be classified into the following categories: bacteria (e.g. *Bacillus subtilis*) and fungi (e.g. *Aspergillus niger*) (Veglio and Beolchini, 1997; Wang and Chen, 2009). Microbial cell walls, outer layers and exopolymers containing various functional groups such as hydroxyl, amino, carboxyl, sulphate, phosphate and imidazoles associated with polysaccharides and protein have significant metal-sorption properties (Wang and Chen, 2009). Microbial biomass is easy to produce using inexpensive growth medium or by-products from various fermentation industries.

2.4.5.1 Bacterial Biomass

The ability of bacteria to accumulate metals is well documented for bacteria strains such as *Bacillus sp., Citrobacter sp.* and *Azobacter sp.*. The bacterial cell wall contains peptidoglycan, a linear polymer of alternating units of two sugar derivatives, poly-N-actetylglucosamine and N-acetylmuramic acid (Wang and Chen, 2009). It is relatively porous and acts as an impermeable barrier (Cho *et al.*, 2010). Polyalcohols known as teichoic acids imbedded in the Gram-positive cell wall with overall negative charge (Cho *et al.*, 2010). Carboxylic, phosphordiesters, phosphoric, amines and hydroxyl groups present in the peptidoglycan, teichoic and teichuronic acids of the membrane cell wall are reported responsible for high metal uptake (Yun *et al.*, 2011).

Teichioc acid, teichuronic acid and lipoteichoic acid are normally not found in Gram-negative cell walls because cell wall of Gram-negative bacteria is much thinner and contains only 20% of peptidoglycan (Cho *et al.*, 2010). Bacteria remove the heavy metal through complexation by the secretion of polysaccharides and other organics from inside the cell or by the adsorption of metals directly to the cell wall (Ledin *et al.*, 1999). The cell wall of bacteria contains functional groups that include carboxyl, phosphoryl, hydroxyl, amino and sulfhydryl groups. These functional groups can act to either hold the metal in place through adsorption (Borrok *et al.*, 2004), or to catalyze metal reduction (Cummings *et al.*, 2007).

Table 2.7 shows the sorption capacities of bacterial biomass to remove metal ions reported in the literature.

Table 2.7 Removal of heavy metal ions onto original and modified bacterial biomass

Bacteria	Modifying Agent	Sorption Capacity (mg/g)				Reference
		Original		Modified		
Pseudomonas sp.	-	Cd(II)	278.00	-	-	Ziagova *et al.*, 2007
Staphylococcus xylosus	-	Cd(II)	250.00	-	-	Ziagova *et al.*, 2007
Arthrobacter nicotianae	-	U(VI) Th(VI)	68.80 75.90	-	-	Nakajima and Tsuruta, 2004
Bacillus subtilis	-	Hg(II)	68.5	-	-	Wang *et al.*, 2010a
Pseudomonas cepacia	-	Cu(II)	65.30	-	-	Savvaidis *et al.*, 2003
Symphortcarpus albus	-	Pb(II)	62.10	-	-	Akar *et al.*, 2009
Bacillus subtilis IAM 1056	-	U(VI) Th(VI)	52.40 71.90	-	-	Nakajima and Tsuruta, 2004
Streptomyces rimosus	NaOH	Zn(II)	30.00	Zn(II)	80.00	Mameri *et al.*, 1999
Bacillus subtilis	Ultrapure water & cationic exchange resin	Cu(II)	29.62	Cu(II)	18.42	Fang *et al.*, 2010
Bacillus subtilis IAM 1026	-	Cu(II)	20.80	-	-	Nakajima *et al.*, 2001

Bacillus sp. is a relatively large (1.5 µm wide, 3 µm long), gram-positive, strictly aerobic or facultatively anaerobic encapsulated bacteria. Among other bacteria, *Bacillus* sp. is identified as a high potential adsorbent for metal sequestration and it is used in commercial biosorbent preparation (Cho *et al.*, 2010). *B. subtilis* is nonpathogenic bacteria which presents high interest for research and industrial applications such as antibiotics production. In addition, *B. subtilis* is a source of industrial enzymes such as amylases used in starch modifications, proteases and cellulases used as additives in laundry detergents. Besides, *B. subtilis* can be readily available in the form of industrial wastes of the industry. The major importance of carboxyl groups of the peptidoglycan as well as a minor contribution of phosphate groups in metal ions uptake by *B. subtilis* biomass were demonstrated by Brierley (1990).

2.4.5.2 Fungal Biomass

Fungi can be classified into filamentous fungi (e.g. *Aspergillus*) and unicellular yeast (e.g. *Saccharomyces*) based on the structure of the fungal wall. Mycelial wall of filamentous fungi appears to be layer structured while yeast cells commonly vary from a spherical to an oval shapes depending on the yeast species, nutrition level and conditions of cultivation (Wang and Chen, 2009). Filamentous fungal biomass of *Aspergillus niger* showed excellent potential for metal ions biosorption due to the high polysaccharide content in the cell walls (Wang and Chen, 2009).

Sorption capacity of *A. niger* towards various metal ions is reported in Table 2.8.

Table 2.8 Removal of heavy metal ions onto original and modified *A. niger*

Fungi species	Modifying Agent	Sorption Capacity (mg/g)				Reference
		Original		Modified		
Aspergillus niger	-	Cr(VI)	117.33	-	-	Khambhaty *et al.*, 2009
Aspergillus niger	Poly(vinyl) alcohol hydrogel immobilized	Cu(II)	17.60	Cu(II)	34.13	Tsekova *et al.*, 2010b
		Cd(II)	69.44	Cd(II)	60.24	
Aspergillus niger	Ca-alginate immobilized	Cu(II)	14.00	Cu(II)	17.00	Tsekova *et al.*, 2010a
		Zn(II)	0.66	Zn(II)	2.40	
		Pb(II)	0.15	Pb(II)	0.15	
		Cd(II)	0.25	Cd(II)	0.30	
Aspergillus niger	Poly(vinyl) alcohol hydrogel immobilized	Cu(II)	14.00	Cu(II)	15.60	Tsekova *et al.*, 2010a
		Zn(II)	0.66	Zn(II)	2.50	
		Pb(II)	0.15	Pb(II)	0.14	
		Cd(II)	0.25	Cd(II)	0.25	
Aspergillus niger	NaOH	Pb(II)	7.42	Pb(II)	2.25	Amini *et al.*, 2008

Table 2.8 (continued) Removal of heavy metal ions onto original and modified *A. niger*

Fungi Species	Modifying Agent	Sorption Capacity (mg/g)				Reference
		Original		Modified		
Aspergillus niger	Cetyl trimethyl ammonium bromide	Cr(VI)	1.50	Cr(VI)	3.10	Mungasavalli *et al.*, 2007
Aspergillus niger	NaOH	-	-	Cu(II) Pb(II)	28.70 32.60	Dursun,2006
Aspergillus niger	Formalin	-	-	Cu(II)	23.62	Mukhopadhyay *et al.*, 2007
Aspergillus niger	NaOH	-	-	Cd(II) Ni(II) Pb(II)	2.20 1.60 4.70	Amini and Younesi, 2009

A variety of ligands may be present in the fungi biomass including carboxyl, amino, phosphate, hydroxyl and sulphydryl groups. Nitrogenated and phosphated biomolecules inside the cell wall of fungi are the major contributors to the adsorption of cations and anions (Gracia-Reyes, 2009). Nitrogenated biomolecules include chitosan, chitin and peptidoglycan; whereas phosphated biomolecules include teichoic acid, lipopolysaccharides and phospholipids. Protonated amine groups create a positive charge on the biomass surface allowing the removal of anions from aqueous solutions at certain conditions. Nitrogen-containing groups can also form complexes with cations because of the present free election pairs. *A. niger* is an economically important fungi species for fermentation of citric acid and enzyme glucamylase. Large quantities of fungal mycelia by-products are available from industrial fermentation processes continue to attract interest in the research for good metal biosorbents.

However, some biomass also indicated limitations related to less sorption efficiency and stability, restricting their commercial application due to the physiological states and surface properties of biomass (Skowronski *et al.*, 2001). Constructive efforts towards structural modifications of biosorbents can lead to the enhancement of sorption efficiency and environmental stability promoting their broader commercial use (Srivastava and Goyal, 2010).

2.5 Novel adsorbents

Graft co-polymerization is a new technique used to improve the stability and mechanical strength of natural biosorbents especially for long term applications since the biosorbent regeneration is necessary feature to increase the cost-effectiveness of the treatment process (Srivastava and Goyal, 2010). Novel adsorbent is attained through graft co-polymerization in which a half of the structure is grafted on another half of structure such as grafting an alkyl acrylate to a polycarbonate, polysaccharides and other cellulosic materials in the solid phase (Wada *et al.*, 2006). Graft copolymerization of adsorbent has attracted great research interest because of the resulting high strength, thermal stability, biodegradability and non-toxicity of the produced adsorbents (Ramakrishna *et al.*, 2005).

Goyal and Srivastava (2009) developed a novel *Zea mays* based biomaterial by using acetylation, succination and graft co-polymerization processes. The novel adsorbent showed increased sorption efficiency from 2 to 15 % and enhanced stability in the reusability cycles from 3 to 5 cycles in the adsorption of Pb(II), Cd(II), Ni(II) and Cr(III) from aqueous solution.

Zheng *et al.* (2010) prepared a graft co-polymerization of acrylonitrile using potassium permanganate as redox initiator onto the corn stalk, which increased the adsorption capacity of the biosorbent towards Cd(II) from 3.81 to 22.17 mg/g. In another study, Hashem (2006) showed the maximum capacity of 39 mg Cu(II)/g of grafted acrylonitrile sunflower stalks.

Shibi and Anirudhan (2002) grafted acrylamide onto banana stalks which increased the adsorption capacity of from 138 to 210 mg/g for Hg(II). Similarly, Bau-Xiu *et al.* (2006) grafted acrylic acid and acrylamide onto cellulose promoting removal of 49.6 mg of Cu(II)/g from aqueous solutions, with regeneration of the material in seven cycles with 90% efficiency.

Yin *et al.* (2008) conducted a study on the removal of Ni(II), Cd(II) and Pb(II) ions from aqueous solutions onto polyethyleneimine (PEI) impregnated palm shell activated carbon (PSAC). They found that the surface area of the PSAC significantly decreased from 1027 to 33 m^2/g due to the impregnation of PEI. However, the modified adsorbent showed increased Ni(II) and Cd(II) adsorption capacities and reduced adsorption capacity for Pb(II) at pH 5.

Pang *et al.* (2011) attempted grafting PEI onto the magnetic porous matrix which was used in removal of Cu(II), Zn(II) and Cd(II) ions from aqueous solutions with high efficiency and a regeneration in four successive cycles with 85% efficiency. Overall, the graft copolymerization improves the adsorption capacity, selectivity and stability of the adsorbents by forming many reactive groups on the adsorbent surface.

Removal of metals from effluents utilizing novel adsorbents is a relatively recent development. Traditionally, activated carbons are used in water treatment industries. However, the high cost of commercial activated carbon limits its wider use. Whereas, activated carbons prepared from locally available waste materials receive growing number of applications.

2.6 Palm shell activated carbon (PSAC)

Malaysia is one of the largest producers and exporters of palm oil contributing 49.5 % to the world production and 64.5 % of world exports (MPOB, 2004). The total oil palm tree plantation area covered up to 4.69 million hectares resulting also in the production of palm shell wastes reaching 4.21 milion tonnes in 2009 (Ng *et al.*, 2011). Some portion of the wastes is burned for heating purposes but mostly it is dumped in areas adjacent to the mill creating serios environmental problems. The utilization of this plentiful and readily available waste material for activated carbon synthesis induces a large-scale recycling mechanism as a part of the sustainable solid waste management programme in the palm oil industry reducing the environmental pollution impact and promoting rational consumption of the natural resources.

Palm shell is suitable for preparation of activated carbon due to its excellent natural structure, high volume of porosity, high specific surface area, high carbon and low ash content (Gua and Lua, 2003). As other carbonaceous materials, palm shells have been successfully converted into a structural activated carbon by physical and chemical activation.

Some researchers obtained palm shell carbon by chemical activation in phosphoric acid (H_3PO_4), potassium carbonate (K_2CO_3), zinc chloride ($ZnCl_2$), potassium hydroxide (KOH) and sodium hydroxide (NaOH) to increase the surface area and narrow micropore distribution of the activated carbon (> 2 nm) (Guo and Lua, 2003; Lua and Yang, 2004; Raymundo-Pinero *et al.*, 2005; Adinata *et al.*, 2007). The chemical reagents may promote the formation of a rigid matrix which is less prone to the loss of volatiles and volume contraction at high temperatures.

In the pursuit of obtaining good quality low cost adsorbents, efforts have been put to increase PSAC adsorption capacity towards heavy metals. Onundi *et al.*, (2010) studied the sorption of Cu(II), Ni(II) and Pb(II) ions onto PSAC from the synthetic wastewater. The adsorbent was acquired from KD Technology Sdn. Bhd. (Kuala Lumpur, Malaysia) and it had surface area of 513.30 m^2/g. The metal solution was diluted with distilled water to mimic the concentration of the semiconductor industrial wastewater. Batch adsorption experiments were carried out to identify the effect of pH and contact time on adsorption of copper, nickel and lead ions from the mixture of metals. The adsorption results showed that the sorption of metal ions increased when solution’s pH increased. Maximum adsorption was observed in the pH range of 4.5 to 6.0. It might be due to the partial hydrolysis of metal ions [M(II)] resulting in the formation of $M(OH)^+$ ions and $M(OH)^{2+}$, which would be adsorbed to a greater extent on a less polar carbon surface of the adsorbent as compared to M(II) ions (Onundi *et al.*, 2010). Furthermore, the authors noted that low solubility of hydrolyzed metal species may be another factor affecting maximum adsorption in pH range of 4.5 to 6.0. The maximum sorption capacity of PSAC reached 1.34 mg/g for Pb(II), 1.58 mg/g for Cu(II) and 0.13 mg/g for Ni(II). The equilibrium was reached within 30 minutes for lead and in 75 minutes for both Cu(II) and Ni(II).

Effect of different temperatures on adsorption of Pb(II) from aqueous solution onto PSAC were studied by Ho and Ofomaja (2005). The sorption was better at elevated temperatures (65 ℃) with maximum sorption capacity of 49.90 mg Pb(II)/g. The results indicated that the sorption was spontaneous and endothermic in nature.

Wan Nik *et al.*, (2006) reported that the optimal treatment for preparation of microporous PSAC with high surface area (1058 m^2/g) involved impregnation of the palm shells with 30% phosphoric acid at activation temperature of 500 ℃ within 2 hours. Percentage removal of metal ions by activated carbon treated with phosphoric acid for Cr(VI) was 100%, followed by 99.8% for Pb(II), 99.5% for Cd(II) and 25% for Cu(II).

Issabayeva *et al.*, (2010) studied the removal of Cu(II) ions from aqueous solution using PSAC with 957.04 m^2/g surface area. Uptake of Cu(II) was noticeably higher at pH 5 than at pH 3 with maximum adsorption capacity of 30.5 mg/g. A work on the removal of Pb(II) from aqueous solutions onto PSAC was conducted by Issabayeva *et al.*, (2006). PSAC showed high adsorption capacity for Pb(II), especially at pH 5 with an uptake of 95.2 mg/g.

Table 2.9 shows a summary on the adsorption capacities and surface areas of the original and modified PSACs for various metal ions. The data are presented in the ascending order of the metal ions adsorption capacities.

Table 2.9 Summary on the adsorption capacities and surface areas of PSAC

Adsorbent	Modifying Agent	Metal ions	Adsorption Capacity (mg/g)		Surface Area (m^2/g)		Reference
			Original	Modified	Original	Modified	
PSAC	-	Pb(II)	95.20	-	957.04	-	Issabayeva *et al.*, 2006
PSAC	-	Pb(II)	82.40	-	-	-	Aroua *et al.*, 2008
PSC	Chitosan and acid	Cr(VI)	60.25	-	-	-	Nomanbhay and Palanisamy, 2005
Palm shell charcoal (PSC)	Chitosan	Cr(VI)	52.68	-	-	-	Nomanbhay and Palanisamy, 2005
PSC	Acid	Cr(VI)	44.68	-	-	-	Nomanbhay and Palanisamy, 2005
PSAC	-	Cu(II)	30.80	-	-	-	Issabayeva *et al.*, 2010
PSAC	PEI	Cr(VI)	12.60	20.50	-	-	Owlad *et al.*, 2010
PSAC	PEI	Ni(II) Cd(II) Pb(II)	6.10 8.50 66.50	9.60 14.10 53.50	1027.00	33.00	Yin *et al.*, 2008
Oil palm empty fruit bunches	-	Zn(II)	1.63	-	-	-	Alam *et al.*, 2008

It can be noticed that number of works on the adsorption of heavy metals ions onto PSAC are limited and so far no research has been reported on biomodification of PSAC by using *Aspergillus niger* and *Bacillus subtillis* biomass. In view of this, the present research was carried out to evaluate adsorption performance of the original and biomodified PSACs in removal of heavy metals from aqueous solution.

2.7 Modifications of activated carbons

Research and development interests to improve activated carbon by modifying it using various types of organic and inorganic compounds have increased in recent years. Modification allows increasing or reducing the presence of surface functional groups on activated carbon surface influencing the adsorption capacity towards metal ions. Modification of activated carbons is an attractive approach for enhancement of heavy metals removal; it can be generally divided into the physical, chemical and biological types.

2.7.1 Physical modification

Thermal treatment significantly improves BET surface area, pore volume and other physical characteristics of activated carbons, which in turn results in the increased total metal ions uptake (Yin *et al.*, 2007). According to Attia *et al.* (2006), thermal treatment at 400 ℃ and 600 ℃ increased the surface area and micropore volume of the activated carbon. The same phenomenon was observed by Yoo *et al.* (2005) who modified activated carbon by using heat treatment at 350 ℃. However, heat treatment may destroy or decompose some oxygen surface functional groups and surface-active components resulting in a loss of adsorption capability due to the increase in alkalinity of the carbon surface (Shafeeyan *et al.*, 2010). Furthermore, the thermal treatment of activated carbon also promotes specific adsorption of certain pollutant compounds from medium since the basic characteristics of activated carbons are amplified in the high-temperature treatment.

2.7.2 Chemical modification

Chemical modification of activated carbon is usually performed by adding some acid, alkali or other oxidizing agents such as sodium hypochlorite, permanganate, dichromate, hydrogen peroxide and ozone to modify the surface binding sites; it also can be performed by impregnating or immobilizing foreign chemical compounds onto the carbon surface.

2.7.2.1 Alkaline modification

Alkaline treatment is a process where sodium hydroxide (NaOH), potassium hydroxide (KOH) and other alkaline reagents with OH^- group react with the surface functional groups of activated carbon exposing additional functional groups on its surface that become available for binding of metal ions. According to Shim *et al.* (2001), surface area, micropore volume, carboxyl and phenol groups of activated carbon fibers (ACFs) decreased; while the concentration of lactone groups increased after the treatment with NaOH, which resulsted in the increased Cu(II) and Ni(II) ions adsorption on ACFs. Chen and Wu (2004) reported that NaOH treatment increased the content of hydroxyl groups without reduction in the specific surface areas. NaOH treatment slightly increased Cu(II) adsorption from 6.15 to 6.75 mg/g within 48 hours at 25˚C. Overall, alkaline treatment may have a negative effect on the adsorption of metal ions due to the decrease in specific surface area or micropore volume of activated carbon (Park and Jang, 2002).

2.7.2.2 Acidic modification

Activated carbon surface oxidation with agent such as nitric acid (HNO_3) represents a typical acidic modification method, which introduces large amount of acidic functional groups and oxygen-containing surface groups on the surface of the activated carbons leading to a more hydrophilic and acidic surface structure. This in turn can effectively enhance carbon’s chelation ability towards metal species. However, acidic treatment may decrease the surface area and pore volume of activated carbon.

Modification of commercial activated carbon by citric acid ($C_6H_8O_7$) to improve adsorption of copper ions from aqueous solutions was conducted by Chen *et al.* (2003). The results showed that the presence of citric acid reduced the specific surface area from 648 to 431 m^2/g; while the total concentration of surface functional groups increased from 0.19 to 0.32 mmol/g. The adsorption capacity of the modified activated carbon increased from 6.14 to 14.92 mg Cu^{2+}/g at 25˚C in 48 hours, 140% higher compared to the unmodified carbon.

Table 2.10 shows adsorption data for various origin activated carbons subjected to the modification procedures. The data are arranged in the order of increasing adsorption capacity and surface area.

Wu and Chen *et al.* (2001) investigated adsorption capacity of chemically modified commercial activated carbon towards Cu(II) ions. The carbon was first modified by HNO_3 or citric acid. The results showed HNO_3 double increased the adsorption capacity of activated carbon; while activated carbon modified with citric acid increased Cu(II) uptake by 90%. Such results are attributed to the increase of total concentration of surface acidic functional groups and negative charge on the carbon surface.

Table 2.10 Adsorption capacity and surface area of chemically modified activated carbons.

Activated Carbon (AC)	Modifying Agent	Metal	Adsorption Capacity (mg/g)		Surface Area (m^2/g)		Reference
			Original	Modified	Original	Modified	
Walnut shell AC	$ZnCl_2$	Hg(II)	-	151.50	-	780.00	Zabihi *et al.*, 2010
Nut shell AC	SO_2 gas	Cd(II)	104.17	142.86	1556.90	1257.10	Fouladi *et al.*, 2009
Commercial activated carbon (CAC)	SO_2 gas	Cd(II)	90.09	126.58	1286.70	1041.30	Fouladi *et al.*, 2009
Peanut shell AC	20% HNO_3	Pb(II)	24.02	35.46	1019.00	867.00	Xu and Liu, 2008
CAC	HNO_3	Cr(VI)	6.40	16.10	853.00	681.00	Huang *et al.*, 2009
CAC	HNO_3	Cu(II)	7.88	15.51	642.00	668.00	Wu and Chen, 2001
CAC	$HNO_3$and NaOH	Cu(II)	7.88	14.42	642.00	646.00	Wu and Chen, 2001
CAC	Citric acid	Cu(II)	7.88	13.22	642.00	624.00	Wu and Chen, 2001
CAC	Citric acid and NaOH	Cu(II)	7.88	11.37	642.00	663.00	Wu and Chen, 2001

Table 2.10 shows that modified walnut shell activated carbon had excellent Hg(II) uptake, expesially considering that the total surface area for the walnut shell activated carbon is lower than other activated carbon (Zabihi *et al.*, 2010). Fouladi *et al.* (2009) indicated the metal removal effciency of SO_2 modified

nut shell AC and SO_2 modified commercial activated carbon was better than unmodified carbon towards Cd(II).

2.7.3 Biological modification

Biological modification is often the most economical alternative compared to the physical and chemical modifications. Biological modification includes immobilization or adsorption of microorganisms into granular activated carbon (GAC). Immobilization of adequately capable microorganism's biomass with an effective adsorbent material such as GAC and polymeric matrix should improve the adsorption potential of biosorbents for metal removal (Yan and Vijayaraghavan, 2001; Rivera-Utrilla *et al.*, 2003).

2.7.3.1 Microorganism immobilized on GAC

It is well known that GAC is a good support media for microbial growth (Xing *et al.*, 2008). Microorganisms can be adsorbed and grow on GAC due to the following reasons:

(1) high adsorption capacity of carbon, which promotes availability and exchange of nutrients and oxygen;

(2) the porous structure and irregular shape of GAC which acts as a shelter providing the microorganism with a protective environment; and,

(3) the presence of a large variety of surface functional groups that affect the adhesion of the microorganisms on the carbon surface (Stewart *et al.*, 1990; Rivera-Utrilla *et al.*, 2001; Moreno-Castilla *et al.*, 2003; Rivera-Utrilla *et al.*, 2003; Yin *et al.*, 2007; Gaur and Shankar, 2008)

Immobilization of miroorganisms on GAC via adsorption can be understood in terms of hydrophobicity and electrostatic interactions (Moreno-Castilla *et al.*, 2003). When the hydrophobicity between miroorganisms and activated carbon surface increases, the Van der Waals's attraction becomes stronger favoring the adsorption process. From an electrostatic point of view, the higher pH of point of zero charge (pH_{pzc} = pH at which the adsorbent has a net zero surface charge) of GAC enhances the adsorption of microorganism biomass due to the stronger attractive interaction predominating between microorganism biomass and activated carbon surfaces. The GAC modified with microorganism biomass can effectively remove contaminants via adsorption and biodegradation mechanism (Moreno-Castilla *et al.*, 2003).

The microorganisms in biologically modified GAC during water treatment bring beneficial features. The life cycle of the carbon bed is prolonged because the microorganisms can convert a portion of recalcitrant organics into biodegradable organic matter by natural preozonation. The attached microorganisms convert the biodegradable portion into biomass, carbon dioxide and residual products preventing saturation of the carbon (Rivera-Utrilla *et al.*, 2001; Rivera-Utrilla *et al.*, 2003; Yin *et al.*, 2007).

The adsorption of heavy metals and organometallic compounds is also enhanced by the metabolism of microorganisms or by the formation of complexes between the metals and the ligands present on the cell's surface, such as extracellular polysaccharides, pigments, carboxyl and hydroxyl groups.

This type of biosorption process can occur in both dead and living cells (Rivera-Utrilla *et al.*, 2003).

All heavy metals are toxic for living microorganism, therefore metal ions removal by living biomass is extremely difficult. Dead biomass and its derived products, on other hand, are not sensitive towards heavy metal toxicity and do not require nutrients for cultivation (Rivera-Utrilla *et al.*, 2003). According to Rivera-Utrilla *et al.* (2001), the pH of point zero charge of activated carbon biomodified with *Escherichia coli (E. coli)* decreased thus increasing carbon's negative surface charge density. Negative surface charge density enhanced the capacity activated carbon to adsorb Pb(II) and Cd(II) ions from 21.5 to 26.4 mg/g and 5.1 to 7.7 mg/g, respectively (Rivera-Utrilla *et al.*, 2003). However, a reduction in the amount of Cr(VI) ions adsorbed by the *E. coli* biomodified activated carbon was observed which is probably due to the anionic behaviour of Cr(VI) ions in aqueous solution (Rivera-Utrilla *et al.*, 2003).

Bacterial and fungal biomass otherwise known as microbial wastes is generated by many fermentation/food industries and it showed high affinity towards metal adsorption (Yun *et al.*, 2011). However, the microorganism biomass has a few drawbacks that limit its practical applications, such as solid-liquid separation problems, clogging problem in the column mode studies and impossible regeneration due to the small size, low density, poor mechanism strength and low rigidity (Vijayaraghavan and Yun, 2007).

Nevertheless, it is believed that combination of adsorption performance of microorganisms biomass and palm shell axtivated carbon (PSAC) should show promising results and significantly enhance the adsoption potential of low cost biosorbents in the removal of heavy metals.

CHAPTER 3

MATERIALS AND METHODS

The first part of this chapter describes experimental procedures for the preparation and characterization of the original palm shell activated carbon and biomodification of the palm shell activated carbon with *Bacillus subtilis* and *Aspergillus niger* biomass. The surface properties analysis of the biosorbents was carried out using Boehm titration, pH_{pzc}, SEM, EDS and FTIR methods. The second part provides details on the adsorption isotherm models and kinetic equations used to evaluate the process of heavy metal ions adsorption onto the biosorbents.

3.1 Preparation of biosorbents

3.1.1 Palm shell activated carbon (PSAC)

The commercial granular palm shell based activated carbon (PSAC) was provided by a local manufacturer “Bravo Green” Sdn Bhd located in Kuching, Sarawak, Malaysia. The PSAC was produced by physical activation process with a steam as the activating agent. It was grounded and sieved to particles size range from 1.0 to 2.0 mm and stored in a plastic container at room temperature (Figure 3.1).

Figure 3.1 Granular PSAC

3.1.2 Bacillus subtilis biomass

Bacillus subtilis culture was provided by Biological Science laboratory of the Universiti Tunku Abdul Rahman (UTAR), Kuala Lumpur and used to biomodify the original PSAC. Conical flasks with nutrient broth were sterilized using HVE-50 vertical autoclave (Hirayama, Japan) at 121 °C for 20 minutes to prevent contamination. The spores of *Bacillus subtilis* were isolated from the stock culture and streaked onto the nutrient agar medium (Merck, Germany). The cultures were incubated at 37 °C in standard size (diameter - 85 mm) plastic Petri dishes for 24 hours (Figure 3.2). Then, a single colony of *Bacillus subtilis* was transferred into a flask containing 100 mL of the nutrient broth (Merck, Germany). The composition of nutrient broth was as follows: peptone from meat, 5 g/L, and meat extract, 3 g/L. The inoculums were incubated at the agitation rate of 220 rpm, 30 °C for 24 hours. The suspension was then centrifuged at 4 °C and 5000 rpm for 15 minutes. The supernatant was removed and the pellet was washed one time with sterile Milli-Q water

(Milli-Q, USA). Finally, 2 mL of wet biomass of *Bacillus subtilis* were resuspended in 40 mL of sterile Milli-Q water for subsequent use in the biomodification procedure.

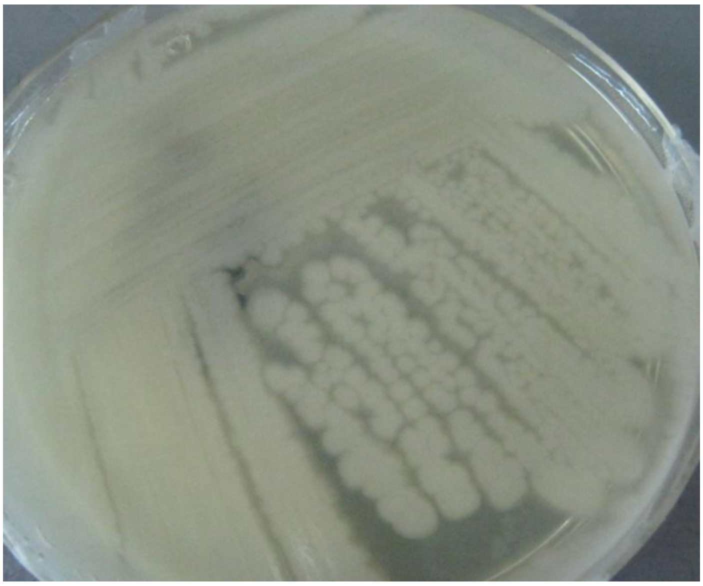


Figure 3.2 Culture of *Bacillus subtilis*

3.1.3 Aspergillus niger biomass

Aspergillus niger was provided by Biological Science laboratory at the Universiti Tunku Abdul Rahman (UTAR), Kuala Lumpur, Malaysia and used to biomodify PSAC. *Aspergillus niger* was cultured on the potato dextrose agar (Merck, Germany) medium and incubated at 37 °C for one week before it was subcultured into a liquid medium (Figure 3.3). The composition of potato dextrose agar was as follows: potato infusion, 4 g/L, D^+ glucose, 20 g/L, and agar-agar, 15 g/L.

The potato dextrose broth consisted of: sucrose (Ram Chemicals, UK), 20 g/L; peptone (BD Bacto^{TM}, USA), 10 g/L, and yeast extract (BD Bacto^{TM}, USA), 3 g/L. The pH of the growth medium was adjusted to pH 5.0 using 0.1 M HCl. Conical flasks (250 mL) containing liquid medium were autoclaved at 121 ℃ for 15 minutes. The fungal spores grown onto potato dextrose agar were suspended in 5 mL of the autoclaved 0.01% Tween 80 solution (Prochem, USA). The fungal culture used for the biomodification process was prepared by incubating 2 mL of fungal suspension in 100 mL of liquid medium and incubated at 30 ℃, 220 rpm for a week. The viable biomass was then filtered through a 0.5 mm pore size of plastic edge mesh strainer and rinsed one time with sterile deionized water. The biomass was blended in a blender (Panasonic, Japan) to make it homogeneous. Biomass (2 mL) were then suspended in 40 mL of sterile deionized water for the use in the biomodification procedure.

Figure 3.3 Culture of *Aspergillus niger*.

3.2 Biomodification of palm shell activated carbon

A total of 40 mL of *Bacillus subtilis* or *Aspergillus niger* suspension was added to a 50 mL centrifuge tube containing 1.2 g of original palm shell activated carbon (Rivera-Utrilla *et al.*, 2001). The contents of the centrifuge tubes were stirred using vortex mixer (Fine PCR, Korea) at 2000 rpm for 2 minutes and the tubes were then placed on an orbital shaker. The temperature and agitation were maintained at 27 ℃ and 45 rpm, respectively, for 24 hours (Rivera-Utrilla *et al.*, 2001). Then the biomodified palm shell activated carbon was filtered through a 0.5 mm pore size of plastic edge mesh strainer and washed carefully with sterile deionized water. The prepared materials were dried in incubator (Memmert, Germany) at 80 ℃ overnight and then were transferred into a desiccator. The dried biomodified palm shell activated carbon with *Bacillus subtilis* (BS-PSAC) and *Aspergillus niger* (AN-PSAC) were stored in the plastic containers at room temperature (Figure 3.4). Figure 3.5 summarizes basic steps of the biomodification procedure of palm shell activated carbon.

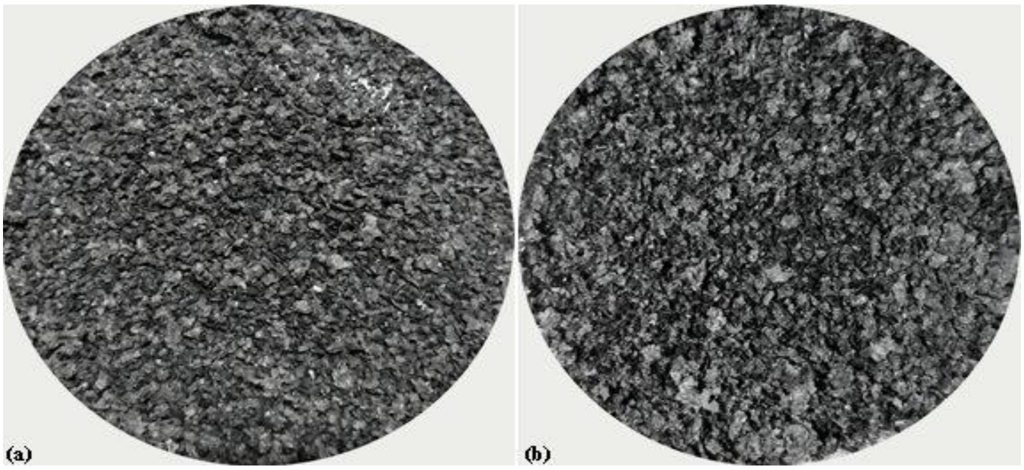


Figure 3.4 Samples of (a) BS-PSAC and (b) AN-PSAC.

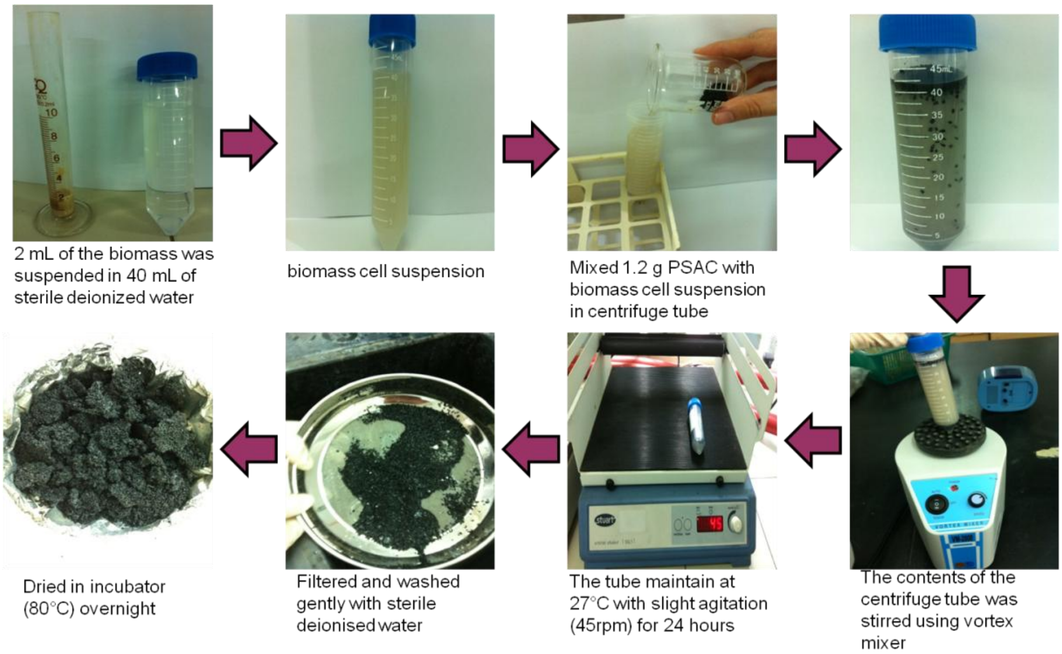


Figure 3.5 Steps of the of biomodification procedure.

3.3 Characterization of biosorbents

3.3.1 Ash content

Ash content of a carbonaceous material is the residue remains of inorganic oxides when the carbonaceous materials are burned off. Ash content can lead to increase hydrophilicity and also have catalytic effect, causing restructuring process during regeneration of used activated carbon (Vigouroux, 2001).

About 1.0 g of biosorbent was weighted and charred at 650 ° in the vertical tube furnace (Lenton, England) overnight. After that, the samples were transferred into a desiccator to cool down and weighted. The ash content was calculated based on the following formula (Gueu *et al.*, 2006):

$$\text{Ash Content (\%)} = \frac{m_1 - m_2}{m_1} x100 \qquad (3.1)$$

where,

m_1 = Weight of the sample before calcinations (g)
m_2 = Weight of the sample after calcinations (g)

3.3.2 Determination of acidity functions

The Boehm titration method was used to determine the acidity functions in the carbonaceous material. In this method, 1.5 g of biosorbent was placed in a 250 mL conical flask and 50 mL of each base solution [sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH), each 0.05 M] was added to the respective flask, which were agitated at 220 rpm and 27 ℃ for 24 hours. After that, 10 mL filtrate aliquots of $NaHCO_3$ and NaOH were taken from the flask and acidified with 20 mL of 0.05 M HCl, while 10 mL filtrate aliquots of Na_2CO_3 were acidified with 30 mL of 0.05 M HCl. The acidified solutions were then back-titrated with 0.05 M NaOH. The endpoint was determined by using both a pH meter and phenolphthalein (color indicator) silmultaneously until pH 7 was measured, at which point the titration volume was noted. The quantity of neutralized base is given by (Sarah *et al.*, 2010):

$$n_{CSF} = \frac{n_{HCl}}{n_B}[B]V_B - \left([HCl]V_{HCl} - [NaOH]V_{NaOH} \right)\frac{V_B}{V_a} \tag{3.2}$$

The concentration of each acidic surface group is given by:

Carboxyl group = $[NaHCO_3]$

Lactones group = $[Na_2CO_3] - [NaHCO_3]$

Phenolic group = $[NaOH] - [Na_2CO_3]$

where,

n_{CSF} = Amount of carbon surface functionalities (µmol/ g)
$\frac{n_{HCl}}{n_B}$ = Molar ratio of acid to base
$[B]$ = Concentration of the reaction base
V_B = Volume of the reaction base
V_a = Volume of the aliquot taken from V_B
$[HCl]$ = Concentration of the acid added to the aliquots
V_{HCl} = Volume of the acid added to the aliquots

3.3.3 Determination of pH of point of zero charge

An treated adsorbent surface has a net positive charge at pH < pH of point of zero charge of original adsorbent, while at pH > pH of point of zero charge, the surface has a net negative charge. A pH drift method was used to establish pH of point of zero charge (Rivera-Utrilla *et al.*, 2001; Khormaei *et al.*, 2007). One hundred mL of 0.15 M $NaNO_3$ solution was placed in an Erlenmeyer flask and N_2 gas was purged through the solution to stabilize pH and prevent dissolution of atmospheric CO_2. The pH was adjusted to initial values of 2, 4, 6, 8, 10 and 12 by adding 0.1 M HCl or NaOH. Biosorbent (250 mg) was added into a flask of a certain pH solution and it was left continuously mixed at 220 rpm for 48 hours at room temperature. At the end of the experiment, the equilibrated solution was decanted and final stabilized pH was measured. The final stabilized pH was plotted against the initial pH, the value of pH at which the plotted curves are crossed is considered to be a pH of point of zero charge.

3.3.4 Determination of surface area and porosity

Total specific surface area, porosity and the pore size distribution of biosorbents were analyzed by nitrogen adsorption-desorption measurements using Sorptomatic 1990 Series analyzer (Thermo Electron, USA) within the range of p/ p °= 0.04 to 0.3 at 77 K. Before the experiment, the biosorbents of known weight (approx 0.1 g) were degassed at 393 K (10^{-4} mmHg) for at least 24 hours to remove the moisture and volatiles. Then the sample was placed into the quantachrome analyzer and put into liquid nitrogen. Once the adsorption-desorption isotherm data was obtained, the specific surface area and monolayer volume was estimated by applying the Brunauer, Emmet and Teller (BET) equation.

BET model is an extension of the Langmuir theory (monolayer adsorption) to multilayer adsorption and can be applied to calculate surface area (m^2/g) of biosorbent material. The assumptions of this model are that the surface is energetically homogeneous or adsorption energy does not change with the progress of adsorption in the same layer. Uppermost layer is in equilibrium with vapor phase and the number of layers becomes infinite at saturation pressure. Besides, there is no interaction between the adsorbed molecules.

The BET equation gives a line for linear regression (Brunauer, 1938):

$$\frac{P}{n_{ads}\,(P^\circ - P)} = \frac{1}{n_m\,C} + \left(\frac{C-1}{n_m\,C}\right)\left(\frac{P}{P^\circ}\right) \tag{3.3}$$

where,

P = Pressure of gas adsorbed (Torr)
P° = Saturation vapor pressure of gas adsorbed (Torr)
n_{ads} = Amount of gas adsorbed (mmol/g)
n_m = Monolayer amount of gas adsorbed (mmol/g)
C = Non-dimensional constant

The slope and an intercept determine the values of n_m and C and can be calculated from the linear plot of the $P/n_{ads}\,(P^{\circ}-P)$ versus (P/P°).

$$n_m = \frac{1}{slope + intercept} \qquad (3.4)$$

$$C = \frac{slope}{intercept} + 1 \qquad (3.5)$$

A calculation range of P/P° equal 0.05 to 0.25 is normally within a good linearity. For relative pressures above the used range, capillary condensation should be accounted for, which is not amenable to the multilayer analysis. The surface area of biosorbent material is calculated according to the equation 3.6 (Reichert, 2005):

$$S_{BET} = \frac{L\, n_m}{V_{mol}}\, a_m \qquad (3.6)$$

where,

S_{BET} = Specific surface area (m^2/g)
L = Avogardros number (6.022×10^{23} mol^{-1})
V_{mol} = Volume of 1 mole of an ideal gas at standard pressure and temperature (22.41 L/mol)
a_m = Area of one molecule of adsorbate (N_2: 16.2 Å^2)

Dollimore and Heal (DH) model is usually used for the determination of the pore volume maximum in the biosorbent. DH method is an extension of the Barrett, Joyner and Halenda (BJH) method which covers adsorption in cylindrical mesopores region via film formation and capillary condensation mechanisms. The core radius is converted into the pore radius using the value of statistical thickness of adsorbed film (*t*-values) from the standard adsorption isotherm (Reichert, 2005).

Dubinin-Radushkevich (DR) equation uses a linear regression analysis to calculate the micropore volume (cm^3/g) of the biosorbents material (Reichert, 2005). This fundamental equation is based on a thermodynamic view of the adsorption process occurring in the micropores region. Adsorption is treated as a filling of the micropores with liquid adsorbate rather than layer by layer adsorption at the pore walls. The DR equation is linearized to obtain the micropore volume from the intercept of the line by plotting $log W$ versus $log^2\left(\frac{P°}{P}\right)$ (Reichert, 2005).

$$log W = log W_o - \left(\frac{RT}{\beta E_o}\right)^2 log^2\left(\frac{P°}{P}\right) \qquad (3.7)$$

where,

W = Volume that has been filled when the relative pressure is P/P °(cm^3/g)
W_o = Total volume of the micropore system (cm^3/g)
β = Non-dimensional affinity coefficient (N_2: $\beta = 0.33$)
R = Ideal gas constant (8.314 J/mol K)
E_o = Characteristic energy (J/mol)

The build-in software Sorptomatic 1990 (Thermo Electron, USA) which encloses the above calculation models was used for determination of surface area and pore size.

3.3.5 Surface morphology analysis (SEM/ EDS)

The surface morphology of biosorbents was evaluated based on the micrographs of the porous structure obtained via S-3400N Scanning electronic microscope (SEM) (Hitachi, Japan) application. The samples were prepared by spreading the biosorbent (0.1 g) over an aluminum stub with the help of double edge tape followed by the biosorbent surface coating with film of gold in a SC-7620 mini sputter coater (Quorum Technologies, UK). The backscattered electrons option on the detector block and stereo (3D) mode on the detection mode was selected to produce observation images in 3D mode.

Backscattered electrons with energy of 30 KeV under SEM are scanned across the surface of biosorbents. Backscattered electrons consist of high energy electrons originating in the electron beam that are reflected or back-scattered out of the sample interaction volume. Elements with higher atomic number appear brighter than elements with lower atomic numbers; backscattered electrons are used to detect contrast between the areas of different chemical compositions. The backscattered electrons emitted from the sample in different directions are detected by semiconductor sensor and produce direct observation of the surface microstructures of the microorganism biomass present on the carbon surface.

Energy dispersive X-ray spectroscopy (EDS) incorporated with SEM provided the elemental analysis in weight percentage (wt %) and atomic percentage (at %) of the samples (biosorbents). EDS detects X-rays generated from the incident electrons of SEM to characterize the elemental composition of the biosorbents.

3.3.6 Fourier transform infrared (FT-IR) spectrometer analysis

Fourier Transform Infra Red (FT-IR) Spectrometer (Perkin-Elmer, USA) was used to observe the changes in the surface functional groups present in the original and biomodified PSACs before and after metal ions adsorption. The dried carbons were first ground in a mortar into a powder form, and mixed with potassium bromide (KBr) (Merck, Germany) powder in the ratio 1:10 in the sample disk. KBr powder was dried in an oven for at least 24 hours at 100 ℃ before use. KBr powder is used to dilute granular activated carbon because the beam of FT-IR cannot pass the black color of granular activated carbon. KBr was chosen because it could transmit throughout most of the infrared region (Skoog and Leary, 1992). The mixture was pressed under 15 tonnes for 2 minutes to form the pellets using a hydraulic pellet press. The pellet was analysed immediately after the preparation. The background from a scan of pure KBr was automatically subtracted from the sample spectra. All spectra were plotted using the same scale of the percentage of transmission (% T) over the range of wavenumbers 400 - 4000 cm^{-1}.

3.4 Batch adsorption experiments

The adsorption experiments were carried out in 250 mL conical flasks placed on an orbital shaker (LabTech, India) at a constant speed of 220 rpm and 27 ℃. Two hundred fifty mg of biosorbent (original PSAC, BS-PSAC or AN-PSAC) was added into 100 mL of metal ions solution (Pb^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+}) with metal ions concentrations ranging from 30 to 300 mg/L. After 24 hours, the biosorbent was removed by filtration through 0.45 µm pore size filter paper (Fioroni, France). The initial and remaining heavy metal concentrations in the solutions were measured using Optima 7000 DV Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) (Perkin-Elmer, USA) according to the standard procedures.

Prior to the experiments, all conical flasks were washed with a detergent, rinsed with distilled water, soaked in 0.1 M nitric acid to avoid any binding of metal ions on the surface of the glassware, rinsed with distilled water and then oven-dried. All experiments were carried out in duplicates.

3.4.1 Preparation of adsorbate solutions

The background electrolyte was prepared by 0.15 M of $NaNO_3$ (Merck, Germany) and 0.1 M of $Pb(NO_3)_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$ and $Cu(NO_3)_2$ (R & M Chemical, UK) were used to prepare heavy metal ions stock solutions. Milli-Q (Milli-Q, USA) water was used in the preparation of all synthetic solutions. All chemicals were of analytical reagent grade. Information on the properties of four heavy metals used in this study is given in Table 2.3 (page 12). The test solutions were prepared by diluting the stock solutions in 0.15 M $NaNO_3$ to the desired metal ion concentrations.

3.4.2 Initial metal ions concentrations

Heavy metal solutions with initial concentration varying from 30 to 300 mg/L were prepared by diluting the stock solution. Sorption experiments were performed by adding 250 mg of biosorbent to 100 mL of metal solution.

3.4.3 pH

pH is an important process parameter in biosorption of metal ions from aqueous solutions since it is responsible for protonation of metal binding sites, solubility and speciation of metal ions in the solution. Effect of initial solution pH was investigated by adjusting pH of the synthetic solutions with 0.1 M HCl and/or 0.1 M of NaOH solutions from pH 3 to 6. The pH of the solution was measured using pH 510 pH meter (Eutech, Singapore). The pH range values were selected based on the report by Department of Environment which identified this range as common for the industrial wastewater in Malaysia (DOE, 2002).

3.4.4 Contact time

Contact time is an important parameter to determine the process kinetics as well as equilibrium time. Solutions containing 100 mg of Pb^{2+}/L and 50 mg/L of Zn^{2+}, Cu^{2+} and Cd^{2+} were prepared by diluting the respective stock solutions. The solution (100 mL) was placed into 250 mL conical flask containing 250 mg of biosorbents. The pH of the solutions varied from 3 to 5. Samples were taken in the intervals of 20 min, 40 min, 60 min, 90 min, 120 min, and then every hour after 2 hours periods until 12 hours to determine the kinetic mechanism of the adsorption. Last two samples were collected after 24 hrs and 48 hrs. The content of the sampled flasks was filtered through 0.45 µm pore sizes filter paper (Fioroni, France). The filtrate was analyzed for the residual heavy metal concentrations using ICP-OES. Repeated experiments were carried out for three adsorbents: original PSAC, BS-PSAC and AN-PSAC.

3.5 Thermodynamic study

It is important to study the effect of temperature on metal ions adsorption as the wastewater temperature naturally may vary greatly. Effects of temperature experiments were performed at 303, 313 and 323 K, at 220 rpm for 24 hours. Respective adsorbent (250 mg) and 100 mL of test solution with metal ions concentration ranging from 30 to 200 mg/L were prepared. pH 5 was used in all experimental runs, as the preliminary batch adsorption experiment showed high metal uptake at this pH. The samples were filtered and analyzed for metals ions concentration using ICP-OES.

Thermodynamic parameters (ΔG°, ΔH° and ΔS°) can be calculated from the variation of the thermodynamic equilibrium constant K° over temperature range (Li *et al.* , 2005). K° can be obtained from the Langmuir's equation by the plots of $\frac{C_e}{q_e}$ versus C_e (Chen *et al.*, 2007),

$$\frac{C_e}{q_e} = \frac{1}{K^\circ} + \frac{C_e}{Q^\circ} \tag{3.8}$$

where,

C_e = Equilibrium concentration (mg/L)
q_e = Amount of heavy metal absorbed (mg/g) at equilibrium
Q° = Maximum adsorption (μmol/g)
K° = Equilibrium constant

The Van't Hoff equation is used to determine the value of the equilibrium constant at different temperature:

$$\frac{d(\ln K^\circ)}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{3.9}$$

Integrated form of Eq. 3.9 gives:

$$\ln K^\circ = -\frac{\Delta H^\circ}{RT} + C \tag{3.10}$$

If *C* is written as: *C* = ($\Delta S^\circ/R$) then, $\ln K^\circ$ can be obtained through (Moradi *et al.*, 2011):

$$\ln K^\circ = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{3.11}$$

The ΔH° and ΔS° values are calculated from the slopes and intercepts of the linear plots of $\ln K^\circ$ versus $1/T$, respectively. ΔH^o is a measure of the amount of heat energy absorbed or released in an adsorption process. Negative value of ΔH^o indicates that the adsorption process is exothermic. The adsorption process is endothermic if ΔH^o is positive. ΔS° measures the degree of randomness or disorder at the interface of adsorbent and metal ions solution during the adsorption process.

ΔG^{o} is the total amount of free and useful energy that can perform work from an adsorption process at the constant temperature and pressure. As such ΔG° is the fundamental criterion of spontaneity and feasibility of adsorption process. Negative value of ΔG° determines the adsorption process as spontaneous at given temperature and the free energy always decreases. ΔG° can be obtained using the following equations (Chen *et al.*, 2007; Moradi *et al.*, 2011):

$$\Delta G^{\circ} = -RT \ln K^{\circ} \tag{3.12}$$

Eq. 3.11 is combined with Eq. 3.12, ΔG° is:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{3.13}$$

where,

ΔH^{o} = Enthalpy change (kJ mol^{-1})
ΔS^{o} = Entropy change (kJ mol^{-1} K^{-1})
ΔG^{o} = Gibbs free energy (kJ mol^{-1})
R = Ideal gas constant (8.3145 J mol^{-1} K^{-1})
T = Temperature (K)

3.6 Data analysis and calculations

3.6.1 Percentage removal and sorption capacity

The percentage removal of heavy metal in the biosorption experiments were calculated using equation (Tan *et al.*, 2009):

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \text{ x } 100\% \tag{3.14}$$

where,

C_i = Initial heavy metal concentration on PSAC (mg/L)
C_e = Equilibrium heavy metal concentration on PSAC (mg/L)

The amount of heavy metal adsorbed on the biosorbent at equilibrium was calculated from the mass balance of the equation (Tan *et al.*, 2009):

$$q_e = \frac{V(C_i - C_e)}{M} \tag{3.15}$$

where,

q_e = Equilibrium heavy metal concentration on PSAC at any time (mg/g)
M = Mass of the adsorbent (g)
V = Volume of heavy metal solution (L).

3.6.2 Adsorption isotherm models

Adsorption isotherm model provides characterization of adsorption system through certain constants values which express the surface properties and affinity of the adsorbent towards adsorbate. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually related to the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium (Han *et al.*, 2006). Two common isotherm models are the Langmuir and Freundlich isotherms. The Langmuir isotherm model suggests monolayer adsorption of metal ions on homogeneous surfaces of adsorbent, while Freundlich isotherm assumes multilayer adsorption on heterogeneous surfaces of the adsorbent.

In this study, both Langmuir and Freundlich absorption isotherm equilibrium models were used for the analysis of the biosorbent metal sorption systems. The linearised form of Langmuir isotherm was used to characterise the adsorption process of heavy metal ions onto palm shell based biosorbents and their maximum adsorption capacity (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{b\,q_{max}} + \frac{C_e}{q_{max}} \tag{3.16}$$

where,

q_e = Amount of metal absorbed (mg/g) at equilibrium
q_{max} = Maximum of Langmuir monolayer adsorption capacity (mg/g)
b = Langmuir constant (L/mg)
C_e = Equilibrium concentration of the metal in the solution (mg/L)

The Freundlich isotherm model (Freundlich, 1906) is the earliest known relationship describing the sorption equation.

$$log\, q_e = log\, K_f + (\frac{1}{n})\, log\, C_e \tag{3.17}$$

where,

K_f = Freundlich adsorption constant
n_f = Adsorption intensity constant

K_f is an indication of the adsorption capacity of the adsorbents; n_f indicates the effect of concentration on the adsorption capacity and represents adsorption intensity (Kumar *et al.*, 2010).

3.6.3 Adsorption kinetics

The study of adsorption kinetics is quite significant aspect in wastewater treatment as it describes the solute uptake rate, which in turn controls the residence time of adsorbate uptake at the solid solution interface. Kinetic data also provides analysis and characterisation of possible reaction mechanisms. The adsorption kinetic data is processed to understand the dynamics of adsorption process in terms of the order of rate constants. Two models are commonly used to evaluate adsorption of heavy metal ions at varying initial concentrations and pH: pseudo-first-order and pseudo-second-order kinetic models (Kumar et al., 2010; Wang et al., 2010).

A linear form of pseudo-first-order-reaction model proposed by Lagergren (1898)

is:

$$log(q_e - q_t) = log\, q_e - \frac{K_1}{2.303}t \tag{3.18}$$

where

q_e = Amount of metal adsorbed on the carbon (mg/g) at the equilibrium
q_t = Amount of metal uptake (mg/g) at time t (min.)
k_1 = Rate constant of pseudo-first-order biosorption, (min^{-1})

A linear form of pseudo-second-order model proposed by Ho and McKay (1999) is:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{3.19}$$

where

k_2 = Rate constant pseudo-second-order (g/mg min)
$h = k_2 q_e^2$ = Iinitial sorption rate (mg/g min)

From the plots of ($log\ q_e - q_t$) versus t and t/q versus t, the constant' values for both first-order and second-order reaction models can be calculated, respectively. The values of q_e, k_2 and h ($k_2 q_e^2$) against C_o in the corresponding linear plots of the pseudo-second-order equation were regressed to obtain expressions for these parameters values in terms of the initial metal ions concentration. Each of this parameters can be expressed as a function of C_o for four heavy metals as reported by Ho and Mckay (1998, 1999).

$$q_e = \frac{C_o}{A_q C_o + B_q} \tag{3.20}$$

$$K_2 = \frac{C_o}{A_k C_o + B_k} \tag{3.21}$$

$$h = \frac{C_o}{A_h B_o + B_h} \tag{3.22}$$

where,

A_q, B_q, A_k, B_k, A_h, and B_h are the model constants.

3.7 Speciation diagrams of metal ions

Visual MINTEQ software (Gustafsson, 2011) is a chemical equilibrium model to simulate equilibrium and speciation of inorganic solutes in natural waters. Visual MINTEQ was developed from the DOS program of MINTEQA2, which was released by the U.S. Environmental Protection Agency (USEPA) in 1999. The software is available online since 2000 (Gustafsson, 2011).

In this project, the latest version of Visual MINTEQ (version 3.0) software was used for the determination of metal ions speciation profiles, solubility, and equilibrium of solid and dissolved phases of electrolytes present in the studied aqueous solutions. The concentrations of the elements involved in the batch adsorption such as anion concentrations (NO_3^-), cation concentrations (Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Na^+) were provided as the input. The parameters such as pH, temperature, concentration and possible solid phases (metal hydroxide) were provided also as an input to generate a speciation distribution of each metal ions species in the solution in a range of pH from 1-14. The speciation data are generated in the form of molar percentages of metal ions relatively to a respective phase, solid or aqueous.

The generated speciation diagrams were used to determine pH of formation and precipitation of metal hydroxide which should be avoided as it interferes with the biosorption process and results in significantly lower metal ions removal.

CHAPTER 4

RESULTS AND DISCUSSION

In this section, the surface characterisation data for the original palm shell activated carbon (PSAC), *Bacillus subtilis* biomodified PSAC (BS-PSAC) and *Aspergillus niger* biomodified PSAC (AN-PSAC) obtained using scanning electronic microscope/energy dispersive X-ray (SEM/EDS) and Fourier transform infrared (FT-IR) spectrometer methods are discussed first. It is followed by the discussion of the batch mode adsorption experiments carried out under varying parameters such as metal ions concentration, pH, temperature and adsorbent material evaluated using isotherm and kinetic models are presented. In addition, metal ions speciation profiles in the test solutions investigated by using Visual MINTEQ (Gustafsson, 2011) software are presented and discussed.

4.1 Characterization of original and biomodified PSAC

Surface characteristion data for the original and biomodified PSAC are presented in Table 4.1. Measurement of the specific surface area showed that the surface areas of AN-PSAC decreased by 26% and BS-PSAC's area decreased by 4% as compared to specific surface area of the original PSAC. Rivera-Utrilla *et al.* (2001) reported that surface area decrease after the activated carbon modification procedure was observed. The decrease in the surface area is probably due to the blockage of carbon pores as a result of microbial mass presence and growth.

Table 4.1 Characteristics of the original and biomodified PSACs

	Original PSAC	BS-PSAC	AN-PSAC
BET specific surface area (m^2/g)	716.89	688.88	530.67
Maximum pore volume (cm^3/g)	0.11	0.15	0.15
Monolayer volume (cm^3/g)	164.90	158.25	121.90
Micropore volume (cm^3/g)	4.85	1.17	0.55
Carboxyl (μmol/g)	0.124	0.196	0.268
pH point of zero charge (pH_{pzc})	9.25	8.60	6.60
Ash content (%)	5.89	6.21	6.83

The maximum pore volume of the biomodified PSAC reached 0.15 cm^3/g as compared to 0.11 cm^3/g measured for the original PSAC. Micropore volume of the original PSAC was 4.85 cm^3/g while BS-PSAC and AN-PSAC showed 1.17 cm^3/g and 0.55 cm^3/g micropores volume, respectively. Concentration of carboxyl functional groups of PSAC increased after biomodification due to the addition of –COOH groups commonly present in the microorganism biomass (Yun *et al.*, 2011). The ash content was low for all PSAC (<10%), with a slightly higher values for BS-PSAC and AN-PSAC as compared to the original PSAC.

Figure 4.1 shows the pH of point of zero charge (pH_{pzc}) for all three adsorbents. pH_{pzc} of the original PSAC was determined to be 9.25; whereas pH_{pzc} of biomodified PSACs showed lower values, 8.60 and 6.60, for BS-PSAC and AN-PSAC, respectively. The results indicated the increase of negative charge density of the biomodified PSAC. The observed changes in the surface characteristics of the original PSAC indicated effect of the biomodification procedure (Rivera-Utrilla *et al.*, 2001).

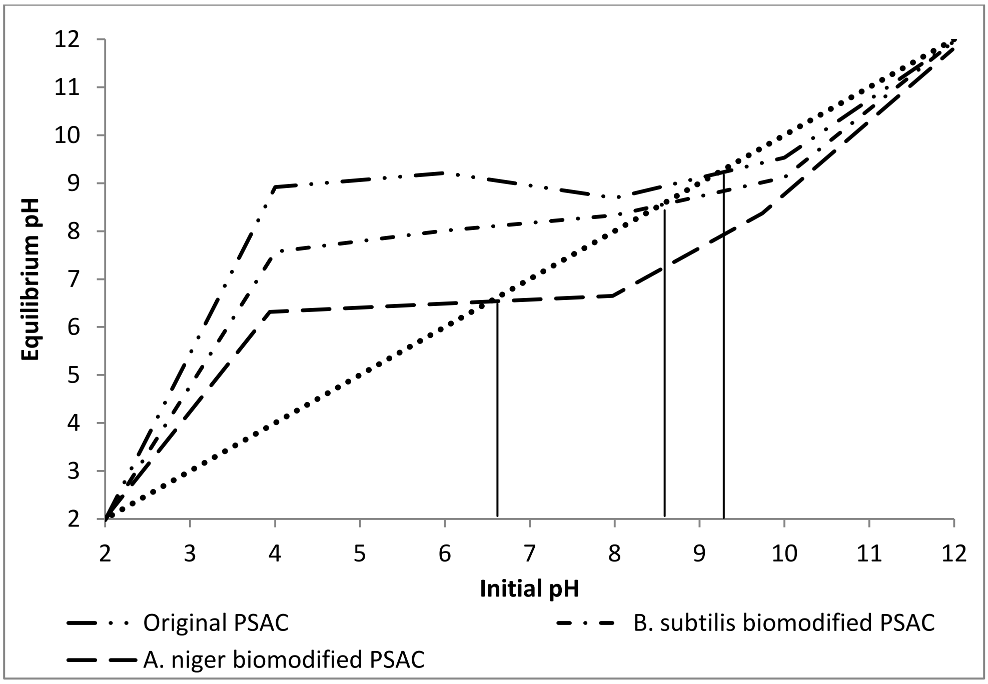


Figure 4.1 Determination of pH zero point of charge (pH_{pzc}).

4.1.1 Surface morphology analysis (SEM/EDS)

Surface morphology of the original and biomodified PSAC was studied using SEM with blackscatter electron at 500x and 550x magnification to identify the surface microstructures and determine its chemical composition. The SEM images of the three biosorbents are shown in Figure 4.2.

The SEM micrograph *(a)* showed numerous orderly structural pores present on the original palm shell activated carbon surface. A comparison of the SEM micrographs before and after biomodification of PSAC showed changes in the surface morphology. Fragments of microbial and fungal biomass attached to the activated carbon surface can be clearly seen on *(b)* and *(c)* images.

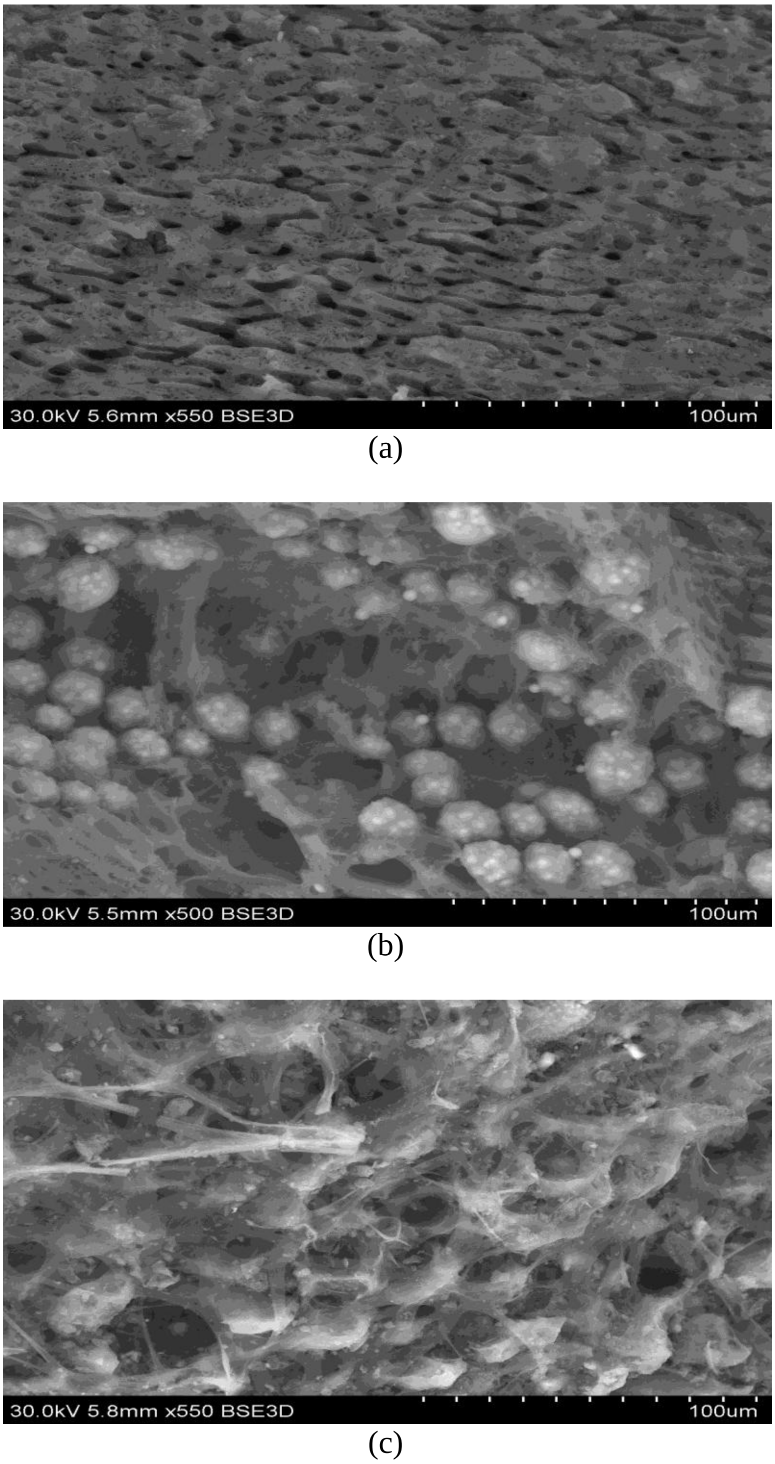


Figure 4.2 SEM micrographs of *(a)* Original PSAC, *(b)* BS-PSAC and *(c)* AN-PSAC

Table 4.2 shows data of the surface compositional measurements, the elements are presented as atomic percentage (At %) measured before and after the biomodification of the PSACs using EDS method. The C/O ratio of the original PSAC decreased from 15.66 to 7.68 after biomodification with *B. subtilis* and it decreased further to 1.96 after biomodification with *A. niger*. The percentage of calcium in the BS-PSAC and AN-PSAC increased from 0.05% to 0.3% and 0.07%, respectively, as compared to the original PSAC. The presence of functional group of bacteria and fungi increase the percentage of oxygen and calcium of activated carbon. This observation is consistent with the changes observed in the surface morphology of PSACs, which unequivocally proves the attachment of the microbial biomass into the carbon matrix during the biomodification process.

Table 4.2 Elemental composition of PSACs samples (EDS analysis)

Element	Atomic Percentage (At %)		
	Original PSA	BS-PSAC	AN-PSAC
Carbon (C)	93.64	87.97	66.09
Oxygen (O)	5.98	11.46	33.64
Calcium (Ca)	0.05	0.30	0.07
C/O ratio	15.66	7.68	1.96

4.1.2 Fourier transform infrared (FT-IR) spectroscopy analysis

Figure 4.3 presents the FT-IR spectra of the original and biomodified PSACs in the range of 400 - 4000 cm^{-1} where the changes in the identified functional groups on the carbon surface can be seen. No significant variations were observed between the three biosorbents.

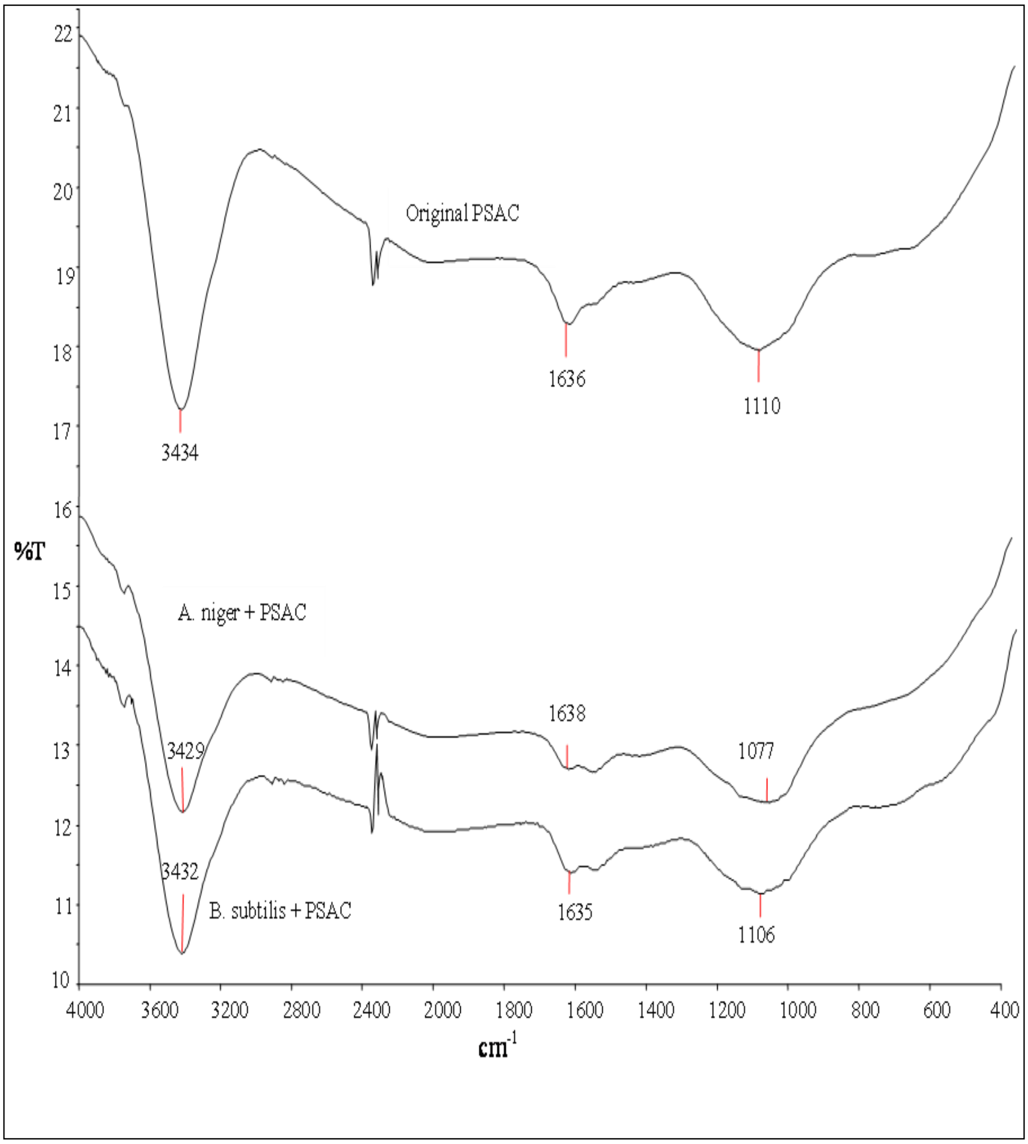


Figure 4.3 FT-IR spectra of the original and biomodified PSACs.

The FT–IR spectrum results are summarised in Table 4.3. A broad band at 3429 - 3434 cm^{-1} indicating the presence of hydroxyl group (-OH) stretching vibrations for the three biosorbents were detected. 1635 - 1638 cm^{-1} band corresponded to the C=C stretching and 1077 - 1110 cm^{-1} band is recognised as C-O stretching (Skoog and Leary, 1992; Marungrueng and Pavasant, 2007). -OH and C-O functional groups are likely to be involved in chemical bonding and responsible for the metal ions adsorption (Ho, 2003). The oxygen of each carbonyl and hydroxyl group is considered as a strong Lewis base due to the presence of nonbonding electron pairs. The oxygen base which is considered as Lewis acid participates in the coordination bonding with metal ions (Rao *et al.*, 2009).

Table 4.3 Functional group of PSACs before and after biomodification

Functional group	Wavenumber (cm^{-1})			
	Standard	Original PSAC	AN-PSAC	BS-PSAC
O-H stretching	3250-3700	3434	3429	3432
C=Cstretch (conjugated)	1610-1640	1636	1638	1635
C-O stretching vibration	1050-1300	1110	1077	1106

4.2 Speciation profiles of heavy metals

The speciation profiles of Pb(II), Cu(II), Cd(II) and Zn(II) in the solution of sodium nitrate as a function of pH were obtained using Visual MINTEQ software (Gustafsson, 2011). The speciation profiles and distribution of species are important to understand ions interactions during the adsorption process. The speciation diagrams present percentage related to the concentration of available metal ions (M^{2+}) over the 0-14 pH range. A row of different concentrations of metals were investigated in this study. However, the speciation profiles are shown only for 100 mg/L metal ions initial concentration, since the profiles for metals concentrations from 10 to 300 mg/L (not shown) were very similar.

Figure 4.4 presents speciation diagram for Pb(II) ions. The major species of Pb(II) in the solution are $Pb^{2+,}$ $PbNO^{3+}$, $PbOH^{+}$ and $Pb(OH)_3^{-}$. Two aqueous forms of Pb(II) are present as $Pb(OH)_2$ and $Pb(NO_3)_2$ species. In pH range between 3 to 6, such species as Pb^{2+}, $PbNO^{3+}$ and aqueous $Pb(NO_3)_2$ are present at concentrations of approximately 55%, 40% and 5%, respectively. These concentrations are maintained until pH 6 when they start decreasing and these species completely disappear around pH 10.

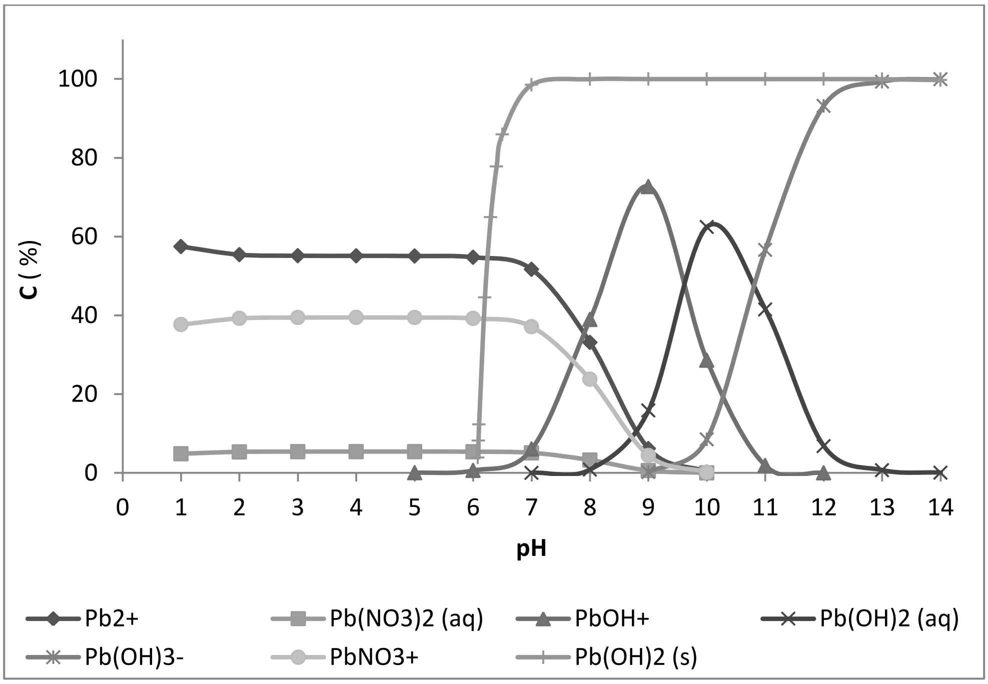


Figure 4.4 Speciation profile of lead ions in the solution (Pb =100 mg/L).

Besides, it was observed that hydrated precipitate of lead, $Pb(OH)_2$(s) forms at pH>6, which normally interferes with the adsorption process of metal ions onto adsorbent surface. Based on the speciation diagrams results it was concluded to conduct all batch adsorption experiments at pH≤6.0.

Lead speciation diagram showed that Pb^{2+} ions are abundant in pH range 1.0 to 6.0 where the percentage of free Pb^{2+} ions is almost 100%. At pH above 6.0, formation of higher concentration of metal hydroxide ($PbOH^+$) is observed (Figure 4.4.) leading to the decrease of free lead ions in the solution and their supposed availability for adsorption process.

Figure 4.5 shows speciation profile of Cu(II) ions at concentration of 100 mg/L. The main species in the pH range 3.0 to 5.0 are Cu^{2+}, $CuNO^{3+}$ and aqueous $Cu(NO_3)_2$. The initial concentration of free Cu^{2+} ions does not change until pH 5; it starts decreasing from pH 5.0 (86.56%) towards pH 6.0 (83.02%). This phenomenon indicates that Cu^{2+} ions are abundant at pH≤5. Therefore, the maximum adsorption capacity of Cu(II) ions on the PSACs is likely to occur at pH 5.

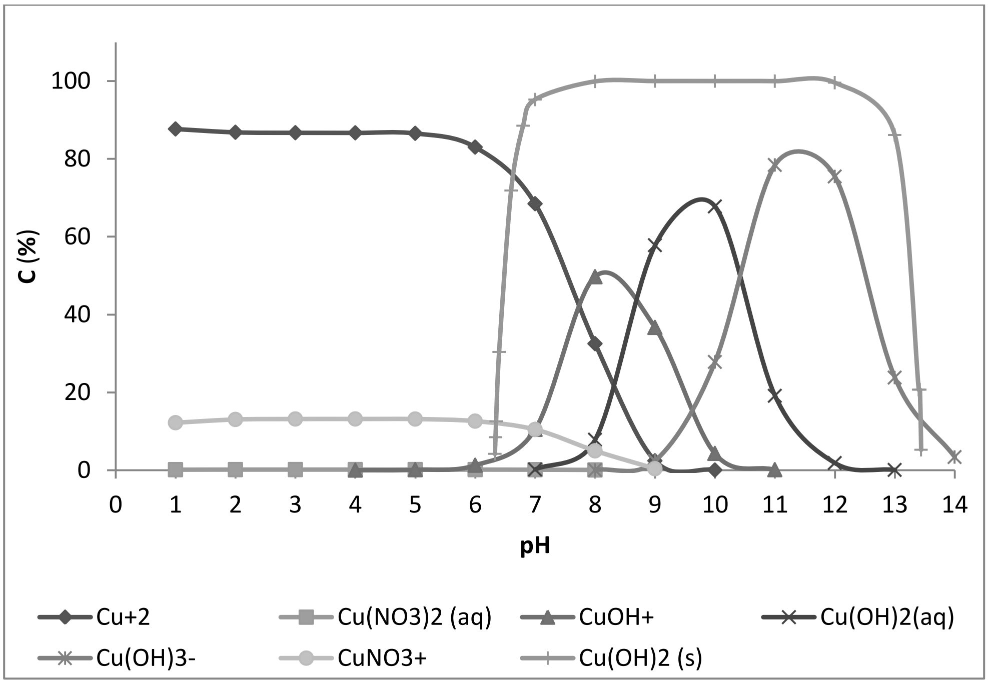


Figure 4.5 Speciation profile of copper ions in the solution (Cu=100 mg/L).

In addition, the speciation diagram indicated formation of $CuOH^+$ ions starting from pH 4 and until pH 11. The formation of hydrated precipitate of copper, $Cu(OH)_2$ starts at pH>6.3 and it reaches 99.9% concentration in pH range from 8.0 to 12.0. Other soluble hydroxides, namely $Cu(OH)_2$ and $Cu(OH)_3^-$, start forming around pH 7.0 and 8.0, respectively.

Figure 4.6 shows speciation profile of Cd(II) at concentration of 100 mg/L. In pH range from 1.0 to 8.0, the main species present are Cd^{2+}, $CdNO^{3+}$ and aqueous $Cd(NO_3)_2$. Free Cd^{2+} ions concentration start decreasing at pH 9 and they completely disappear after pH 12.

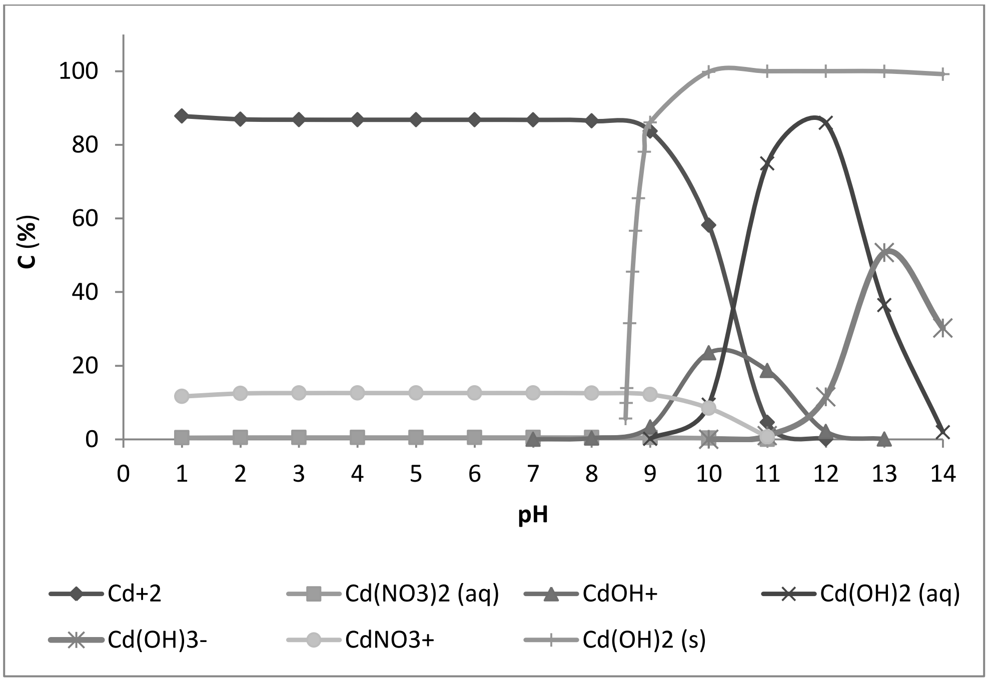


Figure 4.6 Speciation profile of cadmium ions in the solution (Cd = 100 mg/L).

The formation of solid $Cd(OH)_2$ starts at pH>8.6 and it reaches 99.9% precipitation at pH>10. It is noticed that the concentration of Cd^{2+} depletes proportionally to a solid $Cd(OH)_2$ formation in the aqueous solution when. Formation of $CdOH^+$ starts at pH≥7 and it disappears after pH 13. However, less than 1% of $CdOH^+$ occurs between pH 7 to 8. Other soluble hydroxides such as aqueous $Cd(OH)_2$ and $Cd(OH)_3^-$ are also present above pH 9 and 10, respectively.

The speciation profile for Zn(II) is presented in Figure 4.7. The main species present in the pH range from 1.0 to 7.0 are Zn^{2+}, $ZnNO^{3+}$ and aqueous $Zn(NO_3)_2$. Concentration of free Zn^{2+} ions does not change until pH 7 and it disappears at pH 10. The formation of solid $Zn(OH)_2$ starts at pH>7.4 and it reaches 99% precipitation between pH 9 and pH 12.

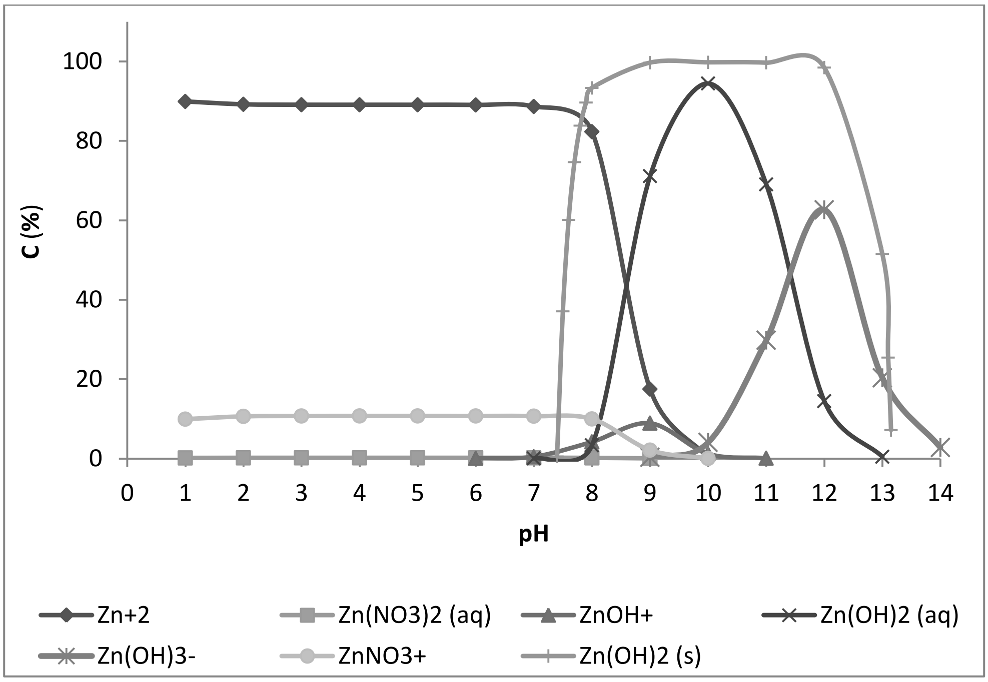


Figure 4.7 Speciation profile of zinc ions in the solution (Zn = 100 mg/L).

It can be observed that the concentration of Zn^{2+} ions depletes proportionally to a solid $Zn(OH)_2$ formation in the aqueous solution. $ZnOH^+$ occurs at pH≥6 and disappears at pH 11. Other soluble hydroxides such as aqueous $Zn(OH)_2$ and $Zn(OH)_3^-$ are present above pH 7 and 9, respectively. The concentrations of $Zn(OH)_2$ and $Zn(OH)_3^-$ start decreasing from pH 10 and pH 12 and the species disappear after pH 12 and 14, respectively.

The speciation profiles for the four metals showed that the metal ions are mostly present as free ionic species or as soluble organometals at lower pH range. However, as pH increases, the solid hydrated precipitates of metal ions start forming as shown in Figure 4.8, which might result in lower availability of metal ions for adsorption onto activated carbon process; hence pH>6 should be avoided.

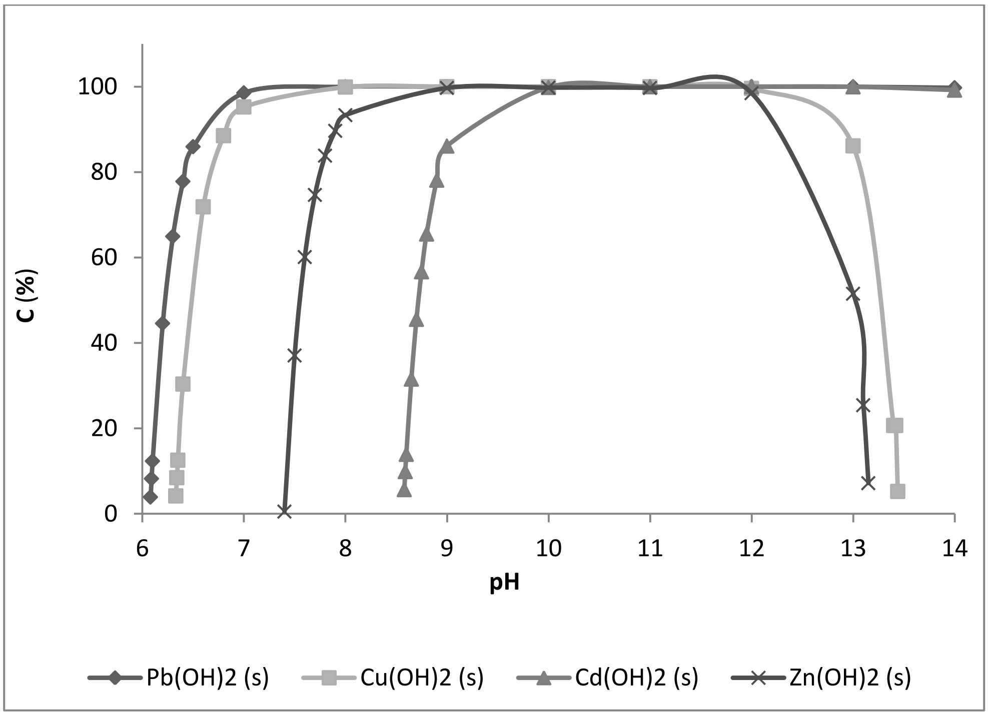


Figure 4.8 Profile of metal precipitation at higher pH (C_i=100 mg/ L)

4.3 Adsorption of heavy metals on original PSAC

4.3.1 Effect of pH

Figure 4.9 shows steady increase in the equilibrium sorption capacity (q_e) of the original PSAC observed in the pH range from 3 to 6 for Pb(II) and Cd(II). For Zn(II), q_e increased between pH 3 to pH 4, then it remained constant until pH 5 and later showed slight increase at pH 6. When pH increased from 3 to 5, an increase in the sorption capacity of Cu(II) by the original PSAC was observed. However, slight decrease was observed at pH 6. The highest sorption capacity of the original PSAC towards Cu(II) ions was observed at pH 5. The optimal pH for Pb(II), Cd(II), Zn(II) was observed at pH 6 and for Cu(II) it was at pH 5.

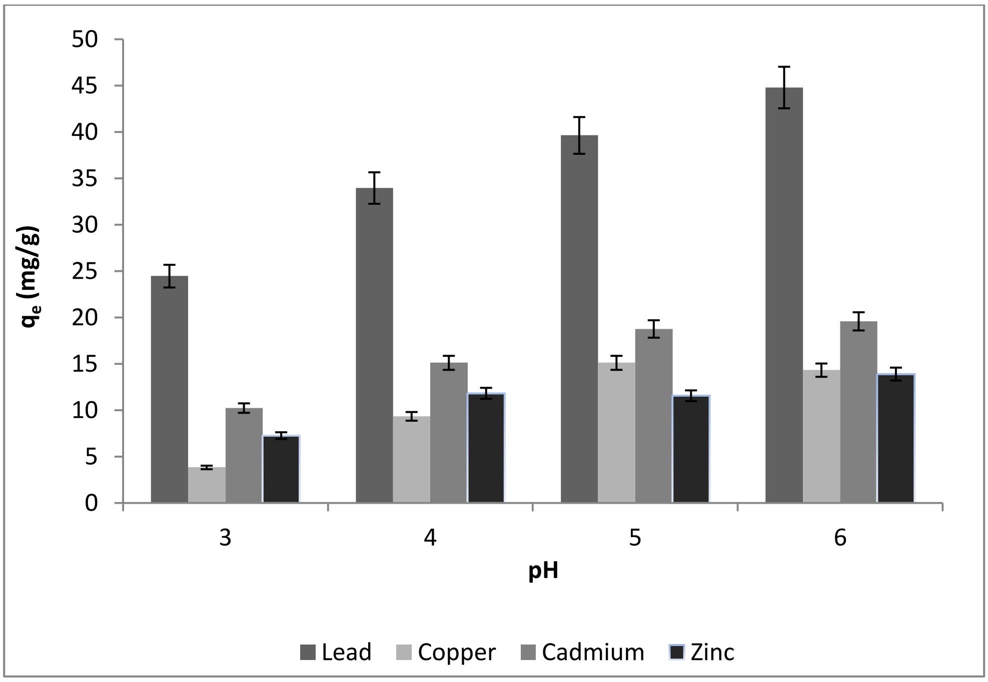


Figure 4.9 Adsorption of metal ions by the original PSAC, $C_{Me(II)}$ = 100 mg/L.

This can be explained by the decrease of free Cu^{2+} ions in the solution at pH 6 as compared to pH 3, 4 and 5 and is associated with copper precipitation as was discussed in section 4.2. Figure 4.10 shows that the percentage of Pb(II), Cu(II), Cd(II) and Zn(II) uptake increased sharply from pH 3 to 4 and became steady in the range of pH 4 to 6.

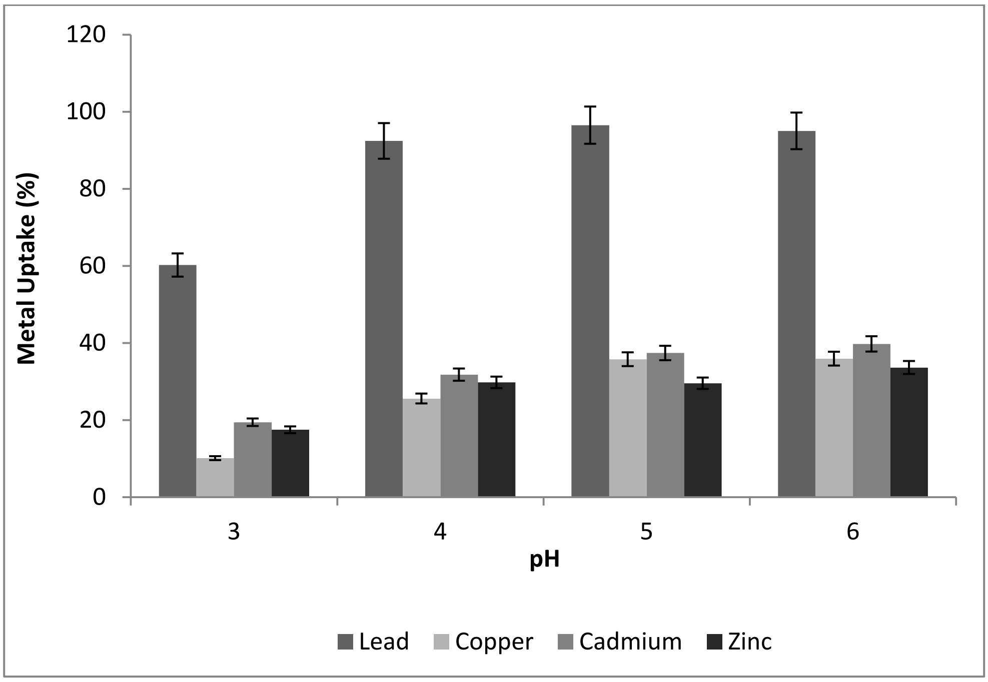


Figure 4.10 Effect of pH on the adsorption of metal ions by original PSAC, $C_{Me(II)}$ = 100 mg/L.

The increase in metal ions removal with increase in pH can be explained in terms of point of zero charge (pH_{PZC}) of the adsorbent and metal speciation occurring in the solution. The pH_{PZC} of the original PSAC was experimentally found to be at pH 9.25 as shown in Table 4.1. At pH lower than pH_{PZC}, the adsorbent is positively charged and the adsorbate species (Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}) are also positively charged. Thus, electrostatic repulsive forces occur between the positive adsorbate species and the surface positive charges of PSAC at $pH \leq 6$. The increase of pH towards pH_{PZC} of the original PSAC resulted in the decrease of the surface positive charge of PSAC due to the lower electrostatic repulsion forces between the sorbate species and the carbon surface functional groups (Rao *et al.*, 2009). The competition effect between H^+ ions and metal ions for the surface binding sites becomes less significant at higher pH; metal ions are easily transported to the surface of the adsorbent from the bulk solution and attach to the negatively charged functional groups on the adsorbent surface.

The lower metal sorption at pH 3 may be explained on the basis of active sites protonation meaning that the carbon surface tends to be more positive resulting in strong electrostatic repulsion between the cationic metal ions and positively charged groups on the surface of PSACs. Besides, higher concentration of H^+ in the solution competes with the metal ions for the same binding sites leading to the decrease in the adsorption of metal ions. These results are in line with Onundi *et al.*, (2010) who reported on the adsorption of Cu(II), Ni(II) and Pb(II) from synthetic semiconductor industrial wastewater by PSAC, whereby the maximum adsorption of metal ions occurred in the pH range between 4.5 to 6.0. The alkaline range of pH was not investigated in this study due to the probable precipitation of insoluble hydroxide complexes occurring at pH>6 according to speciation profile in Figure 4.8. For subsequent experiments, pH 5 was chosen in order to avoid precipation of metal ions and maximize metal ions sorption onto adsorbents.

4.3.2 Effect of initial concentration

Figure 4.11 shows the changes in the equilibrium sorption capacity (q_e) of the original PSAC over a range of initial metals concentrations. Figure 4.11 shows the q_e of PSAC towards Pb(II) ions increases rapidly from 30-120 mg/L because the high availability of adsorbents sites at this lower range of concentration, then q_e become steady up to 300 mg/L which with slight increases between 250-300 mg/L.

As initial metal ions concentration increased from 120 to 220 mg Pb^{2+}/L, slight change in q_e values can be observed which indicates steady phase of adsorption whereby fewer adsorption sites are available. Additional increase in q_e at concentrations 250 and 300 mg Pb^{2+}/L, is probably associated with higher affinity of lead ions towards palm shell activated carbon and also with presence of impurities in PSAC as it was not subjected to any pretreatment.

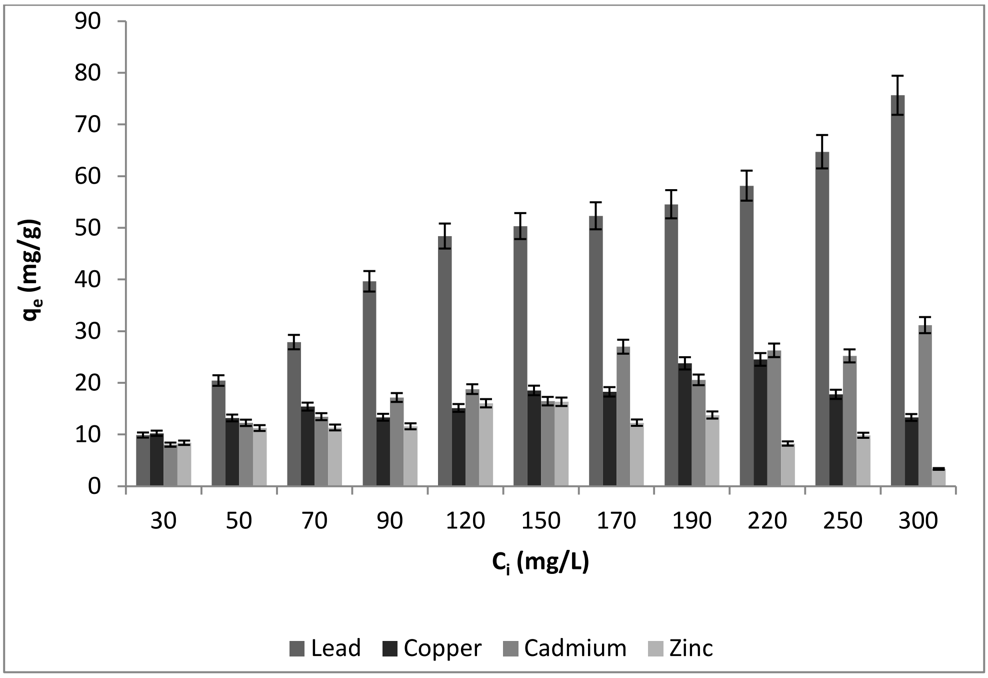


Figure 4.11 Sorption capacity of original PSAC under different initial concentration of metals.

However, this trend is temporarily and unlikely to continue due to complete saturation of adsorption sites which is indicated by steady adsorption uptake from concentration between 120-250 mg/L. This can be confirmed through comparison of q_e and percentage of lead removal shown in Figure 4.11 and Figure 4.12. Thus, Figure 4.12 shows that the percentage of Pb(II) removal was steady at concentrations from 30 to 90 mg/L concentration, then it decreased as the initial concentrations increased from 120 to 300 mg/L.

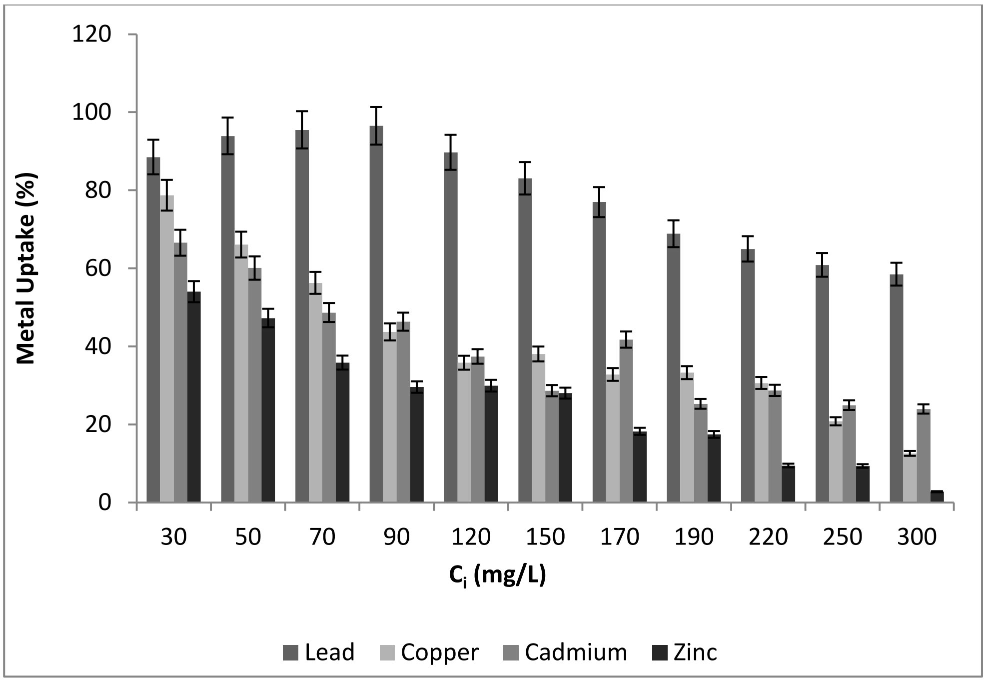


Figure 4.12 Effect of initial concentration on the percentage of metal ions removal using original PSAC.

Actually, the trend shown in Figure 4.11 and 4.12 are comparable, as it can be seen that the percentage of metal removal is steady for concentrations 30-120 mg/L which can corresponds to steady increase in q_e for the same initial lead concentrations. Once initial concentration exceeded 120 mg/L, the removal percentage decreased indicating slower adsorption and insignificant increases in q_e values. Moreover, comparison of q_e and percentage of lead removal allows concluding that once initial concentration is above 120 mg/L, the adsorption of lead ions gradually decreases.

Similar observation was reported by Kumar et al., 2010; Lalhruaitluanga et al., 2010; Wang et al., 2010 which the increase in adsorption capacity is associated with enhancement of the driving force to overcome mass transfer resistance between the aqueous phase and adsorbent phase resulting in higher probability of collision between adsorbate molecule and adsorbent surface.

Figure 4.11 also shows the sorption capacity of the original PSAC towards Cu(II) ions increased from 10.22 to 24.52 mg/g for 30 to 220 mg Cu(II) /L range of initial concentration due to the availability of binding sites on the PSAC surface. However, the sorption capacity of PSAC decreased from 24.52 to 13.28 mg/g in the range of initial concentrations from 220 to 300 mg/L, indicating the saturation of adsorption sites.

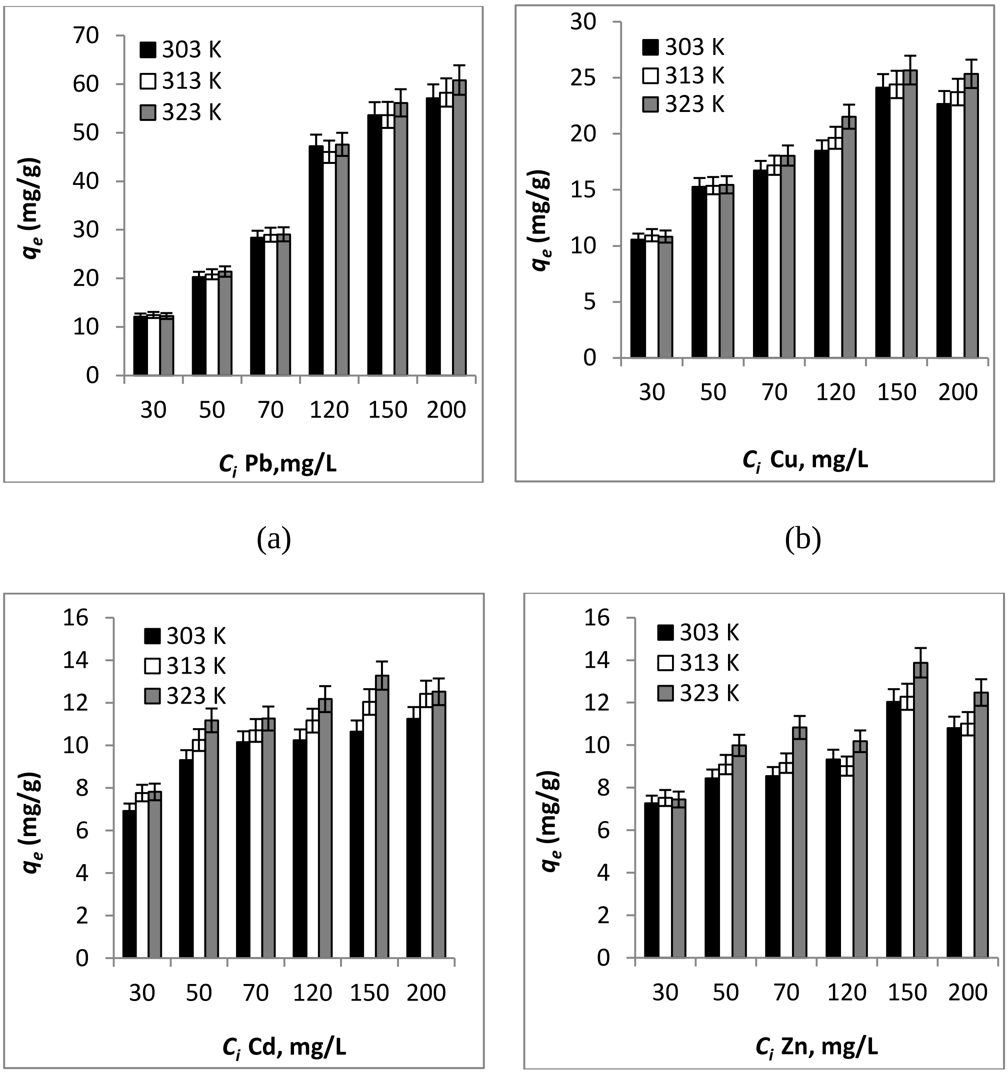
It can be observed that q_e of PSAC towards Zn(II) removal had a similar trend as for Cu(II) whereby it increased as initial Zn(II) concentration increased from 30 to 150 mg/L and it decreased when ions concentration increased from 150 to 300 mg/L. The adsorption capacity of PSAC towards Cd(II) increased from 8.02 to 26.98 mg/g over initial concentrations from 30 to 170 mg/L. Above 170 mg/L, no significant change in removal of Cd(II) ions was observed. The results clearly showed that the adsorption of metal ions on PSAC is strongly dependent on the initial metal ions concentration.

The percentage of Cu(II), Cd(II) and Zn(II) uptake decreased when initial concentration increased from 30 to 300 mg/L due to the fixed quantity of PSAC used in this study. However, q_e of PSAC towards metal ions increased when the initial metal concentration increased due to the initial metal concentration provides the necessary driving force to overcome the resistance to the mass transfer of metal ions between the aqueous phase and the biosorbents phase. The results showed that the percentage of metal ions removal decreased when initial metal concentrations increased although the actual amount of metal ions adsorbed per unit mass of PSAC increased when intial metal concentration increased.

The adsorption results showed a noticeable dominance in adsorption of Pb(II) ions over Cu(II), Cd(II) and Zn(II) ions onto the original PSAC. It is probably associated with the higher surface charge of Pb(II) ions compared to Cu(II), Cd(II) and Zn(II) ions (Canet and Seta, 2001; Moradi *et al.*, 2010). It has been well established that water is attracted to the positively charged cations due to its dipolar nature and the attracted water molecules create a shell around the cation where the hydrated cations are formed. Thus the charge density for Pb(II) is higher compared to Cu(II), Cd(II) and Zn(II) ions leading to the increase in the percentage of metal ions adsorbed onto adsorbent surface. This observation is consistent with Moradi *et al.* (2011) who reported the interaction of Pb(II), Cu(II) and Cd(II) ions in a single walled carbon nanotube.

4.3.3 Effect of temperature

Adsorption studies were carried out at different temperatures with different initial metal concentrations (30-200 mg/L) and adsorbent mass to solution volume ratio of 0.25 g: 100 mL. Figure 4.13 (*a* and *b*) show the sorption capacities for Pb(II) and Cu(II). No considerable differences for lower initial concentrations (30-70 mg/L) over the temperature range of 303 to 323 K could be identified.



(a) (b)

(c) (d)

Figure 4.13 Heavy metal ions adsorption by original PSAC at different temperatures. *(a)* lead; *(b)* copper; *(c)*cadmium; *(d)*zinc at pH 5.

A clear increase in Pb(II) and Cu(II) adsorption by the original PSAC was observed at higher initial metal concentrations, 120 to 200 mg/L. Figure 4.13 (*c* and *d*) show a significant increase in Cd(II) and Zn(II) adsorption at various initial concentrations by the original PSAC over the increasing temperature range. The results indicate more efficient adsorption at higher temperature with the optimum adsorption taking place at 323 K.

Increase in temperature promotes mobility of ions in the aqueous solutions resulting in their increased collision rate and subsequent improved adsorption. Also, at higher temperatures, metal ions are readily dehydrated and therefore their adsorption becomes more favorable (Chen *et al.*, 2007). Similar observation was reported by Moradi *et al.* (2011) for the adsorption of Pb(II), Cd(II) and Cu(II) ions in a single walled carbon nanotube.

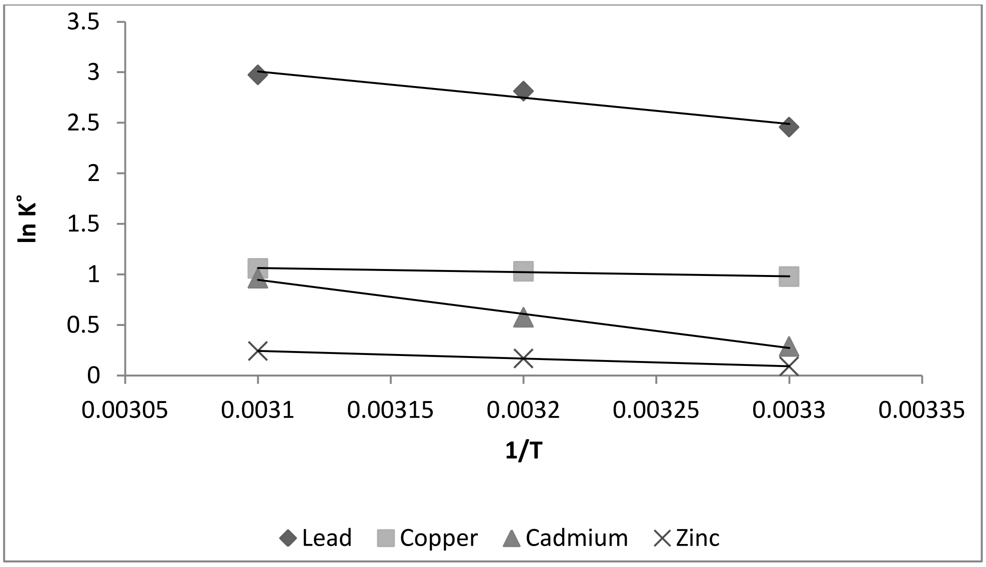


Figure 4.14 Van’t Hoff plot of adsorption of various metal ions onto original PSAC.

Figure 4.14 shows the Van't Hoff plot used for the determination of the thermodynamic parameters of the adsorption process.

Table 4.4 presents thermodynamic parameters estimated based on the experimental data obtained at different temperatures. The adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) on the original PSAC increased along the increase in temperature and the values of enthalpy change ($\Delta H°$) are positive confirming that the adsorption process is endothermic in nature for the tested metal ions, which is an indication of the existence of a strong interaction between PSAC surface and metal ions (Chen *et al.*, 2007).

Table 4.4 Thermodynamic parameters for the sorption of metal ions on the original PSAC.

Temperature (K)	Thermodynamic Parameters		
Lead	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
303	-6.26	21.12	90.35
313	-7.16		
323	-8.07		
Copper			
303	-2.47	3.32	19.12
313	-2.66		
323	-2.86		
Cadmium			
303	-0.68	28.06	94.86
313	-1.63		
323	-2.58		
Zinc			
303	-0.23	6.29	21.50
313	-0.44		
323	-0.66		

The values of changes in the Gibbs free energy (ΔG°) were negative as is expected to be for a spontaneous process under the applied conditions. The decrease in ΔG° over the increase of temperature indicated more efficient adsorption occurring at higher temperatures (Ibrahim, 2011). The values of ΔG° reflect the feasibility of the adsorption, since all values were negative at all temperatures, it indicated that the adsorption of metal ions onto the original PSAC is spontaneous and thermodynamically favorable. Also, a greater negative value of the Gibbs energy implies a greater driving force of adsorption resulting in a higher adsorption capacity (Moradi *et al.*, 2011). As the temperature increased from 303 to 323 K, ΔG° showed greater negative values for all tested metal ions. Hence, the extent of the Gibbs free energy implies that the adsorption affinity of Pb(II) ions towards PSAC is stronger as compared to Cu(II), Cd(II) and Zn(II) affinities signifying that the properties of metal ions play important role in adsorption process as well.

The positive values of entropy change (ΔS°) reflect the affinity of the original PSAC toward the metal ions in aqueous solutions. Also it is indicative of the increased randomness at the adsorbent-adsorbate interface during the adsorption of metal ions onto the surface of PSAC (Moradi *et al.*, 2011). The increase in the adsorption capacity of the adsorbent over tested temperature range is also attributable to the enlargement of the pores and/or activation of the adsorbent surface groups (Han *et al.*, 2006).

4.3.4 Adsorption model isotherm analysis

Table 4.5 presents the estimated parameters of Langmuir and Freundlich isotherm models for the adsorption of different metal ions. It can be noted that the correlation coefficient values, R^2, for the Langmuir model are mostly higher than R^2 for the Freundlich model.

Table 4.5 Parameters of Langmuir and Freundlich isotherm models.

	Langmuir constants					Freundlich constants			
pH	q_{max} (mg/g)	q_{max} (mmol/g)	b (L/mg)	R^2	SSE	K_f	n_f	R^2	SSE
Lead									
3	39.68	0.19	0.04	0.99	0.24	6.31	2.98	0.94	0.01
4	53.76	0.26	0.22	0.99	0.08	16.66	3.79	0.71	0.12
5	59.88	0.29	0.24	1.00	0.01	21.82	4.19	0.74	2.05
6	64.52	0.31	0.28	1.00	0.03	21.35	3.90	0.72	2.50
Copper									
3	7.51	0.12	0.01	0.99	5.66	0.29	1.84	0.97	0.01
4	21.69	0.34	0.05	0.97	2.00	5.54	4.16	0.88	0.01
5	22.17	0.35	0.07	0.91	5.31	6.51	4.30	0.76	0.03
6	17.04	0.27	0.85	0.97	2.51	7.78	5.76	0.73	0.02
Cadmium									
3	12.87	0.11	0.03	0.87	7.19	1.39	2.48	0.67	0.01
4	23.04	0.20	0.03	0.99	0.79	2.95	2.79	0.97	0.01
5	28.74	0.26	0.03	0.95	2.43	3.62	2.61	0.90	0.03
6	31.06	0.28	0.02	0.91	4.19	5.56	3.68	0.79	0.03
Zinc									
3	7.37	0.11	0.08	0.97	11.23	2.17	4.17	0.67	0.38
4	12.29	0.19	0.13	0.94	17.50	3.96	4.36	0.47	0.06
5	14.77	0.23	0.10	0.94	5.29	4.78	4.43	0.63	0.02
6	17.01	0.26	0.04	0.95	4.04	4.51	4.20	0.82	0.01

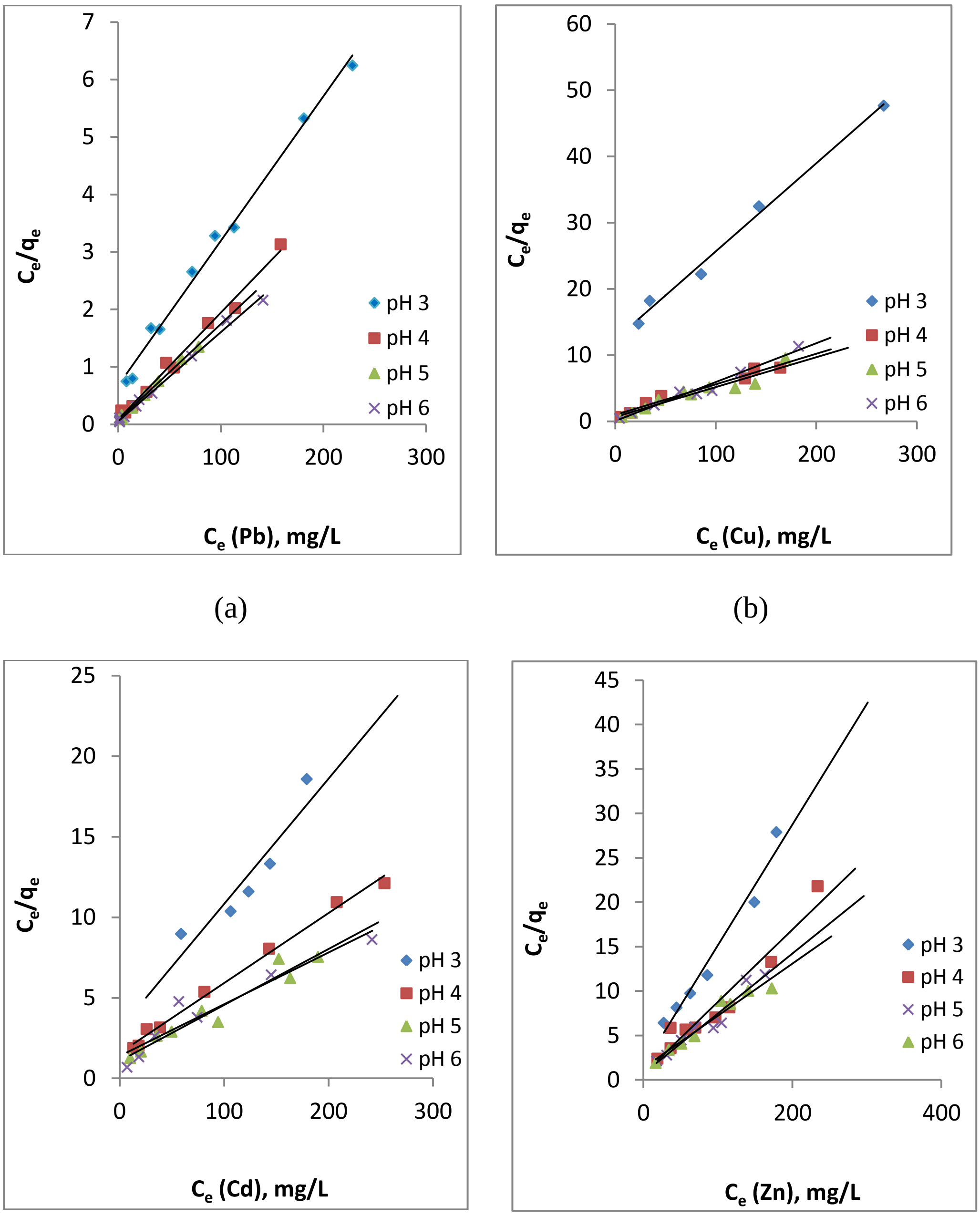
According to the Langmuir model, the maximum adsorption occurs when a saturated monolayer of metal ions is reached on the original PSAC surface and the energy of adsorption is constant and no migration of adsorbate molecules on the surface plane of PSAC is observed.

The constant *b* in the Langmuir equation relates to the energy or the net enthalpy of the adsorption process (Arivoli *et al.*, 2007). The higher the value of the constant *b*, the lower the free energy and the process is more favorable because it requires less energy to sustain. The constant *b* for Pb(II) is higher than for Cu(II), Cd(II) and Zn(II), which means that the system is more energetically favorable for the sorption of Pb(II).

It can be seen from Table 4.5 that the maximum Langmuir monolayer adsorption capacity of the original PSAC towards Pb(II) reached 0.31 mmol/g at pH 6, which is higher than for Cd(II) (0.28 mmol/g), Cu(II) (0.27 mmol/g) and Zn(II) (0.26 mmol/g). The ionic radius of these metals also increases as follows: Pb(1.21Å) > Cd(0.97Å) > Zn(0.74Å) > Cu(0.70Å) (Table 2.3, 12). Normally, cations with larger ionic radius preferentially displace cations with smaller ionic radius (Chirenje *et al.*, 2006) which is in line with the observation with the exception for Cu(II). The Langmuir model indicated that the optimum pH for adsorption of Pb(II), Zn(II) and Cd(II) was pH 6, while for Cu(II) it was pH 5.

Figure 4.15 showed a linear relationship among the plotted parameters indicated the applicability of Langmuir adsorption isotherm. The isotherms for pH 3 are distinct with other pHs for all metals, which is in line with previous observation that adsorption capacity decreased significantly at pH 3.

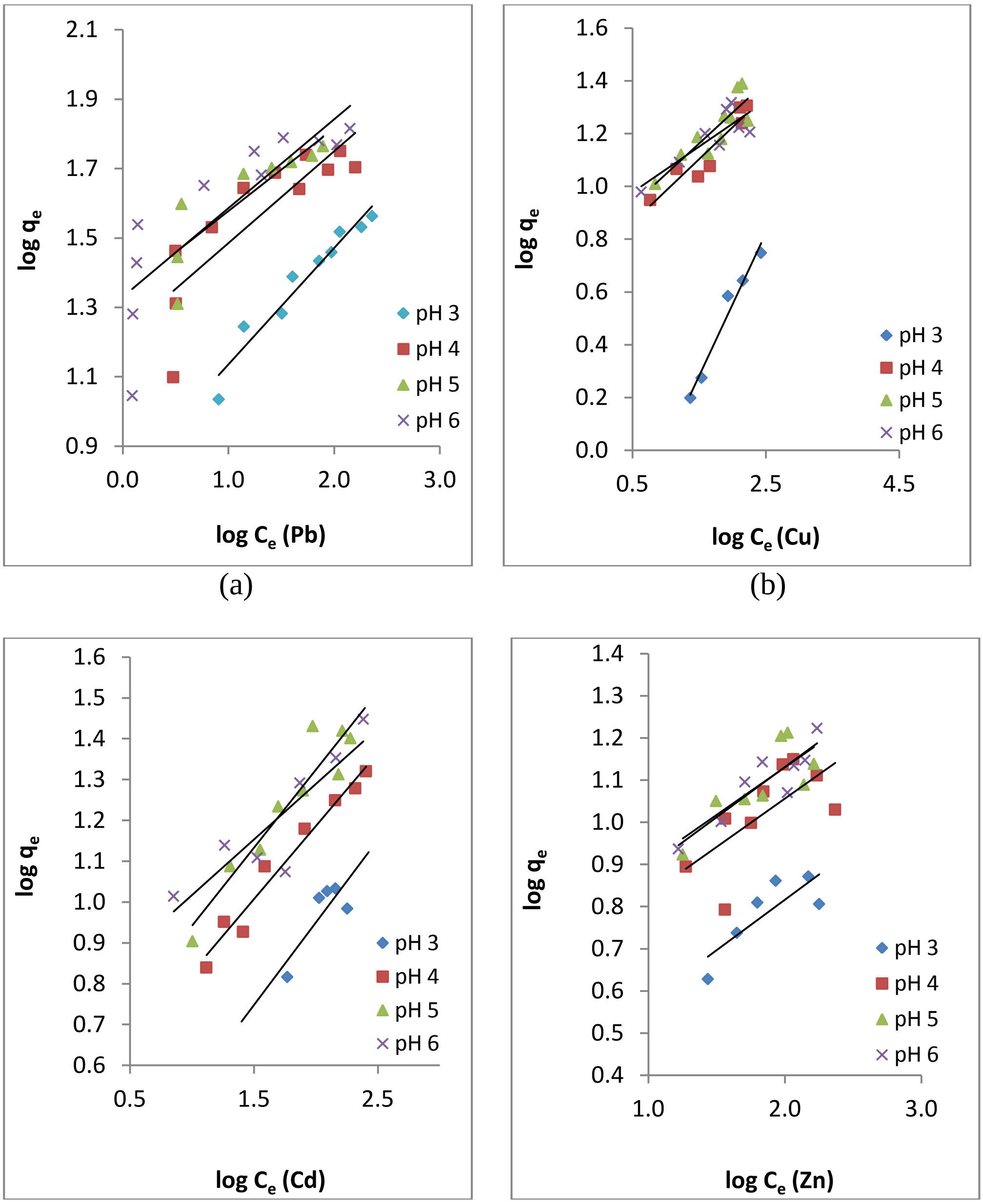
On the other hand, Figure 4.16 showed the applicability of Freundlich isotherm was also analyzed by using the same set of experimental data. It can be seen that the adsorption data points does not fit a straight line well to the Freundlich isotherm. The adsorption data revealed that Langmuir isotherm (Figure 4.15) showed a better fit over the Freundlich isotherm in all the metal ions.



(a) (b)

(c) (d)

Figure 4.15 Langmuir plots for the adsorption of metal ions onto original PSAC at various initial pH and concentration. *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc.



(a) (b)

(c) (d)

Figure 4.16 Freundlich plots for the adsorption of metal ions onto original PSAC at various initial pH and concentration. *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc

The Freundlich isotherm model encompasses on the surface heterogeneity and the exponential distribution of active adsorption sites and their energies (Ong *et al.*, 2007). Parameter n_f is indicative of intensity of the interaction between the adsorbent-adsorbate, showing how strong the metal ions are attached to the adsorbent surface. Table 4.5 presents values of n_f: 3.90, 5.76, 3.68 and 4.20 for Pb(II), Cu(II), Cd(II) and Zn(II) at pH 6, respectively. The n_f values between 1 and 10, indicate favourable adsorption process and the adsorption intensity was favourable over the entire range of tested pH (Vadivelan and Kumar, 2005). The magnitude of the Freundlich adsorption capacity, K_f, is found to be increasing from pH 3 to pH 6 for all heavy metals. This also confirmed that the sorption capacity of the sorbent increases along with pH increase.

4.3.5 Adsorption kinetic studies

Kinetic experiments were conducted to determine the minimum contact time required for the maximum uptake of Pb(II), Cu(II), Cd(II) and Zn(II) by the original PSAC and rates of metal ions removal.

Figure 4.17 and 4.18 show the kinetic data for the first six hours only, as it was earlier determined that the equilibrium sorption capacity (q_e) and percentage uptake were achieved in the first six hours period, respectively. The q_e and percentage of removal achieved in the first six hours were not significantly different from the metal removal obtained after 24 hours period.

The amount of Pb(II) removal increased rapidly in the first 120 minutes, contributing about 60% to the ultimate adsorption, and then the adsorption rate became slower and approached the adsorption equilibrium in about 300 minutes, with an equilibrium adsorption of Pb(II) around 30.10 mg/g or 71.68% removal.

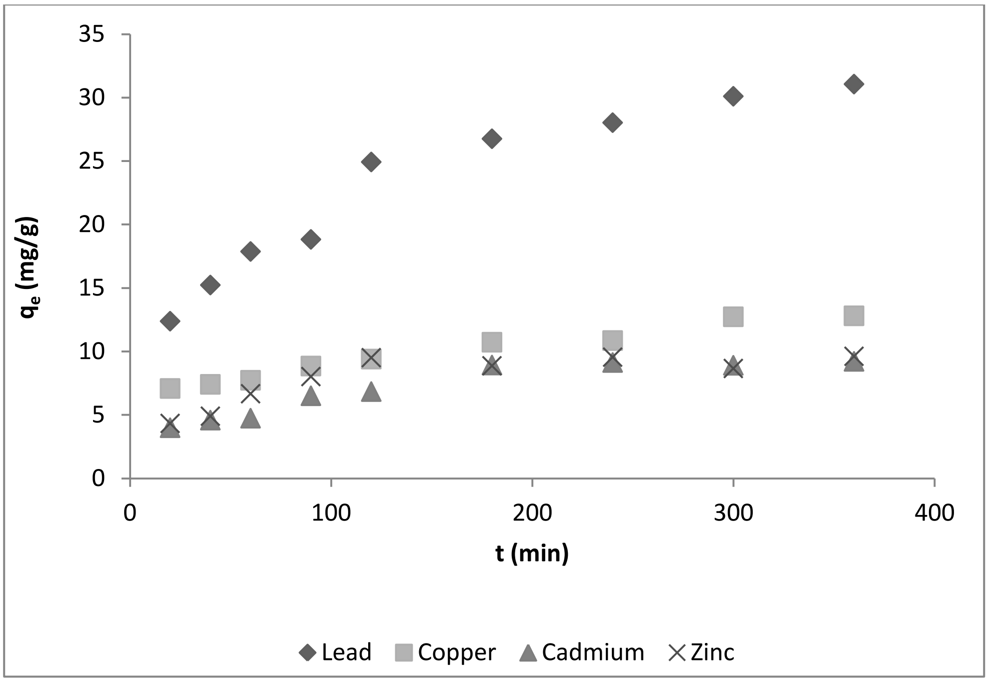


Figure 4.17 Sorption capacities of metal ions vs time at pH 5 (C_{Pb} = 100 mg/L; $C_{Zn, Cu, Cd}$ = 50 mg/L).

Around 45% of Cu(II) was removed by the original PSAC in the first 180 minutes and it took another 120 minutes to reach adsorption equilibrium of 12.73 mg/g. Figure 4.18 shows a rapid initial sorption over the first 180 minutes for Cd(II) with approximately 40% removal; Figure 4.17 shows that the equilibrium uptake reached 8.93 mg/g for Cd(II) by the original PSAC. It was observed that the kinetics of adsorption of Zn(II) was initially rapid in the first 120 minutes and then it slowed down. The maximum removal of Zn(II) occurring in 120 minutes reached 9.51 mg/g or 34% removal.

The results indicated that equilibrium sorption was attained within 300 minutes for Pb(II) and Cu(II); within 180 minutes for Cd(II); and within 120 minutes for Zn(II). The results also showed that a rapid initial sorption was followed by the extended period of much slower uptake of all metal ions.

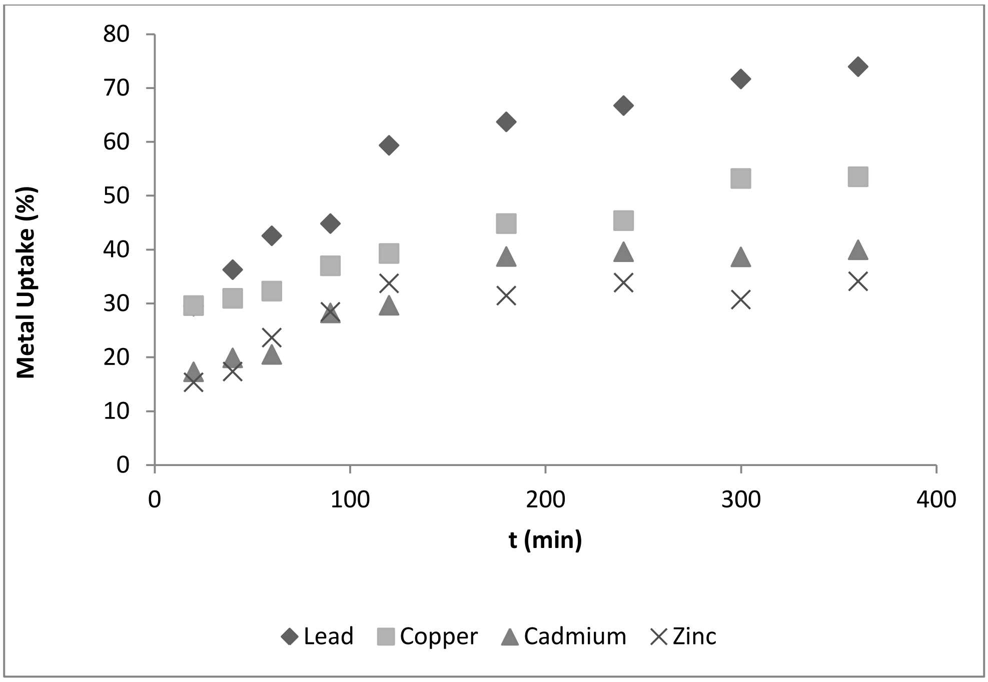


Figure 4.18 Removal of metal ions at different contact time at pH 5 (C_{Pb} = 100 mg/L; $C_{Zn, Cu, Cd}$ = 50 mg/L).

It is explained by the fact that during the initial sorption, a large number of vacant surface sites are available for metal adsorption. After a lapse of time, the remaining vacant surface sites are occupied by the metal ions and the repulsive forces between the metal ions on the solid surface and the bulk phase become greater suppressing further metal uptake. In addition, the metal ions are adsorbed within the carbon pores which become saturated as adsorption progresses. Thus, the driving force for the mass transfer between the bulk liquid phase and the solid phase decreases over time. Further, the metal ions have to traverse farther and deeper into the pores encountering much greater resistance resulting in the slow down of the adsorption process during the later phase (Srivastava *et al.*, 2008; Onundi *et al.*, 2010).

In order to investigate the adsorption kinetic of the tested metal ions onto the original PSAC, pseudo-first-order and pseudo-second-order kinetic models were used and are discussed in the following section.

Table 4.6 presents data for the pseudo-first-order kinetic model. Both factors (q_e and R^2) should be obtained for analysis of adsorption kinetics and modeling data. The calculated equilibrium sorption capacity of metal ions, $q_{e,}$ *cal*, is determined from the pseudo-first-order kinetic model and it indicated that this model poorly estimated q_e since the experimental values significantly differ from the calculated values.

Table 4.6 Parameters of the pseudo-first-order kinetic model.
(C_{Pb} = 100 mg/L, $C_{Cu, Cd, Zn}$ = 50 mg/L; pH 5)

Metal	**Pseudo-first-order rate constants**				
	q_e,*exp* (mg/g)	K_1 (1/min)	q_e,*cal* (mg/g)	R^2	SSE
Pb(II)	31.16	8.52×10^{-3}	22.12	0.96	0.02
Cu(II)	13.15	5.07×10^{-3}	6.84	0.96	0.01
Cd(II)	9.29	8.52×10^{-3}	6.58	0.93	0.01
Zn(II)	9.41	0.02	8.45	0.96	0.01

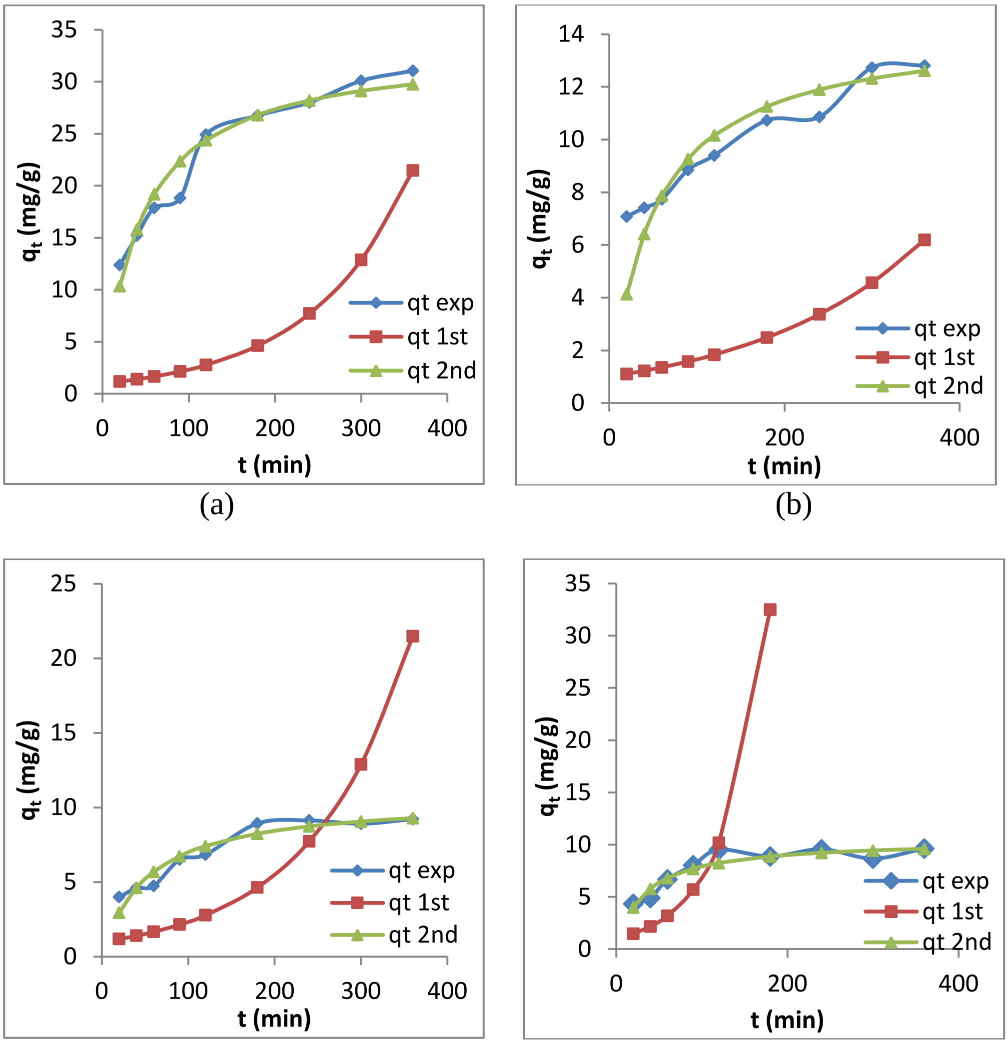
Table 4.7 presents data for the pseudo-second-order kinetic model. All R^2 values obtained for the tested metal ions were equal to one. The $q_{e,}$ *cal*, determined from the pseudo-second-order kinetic model also agreed well with q_e, *exp* indicating that this model fitted well the adsorption process of metal ions onto PSAC surface.

Table 4.7 Parameters of the pseudo-second-order kinetic model.
(C_{Pb}=100 mg/L, $C_{Cu, Cd, Zn}$ = 50 mg/L; pH 5)

Metal	**Pseudo-second-order rate constants**				
	q_e,*exp* (mg/g)	K_2 (g/ mg min)	q_e,*cal* (mg/g)	R^2	SSE
Pb(II)	31.16	6.70×10^{-4}	33.44	1.00	1.15
Cu(II)	13.15	1.41×10^{-3}	14.35	1.00	11.10
Cd(II)	9.29	1.80×10^{-3}	10.63	1.00	14.31
Zn(II)	9.41	2.95×10^{-3}	10.45	1.00	14.77

Figure 4.19 presents pseudo-first-order kinetic model data, where a significant difference between the experimental and modeled data can be seen. However, the experimental sorption capacity (q_e,*exp*) values agreed well with the calculated sorption capacity (q_e,*cal*) for the pseudo-second-order kinetic model for all tested heavy metals. This shows that the pseudo-second-order kinetic model is more suitable to describe adsorption of metal ions onto PSAC surface than the pseudo-first-order kinetic model.

Pseudo-second-order kinetic model indicated that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or the exchange of electrons between the PSAC and metal ions as covalent forces (Ho and McKay, 1999). Pseudo-second-order kinetic model supposed that a monolayer of metal ions is adsorbed on the surface of PSAC and energy of sorption for each metal ion is the same and independent of the surface coverage (Ho and McKay, 1999). Besides, the sorption occurs only on localized sites and involves no interactions between sorbed ions (Ho and McKay, 1999).



(a) (b)

(c) (d)

Figure 4.19 Experimental and modeled kinetics data for adsorption of metals onto original PSAC: *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc at C_i = 100mg/L, pH 5.

The values of SSE are lower for pseudo-first-order model data as compared to pseudo-second-order model data. Based on these observations, adsorption of heavy metals onto the original PSAC is concluded to follow a chemisorption mechanism which requires exchange or sharing of electrons between metal cations and surface functional groups of the carbon. These results agree with Ho and Ofomaja (2005) who reported on the kinetics of Pb(II) ions sorption on palm kernel fibre. Kwon *et al.* (2010) also reported the kinetic data for the sorption of Cd(II), Cu(II), Pb(II) and Zn(II) from aqueous solutions using scoria (a vesicular pyroclastic rock with basaltic composition) that fitted well into the pseudo-second-order model.

Overall, the adsorption data obtained for the original PSAC showed that the adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) was dependent of pH, initial metal ions concentration, contact time and temperature. The optimal pH for the sorption of heavy metals was established to be at pH 6 except for copper (pH 5). As the initial metal ions concentration increased the adsorption of metal ions by the original PSAC also increased; whereas a reverse trend was observed in case of the percentage of metal ions removal, it decreased when initial metal concentration increased. The equilibrium sorption was attained within 300 minutes for Pb(II) and Cu(II); within 180 minutes for Cd(II); and within 120 minutes for Zn(II). The results showed a rapid initial sorption followed by a much slower uptake of metal ions by the adsorbent. It was also found that a higher adsorption took place at 323K for all metal ions implying the endothermic nature of the adsorption process. Adsorption isotherms of all metals were well described by the Langmuir model and the process can be concluded to be monolayer adsorption. The kinetics of metal ions adsorption followed the pseudo-second-order kinetic model indicating the chemisorptions mechanism of metal ions removal.

4.4 Adsorption of heavy metals on palm shell activated carbon biomodified with *Bacillus subtilis* (BS-PSAC)

4.4.1 Effect of pH

The optimal pH condition was determined for the adsorption of metal ions by the BS-PSAC at the initial metal concentration of 100 mg/L. Figure 4.20 shows that the equilibrium uptake of Pb(II) increased sharply from pH 3 to 4 and became fairly constant in the range of pH 4 to 6.

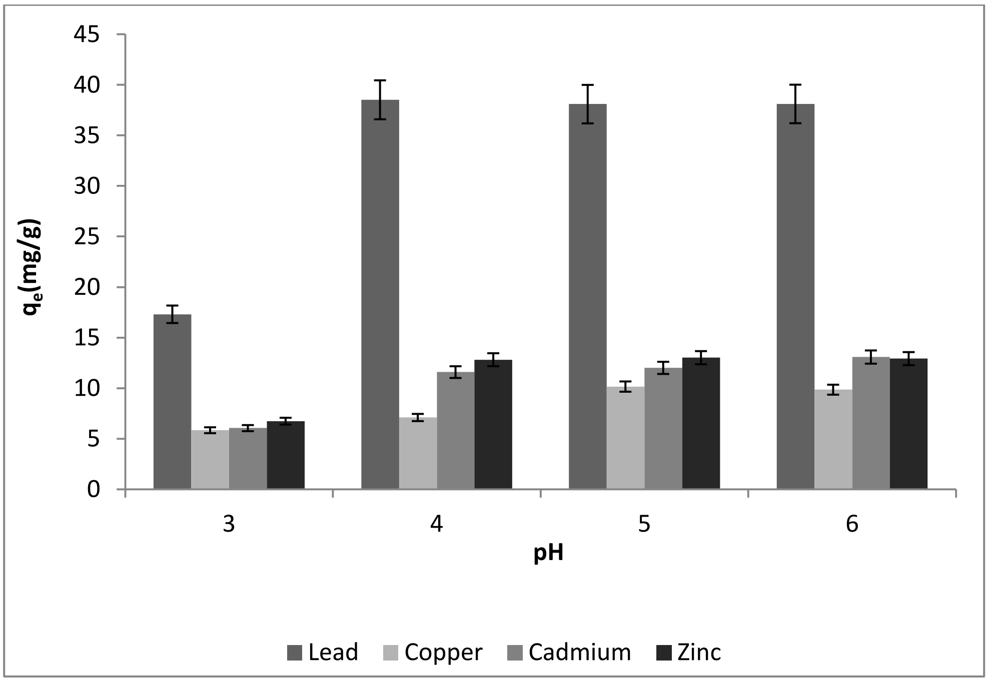


Figure 4.20 Effect of pH on metal uptake by BS-PSAC, $C_{Me(II)}$ = 100 mg/L.

Figure 4.21 shows that the percentage of Pb(II) uptake increased significantly from 44.44% to 90.03% as pH increased from pH 3 to 4. However, the percentage of Pb(II) adsorption increased only slightly from 90.03% to 92.17% in the range of pH 4 to 6. The capacity and percentage of Cd(II) and Zn(II) adsorption by BS-PSAC increased significantly as pH increased from pH 3 to 4. Above pH 4, the adsorption of Cd(II), Zn(II) and Pb(II) ions changed insignificantly. Similar observation was reported by Eba *et al.* (2011), for Pb(II) removal using acid activated carbon prepared from the plant biomass where the metal ions uptake increases greatly from pH 1 to 4. Above pH 4, the adsorption was found increasing very weakly.

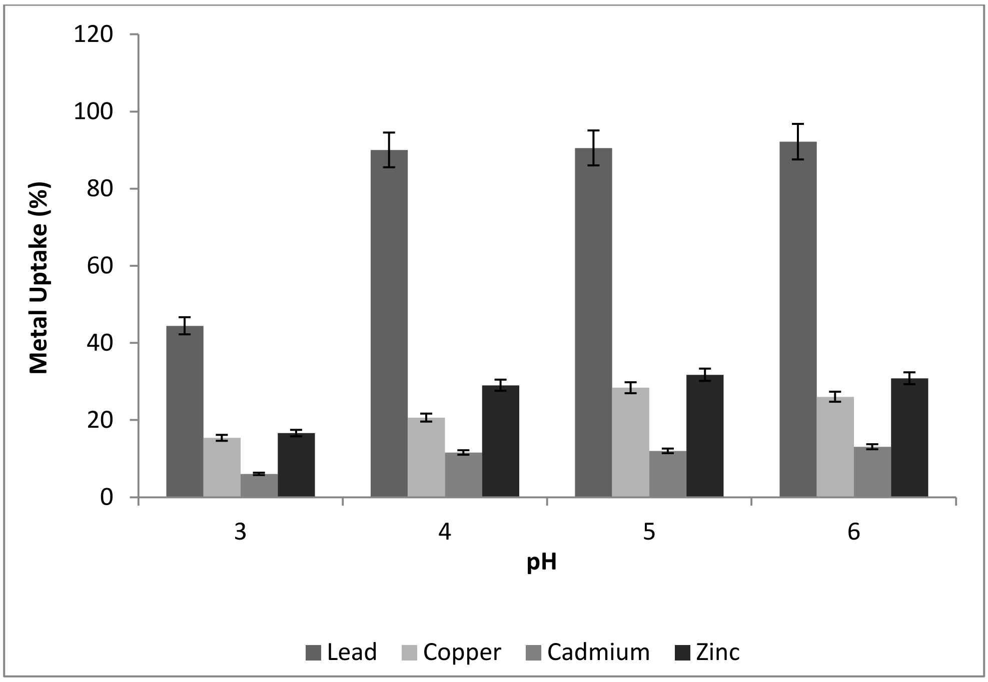


Figure 4.21 Effect of pH on metal removal by BS-PSAC, $C_{Me(II)}$ = 100 mg/L.

No apparent decrease was observed within the pH range of 4 to 6 indicating that presence of *B. subtilis* extended constructive pH range effective for heavy metal removal. The optimal pH for the sorption of Pb(II), Cd(II) and Zn(II) by BS-PSAC was in the range of pH 4 to 6, whereas the optimal pH for the sorption of Cu(II) was pH 5. The percentage removal of Cu(II) increased from pH 3 to 5 and decreased at pH 5 to 6.

Similar to the original PSAC, the sorption behavior of Pb(II), Zn(II), Cd(II) and Cu(II) ions onto the BS-PSAC was dependent on the pH of the solution. Lo *et al.*, (2003) and Adedirin *et al.*, (2011) showed that the biosorption of Cu(II) and Cd(II), respectively, by *Bacillus sp.* biomass increased significantly when pH increased from 2 to 6.

4.4.2 Effect of initial concentration

Figure 4.22 shows the changes in the equilibrium sorption capacity of BS-PSAC by using the initial metal ions concentrations varied from 30 to 300 mg/L. It was observed that with the increase in initial concentration of Pb(II), Cd(II) and Cu(II), the equilibrium sorption capacity increased.

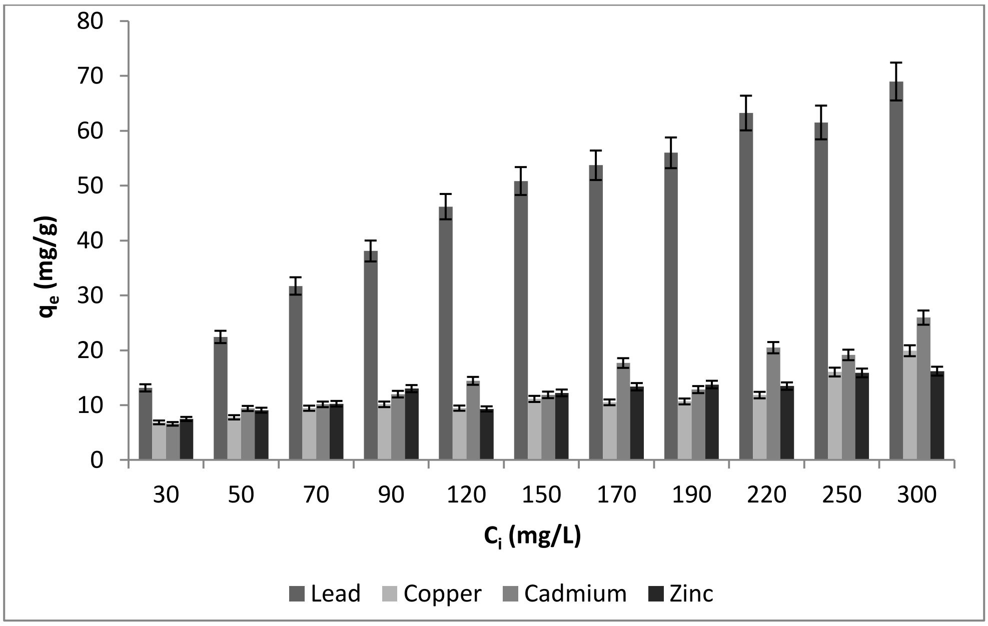


Figure 4.22 Sorption capacities of BS-PSAC for different initial concentrations of metal ions.

This may be due to the fact that at a fixed adsorbent dose, the number of active adsorption sites to accommodate the adsorbate ions remained unchanged; while the number of adsorbate ions to be accommodated increased at the higher adsorbate concentrations. Similar phenomena was observed in removal Pb(II) by using activated carbon, coconut shell and palm shell activated carbons (Eba *et al.*, 2011; Gueu *et al.*, 2006).

Figure 4.22 also shows that the uptake capacity of BS-PSAC increased when initial Zn(II) concentration increased from 30 to 90 mg/L, then it slightly decreased and became fairly steady in the range of initial concentrations from 120 to 300 mg/L indicating the saturation of adsorption sites.

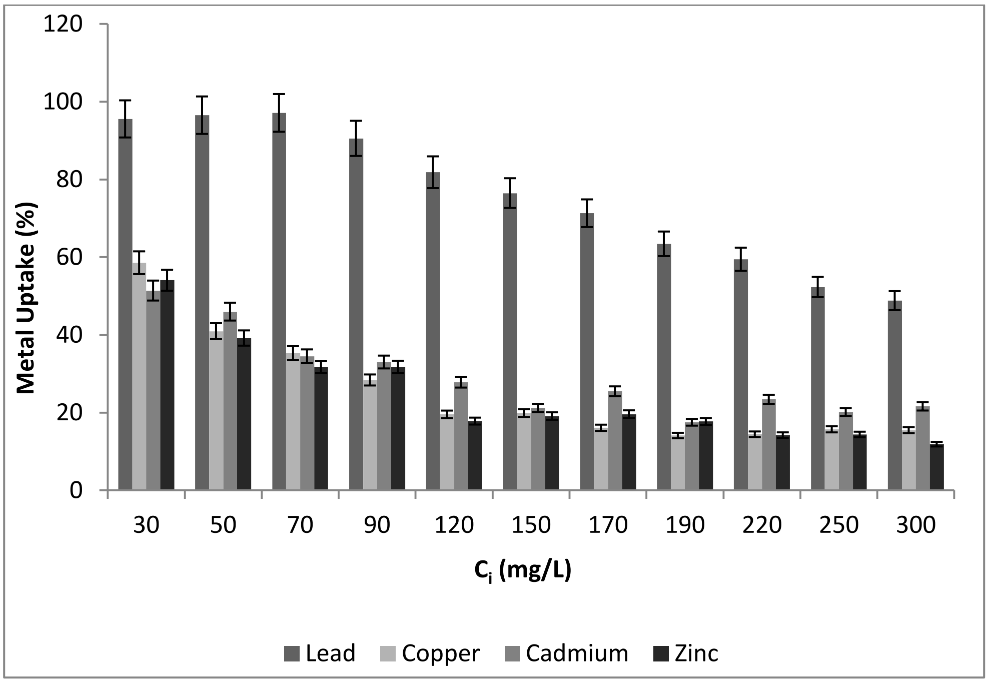


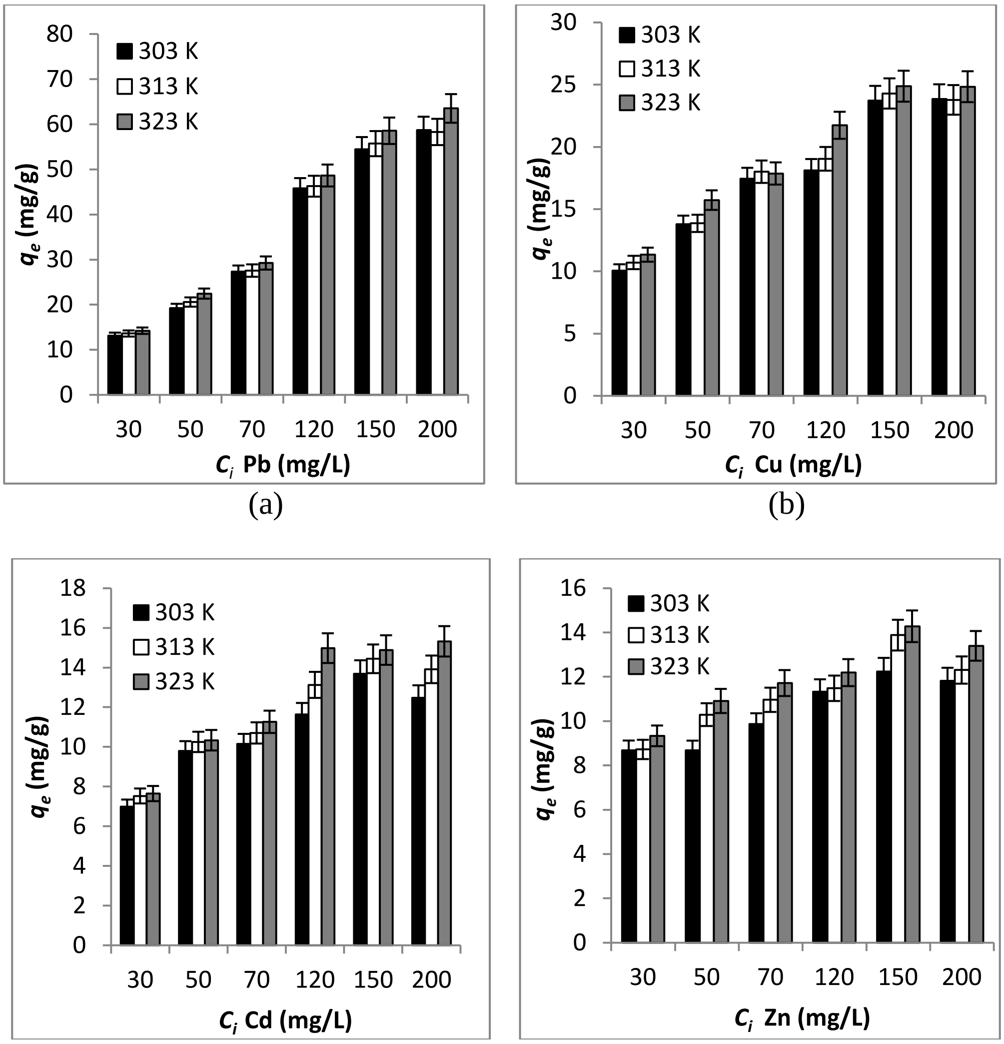
Figure 4.23 Effect of initial concentration on metal removal by BS-PSAC.

Figure 4.23 shows that the removal by BS-PSAC decreased when initial Pb(II) concentration increased. The decrease in removal over the increased concentration may be due to the limited number of available binding sites of the adsorbent since the higher initial Pb(II) concentration required longer removal time by BS-PSAC. Kannan and Veemaraj (2009) also reported the similar observation in the removal of Pb(II) by bamboo dust and commercial activated carbon.

The percentage of Cu(II) and Zn(II) removal decreased when initial concentration increased from 30 to 120 mg/L; no significant difference at and above 120 mg/L concentration in removal of Cu(II) and Zn(II) ions was observed. The percentage of Cd(II) removal decreased in concentration range from 30 to 190 mg/L, and no significant changes took place from 220 - 300 mg/L. Adedirin *et al.* (2011) reported similar observation where the adsorption capacity increased and percentage removal decreased with the increasing of the initial Cd(II) concentration by *B. subtilis* immobilized in agarose gel.

4.4.3 Effect of temperature

Figure 4.24 shows adsorption capacities of BS-PSAC for metal ions at different temperatures and initial metal concentration ranging from 30 to 200 mg/L at pH 5.



(a) (b)

(c) (d)

Figure 4.24 Influence of temperature on the metal sorption by BS-PSAC at pH 5, *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc.

The adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) increased when the temperature increased from 303 to 323 K. The highest temperature for the metal ions adsorption by BS-PSAC was at 323 K. The adsorption increase over temperature is probably caused by the increase in the energy and an enhanced ion exchange of the adsorption process, which facilitates the attachment of metal ions to the surface of the biosorbent. Figure 4.24 also shows that the increase in the initial concentration of Pb(II), Cu(II), Cd(II) and

Zn(II) lead to the increase in adsorption capacity of BS-PSAC at all tested temperatures.

Many authors have reported an increase in metal sorption by activated carbons or *B. subtilis* with an increase in temperature. Gueu *et al.* (2006) observed increase in Pb(II) uptake by activated carbon from coconut and seed hull of the palm tree when temperature increased up to 60 °C. Adedirin *et al.* (2011) also reported increase in Cd(II) adsorption by *B. subtilis* immobilized in agarose gel when temperature increased from 298 to 318 K. Table 4.8 shows the thermodynamic analysis at temperatures from 303 to 323 K.

Table 4.8 Thermodynamic constants for the sorption capacities of metal ions on BS-PSAC.

Temperature (K)	Thermodynamic Parameters		
Lead	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
303	-6.82	2.71	31.44
313	-7.13		
323	-7.45		
Copper			
303	-1.70	25.95	91.24
313	-2.61		
323	-3.52		
Cadmium			
303	-0.09	6.86	22.94
313	-0.32		
323	-0.55		
Zinc			
303	-0.42	20.56	69.24
313	-1.12		
323	-1.81		

The positive value of the enthalpy change (*ΔH*°) for Pb(II), Cd(II), Cu(II) and Zn(II) indicated the endothermic nature of the adsorption process. The positive value of the entropy change (*ΔS*°) indicated that the degree of freedom increased at the solid-liquid interface during the adsorption of metal ions onto BS-PSAC (Saha and Chowdhury, 2011). The value of Gibbs free energy (*ΔG*°) was found to decrease as the temperature increased indicating more efficient adsorption at higher temperature (Ibrahim, 2011). The negative values of *ΔG*° indicated that the adsorption process was spontaneous.

Figure 4.25 shows the Van't Hoff plot of *ln K*° versus *1/T* used for the determination of the thermodynamic parameters such as *ΔH*°, *ΔS*° and *ΔG*°.

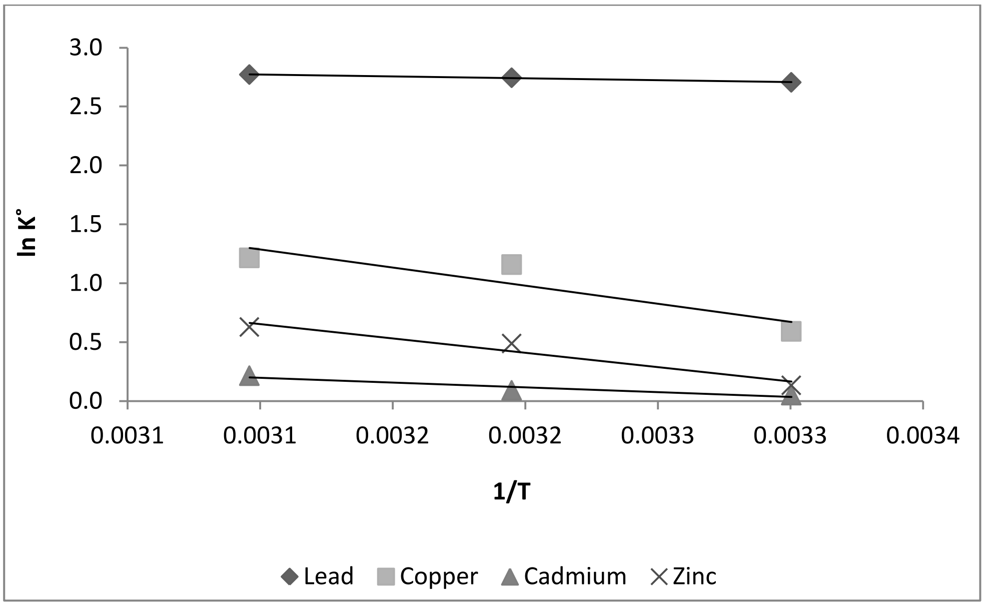


Figure 4.25 Van't Hoff plot for determination of thermodynamic parameters for BS-PSAC adsorbent.

Adedirin *et al*. (2011) reported similar observation in removal of Cd(II) from aqueous solution using *B. subtilis* and *E. coli* immobilized in agarose gel.

Gueu *et al.* (2006) also found that adsorption of Pb(II) ions onto activated carbon from coconut and seed hull of the palm tree was endothermic process.

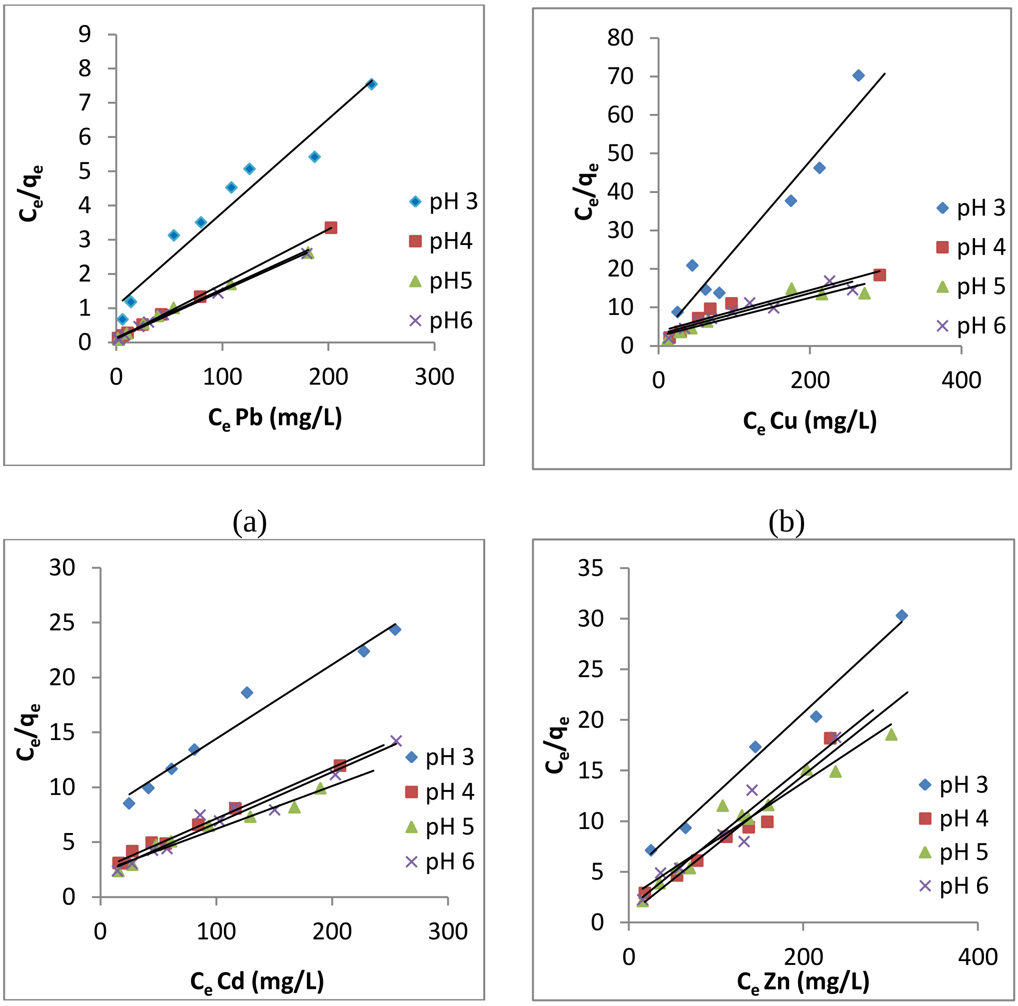
4.4.4 Adsorption isotherm model analysis

Table 4.9 shows the parameters of Langmuir and Freundlich isotherm models for the adsorption of different metal ions by BS-PSAC. It can be observed that the Langmuir model showed higher correlation coefficients (R^2) at various initial concentrations and pH.

Table 4.9 The parameters of Langmuir and Freundlich isotherm models for the adsorption of metal ions by BS-PSAC.

	Langmuir constants					Freundlich constants			
pH	q_{max} (mg/g)	q_{max} (mmol/g)	b (L/mg)	R^2	SSE	K_f	n_f	R^2	SSE
Lead									
3	36.50	0.18	0.03	0.95	1.98	4.67	2.88	0.99	0.00
4	62.50	0.30	0.16	1.00	0.00	17.00	3.68	0.87	0.05
5	68.49	0.33	0.11	0.99	0.04	22.88	4.74	0.95	0.01
6	71.94	0.35	0.12	1.00	0.02	25.67	5.03	0.99	0.00
Copper									
3	4.34	0.10	0.12	0.92	221.62	1.49	4.79	0.29	0.09
4	18.52	0.29	0.01	0.89	19.13	3.00	3.89	0.70	0.03
5	20.08	0.32	0.02	0.88	20.89	2.91	3.21	0.90	0.02
6	18.73	0.29	0.02	0.91	16.27	2.6	3.12	0.88	0.02
Cadmium									
3	14.81	0.13	0.01	0.97	7.46	0.56	1.88	0.99	0.00
4	21.6	0.19	0.02	0.99	0.63	1.48	2.10	0.96	0.01
5	25.58	0.23	0.02	0.96	1.72	1.99	2.27	0.98	0.00
6	21.46	0.19	0.02	0.97	4.29	2.46	2.64	0.92	0.02
Zinc									
3	12.53	0.19	0.02	0.99	4.29	1.00	2.35	0.93	0.01
4	14.56	0.22	0.09	0.95	6.90	2.91	3.16	0.77	0.02
5	17.54	0.27	0.02	0.94	15.59	3.74	4.00	0.81	0.02
6	14.31	0.22	0.05	0.94	11.36	3.23	3.62	0.72	0.03

Adsorption of Pb(II) at pH 3, Cu(II) at pH 5, and Cd(II) at pH 3 and 5 onto BS-PSAC showed some improvement in terms of higher R^2 values estimated for the Freundlich isotherm as compared to the Langmuir isotherm indicating that presence of bacteria biomass altered the surface heterogeneity. The constant *b* for Pb(II) and Cd(II) was greater for Cu(II) and Zn(II) indicating that the system was energetically favorable for the sorption of Pb(II) and Cd(II). Figure 4.26 shows the linearized plots of the Langmuir isotherms for metal ions adsorption by BS-PSAC.

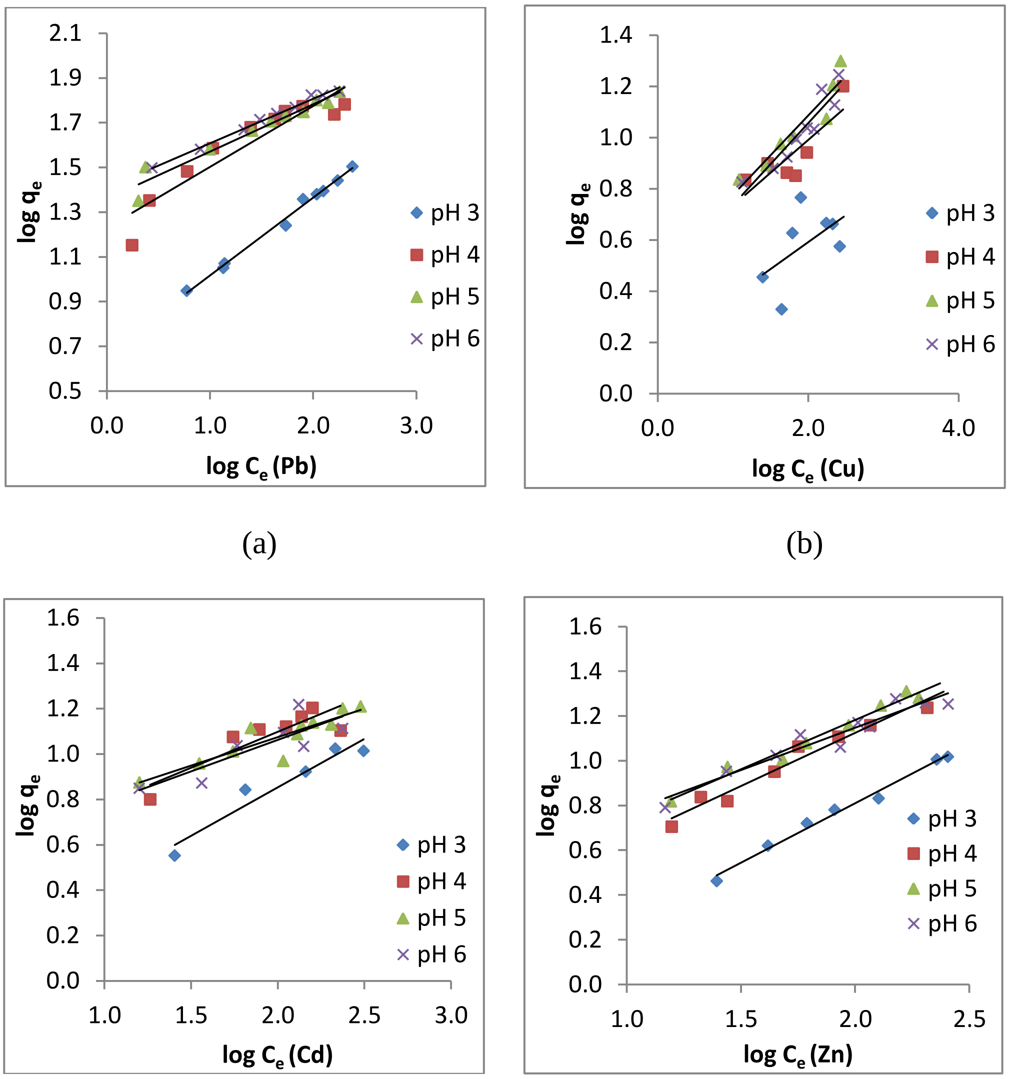


(a) (b)

(c) (d)

Figure 4.26 Langmuir isotherms for the adsorption of metal ions onto BS-PSAC at various pH, *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc.

Figure 4.27 shows the linearized plots of the Freundlich isotherms for metal ions adsorption by BS-PSAC.



(a) (b)

(c) (d)

Figure 4.27 Linearized plot of Freundlich isotherms for the adsorption of metal ions onto BS-PSAC at various pH, *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc.

The optimal pH for the sorption of metal ions was pH 5 except for Pb(II) ions it was pH 6 as can be seen from Table 4.9. The maximum Langmuir monolayer adsorption capacity of the BS-PSAC for Pb(II) reached 0.33 mmol/g at pH 5, higher than for Cu(II) (0.32 mmol/g), Zn(II) (0.27 mmol/g) and Cd(II) (0.23 mmol/g). The maximum sorption capacities of these metals increased: Pb(7.80) > Cu(8.00) > Zn(9.00) > Cd(10.10), corresposnding to the increase of the first hydrolysis constants of these metals (Table 2.3, page 12). The greater the first hydrolysis constant the more readily metal ions are hydrolyzed (Usman, 2008). The observation is consistent with Reddad *et al.*, (2002) who studied the adsorption of Pb(II), Cu(II), Zn(II), Cd(II) and Ni(II) cations onto sugar beet pulp. Pagnanelli *et al.*, (2003) also outlined that the biosorption capacity of *Sphaerotilus natans* followed the hydrolytic properties of metals ions.

K_f values for Pb(II) and Cd(II) ions indicated that the metal uptake of the BS-PSAC calculated by Freundlich isotherm model was increased in the range of pH 3 to 6. K_f for Cu(II) adsorption increased between pH 3 to 4, then it decreased between pH 4 to 6. K_f for Zn(II) adsorption increased between pH 3 to 5 then it decreased between pH 5 to 6. The trend of adsorption capacity between pH 3 to 6 for Cd(II) and Cu(II) calculated by both isotherm model was differ due to the Langmuir isotherm model fitted the adsorption behaviour better with higher R^2 values as shown in Table 4.9.

The n_f values shown in Table 4.9 range between 1 and 10 indicating that the metals adsorption by BS-PSAC was favorable. The sum of squared errors (SSE) estimated for the Langmuir model are much greater than for the Freundlich model because the linearization dependent variables in Langmuir equation always have greater values as compared to those in Freundlich equation.

4.4.5 Adsorption kinetic studies

Figure 4.28 shows the of adsorption capacity of BS-PSAC towards metal ions. Adsorption of Pb(II) ions by BS-PSAC was rapid in the beginning then it stabilized upon achieving equilibrium in about 300 minutes with approximately 32.06 mg Pb/g removal. The adsorption of Cu(II) on BS-PSAC reached equilibrium within the first 240 minutes, with 10.02 mg Cu/g removal. The equilibrium contact time for Cd(II) and Zn(II) was about 180 and 120 minutes, respectively, with removal of 7.83 mg Cd/g and 5.81 mg Zn/g.

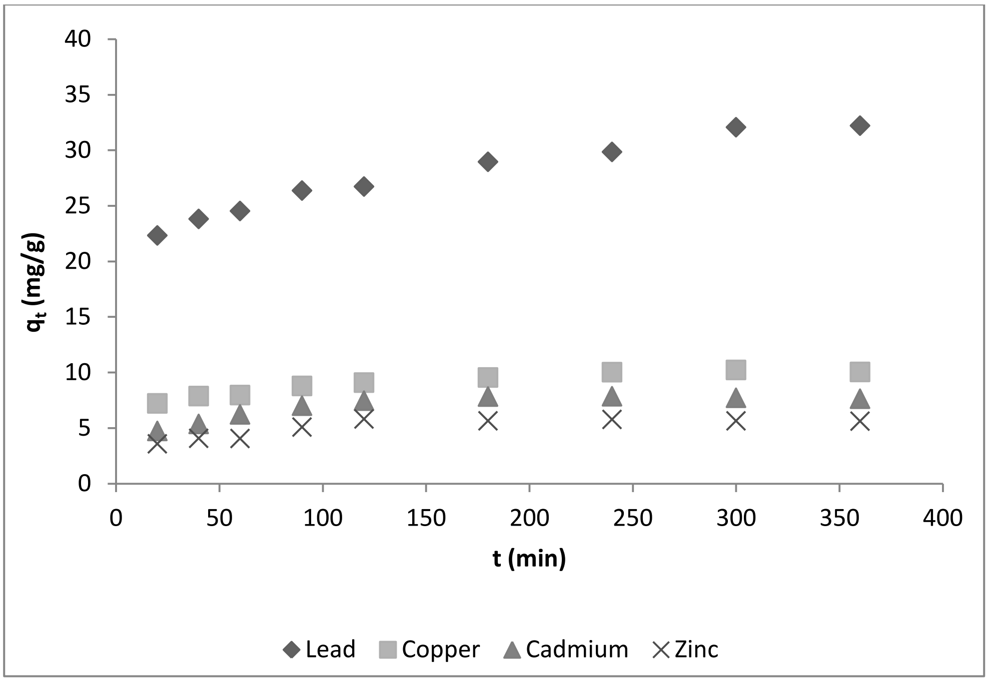


Figure 4.28 Time profiles of metals adsorption onto BS-PSAC (C_{Pb} = 100 mg/L, $C_{Zn, Cu, Cd}$ = 50 mg/L; pH 5).

As illustrated in Figure 4.29, the equilibrium sorption is attanined around 300 minutes for Pb(II), with 76.45% removal. The adsorption of Cu(II) on BS-PSAC reached equilibrium within the first 240 minutes, with 50.8 % removal. The equilibrium contact time for Cd(II) was about 180 minutes, with 40.26 %

removal. The optimal contact time for Zn(II) was about 120 minutes, respectively with around 28.48 % removal.

It was observed that initially the adsorption rate was rapid followed by a much slower rate. This trend might be due to the rapid uptake of metal ions on the surface of BS-PSAC until it reaches saturation level and metal ions gradually diffuse into the porous structure of BS-PSAC, thus resulting in longer contact time to reach equilibrium. The equilibrium contact time for Pb(II), Zn(II), Cd(II) was similar as compare with original PSAC. The equilibrium contact time of BS-PSAC for Cu(II) removal was one hour longer than for original PSAC. In addition, the equilibrium percentage removal of BS-PSAC towards Pb(II), Cu(II) and Cd(II) was slightly higher than original PSAC indicated biomodification with *B. subtilis* increase removal of metal ions from aqueous solution.

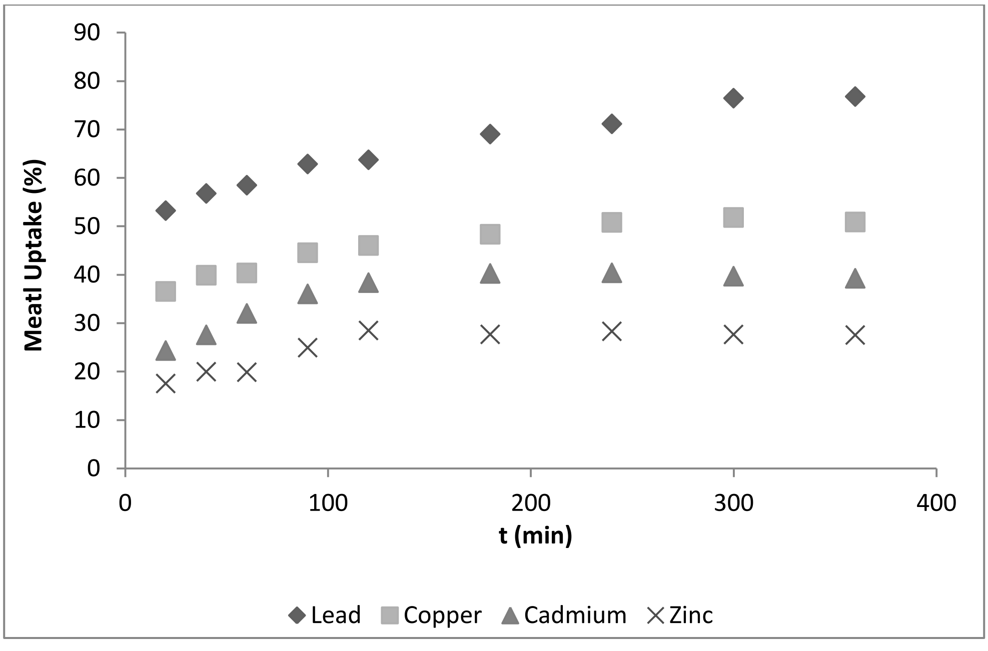


Figure 4.29 Time profiles of metal uptake at pH 5 (C_{Pb} = 100 mg/L; $C_{Zn, Cu, Cd}$ = 50 mg/L).

Table 4.10 presents kinetic data estimated using pseudo-first-order kinetics model. It can be noticed that the modelled q_e values differ from the experimental q_e values for all tested metals.

Table 4.10 Pseudo-first-order constants for metal ions adsorption onto BS-PSAC at pH 5 (C_{Pb} = 100mg/L; $C_{Cu, Cd, Zn}$ = 50 mg/L)

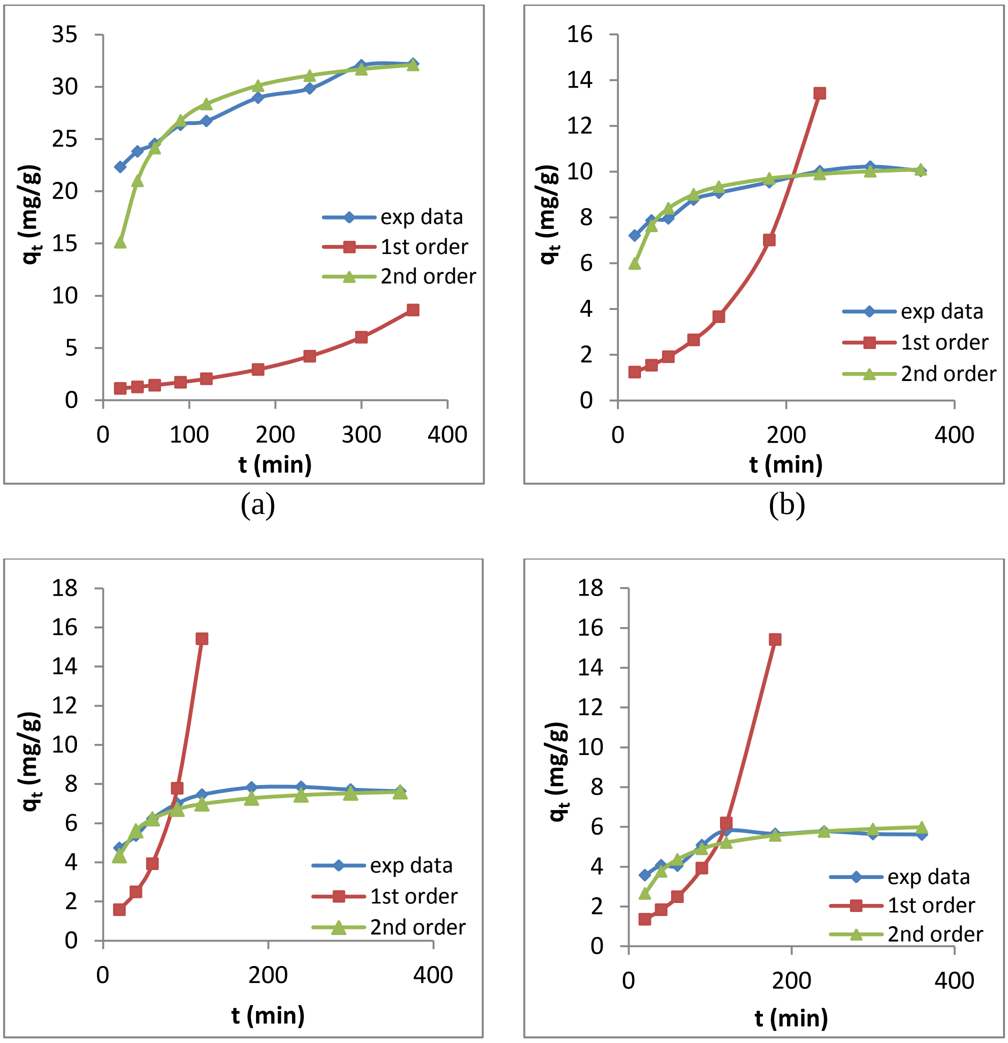
Metal	**Pseudo-first-order rate constants**				
	q_e,*exp* (mg/g)	K_1 (1/min)	q_e,*cal* (mg/g)	R^2	SSE
Pb(II)	32.71	0.00599	11.43	0.99	0.00
Cu(II)	10.05	0.01	3.56	0.97	0.00
Cd(II)	7.78	0.02	5.56	0.98	0.01
Zn(II)	5.81	0.02	3.32	0.85	0.02

Table 4.11 shows kinetic data for the pseudo-second-order kinetic model. The calculated q_e were close to the experimental q_e values. Besides, R^2 for the pseudo-first-order kinetic model varied between 0.85 and 0.99; whereas for the pseudo-second-order kinetic model R^2 reached 1.

Table 4.11 Pseudo-second-order rate constants for adsorption of metal ions onto BS-PSAC (C_{Pb} = 100mg/L, $C_{Cu, Cd, Zn}$ = 50 mg/L; pH 5)

Metal	**Pseudo-second-order rate constants**				
	q_e,*exp* (mg/g)	K_2 (g/ mg min)	q_e,*cal* (mg/g)	R^2	SSE
Pb(II)	32.71	1.14×10^{-3}	34.36	1.00	0.49
Cu(II)	10.05	6.27×10^{-3}	10.53	1.00	1.30
Cd(II)	7.78	0.01	7.95	1.00	4.29
Zn(II)	5.81	5.40×10^{-3}	6.46	1.00	34.10

This suggested adsorption of heavy metal ions was based on the chemical reaction control involving valence forces through sharing or the exchange of electrons between the biosorbent and metal ions as covalent forces (Ho and McKay, 1999; Ju *et al.*, 2006). Figure 4.30 shows plots of the experimental and modell kinetic data obtained for each tested metal. Similarly to the original PSAC, BS-PSAC showed clear predisposition toward chemisorption mechanism (Ho and McKay, 1999.



(a) (b)

(c) (d)

Figure 4.30 Experimental and modeled kinetic data for metal sorption onto BS-PSAC at pH 5: *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc at C_i = 100mg/L.

BS-PSAC was found to be a good adsorbent for Pb(II), Cu(II), Cd(II) and Zn(II). The results show that the optimal pH for the sorption of Cu(II) was around pH 5 except for Pb(II), Cd(II) and Zn(II) it was between pH 4 to 6. It was observed that with the increase of the initial concentrations of Pb(II), Cd(II) and Cu(II) ions, the equilibrium sorption capacity also increased. The adsorption capacity of BS-PSAC increased when initial Zn(II) concentration increased from 30 to 90 mg/L, it then slightly decreased and became fairly constant in the range of initial concentrations from 120 to 300 mg/L. The uptake of Pb(II) and Cu(II) by BS-PSAC was rapid in the beginning of adsorption process then it became constant when the system achieved equilibrium in about 300 and 240 minutes, respectively. The equilibrium contact time for Cd(II) and Zn(II) was 180 and 120 minutes, respectively. It was also found that a higher removal took place at 323K temperature for all metal ions implying the endothermic nature of the adsorption process. The Langmuir model and pseudo-second-order kinetic model fitted well to describe the experimental adsorption data.

4.5 Adsorption of heavy metals on palm shell activated carbon biomodified with *Aspergillus niger* (AN-PSAC).

4.5.1 Effect of pH

Figure 4.321 shows the effect of increase in pH on the adsorption capacity of AN-PSAC. Removal of Pb(II), Cd(II) and Zn(II) ions increased and reached a maximum level at pH 6; whereas optimal pH for the sorption of Cu(II) by AN-PSAC was observed at pH 5. As pH increased more acidic functional groups of *A. niger* biomass dissociated and more metal ions could be adsorbed (Xiong *et al.*, 2010).

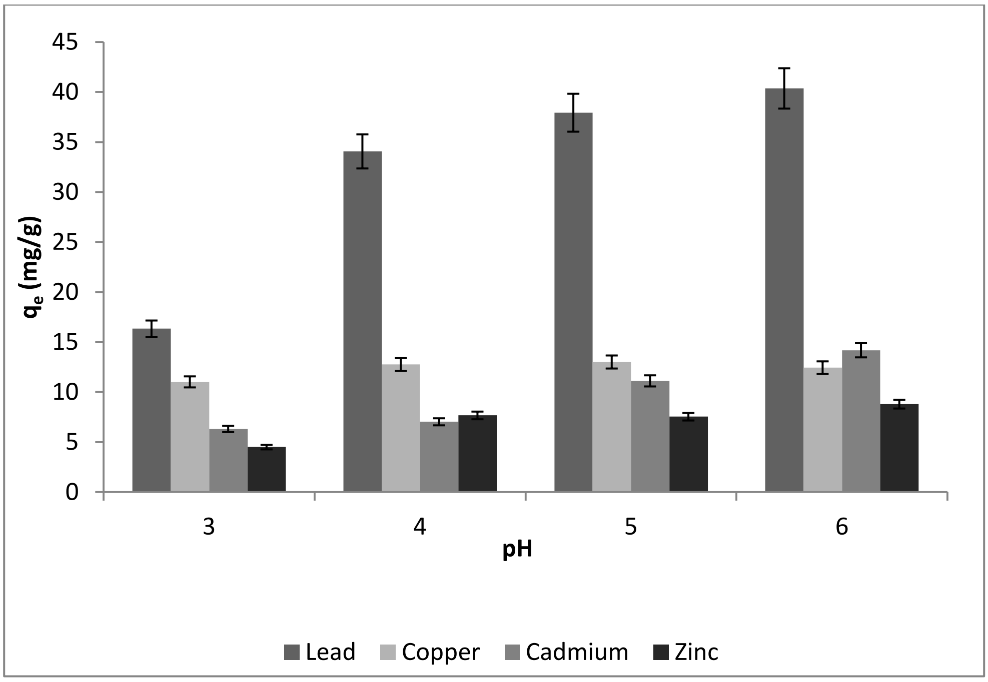


Figure 4.31 Effect of pH on metal ions removal by AN-PSAC, $C_{Me(II)}$ = 100 mg/L.

The competition between metal ions and hydrogen ions for anionic surface functional groups at lower pH (pH 3) resulted in the decrease of metal ions adsorption. Thus, metal ions sorption increased with increase in pH. However, pH>6 above resulted in metal ions precipitation (Figure 4.8; 88).

Figure 4.32 shows the that the maximum removal efficiency of Pb(II) and Cd(II) ions by AN-PSAC was achieved at pH 6; whereas the percentage uptake of Cu(II) decreased at pH>4, and the percentage uptake of Cd(II) achieved equilibrium within the range of pH 4 to 6. Overall, the results showed that pH is important parameter affecting the biosorption of heavy metals.

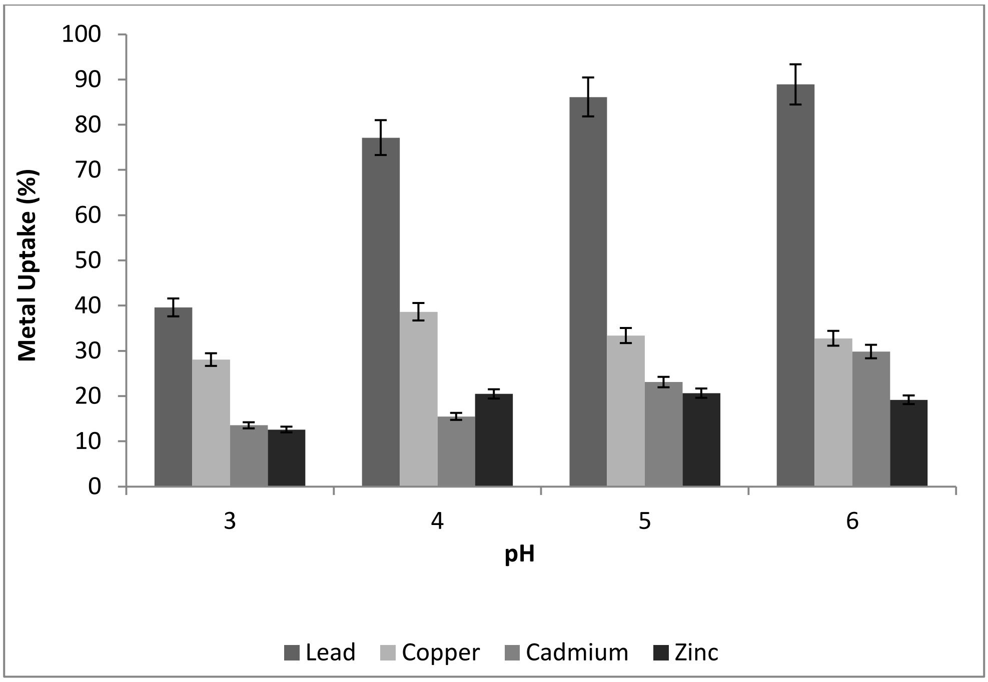


Figure 4.32 Removal of metal ions at different pHs by using AN-PSAC, $C_{Me(II)} = 100$ mg/L.

4.5.2 Effect of initial concentration

Figure 4.33 shows that the adsorption of Pb(II) increased when the initial concentration of Pb(II) increased from 30 to 300 mg/L. Similar trend was observed for Cd(II) adsorption by AN-PSAC. Increase in initial metal concentration increase adsorption uptake of metal ions due to increase driving force to overcome the resistance to the mass transfer of metal ions between the aqueous phase and the solid phase. (Kumar *et al.*, 2010; Lalhruaitluanga *et al.*, 2010).

However, the adsorption no longer increased proportionally with the increase of the initial Cu(II) and Zn(II) concentrations indicating that properties of metal ions play role in the interaction between metal ions and a surface functional groups of an adsorbent.

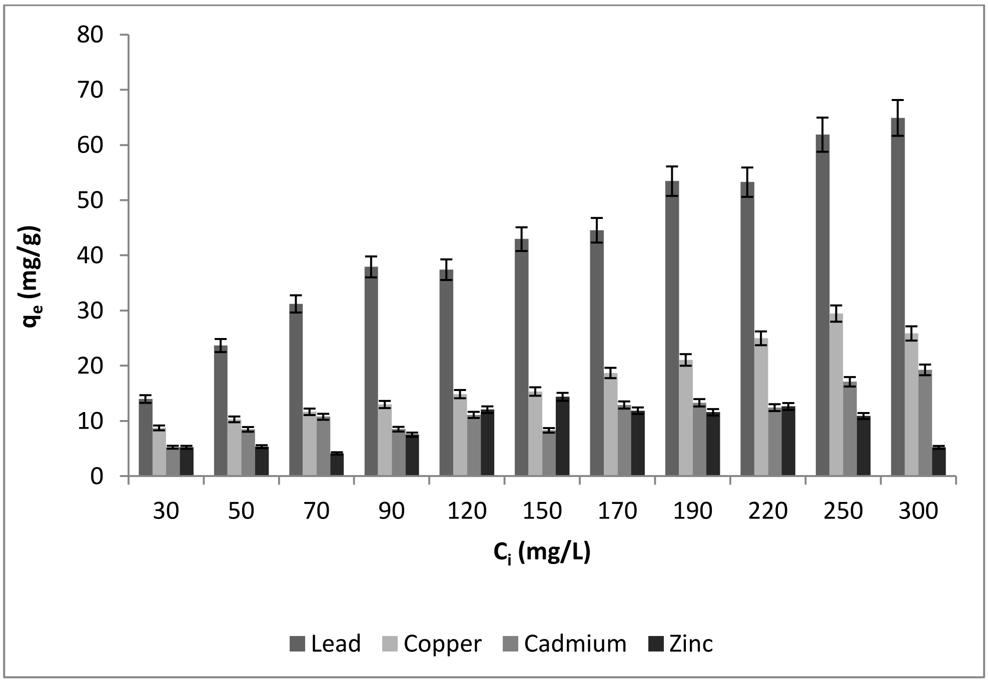


Figure 4.33 Changes in the sorption capacities of AN-PSAC over initial metal concentrations.

It can be observed that q_e of AN-PSAC towards Cu(II) ions increased up to 250 mg/L and then decreased at 300 mg/L; whereas q_e of AN-PSAC towards Zn(II) ions increased up to 150 mg/L with subsequent decrease. The AN-PSAC adsorption capacity increased in the following order: Pb > Cu > Cd > Zn which followed the increase of the density of these metals (Table 2.3, 12).

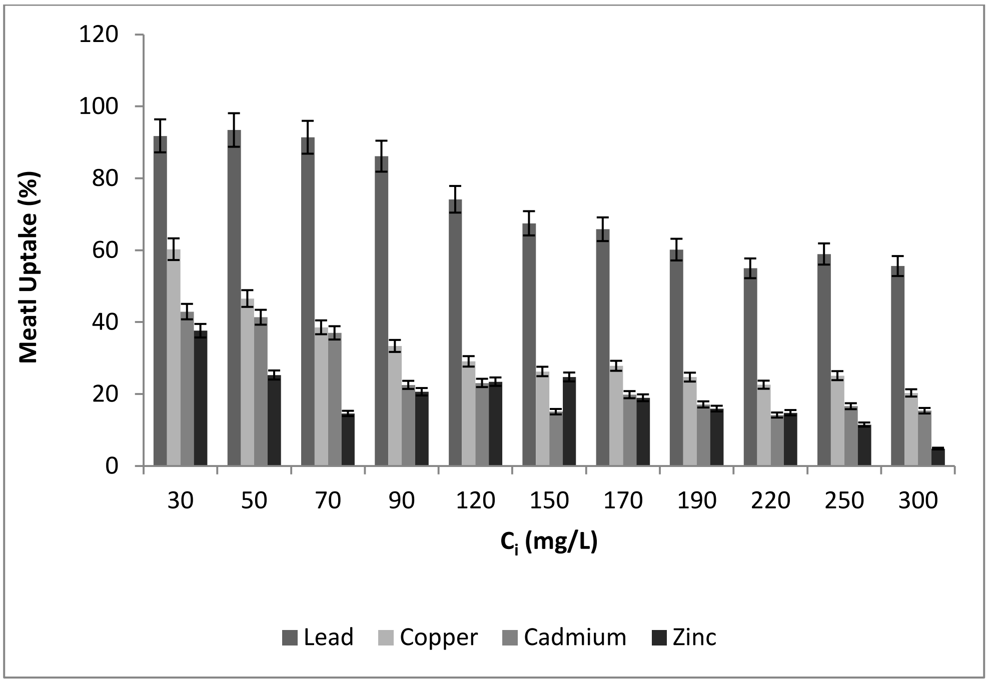
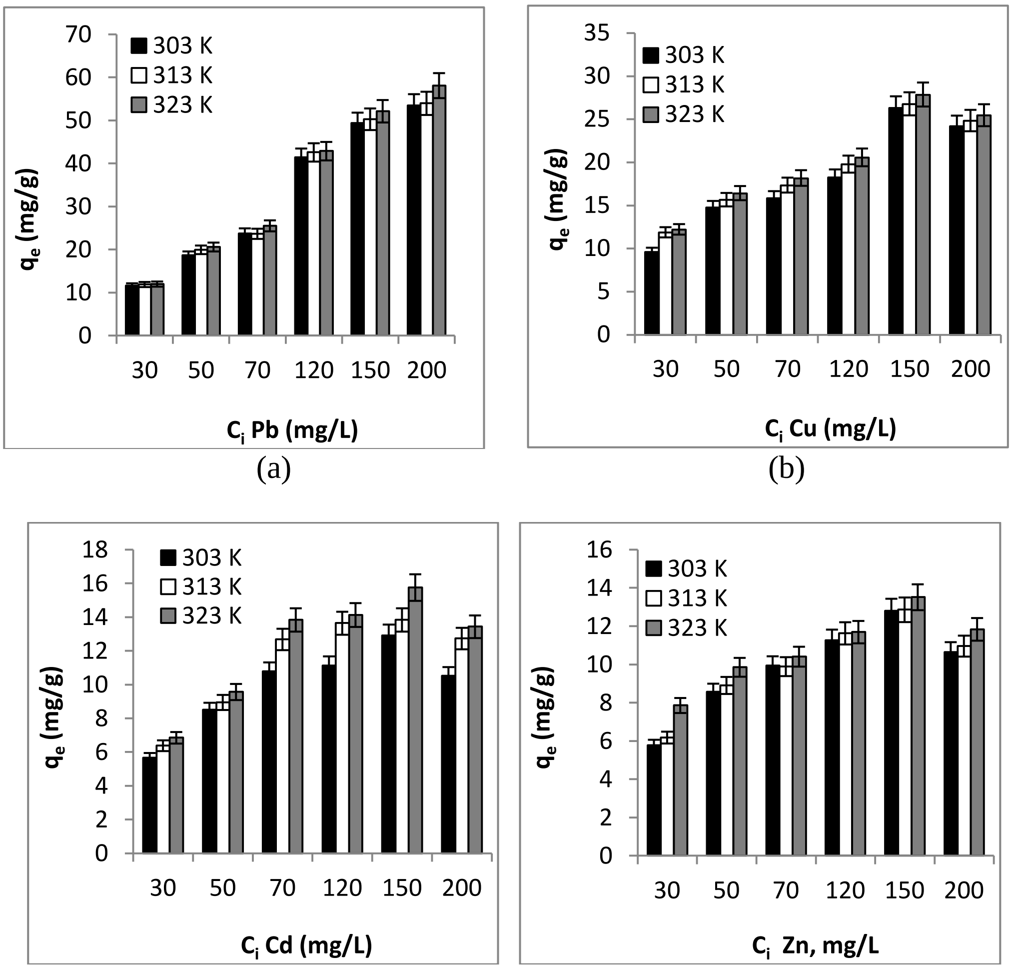


Figure 4.34 Metal removal by AN-PSAC at different initial concentrations.

Figure 4.34 shows a trend where percentage of Pb(II), Cu(II), Cd(II) and Zn(II) removal is inversely proportional to the sorption capacity of AN-PSAC. The percentage uptake of metal ions decreased when the initial concentration increased from 30 to 300 mg/L due to the fixed quantity of adsorbents used in this study. Similar observation was reported by Kumar *et al.*, 2010; Lalhruaitluanga *et al.*, 2010; Wang *et al.*, 2010.

4.5.3 Effect of temperature

Figure 4.35 shows that the sorption capacity by AN-PSAC of Pb(II), Cu(II), Cd(II) and Zn(II) ions increased with the increase of initial concentration and temperature. However, the sorption capacity of AN-PSAC towards Cu(II), Cd(II) and Zn(II) ions increased up to 150 mg/L and decreased at 200 mg/L at all tested temperatures. Besides, q_e values at 323 K for Pb(II), Cu(II), Zn(II) and Cd(II) were higher as compared to 303 and 313 K temperatures, which means that the sorption process by AN-PSAC was endothermic in nature.



(a) (b)

(c) (d)

Figure 4.35 Heavy metals adsorption by AN-PSAC at different temperatures, *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc at pH 5.

Table 4.12 presents thermodynamic parameters estimated based on the experimental data obtained at different temperatures. The positive values of enthalpy change (*ΔH°*) and negative value of Gibbs free energy change (*ΔG°*) confirmed that the adsorption process is endothermic and spontaneous. The increase in negativity of ΔG° values over temperature indicated more efficient adsorption at higher temperature (Ibrahim, 2011).

Table 4.12 Thermodynamic constants for the sorption capacities of metal ions by AN- PSAC.

Temperature (K)	Thermodynamic Parameters		
Lead	*ΔG°* (kJ mol^{-1})	*ΔH°* (kJ mol^{-1})	*ΔS°* (J mol^{-1} K^{-1})
303	-3.21	30.30	110.61
313	-4.32		
323	-5.42		
Copper			
303	-1.11	21.08	73.24
313	-1.84		
323	-2.57		
Cadmium			
303	-0.06	8.78	29.18
313	-0.36		
323	-0.65		
Zinc			
303	-0.05	6.10	20.30
313	-0.25		
323	-0.46		

A positive entropy change value of *ΔS°* reflected the affinity of the adsorbents towards the adsorbate species. Besides, the higher value of *ΔS°* indicated higher randomness and degrees of freedom at the solid-liquid interface during the adsorption of the metal ions onto AN-PSAC (Saha and Chowdhury, 2011).

Figure 4.36 shows the Van't Hoff plot used for the determination of the thermodynamic parameters. An increase in the amount of equilibrium adsorption of each ion with the rise in temperature may be explained by the fact that the adsorbent sites become more active at higher temperatures.

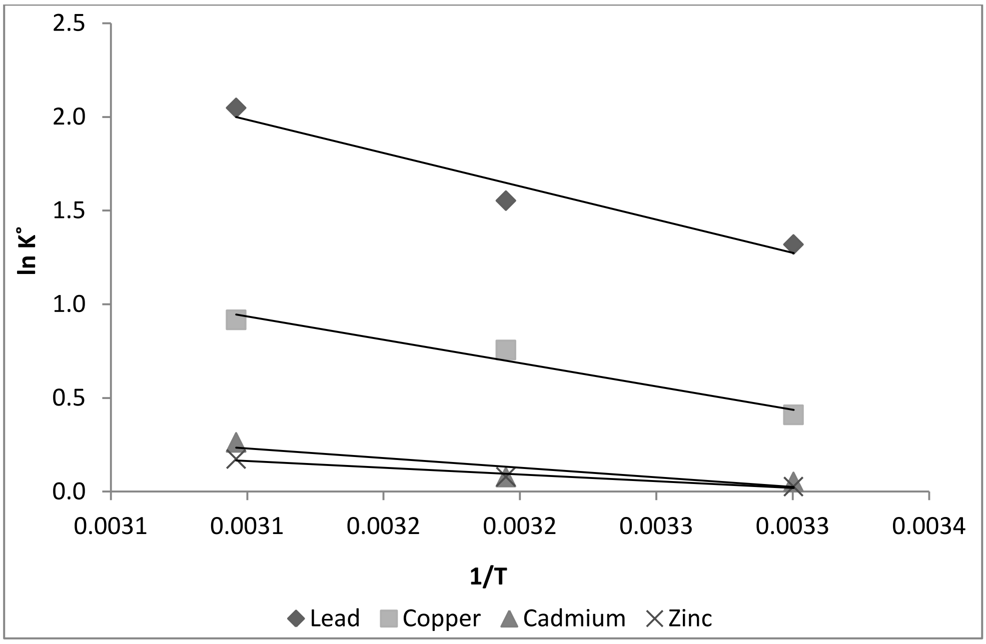


Figure 4.36 Van't Hoff Plot for adsorption of metal ions onto AN-PSAC.

It also can be explained by the fact that the kinetic energy of cations increases at higher temperatures, therefore, the contact between each ion and the active site of adsorbent is sufficient leading to an increase in adsorption efficiency (Moradi *et al.*, 2011). Similar phenomena was observed by Dursun (2006) who showed that biosorption of Cu(II) and Pb(II) on *A. niger* biomass was endothermic and spontaneous.

4.5.4 Adsorption isotherms analysis

Table 4.13 presents parameters of the Langmuir and Freundlich isotherm models for the adsorption of metal ions at different initial pH of solution. The values of R^2 for the Langmuir isotherm model are higher than R^2 for the Freundlich isotherm model.

Table 4.13 The parameters of Langmuir and Freundlich isotherm models for metal ions adsorption onto AN-PSAC.

	Langmuir constants					Freundlich constants			
pH	q_{max} (mg/g)	q_{max} (mmol/g)	b (L/mg)	R^2	SSE	K_f	n_f	R^2	SSE
				Lead					
3	34.25	0.17	0.02	0.91	2.53	4.04	2.74	0.85	0.03
4	54.95	0.27	0.08	0.99	0.08	11.00	3.02	0.93	0.02
5	65.36	0.32	0.07	0.96	0.21	13.51	3.21	0.89	0.02
6	73.53	0.35	0.07	0.99	0.05	12.06	2.72	0.88	0.03
				Copper					
3	10.89	0.17	0.34	0.91	44.81	2.90	3.62	0.50	0.07
4	19.08	0.30	0.05	0.97	5.44	5.96	4.96	0.91	0.01
5	32.36	0.51	0.01	0.92	4.93	2.68	2.51	0.95	0.01
6	25.51	0.40	0.03	0.95	2.48	2.37	2.32	0.92	0.03
				Cadmium					
3	11.44	0.10	0.01	0.88	48.68	0.48	1.81	0.89	0.04
4	13.12	0.12	0.05	0.97	8.39	1.83	2.67	0.90	0.03
5	14.90	0.13	0.03	0.96	4.93	2.45	3.04	0.80	0.03
6	18.28	0.16	0.03	0.91	18.74	4.04	3.81	0.78	0.03
				Zinc					
3	3.01	0.05	-0.09	0.92	313.91	5.84	-9.14	0.13	0.06
4	7.32	0.11	0.14	0.95	32.31	4.56	11.57	0.22	0.02
5	14.99	0.23	0.02	0.91	9.93	1.30	2.31	0.84	0.02
6	9.62	0.15	0.04	0.98	11.77	2.14	11.57	0.79	0.02

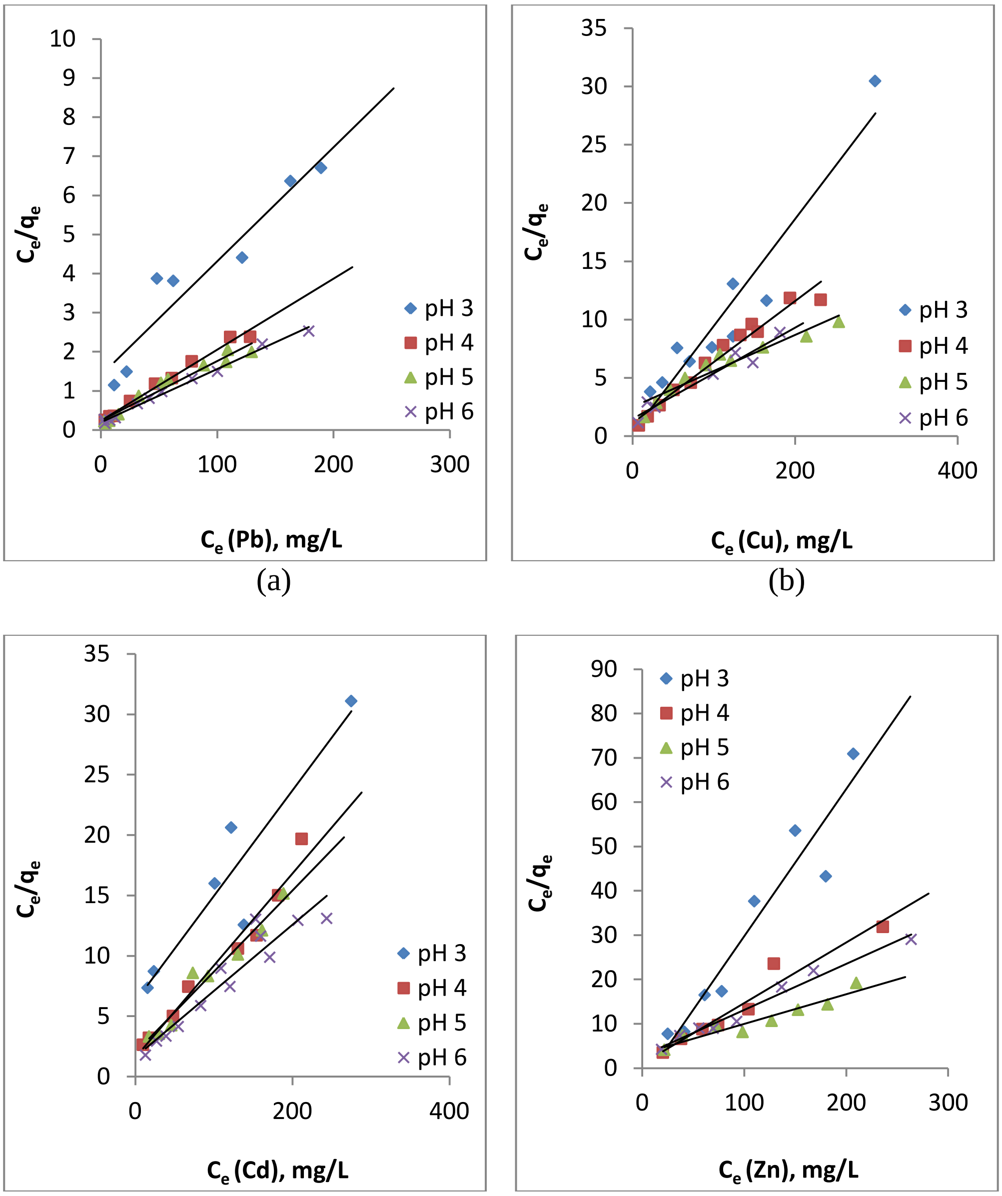
This is in agreement with Tsekova *et al.*, (2010b) who reported that Langmuir isotherm provided an excellent fit ($R^2 > 0.99$) for sorption of Cu(II) and Cd(II) using polyvinvyl alcohol (PVA) immobilized and free fungal biomass of *A. niger*.

Higher values of coefficient *b* in the Langmuir isotherm model signify energetically favorable sorption of metal ions onto AN-PSAC (Arivoli *et al.*, 2007). It can be observed from Table 4.13 that the optimum pH for adsorption of Pb(II) and Cd(II) is pH 6.0; while for Cu(II) and Zn(II) it is pH 5.0 based on the q_{max} values of the Langmuir isotherm model.

The Langmuir adsorption isotherm showed q_{max} of 0.40, 0.35, 0.16 and 0.15 mmol/g (or 25.51, 73.53, 18.28 and 9.62 mg/g) at pH 6.0 for Cu(II), Pb(II), Cd(II) and Zn(II), respectively. The maximum sorption capacity of these metals increased following the increase in the metal's electronegativity order: Cu (1.90) > Pb(1.80) > Cd(1.70) > Zn(1.60) (Table 2.3, 12).

On the other hand, the K_f value for Pb(II) and Cd(II) ions (Table 4.13, page 135) was found to increase from pH 3 to 6 confirmed that the sorption capacity of AN-PSAC towards Pb(II) and Cd(II) increased along with pH increased. Freundlich isotherm model indicated that Cu(II) adsorption increased from pH 3 to 4 then it decreased; whereas Zn(II) adsorption decreased from pH 3 to 5 then it increased from pH 5 to 6. The values of n_f indicate favorable adsorption except for Zn(II) adsorption at pH 3, 4 and 6 which is out of the 1-10 range.

Figure 4.37 shows the Langmuir adsorption isotherms for Pb(II), Cu(II), Cd(II) and Zn(II) ions. The figure showed a linear relationship among the plotted parameters indicated the applicability of Langmuir adsorption isotherm.

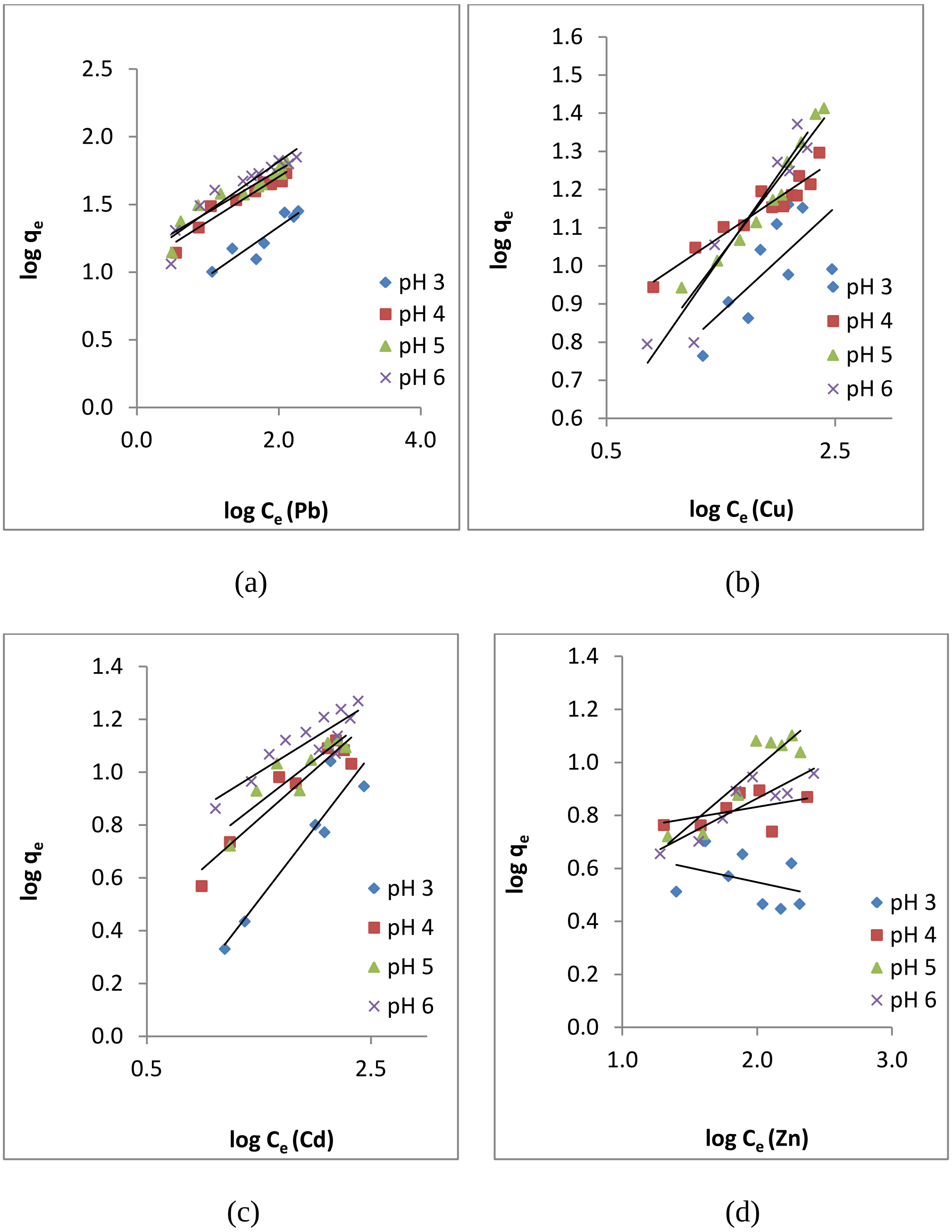


(a) (b)

(c) (d)

Figure 4.37 Langmuir isotherms for the adsorption of metal ions onto AN-PSAC at various pH, *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc.

Figure 4.38 showed the applicability of Freundlich isotherm was also analyzed by using the same set of experimental data. It can be seen that quite poor fit of the Freundlich model isotherms for the experimental adsorption data, especially for Zn(II) adsorption. The adsorption data revealed that Langmuir isotherm (Figure 4.37) showed a better fit over the Freundlich isotherm in all the metal ions.



(a) (b)

(c) (d)

Figure 4.38 Freundlich isotherms for the adsorption of metal ions onto AN-PSAC at various pH, *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc.

4.5.5 Adsorption kinetic studies

Figure 4.39 shows the profile of adsorption capacity of AN-PSAC towards metal ions over time. As for original and BS-PSAC, a rapid initial sorption followed by the extended period of much slower uptake of metal ions. The result shows that the adsorption of Pb(II) on AN-PSAC reaches equilibrium within the first 240 minutes, with an equilibrium uptake of Pb(II) around 24.45 mg Pb/g. On the other hand, the biosorption of Cu(II) onto AN-PSAC increased gradually from 2.81 to 5.72 mg Cu/g and reached equilibrium within 300 minutes; whereas adsorption of Cd(II) and Zn(II) onto AN-PSAC was fast and reached equilibrium within 180 minutes, with removal of 8.04 mg Cd/g and 5.34 mg Zn/g.

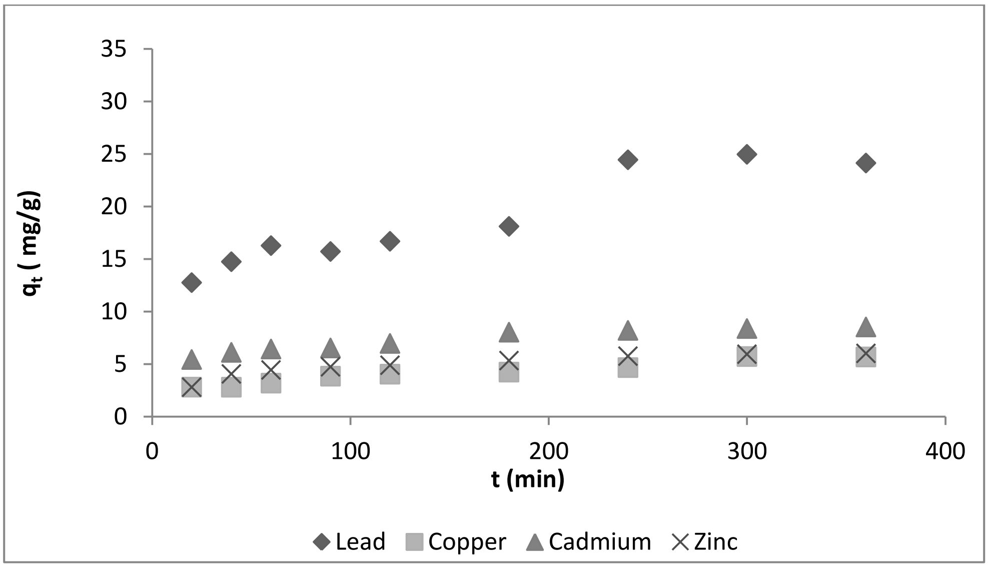


Figure 4.39 Removal rate of heavy metals ions onto AN-PSAC (C_{Pb} = 100 mg/L, $C_{Zn, Cu, Cd}$ = 50 mg/L; pH 5).

Figure 4.40 presents the removal (%) of metals onto AN-PSAC over time. Adsorption of Pb(II) on AN-PSAC reached equilibrium within the first 240 minutes, with around 52 % removal. Adsorption of Cu(II) onto AN-PSAC increased gradually from 17.58 to 35.86 % and reached equilibrium within 300 minutes; whereas adsorption of Cd(II) and Zn(II) onto AN-PSAC reached equilibrium within 180 minutes, with an 39.38 % and 21.44 % removal, respectively.

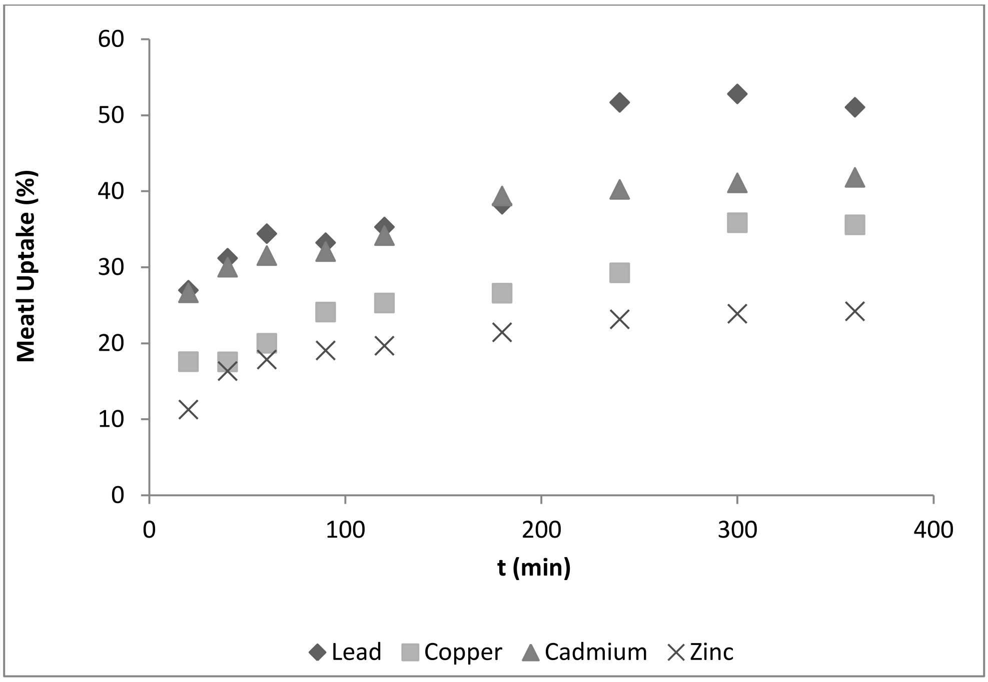


Figure 4.40 Time profile for metal removal onto AN-PSAC (C_{Pb} = 100 mg/L, $C_{Zn, Cu, Cd}$ = 50 mg/L; pH 5).

It was observed that the equilibrium uptake of metal ions did not vary significantly in the period of 180 to 300 minutes from the start of adsorption process. This shows that equilibrium can be achieved in the period of 180 to 300 minutes due to the saturation of the carbon pores with metal ions during the initial stage of adsorption. The equilibrium contact time for adsorption of Zn(II) and Cu(II) by AN-PSAC was 1-2 hours increased as compared with original PSAC and BS-PSAC due to the lowest of micropore volume. The metal ions encountered much stronger resistance to traverse into the micropores of AN-PSAC and resulting in the slowdown of the adsorption. Table 4.14 shows kinetics data for the pseudo-first-order kinetic model; the calculated q_e values were lower as compared to the experimental q_e values.

Table 4.14 Pseudo-first-order model constants for metals adsorption by AN-PSAC (C_{Pb} = 100mg/L, $C_{Cu, Cd, Zn}$ = 50 mg/L; pH 5).

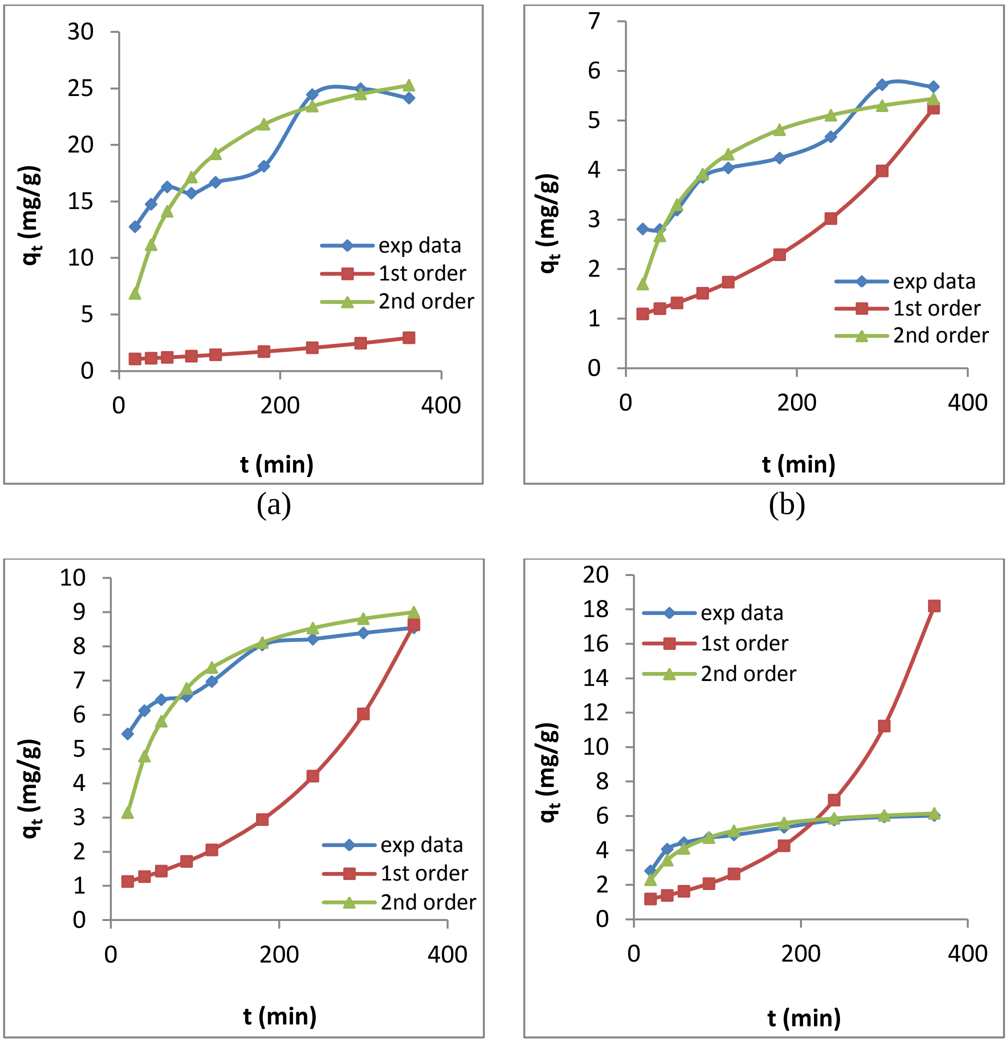
Metal	Pseudo-first-order rate constants				
	q_e,exp (mg/g)	K_1 (1/min)	q_e,cal (mg/g)	R^2	SSE
Pb(II)	25.60	2.99×10^{-3}	12.46	0.86	0.00
Cu(II)	5.81	4.61 x 10-3	3.30	0.96	0.01
Cd(II)	8.61	5.99×10^{-3}	3.33	0.93	0.00
Zn(II)	6.10	8.06×10^{-3}	3.09	0.93	0.02

However, the experimental sorption capacity (q_e,*exp*) values agreed well with the calculated sorption capacity (q_e,*cal*) for pseudo-second-order kinetic model for all heavy metals tested as can be seen in Table 4.15. The values of correlation coefficients (R^2) of pseudo-first-order kinetic model were slightly lower as compared to the values of R^2 for the pseudo-second-order kinetic model.

Table 4.15 Pseudo-second-order model constants for metals adsorption by AN-PSAC (C_{Pb} = 100mg/L, $C_{Cu, Cd, Zn}$ = 50 mg/L; pH 5).

Metal	Pseudo-second-order rate constants				
	q_e,exp (mg/g)	K_2 (g/ mg min)	q_e,cal (mg/g)	R^2	SSE
Pb(II)	25.60	4.93×10^{-4}	30.03	1.00	7.62
Cu(II)	5.81	3.00×10^{-3}	6.24	1.00	96.33
Cd(II)	8.61	2.23×10^{-3}	10.11	1.00	22.68
Zn(II)	6.10	3.70×10^{-3}	6.83	1.00	13.74

Figure 4.41 presents plotted modelled q_e values and estimated ones. Such comparison confirms that adsorption onto AN-PSAC followed the pseudo-second-order kinetic model, i.e. chemisorption mechanism.



(a) (b)

(c) (d)

Figure 4.41 Comparison of experimental and modelled kinetic data for adsorption onto AN-PSAC: *(a)*lead; *(b)*copper; *(c)*cadmium; *(d)*zinc at $C_i = 100$ mg/L, pH 5.

Chemisorption is an adsorption mechanism characterized by a strong interaction between an adsorbate and a substrate surface, as opposed to physisorption mechanism which is characterized by a weak Van der Waals force presence. The sum of squared errors (SSE) for the pseudo-second-order kinetic model is greater than for the pseudo-first-kinetic model because the dependent variables in its linearized equation always have greater values.

The results obtained by Kumar *et al.*, (2012) showed the same trend when Ni(II), Zn(II) and Cr(VI) adsorption by dead *A. niger* biomass showed the best fit in the pseudo-second-order model. Similar observations have also been reported by Liu *et al.* (2006) and Mungasavalli *et al.* (2007) showing that the pseudo-second-order kinetic model predicts the sorption kinetics better than the pseudo-first-order mode.

In this study it was shown that adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) onto AN-PSAC was dependent on pH, initial metal ions concentration, contact time and temperature parameters. The optimal pH for the sorption of Pb(II), Cd(II), Zn(II) was pH 6; whereas optimal pH for the sorption of Cu(II) was pH 5. The adsorption uptake of Pb(II) and Cd(II) increased as the initial concentration increased from 30 to 300 mg/L. However, it is observed that q_e values of AN-PSAC towards Cu(II) removal increased up to 250 mg/L solution concentration and then decreased at 300 mg/L; whereas q_e values of AN-PSAC towards Zn(II) increased in concentration range up to 150 mg/L and then it decreased. The reverse trend was observed for the percentage of metal ions removal by AN-PSAC. The equilibrium sorption was attained within 240 minutes for Pb(II); within 300 minutes for Cu(II); and within 180 minutes for Cd(II) and Zn(II). The results showed a rapid initial sorption followed by a much slower uptake of metal ions by the adsorbents. The adsorption of metal ions on the adsorbent increased over increase in temperature. The thermodynamic study confirmed that the adsorption process for all metal ions is endothermic and spontaneous in nature. Adsorption isotherms of all metals were well described by the Langmuir isotherm model suggesting a monolayer adsorption. The kinetics of metal ions adsorption followed the pseudo-second-order kinetic model indicating the chemisorptions mechanism of metal ions removal.

4.6 Comparison of metal ions uptake efficiencies between the biosorbents

The variations in the removal efficiency by using three adsorbents relate to the type of microorganism biomass used for the biomodification purpose, which is affecting the interactions between sorption sites and metal ions. *Bacillus subtilis* and *Aspergillus niger* have differences in terms of the cell wall structure and its composition since they belong to the different groups of microorganisms.

B. subtilis is a gram-positive bacteria with a thicker peptidoglycan layer which contains many carboxyl groups of glutamic acid responsible for the metal ions deposition. *A. niger* is a filamentous fungi with many carboxyl, phosphate, amine and amide groups in the composition of the cell wall which are important functional groups involved in biosorption of heavy metals (Kapoor and Viraraghavan, 1997).

Table 4.16 shows comparison of maximum sorption capacity (q_{max}) between the three adsorbents. The adsorption capacities for each heavy metal (q_{max}) estimated by the Langmuir model at different pHs are presented in separate table blocks so that the following orders in the adsorption removal can be established.

Table 4.16 Maximum sorption capacity (q_{max}) of three adsorbents.

Lead			
pH	q_{max} (mmol/g)		
	Original PSAC	BS-PSAC	AN-PSAC
3	0.19	0.18	0.17
4	0.26	0.30	0.27
5	0.29	0.33	0.32
6	0.31	0.35	0.35
Copper			
pH	q_{max} (mmol/g)		
	Original PSAC	BS-PSAC	AN-PSAC
3	0.12	0.10	0.17
4	0.34	0.29	0.30
5	0.35	0.32	0.51
6	0.27	0.29	0.40
Cadmium			
pH	q_{max} (mmol/g)		
	Original PSAC	BS-PSAC	AN-PSAC
3	0.11	0.13	0.10
4	0.20	0.19	0.12
5	0.26	0.23	0.13
6	0.28	0.19	0.16
Zinc			
pH	q_{max} (mmol/g)		
	Original PSAC	BS-PSAC	AN-PSAC
3	0.11	0.19	0.05
4	0.19	0.22	0.11
5	0.23	0.27	0.23
6	0.26	0.22	0.15

Based on the presented data, the following orders of adsorption of heavy metals by the biosorbents of this study can be proposed.

For Pb(II): BS-PSAC > AN-PSAC > Original PSAC;

For Cu(II): AN-PSAC > Original PSAC > BS-PSAC;

For Cd(II): Original PSAC > BS-PSAC > AN-PSAC;

For Zn(II): BS-PSAC > AN-PSAC ≈ Original PSAC.

Table 4.16 also shows that BS-PSAC exhibited higher sorption efficiency in removing Pb(II) and Zn(II) at pH 5 as compared to the AN-PSAC and original PSAC. Biomodification of PSAC with bacterial and fungal biomass changed their surface characteristic by increasing the concentration of carboxyl groups, reducing the micropore volume and the pH of point of zero charge with a resulting increase in the density of the negative charge on the biosorbents surface (Rivera-Utrilla *et al.*, 2001). Therefore, biomodified BS-PSAC showed higher Pb(II) and Zn(II) removal efficiency as compared to the original PSAC. The sorption efficiency of BS-PSAC was higher than that of AN-PSAC due to probable blockage of carbon pores (approximately 26%) by *A. niger* biomass; whereas BS-PSAC showed decrease of only 4% in the total carbon surface area due to the greater size of fungal cells (Table 4.1; page 78). Although, the carbon porosity decreased, it did not suppress the metal removal probably due to the adsorptive properties of fungal biomass itself.

The adsorption capacity for Cu(II) by the original PSAC was found to be lower than that of the AN-PSAC, but it was greater than that of the BS-PSAC confirming that the biomodification with *B.subtilis* reduced the adsorption performance of PSAC in removal of Cu(II); whereas biomodification with *A.niger* biomass enhanced the sorption of Cu(II) ions by PSAC. This observation indicated that *A. niger* introduction into the PSAC resulted in increased effectiveness in removing Cu(II) ions as compared to the original PSAC. Akthar *et al.*, (1996) indicated that weak acidic carboxyl groups present in *A. niger*'s cell wall constituents are probable biosorption sites and lead to increased biosorption of Cu(II).

The original PSAC showed higher Cd(II) removal as compared to BS-PSAC and AN-PSAC. Surface area and micropore volume of the adsorbents are the key factors for Cd(II) adsorption since the q_{max} of all adsorbents increased with the increase in the surface area and micropore volume of the adsorbents (Table 4.1; page 78). Larger surface area allows the exposure of a larger number of the active sites.

Overall, the results of this study imply that PSAC biomodified with *B. subtilis* and *A. niger* biomass improved the adsorption performance of PSAC towards metal ions.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research focused on the development of porous hybrid biosorbents with higher adsorption capacity for metal ions removal through biomodification of palm shell activated carbon (PSAC) with *Bacillus subtilis* and *Aspergillus niger*, respectively.

PSAC biomodified with *B. subtilis* (BS-PSAC) and *A. niger* biomass (AN-PSAC) showed increased concentrations of acidic carboxyl surface groups and negative charge density and decreased point of zero charge. Such changes promoted higher adsorption capacity of the developed biosorbents to remove positively charged metal ions through increased electrostatic interactions in the solution. The surface area and porosity of the developed biosorbents decreased, especially for AN-PSAC, as compared to the original and BS-PSAC due to the presence of microbial biomass which was also confirmed by SEM images.

Overall, the Langmuir isotherm model described the adsorption data of the studied adsorbents better than the Freundlich isotherm model confirming monolayer character of adsorption for Pb(II), Zn(II), Cd(II) and Cu(II) ions in aqueous solutions. Higher correlations of R^2 were obtained for BS-PSAC fitted into the Freundlich model reflecting the heterogeneity of the hybrid adsorbent associated with deeper penetration of bacterial cells into the carbon matrix.

Batch adsorption results showed that BS-PSAC had the highest removal efficiency for Pb(II) and Zn(II). Meanwhile, AN-PSAC showed highest capacity for Cu(II) removal and original PSAC showed highest Cd(II) removal. Such differences between the biosorbents related to their physico-chemical properties.

In terms of experimental parameters of adsorption process, the results showed that the optimal initial concentration for Pb(II) removal was 50, 70 and 90 mg/L for the original AN-PSAC, BS-PSAC and PSAC, respectively. The optimal initial metal ions concentrations for removal of Cu(II), Zn(II) and Cd(II) were around 30 mg/L showing no significant differences between the capacity of the studied biosorbents. Such results also indicated higher affinity between palm shells based activated carbons and lead ions.

In terms of pH changes, all three biosorbents behaved quite similarly showing lowest metal ions removal at pH 3. As pH of the solution increased from 4 to 6, adsorption of metals noticeably improved. The optimal pH for the sorption of heavy metals by the original PSAC, BS-PSAC and AN-PSAC was pH 6, except for Cu(II) it was pH 5.

Increase in temperature had positive effect on the metal ions adsorption for all three biosorbents, with optimum around 323 °K, which is associated with the enlargement of carbon pores and subsequent increase in the adsorption capacity.

Effect of contact time was similar between the biosorbents and showed that the optimum removal of Zn(II) and Cd(II) ions was achieved in 120-180 minutes periods. However, the highest Pb(II) and Cu(II) adsorption was observed in 240-300 minutes period. The initial sorption of all metal ions was rapid and it followed by a much slower adsorption of metal ions.

The kinetics data for adsorption of Pb(II), Zn(II), Cu(II) and Cd(II) onto the original and biomodified PSACs showed better fit into the pseudo-second-order reaction model indicating that the rate-limiting step was chemisorption that involved valence forces through exchange of electrons between the adsorbents' surface and metal ions.

Determination of thermodynamic parameters of the studied adsorbents showed positive values of enthalpy change (ΔH^{o}) and negative values of Gibbs free energy change (ΔG^{o}) implying that the adsorption process was spontaneous and endothermic in nature. Also, positive values of entropy change (ΔS°) indicated the affinity of the studied adsorbents toward the metal ions in aqueous solution.

This research can be considered successful as it showed that biomodification with *B. subtilis* and *A. niger* biomass of the original granular palm shell activated carbon demonstrated potential to increase removal of metal ions from aqueous solutions. Besides, one of the significant outcomes of the research is comprehension of the importance of the optimization of the biomodification procedure to substantially improve adsorption performance of biosorbents, which would require a further thorough study.

5.2 Recommendations for future work

Some recommendations are proposed for future research:

Biomodification of PSAC using different amount of microorganism biomass

In this study the biomodification process was conducted using 40 mL of microorganism biomass suspension with 1.2 g of PSAC which was adopted from the experimental process reported by Rivera *et al.* (2001). The uptake capacity of biomodified PSAC could be investigated using more or less amount of microorganism biomass.

Desorption of metal ions and regeneration of adsorbents

Desorption of sorbed metals and the regeneration of adsorbents materials is crucial for keeping the adsorption process cost down and recovers the metals extracted from the solution. The uptake capacity and stability of the adsorbents is investigated as a function of the number of adsorption-desorption cycles. Desorption process can be conducted in a batch system or a continuous flow column using acids such as hydrochloric acid, citric acid, sulphuric acid and other.

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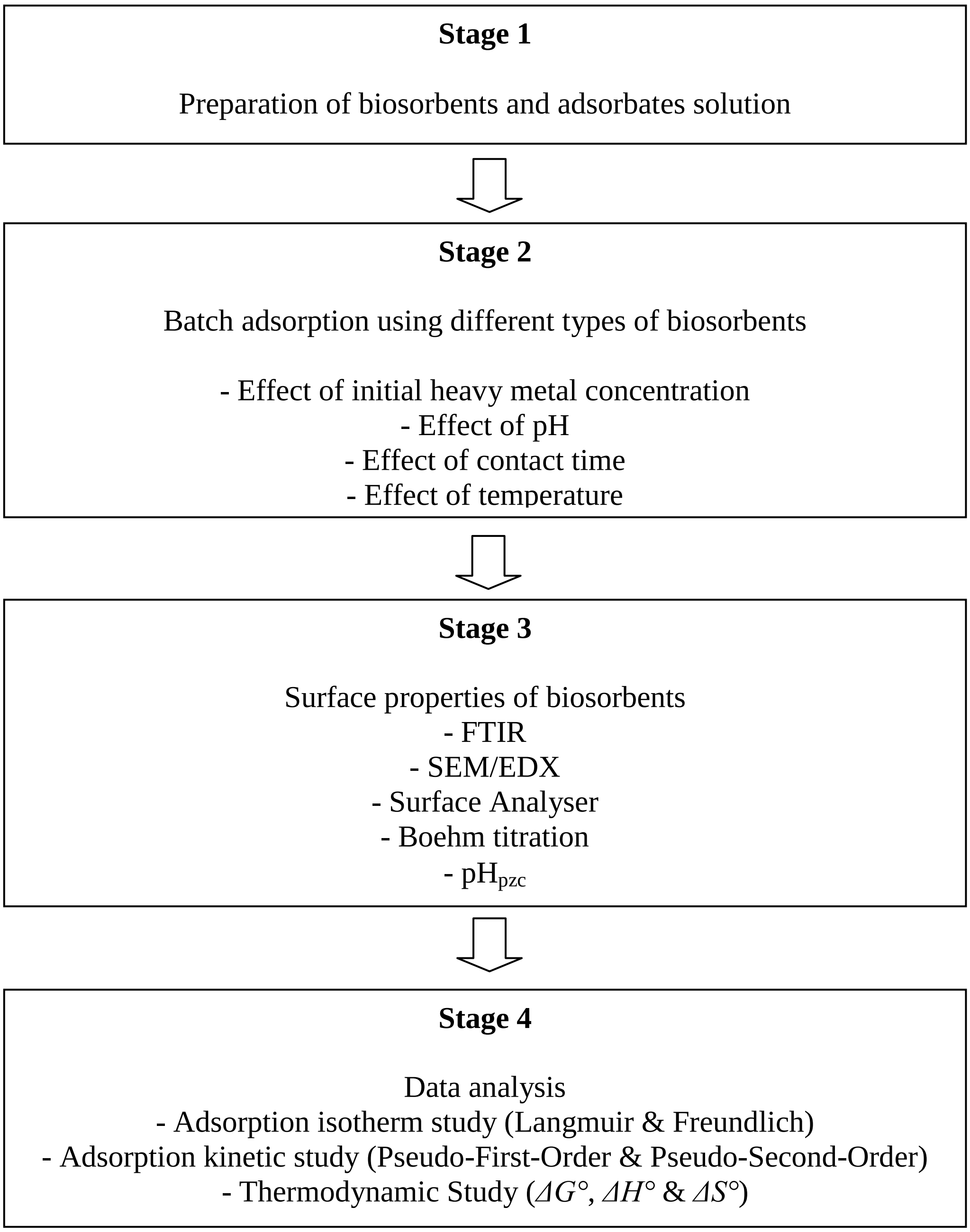
APPENDIX A

EXPERIMENTAL DESIGN OF THE STUDY

The experimental design applied in this study can be summarized as is shown in Appendix A.



Stage 1

Preparation of biosorbents and adsorbates solution

Stage 2

Batch adsorption using different types of biosorbents

- Effect of initial heavy metal concentration
- Effect of pH
- Effect of contact time
- Effect of temperature

Stage 3

Surface properties of biosorbents
- FTIR
- SEM/EDX
- Surface Analyser
- Boehm titration
- pH_{pzc}

Stage 4

Data analysis
- Adsorption isotherm study (Langmuir & Freundlich)
- Adsorption kinetic study (Pseudo-First-Order & Pseudo-Second-Order)
- Thermodynamic Study ($\Delta G°$, $\Delta H°$ & $\Delta S°$)