ULTRASOUND-ASSISTED BIOSORPTION PROCESS FOR THE REMOVAL OF LEAD AND IRON ON LANDFILL LEACHATE USING PRE-TREATED OIL PALM BIOMASS

by

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LIST OF SYMBOLS

Symbols	Descriptions	Unit
A	Weight of filter plus dried residue	mg
A_T	Temkin isotherm equilibrium binding constant	L/g
B	Weight of filter	mg
b	Langmuir constant	L/mg
b_T	Temkin isotherm constant	Dimensionless
C_0	Highest initial concentration of sorbate	mg/L
C_e	Concentration of material remaining in solution after the sorption process	mg/L
C_i	Final concentration of heavy metals	mg/L
D_1	DO of diluted sample immediately after preparation	mg/L
D_2	DO of diluted sample after 5 d incubation at 20° C	mg/L
k_f	Freundlich constant related to adsorption capacity	mg/g
K_{1ad}	Rate constant of pseudo first-order adsorption	g/gmin
K_{2ad}	Rate constant of pseudo second-order adsorption	Min^{-1}
m	Weight of sorbent	mg or g
n	Freundlich constant related to adsorption intensity	Dimensionless
P	Decimal volumetric fraction of sample used	Dimensionless
Q_0	Maximum amount of adsorption	mg/mg
q_e	Amount adsorbed per unit mass of adsorbent	mg/g
q_t	Amount of adsorption at time t	min

R	Universal gas constant	8.314J/mol K
R^2	Regression	Dimensionless
R_L	Separation factor	Dimensionless
T	Temperature	K
t	Time	min
V	Volume of the solution	L
W	Mass of the adosorbent	g
X	Amount of material adsorbed	mg or g

LIST OF ABBREVIATIONS AND SYMBOLS

AAS	Atomic Absorption Spectrophotometry
Ag_2SO_4	Silver Sulfate
Ag	Silver
Am	Americium
As	Arsenic
Au	Gold
ANOVA	Analysis of Variance
BET	Brunauer-Emmett-Teller
BSR	batch Stirred Reactor
BOD	Biological Oxygen Demand
$CaCl_2$	Calcium Chloride
CCD	Central Composite Design
CCRD	Central Composite Rotatable Design
CCFD	Central Composite Face-Centered Design
Cd	Cadmium
Co	Cobalt
COD	Chemical Oxygen Demand
Cr	Chromium
Cu	Copper
DO	Dissolved Oxygen
DOE	Design of Experiment
EFB	Empty Fruit Bunch
EDX	Energy Dispersive X-ray Spectroscopy
$FeCl_3$	Ferric Chloride
FTIR	Fourier Transform Infrared Spectroscopy
HCl	Hydrochloric Acid

Hg	Mercury
$HgSO_4$	Mercury Sulfate
H_2SO_4	Sulfuric Acid
KBr	Potassium Bromide
$K_2Cr_2O_7$	Potassium Dichromate
K_2HPO_4	Dipotassium Phosphate
$MgSO_4$	Magnesium Sulfate
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
Na_2SO_4	Sodium Sulfate
Ni	Nickel
OPB	Oil Palm Bark
OPF	Oil Palm Frond
OPL	Oil Palm Leave
Pb	Lead
$Pb(NO_3)_2$	Lead Nitrate
PBLS	Pulau Burung Landfill Site
PBR	Packed Bed Reactor
Pd	Palladium
Pt	Platinum
Ra	Radium
RSM	Response Surface Methodology
Ru	Ruthenium
SEM	Scanning Electron Microscope
Sn	Tin
Th	Thorium
TSS	Total Suspended Solid

U	Uranium
V_P	Total Pore Volume
Zn	Zinc

PROSES PERJERAPAN-BIO BERBANTU ULTRABUNYI BAGI PENYINGKIRAN PLUMBUM DAN FERUM DARIPADA LARUTLESAP TAPAK PELUPUSAN MENGGUNAKAN BIOJISIM KELAPA SAWIT DIPRARAWAT

ABSTRAK

Empat biojisim berasaskan kelapa sawit yang merupakan pelepah kelapa sawit (OPF), kulit batang kelapa sawit (OPB), daun kelapa sawit (OPL) dan tandan buah kosong (EFB) telah diuji secara mod kelompok bagi penyingkiran Pb (II) dan Fe (III) dari tiga larutan akua (individu dan dwilogam). Eksperimen tersebut telah dijalankan pada julat pemboleh ubah: pH (2-12), saiz perjerapan-bio (200 µm-1400 µm), dos (0.25 g/L-1.75 g/L) dan waktu sentuh (5 min-80 min). Kulit batang kelapa sawit (OPB) menunjukkan kecekapan penjerapan terting pada nilai 80 % dan 78 % bagi plumbum dan ferum dalam larutan dwilogam masing-masing, dan 79 % bagi larutan plumbum dan 77 % bagi larutan ferum, kerana OPB mempunyai luas permukaan dan isipadu liang yang lebih tinggi di bandingkan dengan perjerapan-bio lain. Isoterma Langmuir menunjukkan keputusan terbaik bagi kedua-dua logam dalam larutan dwilogam di antara ketiga-tiga isoterma perjerapan-bio yang dikaji. Kinetik perjerapan-bio dengan padanan ditemukan terbaik pada model pseudo-tertib kedua. Eksperimen berikutnya dijalankan menggunakan OPF, kerana ia merupakan sisa pertanian yang lebih tersedia berbanding OPB. Ia telah diprarawat menggunakan NaCl dan Na_2SO_4 dengan tiga nisbah berbeza, untuk membentuk empat jenis perjerapan-bio-diprarawat dengan empat kod berbeza. OPF yang diprarawat di dalam 1.0Molar NaCl dikodkan sebagai CM1 dan OPF yang diprarawat di dalam 1.0Molar Na_2SO_4 dikodkan sebagai SM1. OPF yang diprarawat di dalam 0.5Molar degan kadar 1:1 dikodkan SCM0.5 dan kombinasi di antara SM1 dan CM1 dengan kadar 1:1 dikodkan sebagai SMCM1. Didapati bahawa perjerapan-bio SM1 adalah perjerapan-bio terbaik bagi penyingkiran ion-ion plumbum. Proses perjerapan-bio berlaku menerusi mekanisma pertukaran ion di antara ion-ion plumbum dan natrium yang hadir dalam OPF yang terubahsuai. Perjerapan-bio CM1 lebih memilih terhadap Fe (III) dan Pb (II) dan ianya adalah disebabkan oleh kehadiran ion-ion klorida pada permukaannya. Di bawah keadaan optimum (dos perjerapan-bio 1.25 g/L dan masa sentuhan 20 min), SCM0.5 menunjukkan kecekapan penjerapan yang paling tinggi pada 98% dan 92% bagi Pb (II) dan Fe (III), masing-masingnya. Data keseimbangan penjerapan telah dipadankan pada tiga model isoterma penjerapan bagi SCM0.5 dan SMCM1. Isoterma Langmuir menunjukkan hasil terbaik untuk ion-ion ferum manakala isoterma Freundlich menunjukkan hasil terbaik untuk ion-ion plumbum. Kinetik bagi proses perjerapan-bio telah dianalisis berdasarkan model pseudo-tertib pertama dan pseudo-tertib kedua. Model pseudo-tertib kedua menunjukkan padanan yang lebih baik bagi kedua-dua logam. Proses perjerapan-bio terbantu-Ultrasonik menggunakan perjerapan-bio terbaik (SCM0.5) telah disiasat pada air larut lesap tapak pelupusan sampah. Proses perjerapan-bio terbantu-Ultrasonik menunjukkan peningkatan yang ketara untuk penyingkiran Pb (II) dan Fe (III) daripada air larut lesap tapak pelupusan sampah berbanding kaedah pencampuran konvensional. Di bawah keadaan optimum (pH 5-6, dos perjerapan-bio 1.75 g/L dan masa sentuhan 20 min), perjerapan-bio plumbum dan ferum menggunakan ultrabunyi telah meningkat daripada 78 % kepada 95 % dan 62 % kepada 83 % masing-masingnya, jika dibandingkan dengan kaedah konvensional. Proses perjerapan-bio terbantu-ultrasonik mencapai penyingkiran logam berat yang paling tinggi dalam tempoh 20 minit berbanding dengan 60 minit bagi kaedah konvensional. Kinetik bagi proses tersebut juga telah dianalisis menggunakan model pseudo-tertib pertama dan pseudo-tertib kedua dan model kedua itu telah menunjukkan padanan yang lebih baik bagi kedua-dua logam. Dengan menggunakan kaedah gerak balas permukaan untuk proses perjerapan-bio berbantu-ultrabunyi, keadaan optimum telah didapati berlaku pada pH 6.07, dos perjerapan-bio 1.6, masa gerak balas 16.30 min dan amplitude ultrasonik 52.4 % yang memberikan penyingkiran Pb dan Fe terbaik pada tahap 94.1 % dan 82.6 %, masing-masingnya.

ULTRASOUND-ASSISTED BIOSORPTION PROCESS FOR THE REMOVAL OF LEAD AND IRON ON LANDFILL LEACHATE USING PRE-TREATED OIL PALM BIOMASS

ABSTRACT

Four oil palm-based biomasses which were oil palm frond (OPF), oil palm bark (OPB), oil palm leave (OPL) and empty fruit bunch (EFB) were examined in batch mode for removal of Pb (II) and Fe (III) from 3 different aqueous solutions (2 single metal solution and bimetal). The experiments were done in certain ranges of variables: pH (2-12), biosorbent size (200 µm-1400 µm), dosage (0.25 g/L-1.75 g/L) and contact time (5 min-80 min). Oil palm bark (OPB) showed the highest adsorption efficiency of 80 % and 78 % for lead and iron in bimetal solution, respectively, and 79 % for lead solution and 77 % for iron solution, because OPB had the higher surface area and pore volume in compare with other biosorbents. The Langmuir isotherm showed the best result for both metals in bimetal solution between the three biosorption isotherms investigated. The best fitted biosorption kinetic is pseudo-second-order model. The following experiments were done using OPF, because it is the more available agricultural waste compared to OPB. It was pretreated using NaCl and Na_2SO_4 with three different ratios, to form four different kinds of pretreated biosorbents with four different codes. The OPF pretreated in 1.0 molar NaCl was coded as CM1 and the OPF pretreated in 1.0 molar Na_2SO_4 was coded as SM1. The OPF pretreated in 0.5 molar with ratio 1:1 was coded SCM0.5 and combination of SM1 and CM1 with ratio 1:1 was coded SMCM1. SM1 biosorbent was found to be the best biosorbent for the removal of lead ions. The biosorption process occurred through ion exchange mechanism between lead ions and sodium ions that were present in the modified OPF. CM1 biosorbent was more selective to Fe (III) than Pb (II) and it was due to the present of chloride ions on its surface. Under optimum conditions (biosorbent dosage 1.25 g/L and contact time 20 min), SCM0.5 showed the highest adsorption efficiency of 98% and 92% for Pb (II) and Fe (III), respectively. The adsorption equilibrium data were fitted to three adsorption isotherm models for SCM0.5 and SMCM1. Langmuir isotherm showed the best result for ferric ions while Freundlich isotherm showed the best result for lead ions. The kinetics of the biosorption process was analyzed based on pseudo-first-order and pseudo-second-order models. The pseudo-second-order models showed a better fit for both metals. Ultrasonic-assisted biosorption process using the most suitable biosorbent (SCM0.5) was investigated on landfill leachate. Ultrasonic assisted biosorption process showed significant improvements for removal of Pb (II) and Fe (III) from landfill leachate comparing to conventional mixing method. Under optimum conditions (pH 5-6, biosorbent dosage 1.75 g/L and contact time 20 min), the biosorption of lead and iron using ultrasound increased from 78 % to 95 % and 62 % to 83 %, respectively comparing with conventional method. Ultrasonic-assisted biosorption process reached the highest heavy metal removal within 20 min comparing to 60 min for conventional method. The kinetics was also analyzed using pseudo-first-order and pseudo-second-order models and the latter model also showed a better fit for both metals. By employing response surface methodology in ultrasound assisted biosorption process, the optimum conditions were obtained at 6.07 for pH, 1.6 mg/L for biosorbent dosage, 16.30 min for the reaction time and 52.4 % of ultrasonic amplitude to give the best Pb and Fe removals of 94.1 % and 82.6 %, respectively.

CHAPTER 1

INTRODUCTION

1.1 General

Hazardous metal contamination of the environment is a significant worldwide concern. Several metals are harmful to living organisms and could have poisonous and carcinogenic effects on human beings (Vijayaraghavan et al., 2011). Heavy metals can accumulate in living tissues causing various diseases and disorders. All heavy metals are non-biodegradable and must be removed from the polluted streams for the environmental quality standards to be met (Witek-Krowiak et al., 2011). At least 20 metals are categorized as toxic and half of these are emitted into the environment in quantities that can pose risks to human health (Nomanbhay and Palanisamy, 2005).

Leachate as one of the wastewater, is one of the major sources of metals discharged to surrounding environment (Wu et al., 2011). Heavy metals in landfill leachate, especially iron and lead, are potential sources of pollution for surface water, ground water, reservoirs that could threaten the environment. Iron and lead concentrations in leachate are normally contributed by iron-based products and lead-based materials (Aziz et al., 2004; Foul et al., 2009).

The parameter limits of effluent for Standard A and B according to the Standards of Malaysian Inland Waters sourced from the Department of Environment Malaysia are given in Table 1.1. The Standard A is applied to the discharge upstream of water supply sources, while, the Standard B is applied to the discharge downstream of water supply sources. The discharged standard values for lead is 0.1 mg/L and 0.5 mg/L for Standard A and Standard B, respectively, while for iron, they are 1.0 mg/L and 5.0 mg/L for Standard A and Standard B, respectively.

Table 1.1 Malaysian Inland Wastewater Discharge Standards for Effluent Discharge (Department of Environment Malaysia, 1974, Department of Environment Malaysia, 2009)

Parameter (mg/L or as stated)	Maximum Permitted Values (DOE, 1974, Oct 2009)	
	Standard A	Standard B
Temperature (°C)	40	40
pH (units)	6.0-9.0	5.5-9.0
BOD at 20° C	20	50
COD	120	200
Suspended solids	50	100
Mercury	0.005	0.05
Cadmium	0.01	0.02
Chromium hexavelant	0.05	0.05
Arsenic	0.05	0.1
Cyanide	0.05	0.1
Lead	**0.1**	**0.5**
Chromium trivalent	0.2	1
Copper	0.2	1
Manganese	0.2	1
Nickel	0.2	1
Tin	1	1
Zinc	2	2
Boron	1	4
Iron	**1**	**5**
Phenol	0.001	1
Free chlorine	1	2
Sulphide	0.5	0.5
Oil and grease	not detectable	10

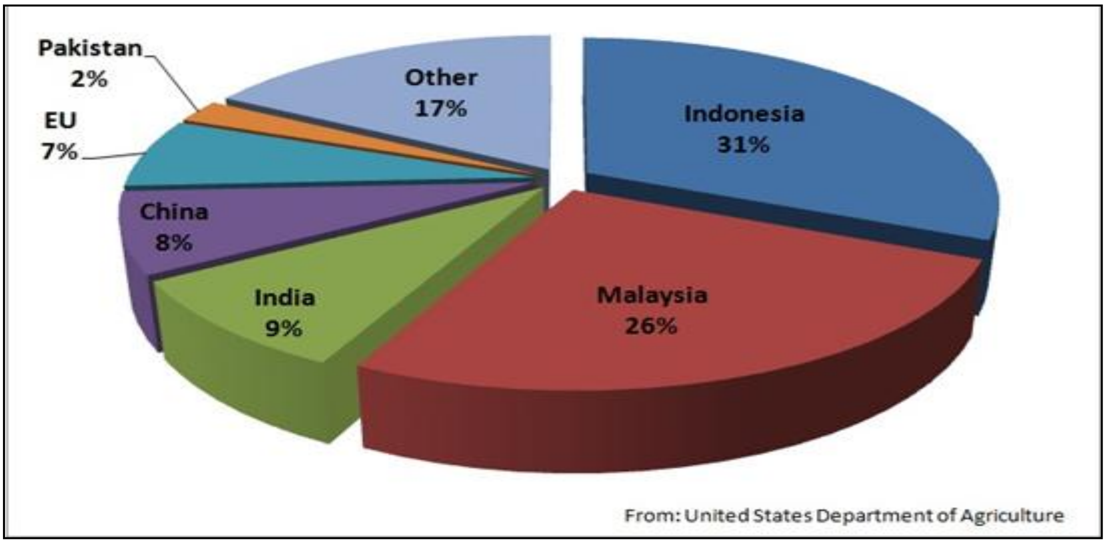
Several processes have been used for removing heavy metals from landfill leachate including adsorption, chemical precipitation, ion exchange, membrane filtration and liquid extraction/electro-dialysis. Among all the methods, adsorption is a more conventional one due to specific selectivity of the metals, low operating cost and no production of secondary toxic compounds (Venkata Ramana et al., 2012).

Some organic and inorganic adsorbents have been proposed for the adsorption method such as zeolites, clay minerals, activated carbon and, trivalent and tetravalent metal phosphates. Carbon-based materials have recently attracted a great deal of interest because of their inertness to the surrounding environment, mechanical stability and highly porous structure with specific surface chemical properties (Shin et al., 2011). Activated carbon as an adsorbent in wastewater treatment has some disadvantages. It remains an expensive material and needs complexing agents to develop its removal performance for inorganic matters. Thus, this condition makes it no longer attractive to be usually used in the industry because of price inefficiency (Babel and Kurniawan, 2003).

Environmental and public health engineers have been searching for low-cost and efficient materials for the treatment of metal-containing wastewaters. It is known for years that biomaterials can bind different heavy metal ions. The major advantages of this system are the reusability of biomaterial, low operating cost, high selectivity, short process time and no secondary production which might be equally toxic (Torab-Mostaedi et al., 2013).

Biosorption is a bioprocess in which toxic heavy metals are removed from aqueous solutions by adsorption onto living or non-living materials of biological origin (Liu et al., 2011). The design and efficient operation of biosorption process has been found to be effective, cheap and environmental friendly (Kumar and Ahmad, 2011; Tan et al., 2011). Replacing commercial adsorbents with cheaper, easily available and biodegradable ones increases the cost effectiveness of this technique and boosts its applicability and extension for real cases (Jellali et al., 2011). Biosorbents are taken from naturally occurring and agricultural waste materials that are cheaper, renewable, biodegradable and available in large quantities (Bhatnagar et al., 2010). One of the largest sources of biomass from agricultural residues in Malaysia is oil palm biomass.

One of the tropical palm trees is oil palm that can be cultivated easily in Malaysia. Malaysian oil palm tree originates from West Africa where it was growing wild and later developed into an agricultural crop (Sumathi et al., 2008). In Malaysia, the expansion of oil palm plantation has occurred each year over the last three decades at a real growth rate of 0.36% per year. In 2010, it is estimated that approximately 48,537 km^2 (4,853,766 ha), or 14.72% of the total landmass was used for oil palm plantations, with approximately 135–145 trees planted per hectare (Abnisa et al., 2013). Figure 1.1 shows that Malaysia is one of the major palm oil producer countries in the world (United States Department of Agriculture, 2012).



From: United States Department of Agriculture

Figure 1.1 World production of palm oil by major producing countries

The enormous expansion of oil palm plantation has generated massive amounts of agricultural wastes in Malaysia. It has been reported that Malaysia currently produces about 30 million tonnes annually of oil palm biomass, including fronds, trunks, empty fruit brunches and fruit wastes (Chan, 1999). The use of oil palm residues as alternative and low cost biomasses can be a promising method for the new generation of biosorbents that can be used for heavy metals removal.

The extraction by shaking was less efficient than extraction by ultrasonic assisted. In fact, ultrasonic-assisted can be carried out within a shorter period of time unlike the shaking method which is carried out for a long period of time yet it has less efficiency in metal ion removal, because most of biosorbents have limited adsorption capacities and the low mass transfer rate and the difficulty for adsorbent to be regenerated limit its development and application. Ultrasound can intensify the mass transfer process and break the affinity between adsorbate and adsorbent by ultrasonic cavitation, which make the use of ultrasound for adsorption/desorption more popular (Lu et al., 2011).

1.2 Problem Statement

Treatment of heavy metals from landfill leachate by biosorption process has been studied by some researchers using different types of biomasses as an efficient and economical method for heavy metals removal. Choi and Yun (2006) was used sludge for removing the cadmium from landfill leachate. The hazelnut shells was used by Turan et al. (2011) as a biosorbent for removing the zinc ion from landfill leachate. However the usage of oil palm biomasses as biosorbent for removing the lead and iron ions are yet to be investigated.

The application of biomasses as biosorbent has been receiving increasing attention due to their less polluting nature and renewable as compared to the conventional adsorbents. Buasri et al. (2012) was used corn cob as a biosorbent for removing the zinc ions from aqueous solution. Pigeon peas hulls was applied for biosorption of iron and nickel ions from aqueous solution by Venkata Ramana et al. (2012). Although different types of biomasses was used for removing the heavy metals from aqueous solution, the usage of biomasses as biosorbents from landfill leachate was lacking and need to be considered for further studies.

Oil palm tree produces many types of biomass wastes such as oil palm frond, oil palm leave and empty fruit bunch. Some of these biomasses have been individually tested by researchers for the removal of heavy metals from wastewater as reported in various literatures (Al-Rub, 2006; Chong et al., 2013; Hossain et al., 2012). But none of the researchers compared the effectiveness of various oil palm biomasses for the removal of heavy metals to identify the proper biosorbent among them.

Chemical modification/pre-treatment of agricultural wastes as biosrbent has been studied by several researchers and the low cost agent has been used as a modification agent in order to attach free groups (El-Ashtoukhy et al., 2008; Lasheen et al., 2012; Mohan and Sreelakshmi, 2008). Mohan and Sreelakshmi (2008) was pretreated rice husk for the removal of manganese, lead, zinc and copper, and this pretreatment was increased the adsorption capacity and adsorption rate constant in compare with raw rice husk. Igwe et al. (2008) was pretreated coconut fiber by thiolation to improving the adsorption capacity of biosorbent for removal of mercury, lead and arsenic from aqueous solution. However, pre-treatment of the oil palm biomasses using different types of reagents in order to adsorbe the desired heavy metals and enhance the biosorption efficiency and selectivity is need to be investigated.

Biosorption of heavy metals using oil palm biomass has some drawbacks. They need long reaction time and are almost immiscible in the waste water (Bhattacharyya and Sharma, 2004; Obuseng et al., 2012a). Bhattacharyya and Sharma (2004) was used *Azadirachta indica* powder for removing lead but the optimum time for the biosorption was 300 min. Therefore, vigorous mixing is required to increase the area of contact between the two phases (biosorbent, waste water). Thus, some solutions need to be found so that the biosorption process will become more efficient and economical. Entezari and Soltani (2008) were used saffron corm for removing the lead and copper from aqueous solution by sono-sorption process and the optimum time for removal of the heavy metals was 20 min. But the usage of ultrasound-assisted biosorption process for removal of heavy metals from landfill leachate was lacking and need to be studied further.

1.3 Scope of Study

In this study, four different parts of oil palm tree i.e oil palm frond (OPF), oil palm bark (OPB), empty fruit bunch (EFB) and oil palm leave (OPL) were used in order to find out the most suitable biosorbent for removal of heavy metals (lead and iron) from landfill leachate. Three types of aqueous solutions (single iron metal solution, single lead metal solution and bimetal solution) were used for comparison and eventually modified for improvement. Four different pretreatments were examined in order to identify the most suitable one to enhance the biosorption capacity of the biomass. These pretreatment methods included treatment with NaCl and Na_2SO_4 at different ratios.

As iron and lead ions are the most predominant heavy metals in the Pulau Burung, Nibong Tebal landfill leachate, hence, they were chosen in this research. Ultrasound-assisted process was also conducted to enhance the biosorption process efficiency for this landfill leachate.

Response surface methodology was employed to optimize the ultrasound-assisted biosorption process. The Langmuir, Freundlich and Temkin isotherms were investigated for their applicability in representing the experimental data. The kinetics of the biosorption process was analyzed using pseudo-first-order and pseudo-second order models.

The characterization of the biomass was carried out using analytical instruments: Fourier transform infrared spectrophotometer (FTIR), energy dispersive X-ray spectroscope (EDX), surface area analyses and scanning electron microscope (SEM). The landfill leachate was characterized to investigate the color, pH and concentration of COD, BOD5, suspended solid and heavy metals.

The potential of the most suitable pretreated biomass for removal of lead and iron from landfill leachate by ultrasound-assisted biosorption system was investigated in this study.

1.4 Objectives

This research project was carried out and arranged to address the following objectives:

- To identify the most suitable oil palm biomass for heavy metal biosorption.
- To determine the most suitable methods of biosorbent modification for improved biosorption capacity and efficiency.
- To evaluate the physical and chemical characteristics of the biosorbents before and after biosorption.
- To optimize the conditions affecting biosorption process i.e. pH, dosage of biosorbent, reaction time and ultrasonic power on the ultrasonic-assisted biosorption process of landfill leachate.
- To determine the reaction kinetics and biosorption isotherm models in the conventional and ultrasound-assisted biosorption process.

1.5 Thesis Organization

This thesis contains of five main chapters. The first chapter (Introduction) introduces the research project, the problem statement, and the scope of the study in brief. In the second chapter (Literature Review), an overview of the reported results related to this study and the main basic knowledge about this project: ultrasonic biosorption, biosorption isotherms, kinetics and others important aspects of the process are discussed in detail. Chapter Three (Material and Methods) includes descriptions on the materials, experimental procedures and instrumental analyses used in this project. The response surface methodology (RSM) designs used including the ranges and the codes are introduced and discussed in this section. This chapter is presented in great detail and arranged in such a way that other researchers can easily repeat it. In Chapter Four, results and discussion on the results obtained in this study are provided. This chapter includes different parts: biosorbent selection, pretreatment, characterization of landfill leachate, using ultrasonic-assisted process, optimization, isotherm experiments and kinetics studies. In Chapter Five (Conclusions), overall conclusions based on the results and findings obtained in the present study are briefly given. Recommendations for future research based on the understanding and knowledge generated in the present study are given in the final chapter (Recommendations).

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals in Landfill Leachate

High concentration of heavy metals such as iron, zinc, lead, copper, cadmium and chromium that are available in untreated leachate could cause serious water pollution and threaten the environment (Foul et al., 2009). There are three mechanism that could increase the concentration of heavy metals in an aerobic landfill.

1. The oxidation of metals sulfides to the more soluble metal sulfates
2. The complexation capacity of oxidized humic acids relative to reduced humic acids
3. The oxidation of sulfides which results in the production of sulfuric acid that reduces the pH and increases the solubility of metal (Aziz et al., 2004).

2.2 Heavy Metals and Necessity of Treatment

Heavy metals are described as those metals with an elemental density above 7 g cm^{-3} (Hodson, 2004). Three types of heavy metals are available, (1) counting toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), (2) precious metals (such as Pd, Pt, Ag, Au, Ru, etc.) and (3) radionuclides (such as U, Th, Ra, Am, etc.)(Wang and Chen, 2006). Effect of heavy metals on ecosystem and human beings due to the type and amount of metals are completely different. It means that a toxic metal even in low concentration has more impact on environment compared to radionuclide. Also, most of the time both surface and ground waters contain heavy metals at concentrations 100 or 1000 times higher than the parameter limits of effluent for the standard according to Maximum Contaminant Level (MCL) value (Srivastava and Majumder, 2008). Because of this, it is essential to develop effective and reliable treatments for the removal of heavy metal ions from wastewaters.

2.3 Treatment Methods for Heavy Metals Removal

Although for young or freshly generated leachate, biological treatment processes are more effective, landfill stabilizes with the passage of time, the biodegradable organic content of the leachate tends to decrease and consequently, the effectiveness of the biological process decreases and physicochemical processes may become one of the appropriate options (Ghafari et al., 2009; Halim et al., 2010).

A number of leachate treatment techniques have been applied with varying degrees of success, including: physicochemical (chemical precipitation, activated carbon adsorption, membrane filtration, ion exchange), biological (aerobic (attached growth or non-attached growth) or anaerobic conditions) (Bohdziewicz and Kwarciak, 2008), spray irrigation to land, reed bed treatment, ammonia stripping, reverse osmosis (Salem et al., 2008) and electrochemical oxidation (Vasudevan and Oturan, 2013). The available methods for the treatment of heavy metals ions are electrochemical, biological treatment, membrane separation, coagulation, filtration, chemical precipitation, solvent extraction, reverse osmosis, solvent extraction, and ion exchange methods (Soetaredjo et al., 2013; Torab-Mostaedi et al., 2013). Each technology has some advantages and disadvantages that are summarized in Table 2.1.

Table 2.1 Conventional metal removal technologies (Al-Rub, 2006; Amarasinghe and Williams, 2007; Rao and Khan, 2007; Volesky, 2001)

Method	Disadvantages	Advantages
Chemical precipitation and filtration	For higher concentrations Difficult separation Low efficiency Excessive sludge	Simple Process Cheap
Chemical oxidation or reduction	Chemicals required (not universal) Climate sensitive	Mineralization
Electrochemical treatment	For high concentrations expensive	Metal recovery
Reverse osmosis	High pressure Membrane scaling Expensive	Pure effluent (for recycle)
Ion exchange	Sensitive to particles Expensive resins	Effective, Pure effluent metal recovery possible
Evaporation	Energy intensive Expensive Excessive sludge	Pure effluent (for recycle)
Adsorption	No disadvantage for treating the heavy metals	Conventional adsorbent

2.4 Physicochemical Treatment

Biological processes are efficient in the treatment of some wastewaters which are rich in volatile fatty acids, but it is not effective for the treatment of more stabilized wastewater due to the presence of recalcitrant organic substances and non-biodegradable compounds (Liu et al., 2012; Saad et al., 2012). For achieving a satisfactory removal of refractory pollutants from the wastewater, several types of physical–chemical treatments have been employed worldwide or some post treatment of biologically pre-treatments, physicochemical process have been used widely to remove the organic solvents and reduce the chemical oxygen demand (Li et al., 2010; Ozturk et al., 2003).

The selection of physicochemical methods depends on many factors, such as: composition of the process wastewater and the pollutant(s); environmental laws; economic parameters and local conditions (Tóth et al., 2011). The main physicochemical methods are absorption (Estay et al., 2013), adsorption (Liu et al., 2013), ion exchange, reverse osmosis (Kukić et al., 2013), extraction (Montesdeoca-Esponda et al., 2013), evaporation, advanced oxidation process (Orescanin et al., 2013), coagulation/flocculation (Birjandi et al., 2013) and membrane processes (Khalaf et al., 2013). But for low concentration of heavy metal ions, adsorption is a much preferable technique and activated carbon has been widely applied for treating industrial wastewater (Nieto et al., 2010).

2.5 Adsorption

Adsorption is one of the most important physicochemical processes in heavy metal removal. Sorption is the ability of certain solids to preferentially concentrate specific substances from solution on to their surface. By using this method, the components of both gas and liquid phase can be separated from each other. There are two different types of adsorption known as physical and chemical. Physical or van der Waals adsorption is the result of intermolecular forces attraction. Chemisorption is the result of chemical interaction between the solid and the adsorbed substance. The adhesive force in chemisorption is generally much greater than that in physical adsorption. Adsorption solids are usually used in granular form, varying in size from

50 μm to 12 mm. The solids must possess certain engineering properties depending upon the application, in which they are used.

On the other hand, three types of interactive sorption behavior could be displayed by a mixture of heavy metals, vis. synergism, antagonism or non-interaction. With synergism, the effect of the mixture is greater than the sum of each of the individual effects of the constituents in the mixture. With antagonism, the effect of the mixture is less than that of the sum of the individual effects of the constituents in the mixture. With non-interaction, the effect of the mixture is equivalent to the sum of each of the individual effects of the constituents in the mixture (Qi and Aldrich, 2008).

An adsorption process is normally controlled by three diffusion steps: (i) transport of the solute from the bulk solution to the film surrounding the adsorbent, (ii) transfer from the film to the adsorbent surface leading to surface adsorption, and (iii) diffusion from the surface to the internal sites followed by binding of the adsorbate on the active sites (Bhattacharyya and Sharma, 2004).

2.6 Biosorption

Biosorption is an adsorption method for heavy metal removal and removal of other pollutants onto low cost adsorbents (Yeddou and Bensmaili, 2007). Among various treatment methods, biosorption method has been extensively used due to remarkable properties of living and non-living micro-organisms in transformation and detoxification of inorganic pollutants (Çolak et al., 2013).

Biosorption can be defined as the ability of biological materials to accumulate compounds as metals and/or heavy metals from wastewater through metabolically mediated or psycho-chemical pathways of uptake (López-Mesas et al., 2011). Biosorption is an inexpensive and socially acceptable technology which involves the use of renewable resources like microbes and plants (biosorbents) to tackle heavy metal and industrial dye problems (Oves et al., 2013).

The main advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metal of interests, short operation time, no production of secondary compounds which might be toxic and minimization of generation of chemical and/or biological sludge, high efficiency, no additional nutrient requirement, regeneration of biosorbents, the possibility of metal and/or heavy metal recovery and valorization of a waste when it is the origin of the biomass (Doğan et al., 2009; López-Mesas et al., 2011; Torab-Mostaedi et al., 2013).

The mechanisms of biosorption of metals have demonstrated that the process generally consists of two distinct stages. The first stage has been described as a passive adsorption of ions and it is likely that a number of different functional groups are involved in this process. This type of metal uptake is rapid and thought to be unrelated to the energy economy of the cell. The second stage of uptake is slower and involves active transport mechanisms requiring cellular energy (Orhan et al., 2006). Biosorption is not restricted to one sorption mechanism only, but comprises several mechanisms such as ion exchange, chelation, precipitation, sorption by physical forces, and ion entrapment in inter- and intrafibrillar capillaries and spaces of structural lignin and polysaccharide networks (Pejic et al., 2009).

2.7 Types of Biosorbent

Many types of biosorbent including fungi, bactria, algae, and industrial and agricultural wastes have been used for the removal of heavy metals from various aqueous solutions.

2.7.1 Bactria and Fungi as Biosorbents

Biosorption method has been extensively used because of remarkable properties of living and non-living micro-organisms in transformation and detoxification of inorganic pollutants and heavy metals. The use of non-living micro-organisms may offer some advantages over living organism, such as lower sensitivity concentration of toxic wastes, lack of requirements for continuous supply of nutrients, easy desorption and recovery, and storage for extended periods at room temperature without putrefaction occurring (Çolak et al., 2013). Free living biomass can promote higher contact with the contaminants during the removal process. However, it is not practical as a clean-up method bacteria and for obtaining a more reliable and reproducible system, bactria can be easily immobilized on a solid matrix (Piccirillo et al., 2013), but living biomass cells often require the addition of fermentation media which increases the biological oxygen demand (BOD) or chemical oxygen demand (COD) in the effluent (Alomá et al., 2012).

Biosorption of heavy metals from wastewater by biological materials has been shown to be subject to the physicochemical properties of microbial biomass materials that adsorb heavy metals efficiently from even very dilute aqueous solution (Abd-Alla et al., 2012). Table 2.2 summarizes the biosorption of several heavy metals using microbial cells.

2.7.2 Algae as Biosorbents

Many aquatic organisms such as algae can adsorb heavy metals from their surroundings. The marine algae are available in large quantities in many regions of the world, and are a kind of promising biologic resources. Marine algae are used as adsorbents due to the presence of polysaccharides, proteins or lipids from the cell walls surface (Bulgariu and Bulgariu, 2012). Microalgae biosorbent seems to be more promising than macroalgae because of the cultivation of microalgae is normally easier and has higher production yield and they have higher performance and efficiency (due to their micron size) and in turn higher specific biosorption area (Abdel -Aty et al., 2013). Metal ion binding to nonliving cells occurs rapidly by cell surface adsorption. The use of dead biomass is more favorable for water as dead organisms are not affected by toxic contaminants (Rajamohan and Sivaprakash, 2008).

Several advantages in applying algae as biosorbent include their wide availability, low cost, high metal sorption capacity, reasonably regular quality, no nutrient requirements and they can be easily collected alonge the shore tide (Areco et al., 2012). Moreover, they are relatively simple to use with no requirement for pretreatment such as drying for transportation and storage (Apiratikul and Pavasant, 2008). A list of different algae that were used as biosorbent is collected in Table 2.3.

2.7.3 Agricultural Materials as Biosorbents

Various side-agricultural products have been reported to show the ability for sorption of heavy metals. The components of agricultural by-products that compose hydroxyl, carbonyl, sulfates, phosphates, amino-groups, carboxylic and ether functional groups bind heavy metals by the donation of an electron pair and form complexes or exchange hydrogen ions for heavy metal ions in solution (Ofomaja et al., 2010). Interest has also been risen in removing heavy metals from solution by binding with agricultural materials such as visible parts of plants, roots, seasonal part, waste wool, nut wastes, tree barks, modified cotton and sawdust (Chubar et al., 2004). This has led to the use of parts of the agricultural products that have no food value for heavy metal removal by sorption process.

Agricultural by-products are high volume, low value and underutilized lignocellulosic biomaterials; contain high fixed carbon content, present a porous structure, high level of cellulose, hemicelluloses and lignin and because of this they show a strong tendency to attract and remove heavy metal ions from aqueous solution (Alomá et al., 2012; Reddy et al., 2012; Witek-Krowiak, 2012). Heavy metal binding onto an agro biomass involves complex processes that comprise a number of mechanisms like adsorption, complexation, chelation and entrapment in capillaries and spaces with in polysaccharide network due to concentration causing diffusion through the cell walls and membrane (Farooq et al., 2010). Some research works on the heavy metal adsorption, properties of naturally occurring and low cost adsorbents represented mainly by agricultural by products and natural fibers are compiled in Table 2.4. The shape of surface area, amount of porous and the functional groups are different in different types of biosorbents and they make a special physical and chemical characterization, because of this reason the process for biosorption are different. Table 2.5 shows some chemical and physical characterization for some agricultural by-products.

Table 2.2 Biosorption of heavy metals using microbial cells

Adsorbent	Heave Metal	pH	Agitation Time	Dose of Absorbent (g/L)	Temperature (°C)	Initial Concentration of Metal (C_0)	Type of Reactor	References
Paenibacillus polymyxa	Cu(II) Ni(II)	5	90 min	1	25	10-90 mg/L	BSR	(Çolak et al., 2013)
Arthrospira platensis	Zn(II) Ni(II) Pb(II)	5-5.5	5-120 min	2	20	0.5, 1, 2 mM/L	BSR	(Rodrigues et al., 2012)
Rhizobium leguminosarum	Cd(II) Co(II)	2-7	0-60 min	2	25	1000 mg/L	BSR	(Abd-Alla et al., 2012)
Pseudomonas putida	Cu(II)	6	5-90 min	250	30	10-40 mg/L	BSR	(Ni et al., 2012)
Magnetospirillum gryphiswaldense	Ag(I) Cu(II)	1-5.5	0-120 min	2-12	10-30	0-600 mg/L	BSR	(Wang et al., 2011)
Bacillus cereus *Bacillus pumilus*	Pb(II)	1-6	5-100 min	1	25	1000 mg/L	BSR PBR	(Çolak et al., 2011)
Pleurotus ostreatus	Cu(II) Ni(II) Zn(II) Cr(VI)	2-6	20-720 min	0.3-8	20-45	20-100 mg/L	BSR	(Javaid et al., 2011)
Oscillatoria Sp. *Phormidium Sp.*	Pb(II) Cu(II) Cd(II)	1-6	0-240 min	1-10	25	10 mmol/L	BSR	(Kumar and Gaur, 2011)
Pseudomonas aeruginosa *Bacillus cereus*	Zn(II)	1-7	0-60 min	1	30	0-200 mg/L	BSR	(Joo et al., 2010)

BSR: Batch Stirred Reactor
PBR: Packed Bed Reactor

Table 2.3 Biosorption of heavy metals using algae

Adsorbent	Heave Metal	pH	Agitation Time	Dose of Absorbent (g/L)	Temperature (°C)	Initial Concentration of Metal (C_0)	Type of Reactor	References
Chlorella vulgaris *Spirulina*	Zn(II) Ni(II) Pb(II)	5-5.5	5-120 min	2	20	0.5, 1, 2 mM/L	BSR	(Rodrigues et al., 2012)
Ulva lactuca	Pb(II) Cd(II) Co(II)	2-6	5-180 min	8	10, 20, 40	0.2-3.4 mmol/L	BSR	(Bulgariu and Bulgariu, 2012)
Ulva lactuca	Cu(II) Zn(II) Cd(II) Pb(II)	2-5.5	24 h	1	25	1000 mg/L	BSR PBR	(Areco et al., 2012)
Anabaena sphaerica	Cd(II) Pb(II)	2-6	5-120 min	1, 10	25	50 mg/L	BSR	(Abdel -Aty et al., 2013)
Nannochloris oculata	Cr(III) Cr(VI)	1-6	5-70 h	1	-	0-500 mg/L	BSR	(Kim et al., 2011)
Corallina mediterranea *Jania rubens* *Ptredocladia capillacea* *Galaxaura oblongata*	Pb(II) Co(II) Cr(II) Cd(II)	2-8	5-120 min	1-40	25	25-300 mg/L	BSR	(Ibrahim, 2011)
Laminaria japonica	Cd(II) Cu(II) Ni(II) Zn(II)	0.5-7	5-1500 min	1	25	0.5-7.5 mmol/L	BSR	(Liu et al., 2009)

BSR: Batch Stirred Reactor
PBR: Packed Bed Reactor

Table 2.4 Biosorption of heavy metals using agricultural waste

Adsorbent	Heave Metal	pH	Agitation Time	Dose of Absorbent (g/L)	Temperature (°C)	Initial Concentration of Metal (C_0)	Type of Reactor	References
Rice straw	Cu(II) Pb(II)	1-6	3-4 h	10-200	30-60	100 mg/L	BSR	(Soetaredjo et al., 2013)
Sugarcane bagasse	Ni(II)	1-6	3-120 min	10	25	10-200 mg/L	BSR	(Alomá et al., 2012)
Moringa oleifera leaves	Cu(II) Cd(II) Ni(II)	2-9	10-100 min	0.010–0.140	20-40	10-1000 mg/L	BSR	(Reddy et al., 2012)
Corn cob	Zn(II)	-	150 min	10-50	30-70	250-1250ppm	BSR	(Buasri et al., 2012)
Moringa oleifera seeds	Zn(II) Cu(II) Ni(II)	2-8	0.5, 1, 2, 4, 6,8,12, 24 h	5	22	1-14 mg/L	BSR	(Obuseng et al., 2012a)
sunflower hulls	Cu(II)	5	3 h	2	20-55	25-200 mg/L	BSR	(Witek-Krowiak, 2012)
Rice Straw	Cd(II)	1-6	1-60 min	2.5-25	25	25-350 mg/mL	BSR	(Ding et al., 2012)
Lemon grass	Cu(II) Zn(II) Cd(II)	3-7	0-240 min	0-5	25	10 mg/L	BSR	(Zuo et al., 2012)
Crok	Pb(II) Cd(II)	2-6	5 min-48 h	2	25	0-1 mM	BSR	(López-Mesas et al., 2011)
Peanut shell	Cr(III) Cu(II)	2-5	0-90 min	0.01-20	20-60	10-1000 mg/L	BSR	(Witek-Krowiak et al., 2011)
Pigeon peas hulls	Pb(II) Ni(II)	2-8	10-120 min	4-18	20-40	25-100 mg/L	BSR	(Venkata Ramana et al., 2012)

Table 2.5 Chemical and physical characterization of agricultural waste as biosorbents

Biosorbent	Pre-treatment	Chemical Characterization	Physical Characterization	Heavy Metal Removal	Reference
grapefruit Peel	0.1 M HCl	Pectin 18.76 % Cellulose 10.52 % Hemicellulose 6.02 % Lignin 4.63 % Protein 3.4 %	Some Cavities in its structure	Cd(II) Ni(II)	(Torab-Mostaedi et al., 2013)
Pigeon Peas Hulls	0.1 N NaOH 0.1 N H_2SO_4	Carbon 45.68 % Hydrogen 7.53 % Nitrogen 0.82 % Sulfur 0.96 % Oxygen 45.01 %	Does not have regular, fixed shape and size	Pb(II) Ni(II)	(Venkata Ramana et al., 2012)
Sunflower Hulls	0.1 M KNO_3	-	Irregular and large number of porous	Cu(II)	(Witek-Krowiak, 2012)
Gum Kondagogu	-	Na^+ K^+ Ca^{2+} Mg^{2+} Cl^- C O	Some irregular particle size with porous structure on the surface	Cd(II) Cu(II) Fe(II) Se(II) Pb(II) Ni(II) Zn(II)	(Vinod et al., 2010)
Moringa Oleifera Bark	Boiling in double distilled water	Carbon 44.8 % Hydrogen 5.9 % Nitrogen 0.8 % Sulfur 0.9 % Oxygen 47.6 %	-	Pb(II)	(Reddy et al., 2010)

2.8 Parameters Influencing Biosorption

Biosorption process is affected by many factors in removing heavy metals such as, pH, contact time, initial concentration of heavy metals, type of biosorbent (species, age), dose and size of biosorbents, presence of other heavy metals, etc.

2.8.1 Effect of pH

The adsorption behavior of heavy metal ions and other contaminants such as dyes, natural organic matters, etc. in aqueous phase strongly depends on pH and may be different for each solute-sorbent interaction (Soetaredjo et al., 2013). Solution pH affects the cell wall metal binding sites and the metal ion chemistry in water (Ibrahim, 2011). The pH controls the extent of surface protonation of the sorbent and the degree of ionization. In very acidic situation, the active sites of the sorbent such as carboxyl and amine groups are protonated and therefore, no complexation is finally observed. When the pH increases in acidic position, the carboxyl groups become more negatively charged and the amino group would carry a partial positive charge (Pelit et al., 2011). In some heavy metals, high concentrations of H^+ ions in the solution also compete with metal species for the adsorption sites on the solid surface. In other heavy metals, at higher pH values, the lower number of H^+ and greater number of ligands with negatives charges result in greater metal ions biosorption (Torab-Mostaedi et al., 2013).

2.8.2 Effect of Size of Adsorbent

The particle size of sorbent is one of the important factors affecting the biosorption process. The heavy metals biosorption decreases with increasing particle size of the biosorbent (Deniz et al., 2011). The size of adsorbent impacts the sorbents