Jatropha Curcas for Phytoremediation of Refinery Sludge

by

Khairul Tasniim Bin Ahmad

Dissertation submitted in partial fulfilment of

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr. Nurlidia Mansor)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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KHAIRUL TASNIIM BIN AHMAD

ABSTRACT

One of the most important environmental problems that arise globally is heavy metal pollution in soil which causes major toxic effect on humans, animals, microorganisms, and plants. Phytromediation is a green technology in which non-edible plants are used to remove by absorbing organic and inorganic contaminant from soil, sediment and water.

This study evaluated the heavy metal concentration in plant tissues of *Jatropha curcas* grown in a mixture of healthy soil and refinery sludge from Petronas Penapisan (Terengganu), Kertih, Malaysia. The plant *Jatropha Curcas* was investigated for its ability to remediate Lead, Zinc and Nickel polluted soil with refinery sludge at ambient conditions. Various levels of single and mixed pollutants were exposed to the plant for more than three month.

The plant seedlings of *Jatropha Curcas* were planted in pot with different refinery sludge to soil ratio at five treatment levels based on the weight percent. The results indicate that the best heavy metal uptake for both Zn and Pb is at *Jatropha Curcas* root. The *Jatropha curcas* found to have a high potential to accumulate high amounts of lead and zinc in its roots, leaves and stems. The plant in medium contaminated soils showed an excellent translocation along the plant parts. This already demonstrates that this plant species was able to tolerate and accumulate a high concentration of heavy metals. This non-edible plant, *Jatropha curcas* can be an ideal option to be grown for phytoremediation in multi-metal contaminated sites and to mitigate the soil pollution.

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ABBREVIATIONS AND NOMENCLATURES

Zn	Zinc
Pb	Lead
Ni	Nickel
AAS	Atomic Absorption Spectroscopy
HNO_3	Nitric Acid
$HCLO_4$	Perchloric Acid

CHAPTER 1

INTRODUCTION

1.1 Background of Study

In the world today, the industrial development, population and urbanization have increased toxic and hazardous wastes on land especially in developed countries. This issue will lead to environmental problems and threaten human health. This problem occurs when waste that could lead to pollution are not treated with proper treatment system. Heavy metal contamination in soil are caused by major industries such as oil and gas, mining, manufacturing, and construction and has occurred since the beginning of the industrial revolution. The concentration of toxic metals has increased exponentially and has caused harm to human and animal health. This is because their existence is prolonged on the ground and remain as a potential threat for many years polluting the ecosystem. Heavy metals are a unique class of toxicants since they cannot be broken down to non-toxic forms. There are ways to recover heavy metals present in contaminated soil. Among them are by using the physico-chemical processes such as ionexchange, precipitation, reverse osmosis, evaporation and chemical reduction. However, these measures are expensive and leaves toxic residues in the soil (M.M. Lasat, 2002). Phytoremediation seems to be an alternative to all these methods in treating the heavy metal contaminants as it is simple, efficient, cost effective and environmental friendly (McCutcheon and J.L. Schnoor, 2003).

1.2 Problem Statements

Wastewater sludge from refinery operations has become a problem for most companies. Wastewater sludge has resulted in companies having to pay approximately RM 3 million per financial year for its disposal service to Kualiti Alam. This problem has become a major concern in reducing the company's expenses from year to year.

The refinery sludge are characterized under the oily sludge. Oily sludge accumulates in large quantities as waste in petroleum refineries. Heavy metal contaminants from oil refining industry is part of the components in wastewater sludge and threat to the ground water. This refinery sludge content may harm the environment without proper treatment while maintaining the sludge treatment plant also has become an issues since there is always faulty with major equipment as per cases in Petronas Penapisan (Terengganu). Hence, phytoremediation can be greener alternative yet low cost method in treating the refinery sludge.

1.3 Objectives

The main objectives of this study are:

i. To quantify Zn, Pb, and Ni concentration in growth medium before planting and after harvest.

ii. To investigate the ability of *Jatropha Curcas* in extracting Zn, Pb, and Ni from the refinery sludge.

iii. To study the phytoextraction potential of *Jatropha Curcas* by using different ratio of refinery sludge and normal soil.

1.4 Scope of Study

This study involves Phytoremediation method using plants to remediate wastewater sludge containing heavy metal derived from oil refinery operations. Thus, the study is set to examine the extraction of the heavy metals from the contaminated refinery sludge into the plant (*Jatropha Curcas*). This study is limited to investigate the ability of *Jatropha Curcas* to extract the heavy metals and does not cover the hydrocarbon potential extraction.

CHAPTER 2

LITERATURE REVIEW

Globally, enormous quantity of waste are produced during the exploration, production, refining and derivation of petroleum products. The petroleum refinery plant that process crude oil will generate oily sludge as waste end products. The oily sludge is classified under low biodegradable (G Nkeng et al., 2012). It will cause environmental problems with significant implication to economic development and human health. However, petroleum-based contaminants have been shown to degrade under various anaerobic conditions, including nitrate reduction, sulphate reduction, ferric iron reduction, manganese reduction and methanogenic conditions (S Maletic et al., 2013).

There are various sources of these oily sludge including storage tank bottoms, oil-water separators, dissolved air floatation units, cleaning of processing equipment, and biological sludge from waste water treatment units (NM Rahim, 2012). One of the major problems faced by oil refinery is the safe disposal of oily sludge in the environment. This is because many of the constituent of oily sludge are carcinogenic and potent immuno-toxicants. The standard of practice among petroleum refinery operators in Malaysia for handling the solid waste is using the third party companies which comprises spending millions of Ringgit on the treatment of oily sludge. Generally, the composition of the refinery sludge may contain up to 10-30 wt% hydrocarbons, 5-20 wt% solids and the remainder is water (N.M.Mokhtar et al., 2011). The solids that contain heavy metals contaminants also are not subjected to degradation. Most common heavy metal contaminants are lead, cadmium, chromium, copper, mercury and zinc (A. M. Beddri & Z Ismail, 2007).

Therefore, the oily sludge that contain heavy metals can be removed using a method known as phytoremediation. Phytoremediation is the use of plants for the removal of contaminants and metals from the soil and water. Phytoremediation is evolving into a cost-effective means of managing wastes, especially excess petroleum hydrocarbons, polycyclic aromatic hydrocarbon, explosives, organic matter, and nutrients (A. M. Beddri & Z Ismail, 2007).

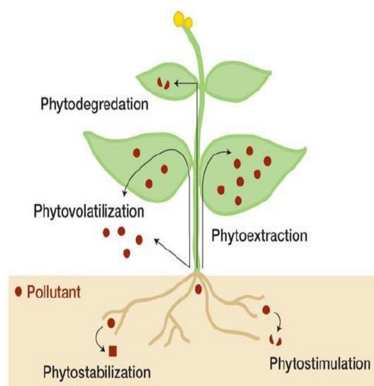

Figure 1 : Phytoremediation Process at Plant Parts

Remediation of heavy metals from refinery sludge could be carried out using physico-chemicals processes such as ion-exchange, precipitation, reverse osmosis, evaporation and chemical reduction. However, these measures are costly and leave toxics in soil. Among the several technologies for the treatment of the oily wastes, phytoremediation seems to be the an alternative method for which plant is applied to absorb, transform and detoxify heavy metals in the oily sludge from the refinement and petrochemical industry. This method is simple, efficient, cost effective and environmental friendly (J Luhach & S Chaudhry, 2012). This prevents the contamination of superficial and ground water, the contamination of the surrounding air and reduces the risk of fires, explosions, poisoning of the food chain and destruction of green areas.

Table 1: Cost Comparison between Phytoremediation and Other Technologies

Contaminant	Phytoremediation Costs	Estimated Cost using Other Technologies	Source
Metals	$80 per cubic yard	$250 per cubic yard	Black (1995)
Site contaminated with petroleum hydrocarbons (site size not disclosed)	$70,000	$850,000	Jipson (1996)
10 acres lead contaminated land	$500,000	$12 million	Plummer (1997)
Radionuclides in surface water	$2 to $6 per thousand gallons Treated	none listed	Richman (1997)
1 hectare to a 15 cm depth (various contaminants)	$2,500 to $15,000	none listed	Cunningham et al. (1996)

Source: J Chappel, 1997

Various studies show *Jatropha curcas* as a potential plant for remediation of heavy metals-contaminated soil. The bioaccumulation potential in the *Jatropha Curcas* is a strong factor in remediation of soil contaminated by heavy metals. In this study, *Jatropha Curcas* was selected due its characteristics as a non-edible plant which can easily grow in tropical areas. It is also known to have commercial viability for the production of biodiesel, The *Jatropha Curcas* growth is related to root system. The root propagation will affect the amount of uptake heavy metal since the root is the main part of plant that contacts the soil. On that concern, most of commercial agricultural of *Jatropha curcas* consider the plant spacing while cultivating the plan. Jatropha is resistant to drought and pest and produces seeds containing 27-40% of oil (M.M. Lasat, 2002). *Jatropha curcas* is found very efficient in accumulating heavy metals, causing almost no damage to the plant biomass.

2.1 Chemical analysis

The analysis of petroleum sludge (wt %) from previous study can be seen in the table below. The sludge was analyzed by characterizing it into structural components (proximate analysis) and chemical elements (ultimate analysis). The moisture and ash contents are important parameters affecting the heating value directly (Kataki R. & Konwer D, 2002). The lower heating value could also cause by the low fixed-carbon and high oxygen contents in the sample (McKendry P, 2002).

Table 2 : Ultimate Analysis of Petroleum Sludge (wt %)

	Moisture content	Volatile matter	Fixed carbon	Ash
Dried sludge	3.1	58.6	11.4	27.3
Wet sludge	75.3	9.9	8.1	6.7
Literature	33.0	ND	ND	12.3
Coal	4.8	8.3	43.6	8.3

Source: N.M. Mokhtar et al., 2011

Table 3 : Proximate Analysis of Petroleum Sludge (dry basis, wt %)

	C	H	N	S	O(by different)	HHV (MJ kg-1)
In this study	45.0	6.6	7.0	1.7	39.71	20.5
Literature [8]	59.9	10.0	0.1	2.1	27.8	22.4
Coal [15]	81.5	4.0	1.2	3.0	3.3	23-28

ND: Not determined *Source: N.M. Mokhtar et al., 2011*

From the results obtained from previous, It can be observed that these petroleum sludge contains high oxygen weight percent (wt %) and low carbon as well as sulfur compared to coal. High content of oxygen (39.7 wt %) will give the lower high heating value hence produce highly oxygenated liquid and solid products. On the other hand, nitrogen and ash seem to have higher in weight percentage which the contents are vary significantly among them. The large number of functional groups and low number of aromatic structure in wet sludge are expressed via the large amount of volatile matter in wet petroleum sludge (Al Futaisi et al., 2007).

Table 4 : Main Inorganic Elements in the Sludge (dry basis, mg/kg)

	Fe	Cu	Cr	Zn	Co	Ni	Ca	Mg	Na	K	Sn	Au	Al
This study	1,850	9	ND	141	ND	ND	ND	250	222	ND	23	31	590
Literature	43,826	590	427	4,206	26	631	17,775	6,038	2,958	83,487	NA	NA	NA

NA: Not available ND: Not detected *Karayildirim et al., 2006*

Table 4 shows the main inorganic elements of the sludge in mg/kg. Apparently, the content of heavy metals are lower compared than those reported in literature (Karayildirim et al., 2006). Based on the results obtained, the higher content of Fe, Al, Mg, Na and Zn metals in the refinery sludge can be the measurement for this waste to be classified either waste oil or oily sludge from wastewater treatment plant of oily refinery or crude oil terminal. In order to determine the ability of sample to absorb energy, it is very essential to analyze the main inorganic elements content in the petroleum sludge as some oxides compounds are able to increase maximum heating temperature.

Characterization of refinery sludge and legal aspects concerning disposal options. The content of heavy metals was monitored for 20 months in 18 sampling events. Heavy metals can interfere with the metabolism of microorganisms because they interact with the extracellular enzymes of fungi and bacteria and inhibit biodegradation, whereas Cd and Hg are in general the most toxic metals for all white-rot fungi (Baldrian P, 2003). Mercury and its compounds are common components of crude oil and the products derived from it. Chemical treatment to remove mercury from sludge has been studied, but it is not common in the petroleum industry (Huebra M et al., 2003). Mercury had the most seriously high values: even the lowest concentration measured was above the threshold limits of all EU and Swedish regulations. The second most contaminating metal present was Nickel. The mercury content found in refinery sludge, on its own, is enough to place the sludge among the most hazardous wastes, thus ruling out most disposal options.

CHAPTER 3

METHODOLOGY

The refinery sludge was generated mainly from chemical and physical treatment unit at Petronas Penapisan Terengganu refinery wastewater treatment plant which located in a district of Kerteh, state of Terengganu, Malaysia. The physical and chemical treatment are circled as in Figure 2. The refinery sludge was treated in a sludge storage tank before dewatered in drying plant. The sample is in a form of black colored semi-solid cake which has a very high hydrocarbon content and other complex compounds with high molecular weight hence makes it highly intractable to degrade. For experimental purposes, the sample collected was placed in the laboratory of chemical engineering to preserve the originality of its characteristics.

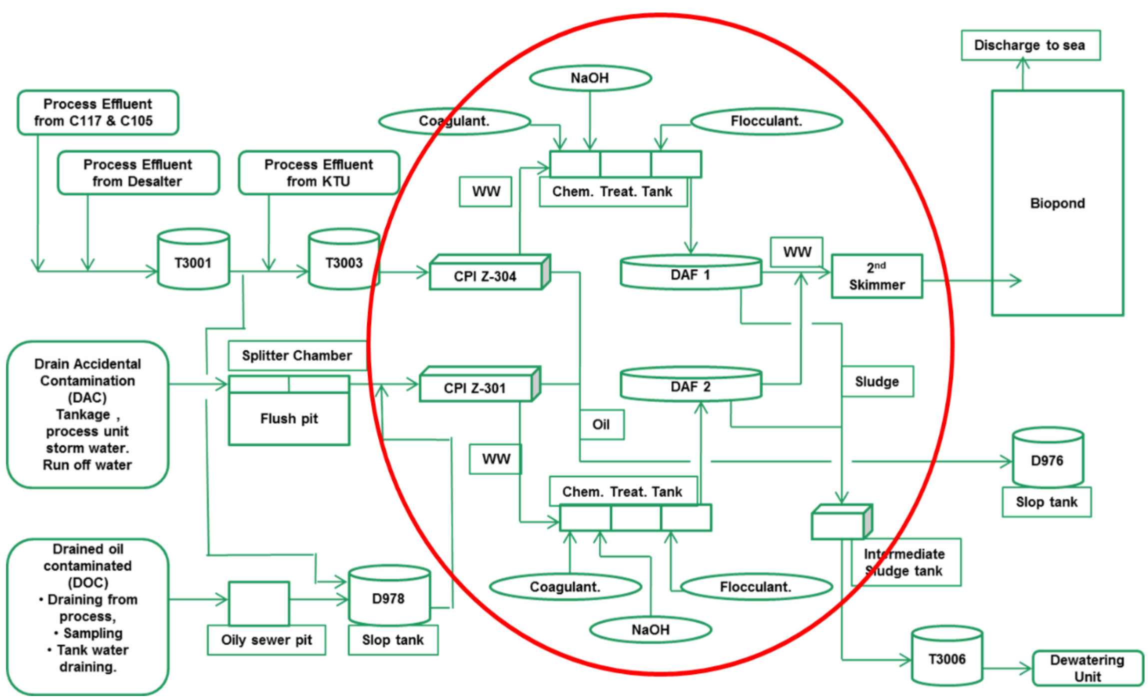

Figure 2 : Schematic Flow Diagram of WWTP for Petronas Penapisan Terengganu

3.1 Preparation of Pot Experiment

In this research, the plant of *Jatropha curcas* were planted in different refinery sludge to soil ratio of weight percent at six treatment levels. The phytoremediation method was measured by pot experiments to which healthy plants of *Jatropha curcas* at a height of 10-15cm each were selected and placed in each pot containing approximately 2kg of planting media (soil). Planting media differs in their weight composition between fresh soil and refinery sludge. There are six different levels of metal contamination were prepared by mixing the refinery sludge and the fresh soil. The refinery sludge was mixed with soil to give an amount of 2kg for each plant pot. Then, *Jatropha curcas* plant were planted on six different planting medias that are T0 (100% fresh soil) as a control, T1 (80% fresh soil and 20% refinery sludge), T2 (60% fresh soil and 40% refinery sludge), T3 (40% fresh soil and 60% refinery sludge), and T4 (20% fresh soil and 80% refinery sludge). As mention, in this experiment planting media with no contaminated soil (refinery sludge) was treated as a control. This pot experiment was carried out in the greenhouse of Faculty Chemical Engineering at Universiti Teknologi Petronas. The pot experiment is done under the ambient temperature. The heavy metal analysis for different components of plants and planting media before and after harvest were performed using AAS to identify each parts of *Jatropha curcas* plant that accumulated with heavy metals.

Figure 3: The Pot Experiment Setup in UTP

3.2 Heavy Metal Analysis

After 90 days of experimental set up the harvested plant samples were prepared for analysing method. The concentration of heavy metals accumulates in plant samples of *Jatropha curcas* were determined using Atomic Absorption Spectrometry (Perkin Elmer AAnalyst 400). The AAS was calibrated for all the metals by running different concentrations of standard solutions. Average values of three replicates were taken for each determination. The detection limits for Pb, Zn, and Ni were 3.0, 1.60, and 3.0 mg L^{-1}, respectively. AAS is chosen due to the availability and easy features to operate. The ability for AAS to assess the concentration of an analyte in a sample makes it a method of choice. The heavy metals contain were analyzed with one gram of the soil from each pot was digested in acidic mixture of HNO3: HClO4 to get their concentration of heavy metals. At the end of the process the leaves, root and shoot from harvesting *Jatropha curcas* plant were separated and digested as in case of soil samples.

Figure 4: Atomic Absorption Spectrometry (Perkin Elmer AAnalyst 400)

3.3 Sludge Sample Analysis

The sludge samples were collected from Petronas Penapisan Terengganu, Kertih Malaysia in early of March 2013. The collected samples were stored into separate plastic container and stored at ambient temperature prior to treatment. The sludge samples were homogenized by manual mixing, air-dried for 24 hours, disaggregated using a pestle and mortar made by porcelain.

3.3.1 Digestion of Sample with Aqua- Regia

An aliquot of 0.200 g of powdered sludge of each sample was taken in a silica crucible (150 cm^3). Then 1M concentrated hydrochloric acid (9 cm^3) was added followed by 1 M concentrated nitric acid (3 cm^3). The content of the crucible was carefully heated in hot block nearly to dryness in fume hood. After cooling the crucible at room temperature, distilled water was added to the sample and was filtered through a filter paper (Whatman No. 42). The filtrate was collected in a measuring flask and was preserved for the determination of Pb, Zn, and Ni. All reagents used were of Analytical Grade (AR) chemical including standard stock solutions of known concentrations of different heavy metals.

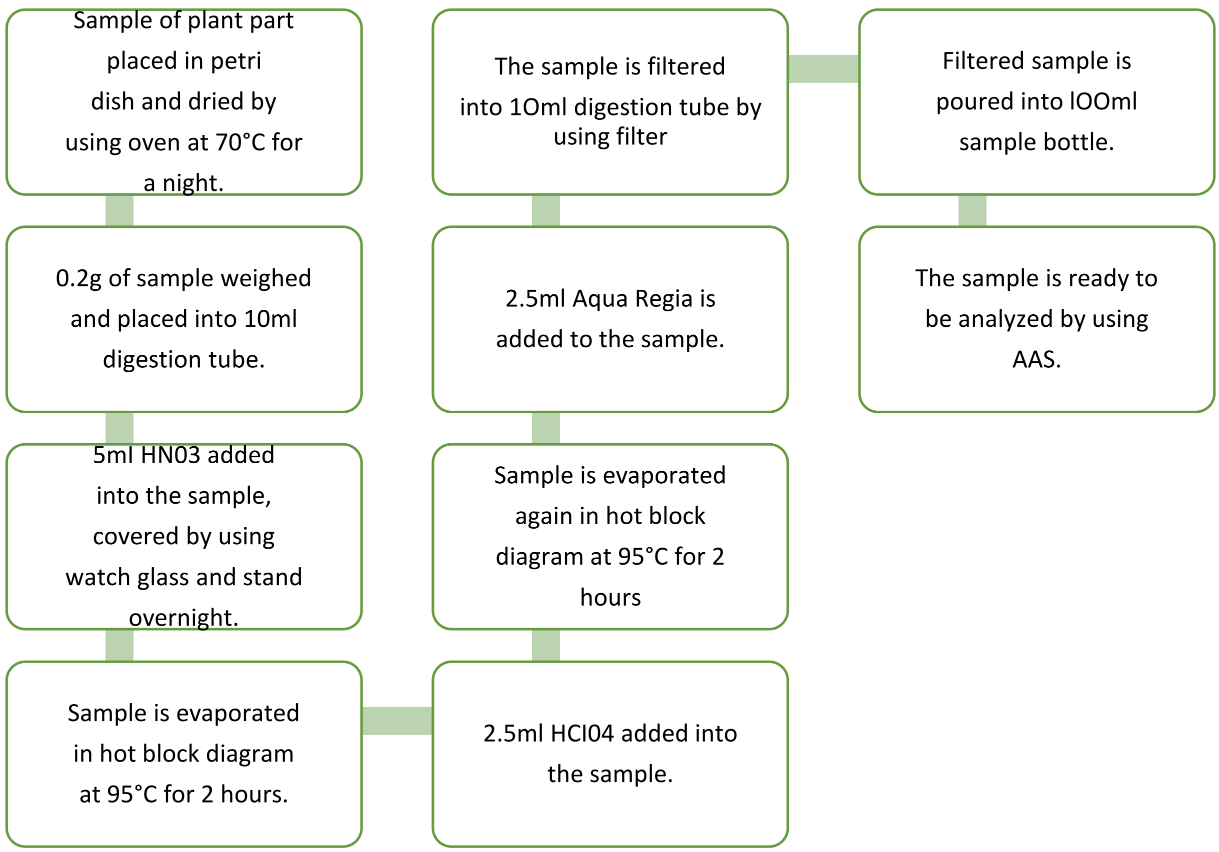

Figure 5: Summary of Sample Analysis Methodology in a Block Diagram

CHAPTER 4

RESULT AND DISCUSSION

4.1 Result and Data Analysis

The calibration curves for each analyzed heavy metal were set up to traceable limit to ensure the accuracy of the Atomic Absorption Spectroscopy. The max traceable limit are different for lead (Pb) which is 10ppm while for Ni and Zn are the same at 4ppm. This calibration curve is done so that the results of the determination were correct and reliable. Standards with the concentration of 0 ppm, 1ppm, 2ppm, and 4ppm were set correspondingly for the calibration of the Atomic Absorption Spectroscopy. The calibration curve of properly prepared standards and an accurate AAS should result as a linear curve. The data on the calibration for Zinc, Lead and Nickel are seen in Figures 6, 7 and 8 respectively.

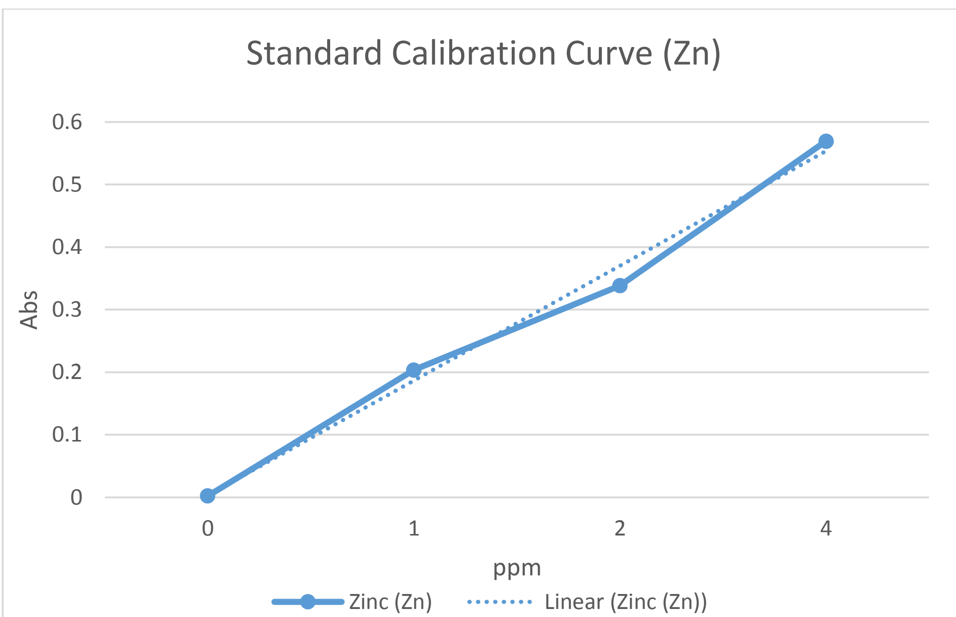

Figure 6: Zinc (Zn) Calibration Curve

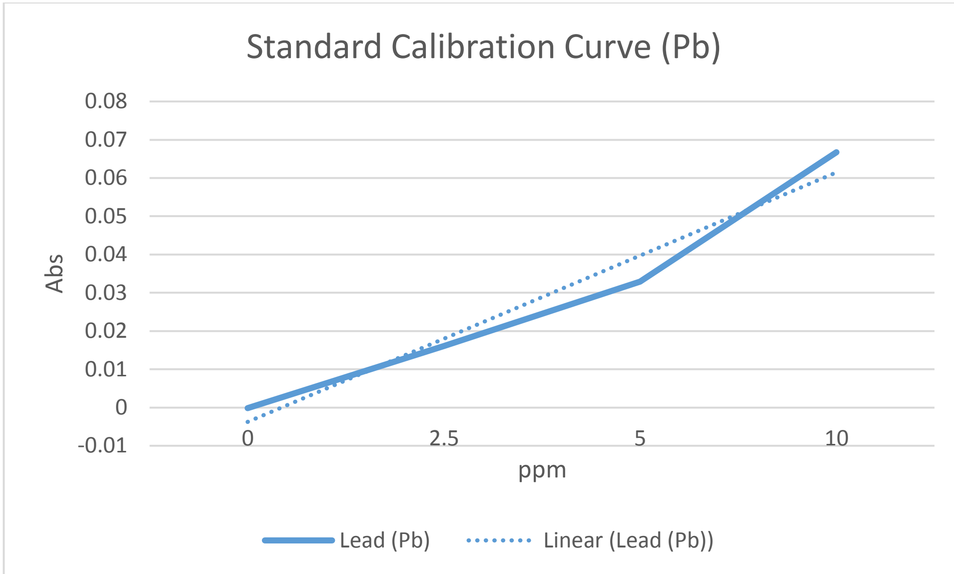

Figure 7: Lead (Pb) Calibration Curve

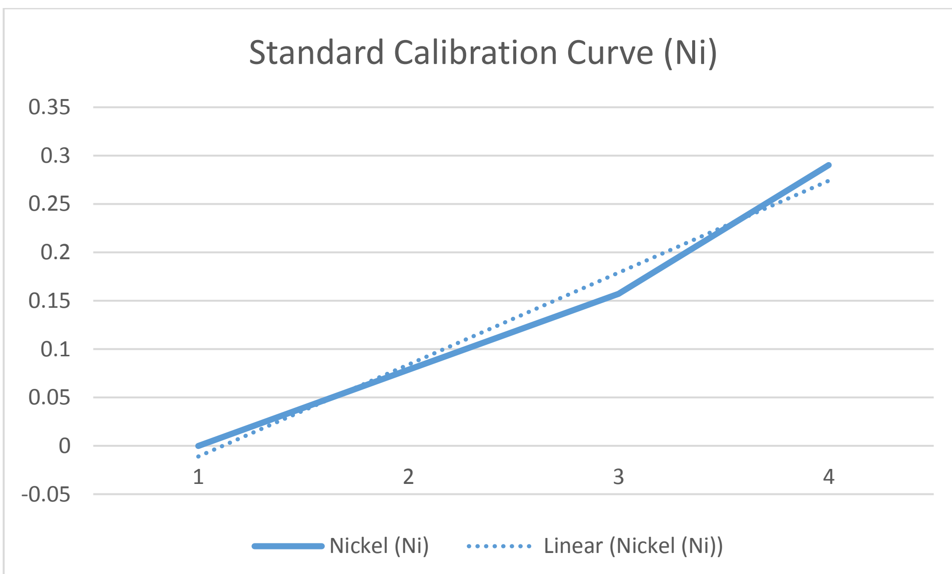

Figure 8: Nickel (Ni) Calibration Curve

After achieving the linear calibration curve of the Atomic Absorption Spectrophotometer, the mixed soil samples and plant parts samples were tested for the heavy metals: Zinc, Nickel and Lead. The data collected on these tests are presented in tables below. Table 5, 6, 7 and 8 presents a raw data collected of the concentrations in heavy metals for all samples. All data was expressed as parts per million (ppm). The heavy metal concentration in each sample were determined using equation to convert into concentration per sample size.

Metal Concentration (mg/kg) = $\frac{A \times B}{grams\ of\ sample}$ where:

A = concentration of metal in digested solution, mg/L (ppm)
B = final volume of digested soltion, mL (Lefevre, 1991)

Table 5: Raw Data of Zinc (Zn),

Zinc			
Sample	PPM	ABS	Heavy Metal Concentration, mg/kg
Shoot	0.25	0.071	12.5
Root	3.8	0.5621	190
Stem	0.67	0.1288	33.5

Table 6: Raw Data of Lead (Pb)

Lead			
Sample	PPM	ABS	Heavy Metal Concentration, mg/kg
Stem	0.35	0.0019	17.5
Shoot	0.33	0.0018	16.5
Root	0.36	0.002	18

Table 7: Raw Data of Nickel (Ni)

Nickel			
Sample	ABS	Conc, ppm	Heavy Metal Concentration (mg/Kg)
Shoot	0.0004	-0.15	-7.5
Root	0.001	-0.13	-6.5
Stem	-0.0001	-0.17	-8.5

Table 8: Raw Data of Mixed Soil Sample (Zn)

Zn			
Sample	PPM	ABS	Heavy Metal Concentration (mg/Kg)
Control	3.41	0.5076	170.5
T1 (20%)	5.76	0.8319	288
T2 (40%)	3.39	0.5046	169.5
T3 (60%)	3.91	0.5775	195.5
T4 (80%)	4.69	0.6852	234.5
Refinery Sludge	5.02	0.7303	251

Table 9: Raw Data of Mixed Soil Sample (Ni)

Ni			
Sample	PPM	ABS	Heavy Metal Concentration (mg/Kg)
Control	0	0.0047	0
T1 (20%)	0.16	0.0094	8
T2 (40%)	-0.07	0.0029	-3.5
T3 (60%)	-0.08	0.0025	-4
T4 (80%)	0.08	0.0071	4
Refinery Sludge	1.09	0.0365	54.5

After running an analysis of the samples, the results revealed that the sample for plant parts are all negative for Nickel but T1, T4 and refinery sludge samples were positive. Hence, the data for Nickel will not be discussed in this chapter.

4.2 Heavy Metal Accumulation in Different Plant Parts of *Jatropha Curcas* (Before Harvesting)

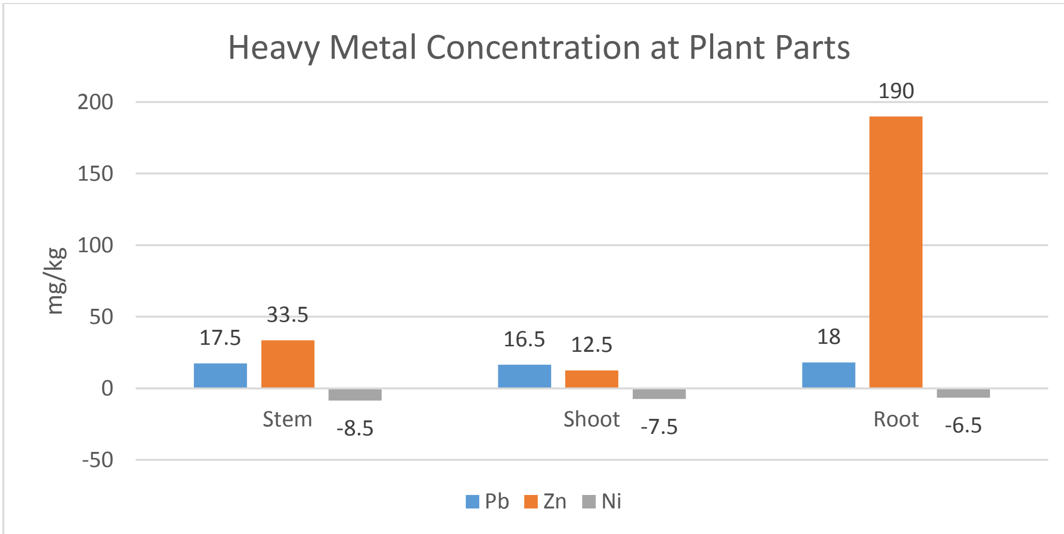

Figure 9: Heavy Metal Concentration at Plant Parts Samples

The concentrations of Pb, Zn, and Ni in plant parts (stem, shoot and roots) at the first month after planting are shown in Fig 9. The accumulation of Zn was observed in the roots of the plants which is the highest concentration detected at 190mg/kg. Meanwhile, the lowest value were shown at shoot at 12.5mg/kg. The concentration of Pb found at the plant parts are lower than Zn and gives almost similar value 17.5, 16.5, and 18 for stem, shoot, and root respectively. The highest accumulation for Pb is also at root. The concentration of nickel gives all negative value at the plant parts. The possibility of this scenario which either nickel content in the plant parts are too low or lower concentration of nickel in the mixed soil sample. Furthermore, the roots of *Jatropha Curcas* were found to absorb high levels of Pb and Zn as compared to the shoot and stem. This shows that *Jatropha Curcas* has already absorb the heavy metal in the mixed soil samples. This graph represent that the plant is in its initial stages of extraction. Therefore, concentration of selected heavy metals is formed mainly at the roots. According to J.Luhach (2012), *Jatropha Curcas* is not a good Ni accumulator due to the fact that it absorbed small amounts of Ni compared to other elements.

4.3 Analysis of Concentration for Pb, Zn, and Ni in Raw Refinery Sludge and Mixture Soil Sample

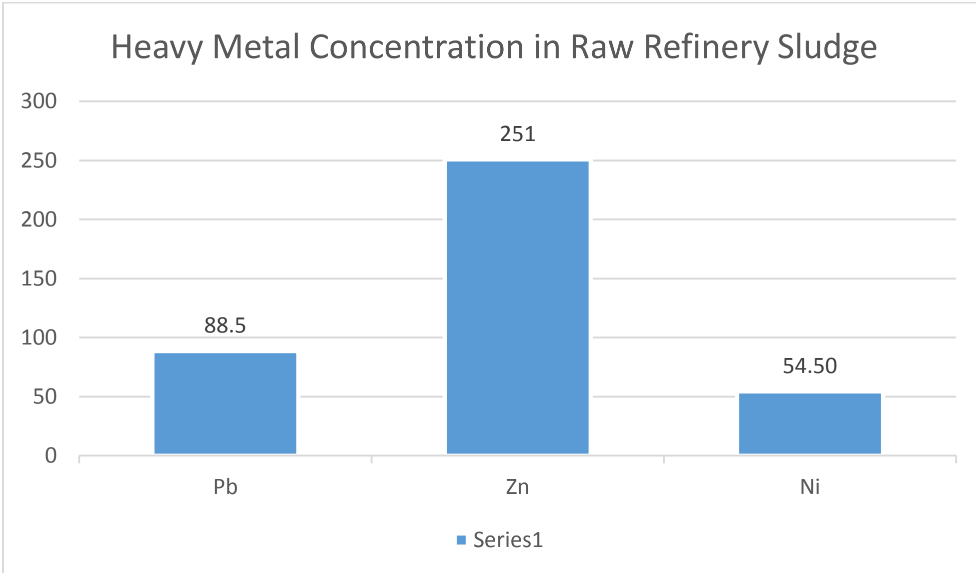

Figure 10: Heavy Metal Concentration in Raw Refinery Sludge, mg/kg

Figure 10 represent the three heavy metal concentration analyzed by AAS from raw wastewater sludge. The result shows that Zn gives the highest concentration at 251mg/kg among the three elements that were analyzed while Ni is the lowest at 54.5mg/kg. As previous result from the concentration of plant parts, Ni also shows a low concentration value which indicates that Ni already has low initial value at raw sludge. So, this low Ni concentration will affect the plant ability to uptake more Ni in the mixed soil sludge samples thus gives very low value as shown in Figure 11.

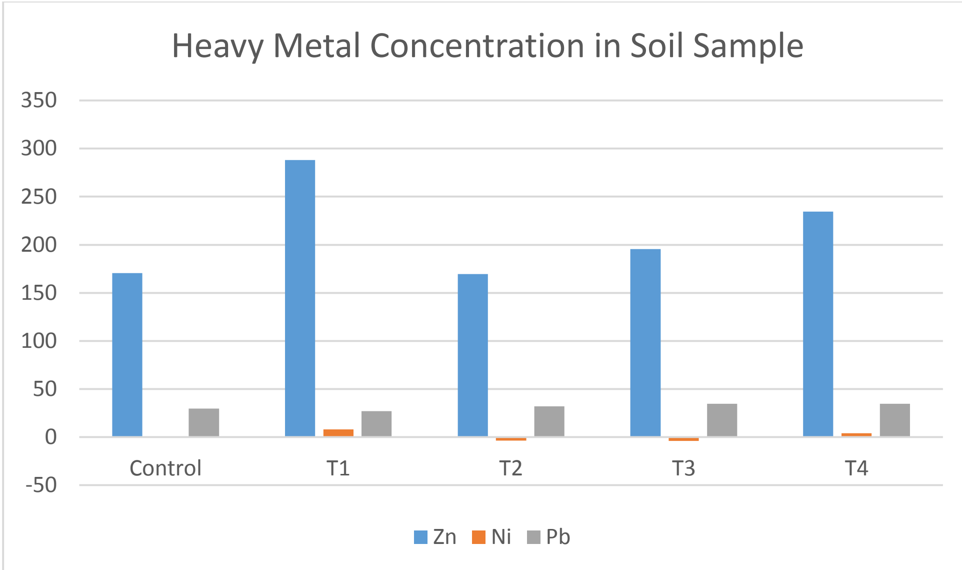

Figure 11: Heavy Metal Concentration in Soil Sample

From Figure 11 the T1 for Zn gives highest value compared to others. Theoretically, the T1 should be lower than T2 since T1 only has composition of 20% refinery sludge. This could be the result of sampling inconsistency due to the soil and sludge were not in homogeneity state. Therefore, the sampling should be done carefully and ensure that the mixture sludge and soil in sample were properly mixed before further analysis done on the sample.

4.4 Heavy Metal Accumulation in Different Plant Parts of *Jatropha Curcas* (After Harvesting)

Figure 12 and Figure 13 represent the analysis of concentration data for three *Jatropha Curcas* plant parts after harvesting. The three plant parts analyzed were shoot, root and stem. The plant harvesting sampling process was carried out to obtain a data comparison between before planting and after harvesting. These Pb and Zn value were taken after up to three months planting in various sludge to soil ratio.

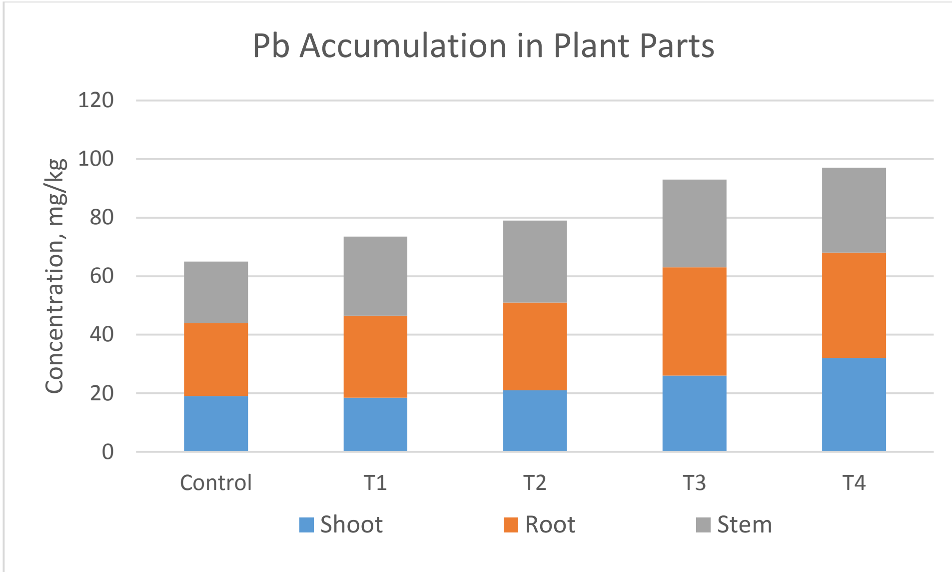

Figure 12: Pb Concentrations in Different Plant Parts of *Jatropha Curcas* after Harvesting

From Figure 12, the recorded absorption trend ranging from Control to T4 are almost equalize in pattern but concentration increased from control to T4. The absorption of Pb at T3 for root parts are higher compared to other sample. Figure 13 shows Zn accumulation in plant parts after harvesting. The graph trend shows that all samples recorded high concentration of Zn at root of *Jatropha Curcas* as compared to shoot and stem with control sample gives the highest recorded value at 250 mg/kg. The concentration of Pb increased as the sludge ratio increased but for Zn, the graph trend decreased as the refinery sludge ratio increased. This situation indicates that Pb and Zn were successfully extracted from soil samples and accumulated mainly at root. All the result are attached at the Appendix C. By referring at Figure 13, it can be observed that the concentration value for heavy metal uptake at plant parts decreased as the soil to sludge ratio increase.

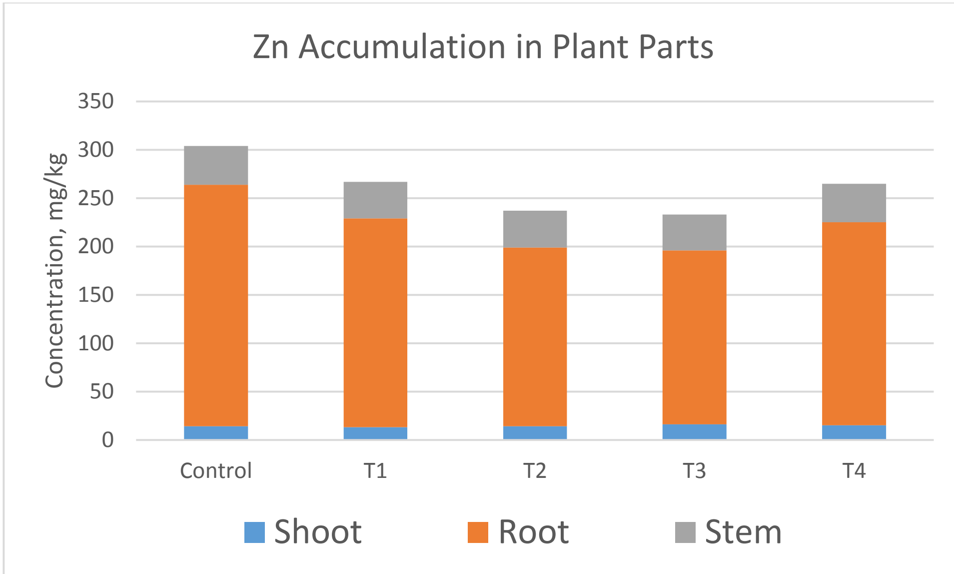

Figure 13 Zn Concentrations in Different Plant Parts of *Jatropha Curcas* after Harvesting

4.5 Comparison of Initial and Final Concentration of Zn and Pb in Soil Samples

Table 10: Heavy Metal Removal Efficiency (Zn and Pb)

Removal Efficiency		
	Zn	Pb
Control	24.93%	20.34%
T1	39.76%	11.11%
T2	-7.96%	7.81%
T3	5.56%	5.80%
T4	5.54%	1.45%

By referring to Table 10, all values from Control to T4 parameter gives positive values except for T2 at Zn.

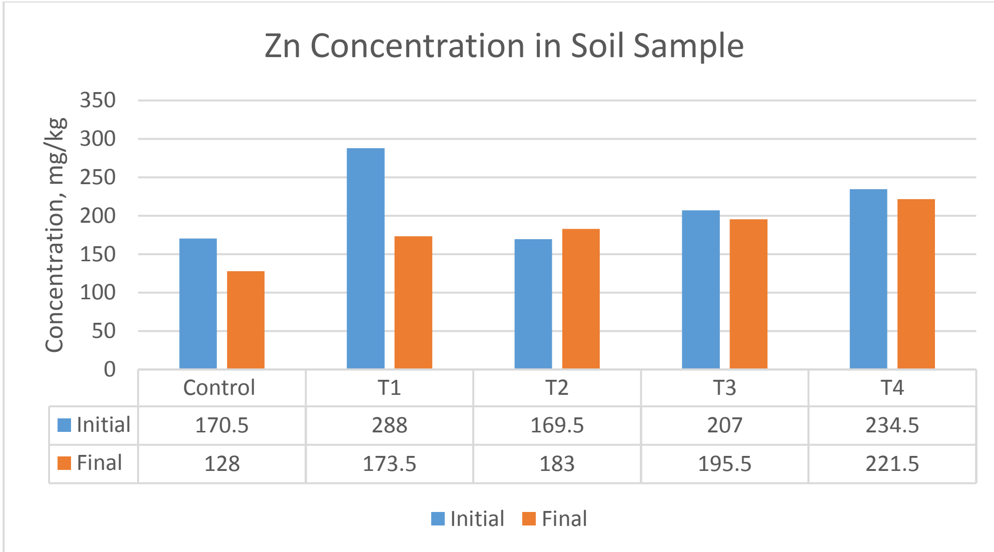

Figure 14: Comparison of Initial and Final Concentration of Zn

Figure 14 and 15 shows all the parameters gives a decreasing pattern in comparing initial and final concentration of samples except for T2. The removal efficiency value for Nickel were also negative. This might be due to external interference that influence the analysis result such as unequal distribution of heavy metals in normal soil before mixture. This proves the theory that rate of heavy metal uptake correspond with the initial concentration of pollutant in the soil.

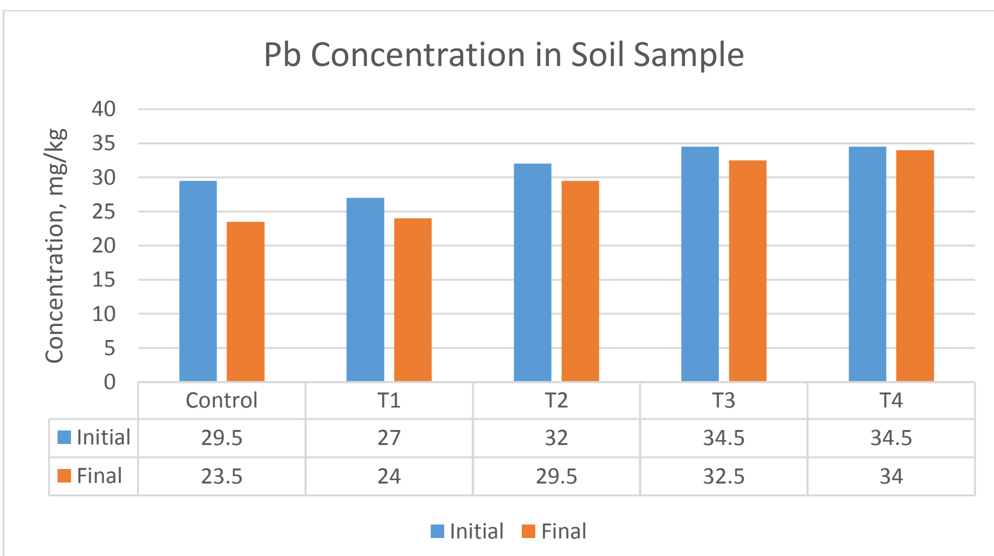

Figure 15: Comparison of Initial and Final Concentration of Pb

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

By referring to previous studies, the cultivation of *Jatropha curcas* in a refinery sludge takes up to 4 months for the result to take effect. As can be seen from the result, the accumulation of heavy metals in *Jatropha Curcas* tends to occur mainly in the roots.

The *Jatropha curcas* plant was found capable in removing the heavy metals. The roots of *Jatropha Curcas* were found to be suitable for taking up heavy metals from refinery sludge except for Nickel element. It was found to be less effective on *Jatropha Curcas* uptake ability provided that the initial concentrations of toxics were not very high. Therefore, *Jatropha Curcas* can be an ideal option for phytoremediation in multi-metal contaminated sites.

As a conclusion, the relevancy of the stated objectives towards the studies has been verified by the previously done researches. It is suitable to investigate the ability of *Jatropha curcas* in extracting Zn, Cr, and Ni from the refinery sludge by cultivating plant in mixed soil with refinery sludge. Furthermore, there are a few recommended future work area which need to be improved in undergoes this research.

1. Study on the effects of hydrocarbon towards plant ability to perform phytoextraction. Hydrocarbon contamination in soil are one of most common groups of persistent organic contaminants. It is measured in Total Petroleum Hydrocarbon (TPH).
2. Analysis on the initial toxicity level of the refinery sludge sample as the plant may not survive in very high toxic condition. The mixed soil and sample need to be under allowable toxicity condition for the plant to survive (LeFevre, 1991).

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APPENDIX

APPENDIX A – Sample Concentration per Sample Size Calculation

Metal Concentration (mg/kg) = $\frac{A \times B}{grams\ of\ sample}$ where:

A = concentration of metal in digested solution, mg/L (ppm)

B = final volume of digested soltion, mL (Lefevre, 1991)

Example:

Values are referred from Zinc (Zn) Control Initial values.

Zn			
Sample	PPM	ABS	Heavy Metal Concentration (mg/Kg)
Control	3.41	0.5076	170.5

$$\frac{3.41\frac{mg}{l} \times \frac{10\ ml}{1000ml} \times 1l}{0.2g \times \frac{1kg}{1000g}} = 170.5\,\frac{mg}{kg} = 170.5\ ppm$$

APPENDIX B – Project Gantt Charts

	FINAL YEAR PROJECT	1	2	3	4	5	6	7	MID SEMESTER BREAK	8	9	10	11	12	13	14
Item	Details/Week															
	PROJECT EXPERIMENT WORKSCOPE															
1	Project Topic Selection															
2	Study on the Project Research Method															
3	Research on the Availability of *Jatropha curcas* plant															
4	Listing of Experiment Apparatus															
5	Cultivation of *Jatropha curcas*															
6	Laboratory Equipment Familiarization															
7	Sampling of Sludge and Soil Mixing															
8	Sludge and Soil Characterization Analysis															
9	Observation of Plant Physical Traits															
10	Sampling for Leaf, Stem, Root, and Fruit															
11	Lab Analysis															
	PROJECT DOCUMENTATION TIMELINES (FYP)															
1	Selection of Project Topic															
2	Preliminary Research Work															
3	Submission of Progress Report															
4	Continues of Project Work															
5	Pre Sedex															
6	Submission of Dissertation Draft															
7	Submission of Final Dissertation															

APPENDIX C – Data for Concentration Analysis

Pb						
	Shoot, mg/kg		Root, mg/kg		Stem, mg/kg	
	Initial	Final	Initial	Final	Initial	Final
Control	16.5	19	18	25	17.5	21
T1	18	18.5	26	28	24.5	27
T2	23	21	28	30	27	28
T3	25	26	35	37	29	30
T4	31	32	34	36	26	29

Zn						
	Shoot, mg/kg		Root, mg/kg		Stem, mg/kg	
	Initial	Final	Initial	Final	Initial	Final
Control	12.5	14	190	250	33.5	40
T1	12	13	210	216	32	38
T2	14	14	180	185	35	38
T3	15	16	173	180	34	37
T4	14	15	180	210	36	40