Ni (II), Cd (II) AND Cr (IV) CONTAMINATION IN GROUNDWATER AT PULAU BURUNG DECOMMISSIONED LANDFILL SITE AND METAL BIOSORPTION USING *TRICHODERMA* SP.

CHEW ANN WON

UNIVERSITY SAINS MALAYSIA

2011

Ni (II), Cd (II) AND Cr IV) CONTAMINATION IN GROUNDWATER AT PULAU BURUNG DECOMMISSIONED LANDFILL SITE AND METAL BIOSORPTION USING *TRICHODERMA* SP.

by

CHEW ANN WON

Thesis submitted in fulfillment of the requirements

for the degree of

Master of Science

July 2011

ACKNOWLEDGEMENT

First of all, I would like to acknowledge my deepest gratitude to my most respected supervisor, Professor Nik Norulaini Nik Ab. Rahman for her excellent guidance, invaluable teaching, encouragement, patience and tolerance during the period of conducting this research studies and writing this dissertation.

Next I would sincerely thank my school dean Assoc. Prof. Dr. Habibah Hj. Lateh and also staff at School of Distance Education which helped me a lot. In the meantime, I also like to express my thanks to Professor Ir. Dr. Mohd Omar bin Abd. Kadir for his advice and friends, colleagues and staff of School of Technology Industry for the kind support showed during my research work.

I highly appreciate the cooperation from all the technicians and lab assistants who kindly provide their help especially Encik Shamsul Zoolkiffli, Encik Khairul and Cik Noraida from School of Technology Industry and staff from Electron Microscopy Unit in School of Biological Science USM.

Finally, I really appreciate the assistance from staff in IPS for postgraduate program and million thanks to my parents for their concern, moral support and patience throughout my research study.

CHEW ANN WON

TABLE OF CONTENTS

CHAPTER 2 – LITERATURE REVIEW

CHAPTER 3 - EXPERIMENTAL MATERIALS AND METHODS

CHAPTER 4 – RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

PBLS	Pulau Burung Landfill Site
APHA	American Public Health Association
USEPA	United State Environmental Protection Agency
WHO	World Health Organization
NSDQW	Nigerian Standard for Drinking Water Quality
EQA	Environmental Quality Act
EEC	European Economic Community
CDWG	Canadian Drinking Water Guidelines
DOE	Department of Environment
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
AAS	Atomic Adsorption Spectrophotometer
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
REE	Rear Earth Elements
FT-IR	Fourier Transform Infrared
JICA	Japan International Cooperation Agency
CPE	Chlorinated Poly Ethylene
PVC	Poly Vinyl Chloride
EPDM	Ethylene-Propylene Diene Monomer
PP	Polypropylene

HDPE	High Density Poly Ethylene
SPS	Structural Preservation Systems
PET	Poly Ethylene Terephthalate

LIST OF SYMBOLS

r^2	Correlation coefficient
k_f	Freundlich constants
n	Freundlich constants
C_e	Equilibrium for liquid phase ion concentration (mg/L)
q_e	Equilibrium solid phase ion concentration (mg/L)
q_{max}	Maximum sorbate uptake (mg/g)
b and b=1/K	Coefficient related to the affinity between sorbent and sorbate
C_f	Final equilibrium sorbate concentration (mg/L)
q	Sorbate uptake (mg/L)
C_i	Initial sorbate concentration in solution (mg/L)
V	Volume of solution (L)
S	Amount of the added biosorbent on dry basis (g)

LIST OF APPENDICES

PENCEMARAN Ni (II), Cd (II) DAN Cr (IV) DALAM AIR BAWAH TANAH DI TAPAK PELUPUSAN SAMPAH PULAU BURUNG OLEH LOGAM BERAT SERTA PENJERAPAN LOGAM BERAT MENGGUNAKAN *TRICHODERMA* SP.

ABSTRAK

Pengumpulan bersejarah logam berat di tapak pelupusan sampah telah menyebabkan bertambahnya proses larut lesap ke dalam air bawah tanah di seluruh dunia. Pertambahan kepekatan logam berat dalam air bawah tanah menyebabkan masalah alam sekitar bagi kebanyakan tempat. Disebabkan hal yang demikian, objektif-objektif dalam penyelidikan ini adalah untuk menentukan kepekatan ion-ion logam (Ni, Cr dan Cd) dalam air bawah tanah di tapak pelupusan sampah Pulau Burung yang terletak di Hutan Simpan Byram (5º 24' N, 100º 24'E) di Pulau Pinang, Malaysia, mengesan struktur dan fungsi *Trichoderma* sp. sebelum dan selepas rawatan air yang dicemari logam berat dan aplikasinya menggunakan proses penjerapan. Dalam kajian ini, pengumpulan sampel air bawah tanah dilaksanakan setiap bulan dari Mei hingga Disember 2008 dan analisis dijalankan dengan menggunakan AAS. Selain itu, kaedah penjerapan yang menggunakan *Trichoderma* sp. dijalankan. Kajian struktur sel dan morfologi pada *Trichoderma* sp. telah dijalankan dengan menggunakan Mikroskop Elektron Pancaran (TEM) dan Mikroskop Elektron Penskanan (SEM). Kajian "Biosorption" pada Ni, Cd, dan Cr oleh *Trichoderma* sp. menggunakan "Freundlich isotherms " dan "Langmuir isotherms" serta rawatan pada air bawah tanah yang tercemar daripada PBLS dijalankan bagi menilai keupayaannya untuk jerap logam berat. Tambahan pula, "Fourier Transform Infra Red Test" juga dijalankan sebelum dan selepas rawatan air bawah tanah.

Jesteru, "Langmuir isotherm" didapati lebih sesuai digunakan berbanding "Freundlich isotherm". Penemuan kajian menunjukkan air bawah tanah mengandungi bahan pencemar logam berat dengan pengumpulan yang tinggi pada pertengahan tahun bulan Mei hingga Ogos 2008 dan mulai berkurang sehingga akhir tahun. Selain itu, didapati bahawa logam berat seperti Ni, Cr dan Cd adalah tinggi diantara logam-logam berat yang dianalisis. Keupayaan jerapan maksimum oleh nikel, cadmium dan kromium oleh *Trichoderma* sp. adalah sebanyak 0.1353 (pH4), 0.374 (pH8) dan 0.0527 (pH 10). Keputusan eksperiment juga menunjukkan bahawa *Trichoderma* sp. dapat menjerap dan mengikat sesetengah logam berat dengan kehadiran kumpulan-kumpulan amino dan hidroksil berdasarkan kajian FTIR. Kesimpulannya, *Trichoderma* sp. merupakan penjerap logam yang baik.

Ni (II), Cd (II) AND Cr (IV) CONTAMINATION IN GROUNDWATER AT PULAU BURUNG DECOMMISSIONED LANDFILL SITE AND METAL BIOSORPTION USING *TRICHODERMA* SP.

ABSTRACT

Historical accumulation of heavy metals in landfills has caused an increased leaching in groundwater all around the world. The elevated concentration of heavy metals in groundwater can cause environmental problems in most of the surrounding areas. The main objectives of this study are to determine the concentration of metal ions (Ni, Cr and Cd) in the groundwater of Pulau Burung landfill located within Byram Forest Reserve at 5º 24'N, 100º 24'E in Penang, Malaysia, to study the biosorption of *Trichoderma* sp. on nickel, cadmium and chromium in the contaminated groundwater, identify the changes in the functional groups of *Trichoderma* sp. before and after treatment and its applicability on adsorption isotherms models to determine its biosorption capacity. In this research, monthly samplings of the groundwater within the site were conducted from May to December 2008 and analyzed for the concentrations of heavy metals using AAS. Studies on the fungal, *Trichoderma* sp. on its cell structure and morphology were performed using Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM). Biosorption studies on Ni, Cd, and Cr by fungi (*Trichoderma* sp.) using Freundlich and Langmuir adsorption isotherms together with the treatment on raw contaminated groundwater from PBLS is used to assess its ability to adsorb the heavy metals. Finally, biosorption using *Trichoderma* sp. is used to treat the raw contaminated groundwater and a Fourier Transform Infra Red Test on the fungus was carried out before and after the treatment of the groundwater to identify the functional groups. Findings through the analysis of the groundwater showed presence of pollutants containing heavy metals with higher accumulation during mid year from May till August 2008 and started to plummet slowly until the end of the year. It is found that concentrations of heavy metals such as Ni, Cr and Cd are among the highest of the heavy metals. Langmuir adsorption isotherm was found to fit the experimental data better than Freundlich adsorption isotherm and the maximum adsorption capacity of nickel, cadmium and chromium for *Trichoderma* sp. are 0.1353 (pH4), 0.374 (pH8) and 0.0527 (pH 10) respectively. The results show that both live and dead *Trichoderma* sp. biomass can adsorb and bind some heavy metals up to 100% after 72 hours contact time since it possesses amino and hydroxyl groups based on the FTIR study. Overall, *Trichoderma* sp. is a good metal biosorbent.

CHAPTER 1

INTRODUCTION

1.1 Landfill in Malaysia

The enhanced development and economic growth in Malaysia have brought on many significant changes over the past ten years especially in urbanization and industrialization. Such changes had brought about an increase in waste generation and various problems to the society and environment as a whole. There are 260 landfills nationwide and 111 of the landfills will be closed down and yet another 10 new landfills will be built. This signifies that landfills will still keep increasing in future and more pollution due to landfills will occur if the expected landfills performance does not improve. Fauziah and Agamuthu (2005) stated that there were on the average 0.7 to 1.3 kg per capita of wastes generated by Malaysians and these are being disposed at the 260 landfills all over the country. Besides that, it was estimated a total volume of 3.0 million leachate per-day will be generated throughout the country and currently a total of 31,000 tonnes of municipal solid wastes are produced in Malaysia everyday and are highly heterogeneous (Agamutu et al., 2009). The leachate produced by the landfills is not only high in BOD and COD but also high in heavy metal concentrations which could pose serious problem to the soil, surface water and groundwater.

1.2 Pulau Burung Decommissioned Landfill Area

The area used for the study is a decommissioned landfill site located within Byram Forest Reserve at 5º 24' N, 100º 24'E in Penang, Malaysia with a total area of 66 hectares equivalent to 26,400m² as shown in Plate 1.1. The Pulau Burung was initially a mangrove island separated by a canal from the mainland. The landfill operated as municipal waste disposal is a re-circulatory system using Fakuoka Method from Japan. The topography of the area in and around the vicinity of the landfill is a flat marsh area especially at the mouth of Tengah River, with local elevation at the site ranging from a high of 1.002m above sea level to a low of 0.662m. The main lithology of the area based on soil investigation work done previously is mostly consisting of silt, sand and gravel (Geolab, 2007). The climate of the area is classified as typical of peninsula Malaysia (equatorial) characterized by uniform temperature (daily mean maximum and minimum of 34˚C and 30˚C respectively) high humidity (80%-90%). The design disposal amount of municipal waste at the site is about 2,000 tonnes daily. According to Aghamohammadi et al. (2007) the site has natural marine clay liner. The Pulau Burung landfill site (PBLS) was designed, built and operated by a private company which is responsible for the implementation, construction and operation of the landfill.

Plate 1.1 Pulau Burung Landfill Site (Dated: 1st December 2009)

1.3 Problems of Groundwater Contamination and Conditions

Many researchers have reported on the contamination of groundwater related to landfills and proofs of groundwater contamination due to landfills are prevalent (Kjeldsen et al., 1993; Al-Tarazi, et al., 2008; Al Sabahi et al., 2009; Oyeku and Eludoyin, 2010). For example in New Delhi a growing capital city of India is facing problems in groundwater quality and quantity. Groundwater is an important water source for living due the scarcity of surface water in the country. Results of sampling and analysis showed that the leachate from Bhalaswa landfill contaminated the groundwater found in nearby locations (Jhamnani and Singh, 2009). In Yemen, a landfill situated at Al-Sahool area, north of Ibb City, showed contamination of groundwater with high concentrations of Pb, Ni, Cu, Cl, Ca, Mg, NH_3, hardness and total dissolved solid (TDS) due to the migration of leachate from the landfill (Al Sabahi et al., 2009).

Investigation on leachate characterization and groundwater found close to the landfills were done to understand the link between groundwater and leachate contamination including heavy metal contamination and remedial measures by Mor et al., (2006) on Gazipur landfill site in Delhi, India. Another investigation by Abu-Rukah and Al-Kofahi (2001) on El-Akader landfill site located in north Jordan reported on the physical and chemical parameters of the groundwater especially on heavy metals like Pb, Fe, Mn, Cd and Zn. Their study on eleven sites revealed that the groundwater nearby in an area of 6 km from the landfill was affected and the chemical parameters examined exceeded the permissible limits. Another similar research on groundwater conducted in the surrounding landfill in the Athens region of Greece by Fatta et al. (1997) concluded that the contaminants including heavy metals showed an increase of concentrations and very much affected by the landfill. They discovered that contaminant migration depends on the composition of the leachate entering the groundwater system.

Despite the increasing number of newly emerging landfills in Malaysia, the old decommissioned landfills such as the PBLS have not been given enough priority to solve its leachate problem that is contaminating ground water and the surrounding soils. Quite often research on Pulau Burung had been done to manage the problems of leachate, high amount of COD and BOD by using various methods (Hamidi et al., 2007 and Talebi et al., 2009). However, little groundwater investigation has been done especially on the metals contamination.

The Olusosun landfill in Ojota area of Lagos State in Nigeria is considered the largest of all landfills in Lagos area and investigation had confirmed that the groundwater contains heavy metals concentration exceeding the maximum recommended (WHO, 2008) limits (Oyeku and Eludoyin, 2010). They further reported that the pH ranges from 3.8 to 12.4 and have proofs showing that the contaminants could spread up to 2 km radius of the landfill. This is due to the uncontrolled dumping of lead batteries and spent petroleum products which caused the high levels of Cu, Pb and Fe available in groundwater.

An assessment of the groundwater contamination had been performed by Reyes-Lopez et al. (2008) in Guadalupe Victoria landfill which is located within Colorado River delta system in Baja California. Studies showed evidence of infiltration of leachate in groundwater near the landfill by using interpretation of resistivity values (where presence of leached contaminants is confirmed by low resistivity value), difference in conductivity, high value of COD and high ionic concentration which indicated that the leachate extended up to 25m away. Geophysical studies conducted by them also showed that the landfill leachate contaminant plume could extend for 20 to 40 m from the south-east and north-west edges of the landfill.

Panthee (2008) discovered that Gokarna landfill site in Nepal faces the problem of insufficient drainage to channel all the surface water, creating a depressed area in the middle part of the landfill site. Besides that another landfill site at Pokhara has been reported on the possibility of leakage of leachate and contamination of groundwater due to the puncture of the geomembrane.

Considering the significance of the pollution to the environment, numerous studies have been conducted on treating the leachate contaminated water with heavy metals (Ting and Choong, 2009; Morales-Barrera and Christiani-Urbina, 2008; Cossich et al., 2002; Mule and Melis, 2000).

1.4 Using Fungi as a Biosorbent of Contaminants

Due to the contamination of heavy metals nowadays various biosorbent had been used through biosorption process to remediate heavy metals in contaminated water (Volesky, 2007; Vijaepraghavan et al., 2004; Huang et al., 2001; Murugesan et al., 2006). However fungus had been slowly becoming more popular in biosorption of metal contaminated water.

For instance, Akhtar et al. (2007) documented that the fungus *Trichoderma harzianum* is capable of uranium biosorption with biosorption capacity of 612mgUg^{-1} and 99.9% of uranium recovery. Analytical grade of uranyl acetate dehydrate were used for the biosorption studies and the *Trichoderma harzianum* showed pseudo-second-order kinetics in biosorption pattern and is better than algae biomass in biosorption.

According to Wuyep et al. (2007) samples of wastewater from petroleum refinery effluent treated with fungal biomass, *P. squamosus* demonstrated biosorption capability by entrapping heavy metals in the mycelia. They achieved significant biosorption of heavy metals like Cr, Mn, Fe, Ni, Cu and Pb having maximum adsorption for cationic metal ions in the range of pH 4-6.

Biosorption of fungal reported by Yazdani et al. (2010) on *Trichoderma atroviride* isolated from a polluted river near an industrial area showed 50.3 to 85.4%

adsorption and 9.6 to 47.1% absorption of heavy metal (Cu). However they also mentioned that the findings still need further studies to confirm the practical use of the fungal under field conditions.

Javaid and Bajwa (2008) reported that fungal species of Basidiomycetous exhibited maximum biosorption on heavy metals in the order of: Ni(II) > Cu(II) > Zn(II) from effluent taken from an electroplating industry,.

Majority of the studies are conducted using artificial solutions and wastewater effluent and it is doubtful as to whether these research finding are equally applicable to the local environment such heavy metals contaminated groundwater near landfill.

1.5 Objectives of Study

The objectives of this study are to

I. Determine the concentrations of metal ions (Ni, Cd and Cr) in the groundwater of Pulau Burung decommissioned landfill areas.

II. To study the biosorption of *Trichoderma* sp. on nickel, cadmium and chromium in the contaminated groundwater.

III. To evaluate and identify the functional groups on *Trichoderma* sp. and the changes before and after treatment.

IV. To evaluate the applicability of Freundlich and Langmuir adsorption isotherms models to determined the biosorption capacity of the biomass.

1.6 Outline of Thesis

Chapter 1 presents some general view and introduction to the landfills in Malaysia especially the study area of Pulau Burung decommissioned landfill site with its lithology and geographical conditions. The significance of studies and objectives are clearly outlined throughout the flow of the research studies.

Chapter 2 reviews the landfill design in Malaysia and heavy metals pollutions followed by the extensive review of literature studies done for biosorption and bioremediation especially using fungus, *Trichoderma* sp.

Chapter 3 describes on the experimental methods and analysis where a detail process is mentioned to provide a clear map for the next discuss chapter.

Chapter 4 describes on the studies of groundwater in Pulau Burung decommissioned landfill site. The heavy metals data collected with analysis can be speculated and determined more specifically through the investigation of interrelationship between metals in the contaminated groundwater based on information from the Pulau Burung management itself. Besides that, reports on the initial study of the selected fungal (*Trichoderma* sp.) using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) also presented in this chapter. Lastly, the reports on the novelty of this study especially the investigation of the ability of the fungal to remove heavy metals using artificial heavy metal contaminated water by using Freundlich and Langmuir adsorption isotherms application to verify the *Trichoderma* sp. adsorption performance and the achievement of biological treatment using *Trichoderma* sp. on raw contaminated groundwater obtained from the Pulau Burung decommission landfill site based on its ability to accumulate heavy metals.

Chapter 5 presents the overall conclusions and findings for the complete research work.

Chapter 6 provides recommendations with valuable strategies and improvement in the next coming studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Landfill Design

Landfill design is classified by the type and concentration of pollutants of the wastes. Different types of wastes require different liner systems. A typical landfill consists of capping layer, landfill gas collection system, waste layer, drainage layer with leachate collection system and base liner. The most important protection system for environment from landfill contamination is the landfill liner system or also known as the landfill containment system. The system of containment or the lining system (artificial or synthetic) can contain all the leachate produced during degradation of landfill waste thus providing protection to the groundwater and soils around it.

According to Holzlöhner and Meggyes (1996), Holzlöhner et al. (1995) and Holzlöhner et al. (1999) the fundamental requirements for landfill establishment are suitable landfill sites, linear sealing system, pre-treatment of waste, capping system with gas drainage system and leachate drainage system. The landfill site mostly depends on geological conditions for example stable subsoil and low water permeability as natural barrier. The liner sealing system operating as technical barrier and usually combination of successive clay liners covered by geomembrane (with thickness of 2.5 mm or 3 mm). However for pre-treatment of waste in a municipal landfill the waste itself with the content of organic substances and concentration of the waste (heavy metals, organic, etc.) must not exceed certain value (limiting value), while leachate from the landfill must be collected, treated and periodically analyzed.

As for the capping system it is commonly applied after the end of an active phase landfill. The capping system has their own component and preferentially a composite system with geomembranes, gas drainage, etc. The following figure, Figure 2.1 shows a typical landfill design.

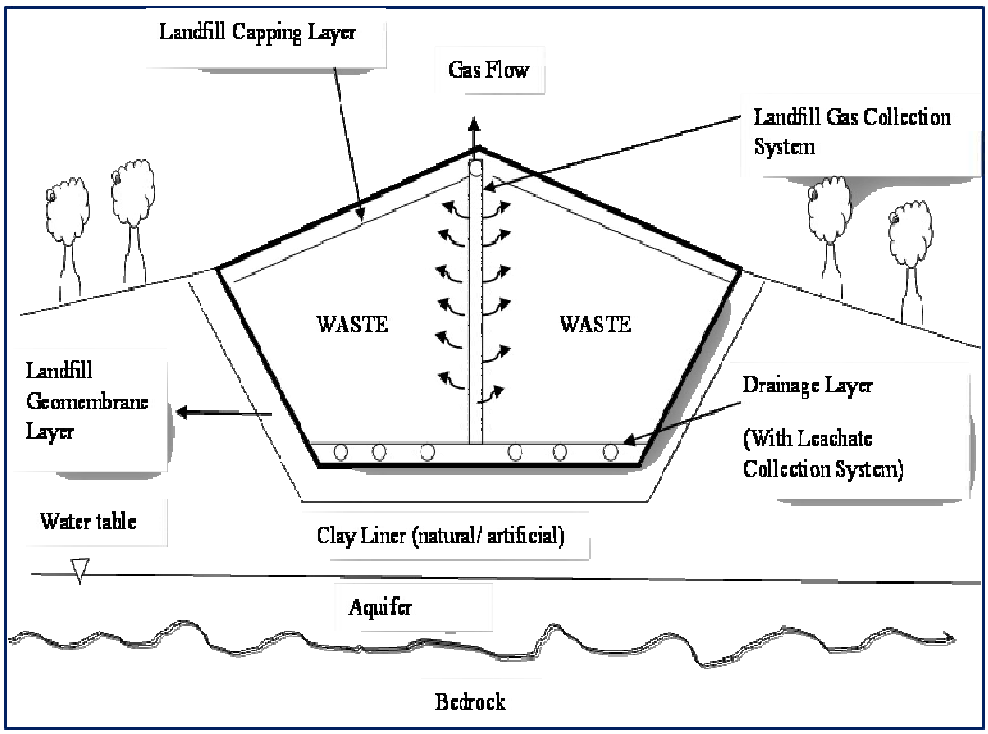

Figure 2.1 A typical landfill design.

(Adapted from: Bulc et al., 2004; Chong et al., 2005)

Based on studies done by Edil (2003) even though improvement of landfill technology has been significantly developed in the last few decades there are still issues of contamination by landfill leachate on groundwater and surface water. In landfill design the liner system is considered as one of the important elements of a modern built landfill. Even in China the government has prescribed standard municipal solid waste landfill bottom liners which showed the importance of the liner system to landfills in order to contain contaminants from polluting the environment (Du et al., 2009). Attempts in preventing contamination of ground and surface water in landfill design had also been studied by Bulc et al. (2004) such as the landfill site at Ormoz in Slovenian territory. According to Bulc et al. (2004) early problems such as untreated leachate flow which contaminate the groundwater after a period of time had caused the authority to come out with a rehabilitation plan (constructed wetland) where a natural approach is also applied on the landfill which involves containment of waste by sealing the site with low permeability materials which allows the landfill to become a bioreactor by allowing controlled infiltration of rain water. With such constructed wetland technology the leachate will flow from the drainage system into the compensation basin and then into four interconnected beds of constructed wetland with an intermittent hydraulic load and fortified with a clay layer upon which a 2mm HDPE foil to ensure impermeability. Besides that plants such as *Phragmites australis* are planted in the beds and the purified water is channeled into a sump with an outflow into an assembly basin which recycle back to the landfill by an irrigation system in which densely planted with fast growing hybrid poplar tress(*Populus deltoids, Populus euamericana)*.The constructed wetland (CW) is design as part of an integrated system which is now currently practiced in many countries such as in England, Denmark, Germany, Australia, Switzerland, USA, Sauth Africa, Newzealand and elsewhere (Bulc et al., 1998).

Foose (2010) developed an analytical equation in evaluating the effectiveness and equivalency of landfill liners to understand the impact of landfills on groundwater quality. Foose et al. (1999, 2002) had done much research on models that presented on diffusion through intact composite liners and three-dimensional (3D) advection. However the effectiveness of the composite liners from preventing groundwater pollution and effect on groundwater quality was not addressed.

2.2 Groundwater Pollution Due to Landfill

Landfills are a major source of contamination to groundwater (USEPA, 1984), and many investigations had been done in the past (Jhamnani and Singh, 2009; Saarela, 2003; Abu-rukah and Kofahi, 2001). Landfills are places for dumping of domestic wastes. It is always reported that areas near landfills will always have a greater possibility of groundwater contamination due to the potential pollution source of leachate originating from the nearby site. Thus the variations in leachate composition could reflect differences in waste composition and also the infiltration of water through the top of the landfill (Kjeldsen et al., 1993). In addition, according to Ragle et al. (1995) which performed a leachate study at a large, operating, regional municipal solid waste landfill site near Seattle, Washington, USA, stated that composition of leachate and its release rates vary between the old and the new areas of the landfill.

According to Fatta et al. (1999) in the study of landfill leachate and its impact on groundwater reported that groundwater near landfill site cannot be made as source of potable water and not suitable for irrigation of water as it is typically heavily contaminated. In England and Wales, a recent groundwater pollution point-source survey (Environmental Agency, 1997) had identified 1200 point sources and 64% are meant to cause groundwater contamination and landfill as one of the causes was also included (Rivett et al., 2002).

Case studies from Nepal by Panthee (2008) mentioned on the contamination of groundwater pollution due to landfill because of some factors such as lack of technical studies and consideration during designing and operation of the landfill. Among those problems include clogging of drainage carpet materials at high load due to compaction, airing problems, defection of geomembrane and puncturing and cracking of clay lining. Chemical reactions which occur between leachate and drainage materials or clay liner are also problems which happened at the landfill in Nepal and causes contamination in groundwater system there.

Contaminated groundwater due to landfill also present serious health problems to those nearby populations as assessed by several studies such as populations living near landfill site in Great Brittain (Jarup et al., 2002) and in area of Campania in Italy (Comba et al., 2006). Hence, those residents would have commonly used the groundwater for daily domestic purpose and unfortunately findings of the exposed population due to groundwater did not demonstrate an increased risk and evidence is not sufficient and unclear.

2.3 Groundwater and Drinking Water Standards

The United States of America uses a large fraction of groundwater for public and private consumption in many urban and rural areas as well as for irrigation and livestock in key agricultural regions (Davidson et al., 2009). Besides that in Northern New England it is reported recently that more than 40% of its population in the region use groundwater as primary drinking water source and it is also reported that groundwater in the regions are also contaminated especially by arsenic (Moller et al., 2009). Groundwater has been used as drinking water in the Netherlands (Appelo et al., 1999; de Vet et al., 2009).

However, there are challenges involved in treating the raw groundwater for drinking water purposes as the groundwater contains contaminants either inorganic, organic and microorganism. Indeed nationwide in the Netherlands, people are consuming groundwater without realizing the contamination (Smeldley and Kinniburgh, 2002).

Therefore due to the heavy metal contaminations in water, all the countries in the world had their own drinking water standards established to protect the health of their citizens.

A developing country like Malaysia also has its own standards for drinking water which is the Environmental Quality Act, 1974, Standard A which applies to areas upstream (of surface or above subsurface water) to the point of water intake just for the purpose of human consumption including drinking (DOE, 2007). Based on Gammie (2001) the US drinking water industry is regulated by the Safe Drinking Water Act of 1974 (as amended in 1986 and 1996).

Table 2.1 The national/international guidelines/standards (World Health Organization, Nigeria, Malaysia, USA, Canada, UK/EEC and Australia)

Heavy Metals	WHO	Nigeria NSDQW	Malaysia EQA, 1974, Std. A	USEPA Primary D.W.S.	USEPA Secondary D.W.S.	Canada CDWG	UK (EEC) 2000	(Australia) 1996
Cd	0.003	0.003	0.01	0.005	-	0.005	0.005	0.002
Cr	0.05	0.05 (Cr^{6+})	0.05(Cr^{6+}), 0.2 (Cr^{3+})	0.1	-	0.05	0.05	0.05
Ni	0.07	0.02	0.2	0.1	-	-	0.02	0.02
As	0.01	0.01	0.05	0.05	-	0.025	0.01	0.007
Zn	5	3	2		5	5	-	3 AO
Mg	50	0.20	-		-			
Pb	0.01	0.01	0.1	0.015	-	0.01	0.025 (2003-tap)	0.01
Hg	0.001	0.001	0.005	0.002	-	0.001	0.001	0.001
Ca	50	50	-		-			
Fe	0.3 (AO)	0.3(Fe^{2+})	1.0		0.3	0.3(AO)	0.2 (AO)	0.3 (AO)
Cu	2.0	1.0 (Cu^{2+})	0.2	1.3	1.3	1	2	2
Al	0.2 (AO)	0.2	-	-	0.05-0.2	0.1	0.2 (AO)	0.2 (AO)

AO: aesthetic objective.
Sources: World Health Organization (2008); Standards organization of Nigeria (2007); Gammie (2001); Department of Environment, Ministry of Natural Resources and Environment, Malaysia (2007).

2.4 Heavy Metals and Pollution

"Heavy metals" is hype in environmental field especially in research area, where everyone will come across this word. Based on the work done by Wang and Chen (2006) there are three categories of heavy metals such as toxic metals (Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (Au, Pd, Pt, Au, Ag, Ru, etc.) and radionuclides (U, Th, Ra, Am, etc.). According to Watts (1998) who reported that heavy metals are elements with atomic number greater than 26 (atomic number for Fe) or any metals with densities greater than 5.0 g/cm^3 (Jarup, 2003).

Hence the heavy metals with their common occurrences in biota environment either natural or as an anthropogenic source have caused anxiety among many of us who are concern about the effects or influence of heavy metals on life forms (Zvinowanda et al., 2009; Melikadze, 2005; Sheikh et al., 2007). Commonly these heavy metal contaminations appeared in various countries. For example in England heavy metals can be detected in some amounts in soil and groundwater (Thornton et al., 2000; Rivett et al., 2002;) and also in India where interesting incidents of heavy metal contamination in Ganga river (which is an important and sacred river of India) is reported of high level of heavy metals such as Fe(0.025-5.49 mg/L), Mn (0.025-2.72 mg/L), Zn (0.012-0.370 mg/L), Ni (0.012-0.375 mg/L), Cr (0.001-0.044 mg/L) and Pb (0.001-0.250 mg/L). All the reported readings of heavy metals are more than 92% of the sample range obtained.

Therefore due to heavy metals characteristic of toxicity, ability to accumulate, causing health complications and posed a high risk to the environment had prompted investigations in every field, every elements of heavy metals and every location where there is groundwater, surface water, marine sediments and soil. (Jarup, 2003; Demirel, 2007; Wiwanikit, 2008; Wang et al., 2010; Wyzga and Ciszewski, 2010)

In general, incidents reporting of heavy metal pollution are scattered all around the world for examples the floodplains of the lower Rhine river in the Netherlands is reported to contain large amounts of heavy metals over the years and could reach a value of 0.03 g/m^2 Cd, 0.7 g/m^2 Cu, 1.1 g/m^2 Pb, and 5.0 g/m^2 Zn during flood (Middelkoop, 2000); In China, due to industrial emissions, wastewater, solid wastes and human activities the average contents of heavy metals may reach up to 3.16 mg/kg Cd, 99.3 mg/kg Cu, 81.4 mg/kg Pb, and 147 mg/kg Zn in the soils of a wastewater irrigation zone in certain areas and could pollute the drinking water and food thus threatening the human health (Cheng, 2003).

The soils from the city of Palermo (Sicily) in Italy is contaminated with heavy metals like Cd, Cr, Ni, V, Mn, Zn, Co, Cu, Pb, Hg and Sb, where in the investigated urban soils the heavy metals concentrations medians of Hg, Pb, Zn and Cu are 0.68, 202, 138 and 63 mg/kg respectively (Manta et al., 2002). For instant, metal pollutants (such as lead, chromium, mercury, arsenic, cadmium, gold, silver, copper, nickel, uranium, zinc etc.) are a serious concern which is widely used in industry particularly in metal-working products, electronics, production of jewelleries, paint pigments, pottery glazes, ink, dyes, rubber, plastics, pesticides, and even in medicines.

These heavy metals can enter the environment wherever they are produced, used, and ultimately discarded as wastes. The heavy metals are toxic as ions or in compound forms, soluble in water and may be easily absorbed into living organisms which can bind to vital cellular components such as structural proteins, enzymes, and nucleic acids thus interfere with their functioning causing severe physiological and health effects (Landis et al., 1999) particularly in humans even in small amounts of metals. The following Table 2.2 shows the effects of heavy metals on human health.

Table 2.2 Heavy metals and its health effects

Heavy Metals	Health effect/ Hazards
Cadmium (Cd)	Diarrhea, excessive salivation, loss of consciousness, growth retardation, abdominal pain, impaired kidney function, hypertension and liver dysfunction, hypertension and cardiovascular problems (humans), and arterial hypertension, castration effect , Itai-itai disease.
Chromium (Cr)	Carcinogenic effect (Cr (VI, III)), growth depression, liver and kidney damage (when fed 50 ppm of Cr (VI)). Bronchogenic cancer (due to inhalation of chromic (Cr (VI)) acid vapor or dusts of Cr (III) salts), ulceration and carninoma dermatitis.
Nickel (Ni)	Gastric ulcers, thyrotoxicosis and cancer, tumors, growth retardation; reduction in the activity of enzyme in liver, kidney and heart, nose cancer, degeneration of heart and tissues, daffiness, nausea, vomiting, headache.
Arsenic (As)	Acute poisoning, gangrene (Black-foot disease), severe gastrointestinal disease, skin, liver and nerve tissue injuries.
Copper (Cu)	Stomach irritation and nausea, growth depression, liver, brain and kidney damage (Jaundice, Wilson's disease)
Mercury (Hg)	Brain cells, physical and emotional disturbance, anxiety, lack of concentration, death (0.03 ppm in water is highly toxic).
Iron (Fe)	Hemochromatosis, tension in gastrointestinal tract, liver damage.
Zinc (Zn)	Gastrointestinal disturbance, nausea, anemia, hinder of bone growth, blurred vision, pain and muscular weakness disease.
Lead (Pb)	Kidney damage, DNA and RNA brain and central nervous system damage, inhibit the formation of haemoglobin, aggression mania, illusion, schizophrenia symptoms and behavioral problems.

Source: Jackson et al. (1999); Luckey et al. (1975); Singh (2005), Förstner and Wittmann (1983); Alloway and Ayres (1993); Nebel and Wright (1996); Mohammed and Najar (1997).

2.5 Incidence of Landfill Leachate and Groundwater Contamination

Heavy metal is a major problem in groundwater contamination originating from wastes in landfill such as electronic waste including used batteries, electroplating waste, painting waste and other kinds of waste. There is no separation of hazardous waste from non hazardous wastes or other municipal solid wastes that could increase the heavy metals in the dumpsites and raise environmental effects in long term periods (Esakku et al., 2003).

Based on a case study in Shanghai in China, results demonstrated that the main heavy metal contaminants were Zn, Cr, Cu and Pb, followed by Ni, Cd and Hg and that mostly composed of putresible waste and miscellaneous indistinguishable particles which are the major contributor of the heavy metals in the municipal solid waste dump (Zhang et al., 2008).

In general the wastes in landfills generated the leachate and are highly concentrated with contaminants such as dissolved organic matter and inorganic compounds with heavy metals (Mn, Cd, Cr, Cu, Pb, Ni, Zn, etc.) and also xenobiotic substances (Kulikowska and Klimiuk, 2008; Ogundiran and Afolabi, 2008; Tengrui et al., 2007; Kurniawan et al., 2006 and Christensen et al., 2001). The migration of leachate or pollutants from landfills to groundwater system has been examined in several field investigations and monitoring, which have established the general possibilities, caused and distribution of the pollutants within the subsurface in several countries for instance like Vejen landfill in Denmark (Christensen et al., 1994; Brun et al., 2002). It can be deduced that the presence of unregulated landfill sites or old landfill sites has left a legacy of groundwater contamination incidents. For example, according to Tatsi and

Zouboulis (2002) hydrological study, a landfill operates near Thessaloniki (North Greece) that the groundwater there are facing leachate infiltration and is contaminated.

A field study on 43 landfill sites in Southern and central Finland by Assmuth and Strandberg (1993) showed evidence of groundwater contamination which had gone unnoticed, despite having had addressed the quality of the groundwater due to leachate fluxes. The concentration of pollutants in the groundwater especially heavy metals were compared to other countries such as Germany, United State of America , Canada, Finnish and Scandinavian which have depicted incidents of groundwater contamination related to landfills. Besides that according to Assmuth and Strandberg (1993) again the groundwater quality near landfill maybe due to many reasons such as leachate concentration gradients, hydro-geochemical conditions, samplings equipment and procedures, sample silt contents and other possible contamination sources which are mentioned in their studies.

In another research done by Rapti-Caputo and Vaccaro (2006) in Italy which conducted hydrogeological and geochemical monitoring on groundwater system proved that the groundwater near landfill of Sant' Agostino (Ferrara Province, Northern Italy) is highly contaminated by heavy metals (Al, Zn, Cl, Cr, Ni and Pb) from landfill leachate.

The lithological and hydrological variability for instant the geological setting which situated below the piezometric level of the unconfined aquifer could cause possible contamination. In addition, low water depth also causes the aquifer to be vulnerable to the diffusion of leachate naturally.

2.6 Heavy Metals and Bioremediation

Remediation of heavy metal contaminated water is an acute environmental issue in most countries, especially those with a water deficit crisis. Thus many conventional methods for heavy metal remediation in aqueous solutions are said to be expensive and might not be very efficient (Kapoor and Viraraghavan, 1995, Rhadika et al., 2006 and Tripathi et al, 2007). Chemical precipitation and filtration cause difficulties in separation of solid-liquid particles when present in higher concentrations which resulted in large amount of sludge being produced (Aguinaldo, 2009).

According to Volesky (2001) chemical oxidation and reduction where the chemical required is not universal and slow in the process of biological system (reaction with structure of biomass), as for reverse osmosis will cause scaling problems and also expensive in usage. In addition ion exchange, membrane technology and activated carbon are reported to be expensive and cause difficulties when frequently use especially when come to large scale treatment of heavy metals contaminated water and waste water.

Besides that according to Veglio and Bolchini (1997), Wang and Chen (2006) and Volesky (1990a) remediation using chemical precipitation and electrochemical treatment are said to be ineffective when the metal ion concentration is low (1 to 100 mg/L) which produces large amount of sludge.

As a result many had turn to biosorption as an alternative method which nowadays had achieved growing importance for metal removal, metal recovery and waste purification. Biosorption can be defined as a fast and reversible reaction of the heavy metal with microorganism biomass (Klimmek et al., 2001; Hussein et al., 2004; Popuri et al., 2007) and also as the accumulation and concentration of pollutants from