LEACHATE TREATMENT – CHITOSAN AS AN ADSORBENT FOR HEAVY METAL IONS

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ABSTRACT

Leachate contains several of heavy metals which become potential pollution for water resources (ground and surface) and the soils. Chitosan reported to be an effective adsorbent to remove heavy metals in leachate. The main objective of this study is to evaluate the effectiveness of heavy metal ions removal from leachate using chitosan. Iron (II) solution was used for synthetic sample analysis to determine the optimum operating condition of the sample in the function of pH, contact time, agitation speed and chitosan dosage. The result indicated that the optimum conditions for chitosan to be the most effective to adsorb metal ions is at pH sample 9, agitation speed 50 rpm, contact time 20 min and the dosage of chitosan 30 mg/L. For actual leachate sample analysis, the highest percentage of metal removal obtained at 50 mg/L of chitosan dosage. The adsorption percentage for Iron ions is 36.8 % while the adsorption percentage for Managanese ions is 28.6. A treatment system for leachate is proposed in this study. The design of treatment system that consists of pH stabilization tank, metal adsorption tank and sedimentation tank is based on the optimum operating condition. The tanks are design to treat $1m^3$ of leachate at a time with chitosan dosage provided is $300g/m^3$.

ABSTRAK

Air larut lesap mengandungi pelbagai jenis logam berat yang menjadi pencemar kepada sumber air dan tanah. “Chitosan” dilaporkan menjadi ejen penyerap yang berkesan untuk menyingkirkan logam berat di dalam air larut lesap. Objektif utama kajian ini dilakukan adalah untuk menilai tahap keberkesanan penyingkiran ion logam berat dari air larut lesap dengan menggunakan Chitosan. Larutan Ferum (II) digunakan dalam analisis sampel sintetik untuk mencari keadaan optima operasi bagi sampel dalam fungsi pH, masa, kelajuan putaran dan sukatan dos Chitosan. Keputusan yang diperoleh untuk keadaan optima bagi Chitosan menyerap ion logam berat dengan paling berkesan adalah pada pH larutan 9, kelajuan putaran 50 rpm, masa 20 minit, dan sukatan dos Chitosan sebanyak 30 mg/L. Bagi analisis sampel air larut lesap, peratusan tertinggi penyingkiran logam diperoleh dengan penggunaan 50 mg/L sukatan dos Chitosan. Peratusan penyerapan untuk ion Ferum ialah 36.8% manakala peratusan penyerapan bagi ion Mangan ialah 28.6 %. Satu sistem rawatan untuk air larut lesap dicadangkan dalam kajian ini. Rekabentuk sistem rawatan ini yang mengandungi tangki penstabilan pH, tangki penyerapan logam dan tangki pemendapan adalah berdasarkan keadaan optima operasi. Kesemua tangki yang digunakan adalah direka untuk merawat $1m^3$ air larut lesap pada satu masa dengan penggunaan sukatan dos Chitosan sebanyak 300 g/m^3.

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LIST OF SYMBOLS

mg/L	-	Milligram per liter
g/m^3	-	Gram per meter cubic
rpm	-	Rotation per minute
ppm	-	Part per million
C_o	-	Initial concentration
C_f	-	Final concentration
V	-	Volume
W	-	Weight

LIST OF ABBREVIATIONS

Fe	-	Iron
Cu	-	Copper
Zn	-	Zink
Hg	-	Mercury
Mn	-	Manganese
BOD	-	Biological Oxygen Demand
COD	-	Chemical Oxygen Demand
SS	-	Suspended Solids
TSS	-	Total Suspended Solids
NaOH	-	Sodium Hydroxide
HCl	-	Hydrochloric acid
HNO_3	-	Nitric acid
HDPE	-	High Density Polyethylene
GAC	-	Granular Activated Carbon Filter

CHAPTER 1

INTRODUCTION

1.1 Introduction

Solid waste is all kind of garbage, refuse, trash and other discarded solid materials which were generated from human activities especially from residential, commercial establishments (e.g., restaurants, banks) and institutions (e.g., hospitals, schools). Usually wastes are managed by municipal authorities. Nowadays, solid waste disposal practices became a huge problem in every country with increasing concern for the environment. People generated solid waste in the form of bottles, boxes, clothing, plastic bags and much more results in million tones of solid waste generated per year. If all of the trashes are not managed properly, they'll pose a major threat to human, animals and the environment.

In Malaysia, there are about 7.34 million tones of solid waste generated in year 2005 that's enough to fill up 42 buildings the same size as Petronas Twin Towers (Chandravathani, 2006). Municipal authorities has used many methods in managing the waste properly so that it's doesn't pose any harm to human health. Composting, incineration, open dumping, reuse and recycling are some example in managing waste. However, landfill is the most common method to manage solid waste in Malaysia. Landfill has become the most popular method because it traditionally been the least-cost disposal option and it is a solid waste management necessity nowadays. Combination of reduction, recycling, composting or incineration are still can't manage the entire solid waste produced currently.

The use of landfill to manage solid waste has produced a hazardous liquid named as "leachate". Leachate can be defined as a liquid that is generated when water or another liquid comes in contact with waste. (Amalendu, 2004). Leachate is a contaminated liquid that consists of different organic and inorganic compounds that may be either dissolved or suspended. As a contaminated liquid, leachate poses potential pollution to both groundwater and surface water and also it will contaminate the soils in areas adjacent to landfill sites. There are many methods used to treat leachate from the landfill. The treatment can be carried out on or off site by physical, chemical or biological methods. For this study, it will be focus on leachate treatment by a natural polymer named "Chitosan".

In some older landfills, generally leachate was directed to the sewers for treatment. Toxic metals from leachate passing through the sewage treatment plant concentrate in the sewage sludge making it difficult and dangerous to dispose off to land without incurring a risk to the environment. In order to make the leachate less dangerous, toxic metals in the leachate need to remove first. Thus, chitosan could be used widely as adsorbent for metal ions in primary treatment of leachate before lechate directed to the sewers for other treatment. Chitosan has been chosen as an adsorbent for metal ions in leachate because chitosan are the second most abundant natural polymer on earth. It is readily available and one of the most appealing aspects of chitosan is it 100% biodegradable. Specifically, chitosan is a biocompatible, antibacterial and environmentally friendly polyelectrolyte. The possibility for chitosan to bring pollution to the environment is nearly zero. That is why chitosan been chosen to become one of the most effective adsorbent for metal ions in leachate and wastewater.

The general layout of leachate treatment shows in Figure 1.1. First, collected leachate will undergo screening process in purpose of removing suspended, huge and hard materials from entering the treatment plant. Then, screened leachate will undergo grit separation process before the treatment with chitosan. Treatment with chitosan will reduce heavy metal ions concentration in leachate. By reducing the concentration of heavy metal ions, leachate is safer to direct to wastewater treatment plant. In wastewater treatment plant, leachate will undergo other treatment as experienced by sewage. After undergo several treatment process in wastewater treatment plant, the leachate now becomes decontaminated and is safe to be discharge to the water works or to the rivers.

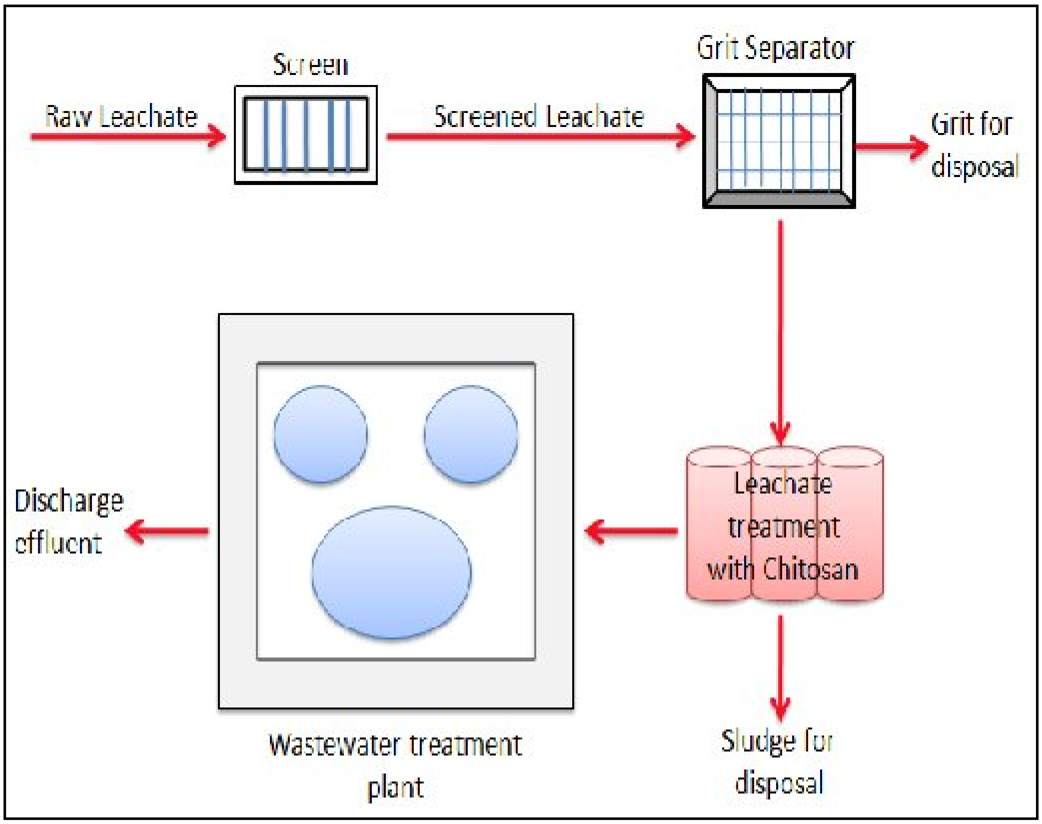

Figure 1.1: General layout of leachate treatment before directed to wastewater treatment plant.

Heavy metals are the metals whose density is greater than 5 g/cm3, e.g. Iron (Fe), Copper (Cu), Zink (Zn), Mercury (Hg), Manganese (Mn), and others. Iron concentration in leachate is normally contributed to by iron-base material waste, such as concentration materials, paints, pigments, color compounds, polishing agents and electrical materials. Different types of solid waste, will contribute to different type of metal ions. The efficient methods of heavy metal ions removal from wastewater and leachate are adsorption, chemisoption and biosorption (Kaminski *et al*., 2007). The most popular adsorbates, reported in the literature are gels of silicic acid, activated carbon, zeolites, tree bark, biomass, lignin, dried mushrooms and chitosan. Chitosan is a derivative of chitin. It is found in the insect's shells, fungi cell walls and in the shells of crustaceans. Commercial value of chitosan is its affinity to heavy metal. In the previous research, chitosan has been found to be effective at removing heavy metal from water sources. Most important thing is chitosan is 100% biodegradable compound. So, it doesn't bring pollution to the environment. In wastewater treatment, chitosan is used as an effective coagulant/flocculant alternative to conventional inorganic coagulants such as alum and ferric chloride. Chitosan is capable for binding the negatively charged particles, heavy metals and oils.

1.2 Problem Statement

Leachate is a contaminated liquid containing high concentration of heavy metals produced from sanitary landfill. The organic strength of landfill leachate can be 20 to 100 times the strength of raw sewage, making landfill leachate as a potential source of pollution for water and soil in adjacent area of the landfill. Beside poses contamination to soil and surface water, this contaminated liquid tends to infiltrate into the earth to the aquifer system and into groundwater. To prevent the pollution, leachate need to be treated so that it is safe to release to the environment. To provide a good treatment for landfill leachate, leachate characteristics need to identify first. Some of the leachate treatments available nowadays are cost expensive. Lower cost system with high performance needs to identify and develop for leachate treatment, so that municipal authorities tend to manage waste and its by-product very well and more efficient.

1.3 Objective

There are three objectives for this study based on the problem statement. The objectives are as below:

1- To determine the characteristics of landfill leachate in Jerangau-Jabor Landfill.
2- To analyze the effectiveness of using "Chitosan" as heavy metal ions removal in leachate.
3- To propose alternative leachate treatment system with lower cost.

1.4 Scope of Study

This study mostly focuses on leachate. The leachate samples are obtained from Jerangau-Jabor Landfill in Kuantan District with cooperation from Majlis Perbandaran Kuantan (MPK) and Alam Flora Sdn. Bhd. Figure 1.2, Figure 1.3, and Figure 1.4 show the activities in Jerangau-Jabor Landfill. Leachate characteristics are identified in terms of physical and chemical characteristics. A series of experiments are conducted to determine the chemical characteristics based on the parameter of pH, biological oxygen demand (BOD), chemical oxygen demand (COD), and metal ions. For physical characteristics, observation for the leachate color, odor, temperature and suspended solids (SS) are done. The main focus of this study is for analyzing the removal of heavy metal ions in leachate by using chitosan. The apparatus used for this process is Spectrophotometer DR2500. Before analyzing the effectiveness of chitosan for metal ion removal in leachate, a series of synthetic analysis is conducted using aqueous solution containing Iron (Fe) as the metal in the sample. It is on purpose to measure the optimum pH, time contact, agitation speed and the optimum dosage for the treatment. Finally, lower cost of leachate treatment system using chitosan proposed as a cost effective treatment compared to other conventional treatment.

Figure 1.2: Solid waste dumping activities in Jerangau-Jabor Landfill site.

Figure 1.3: Separation and collection of plastic materials for recycling process.

Figure 1.4: Plastic-base waste collected for the recycling process in the factory.

1.5 Significant of Study

The study on leachate treatment by using chitosan is important in order to improve the efficiency and provide variation methods of leachate treatment. Leachate treatment by using chitosan will become other alternative treatment which could reduce the overall cost of conventional leachate treatment. This study will analyze the effectiveness of chitosan as adsorbent for heavy metal ions in leachate. End of this study, one method of lower cost leachate treatment will be proposed. This treatment can be used and practice widely by municipal authorities in order to control and reduce pollution posed by leachate from sanitary landfill all over Malaysia.

CHAPTER 2

LITERATURE REVIEW

2.1 Leachate

Leachate is a contaminated liquid which is produced when water passes through solid waste after precipitation in sanitary landfill. From previous studies, leachate is reported to have both organic and inorganic compound whether it's suspended or dissolved in that contaminated liquid. (Paul, 2005; Amalendu, 2004). Leachate is a potentially polluting liquid; could bring harmful effects to the surface and ground water surrounding a landfill site. Many factors influence the production and composition of leachate. One major factor is the climate of the landfill. If the landfill have climate with higher level of precipitation, there will be more water entering the landfill and therefore more leachate is generated. Jerangau-Jabor Landfill located in Pahang is in east coast region and it will have monsoon in November and December. Thus, more leachate will produce during these months every year. Another factor is the topography of the landfill which influences the runoff patterns and again the water balance within the site. Carefully controlled manner need to perform before leachate returned to the environment safely (Salem *et al.,* 2008).

2.1.1 Leachate Production

Leachate is generated as a consequence of water percolation through the solid wastes, biochemical processes in waste's cells and the inherent water content of wastes themselves which will dissolve soluble components out of the solid materials. Figure 2.1 shows the schematic diagram for leachate production. The production of leachate will increase with the increasing of precipitation process. Degree of contamination of leachate is affected by the waste types as a result of biodegradation process. Leachate from biodegradable landfill may contain large amount of organic matter with significant concentration of substances such as ammonia-nitrogen, heavy metal, chlorinated organic and inorganic salts. All these matters are toxic to many organisms especially to aquatic life and can cause harm to human health. (Salem *et al*., 2008; Renou *et al*., 2007; Amalendu, 2004).

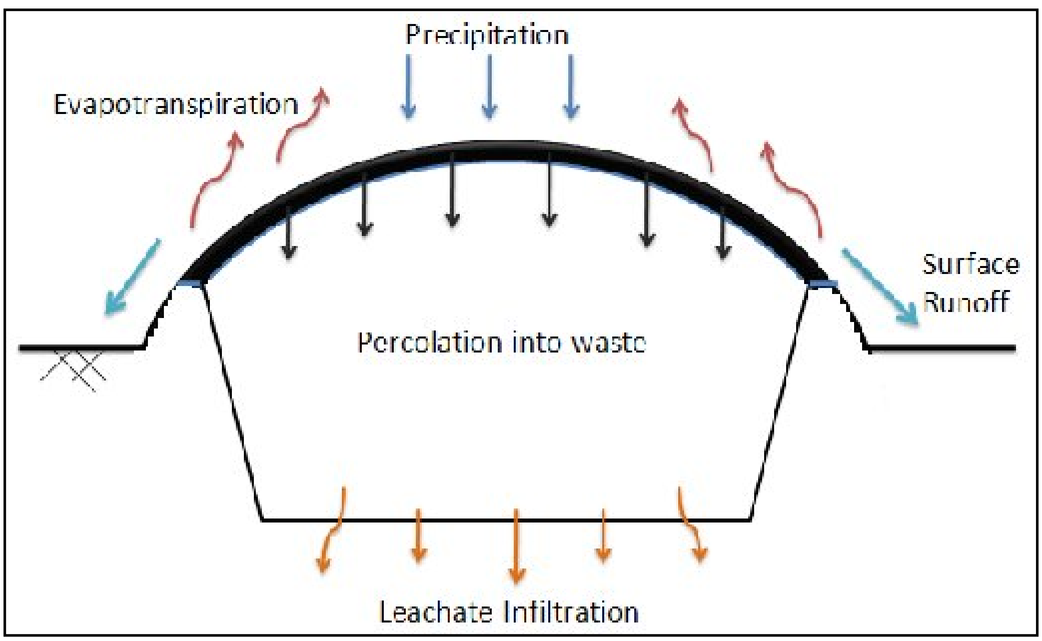

Figure 2.1: Schematic diagram for landfill leachate generation (Amalendu, 2004)

Volumetric flow rate and the composition are two factors characterizing the leachate. Leachate quantity is influence by the degree of precipitation (e.g., rain, snow, etc.) on the landfill site, the surface runoff, evapotranspiration and infiltration or intrusion of groundwater percolating through landfill. All these factors categorized in the climate element which bring great effect to the production of leachate. Groundwater intrusions will increase the leachate quantity and it would be happened if the landfill site construct below the groundwater table. Besides the climate, the production of leachate also influences by the nature of the waste itself namely in water content and its degree of compaction. Leachate production could be greater with less compaction which will reduce the infiltration rate (Renou *et al*., 2008).

Factors that affect the leachate quality vary in many elements such as the landfill age, degree of precipitation, seasonal weather variation, waste types and composition (depending on lifestyle of the surrounding populations) (Renou *et al*., 2008). Composition and solubility of the waste constituents become two primary factors that affect the leachate quality. Changing in waste composition due to biodegradation and weathering will then change the quality of leachate with time. Figure 2.2 shows the stages of leachate production with the quality of contaminated liquid produces. In the early stages of waste decompositions, the leachate is generated under aerobic conditions. Complex solution with nearly neutral pH will produce. This stage will lasts only for a few days or weeks. Under aerobic condition, leachate temperature will increase to 80^{o} – $90^{o}C$ cause by the heat production during this process. As decomposition process developed, the waste will undergo anaerobic process.

In the early anaerobic condition (acidic/acetogenic phase), leachate will develops high concentration of soluble degradable organic compounds with strongly acidic pH. Ammonium and metal concentration will rise as the consequence of the anaerobic condition. After several months or years, methanogenic conditions are established. Leachate will become neutral or slightly alkaline but it still contains significant quantities of some pollutants. As biodegradation near to completion, aerobic condition returned. Now, the leachates eventually cease to be one of hazardous liquid that may pollute the environment if suitable treatment doesn’t perform to treat it (Salem *et al*., 2007).

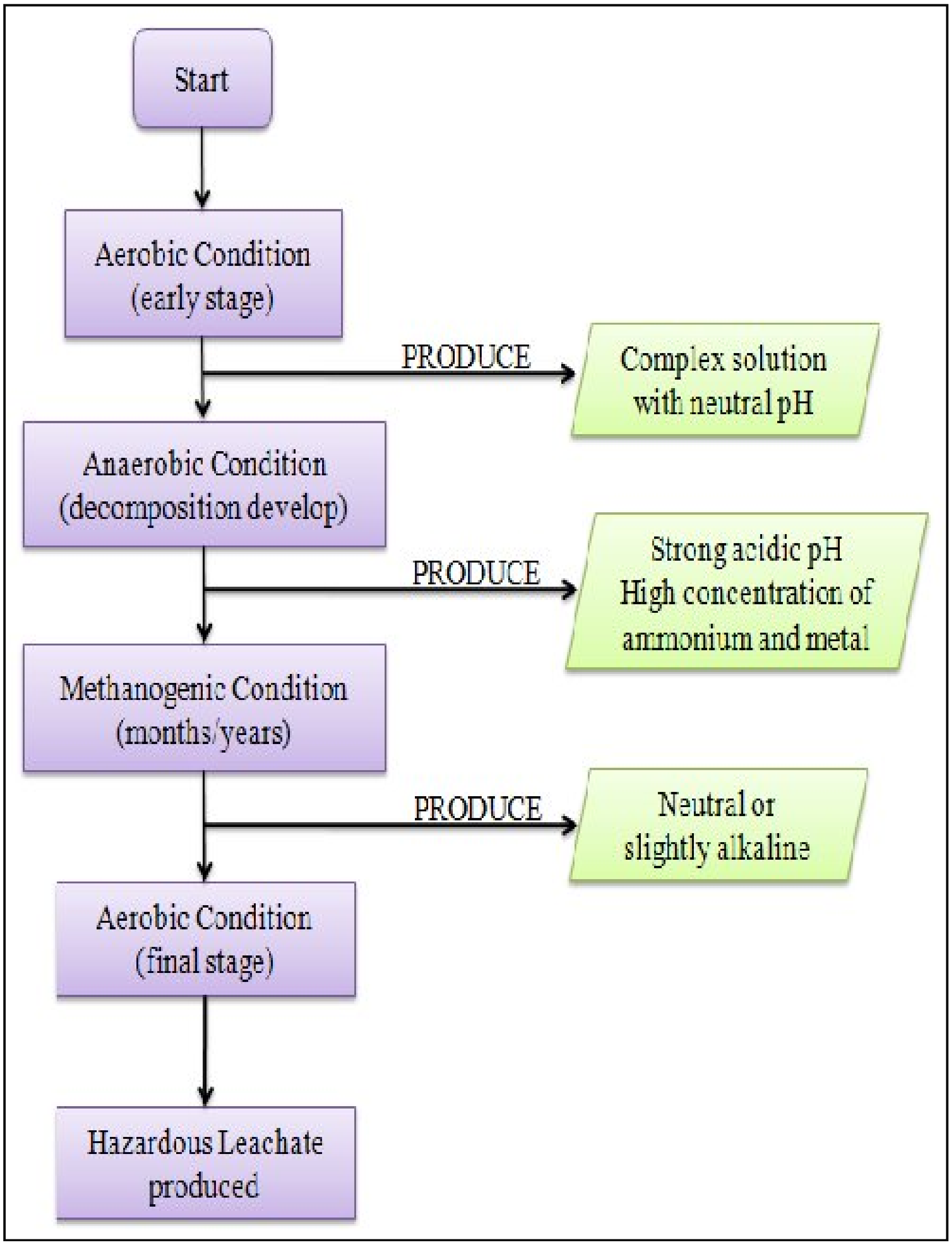

Figure 2.2: General leachate production stages in a landfill (Salem *et al.*, 2007).

2.2 Heavy Metal

The characteristics of the landfill leachate can usually be represented by the basic parameters; chemical oxygen demand (COD), biological oxygen demand (BOD), pH, suspended solids (SS), ammonium-nitrogen (NH_3-N) and heavy metals. Previous studies have mentioned that the age of the landfill and thus the degree of solid waste stabilization has significant effects on leachate characteristics. All of these parameters will become a basic guidance in performing the treatment for the leachate.

Heavy metal is one of the parameters in leachate that needs to be removed. Heavy metals are stable and tend to persist and accumulate in the environment. Heavy metals defined by Kaminski *et al*., (2008) are the metal whose density is greater than $5g/cm^3$. Examples of the metal are Fe, Cu, Zn, Pb, Hg, Cd, Cr, Se, and others. Heavy metal ions could pose huge danger to human life. They are easily transported from womb to embryo, overcome blood-brain barrier, can react with proteins and destroy nucleic acids (Kaminski *et al*., 2008). Knowing of the toxicity and danger associated with bioaccumulation and metals entering the food-chains have led to the growing of awareness of the importance of metal recovery and possible reuse for past two decades. Table 2.1 shows the heavy metal composition in landfill leachate on the selected country based on the age of the sanitary landfill.

There is tremendous need to control heavy metal emissions into the environment. Use of biological materials, including living and non-living micro-organisms, in the removal and possible recovery of toxic substances from industrial wastes, has gained important credibility during recent years. This is due to good performance, the availability and low cost of the materials. The natural affinity of biological compounds for metallic elements could contribute to the purification of metal-loaded wastewater (Shetty, 2006). Some of the traditional methods for heavy metal removal in wastewater are now extremely expensive and uneconomical especially for developing countries, where large volume of the waste are generated

(Volesky, 2001). Therefore, there is requirement for developing new technology and methods in wastewater treatment. Biosorption is a feasible option because of it is both efficient and cheap. Biosorption compared to other conventional methods, has low operating cost, minimization of volume of chemical and biological sludge to be disposed off and high efficiency in detoxifying very dilute effluents (Shetty, 2006).

Table 2.1: Heavy metal compositions in landfill leachate (Renou *et al.*, 2008).

Age	**Landfill Site**	**Fe**	**Mn**	**Ba**	**Cu**	**Al**	**Si**
Y	Italy	2.7	0.04	-	-	-	-
MA	Canada	1.28-4.90	0.028-1.541	0.006-0.164	-	<0.02-0.92	3.72-10.48
MA	Hong Kong	3.811	0.182	-	0.12	-	-
MA	South Korea	76	16.4	-	0.78	-	-
MA	Spain	7.45	0.17	-	0.26	-	-
O	Brazil	5.5	0.2	-	0.08	<1	-
O	France	26	0.13	0.15	0.005-0.04	2	<5
O	Malaysia	4.1-19.5	15.5	-	-	-	-
O	South Korea	-	0.298	-	0.031	-	-

Y: young; MA: medium age; O: old; all values in mgL^{-1}

2.3 Biosorption of Heavy Metal

Definition of biosorption is the accumulation and concentration of pollutants from aqueous solution by the use of biological materials thus allowing the recovery and/or the environmentally accepted disposal of the pollutants (Gray, 2004). A combination of active and passive transport mechanisms normally involve in biosorption. First, the metal ion diffuses to the surface of the cell walls of the micro-organism, and then it binds to the cell wall surface that exhibit some chemical affinity for the metal (Gray, 2004). Metal sequestration can occur by adsorption process, complexation, chelation, ion-exchange, and coordination. There are many different types of biosorbents available, such as:

- Active biomass belonging to algae, bacteria and fungi.
- Non-active kind of biosorbents which is essentially a waste product or byproduct of a fermentation process.
- Abundant natural materials or polymers.

Acetamido groups in chitin, amino and phosphate groups in nucleic acids, amino, amido, sulfhydryl and carboxyl groups in proteins and hydroxyls groups in polysaccharides are several chemicals groups in biomass that could potentially attract and sequester metal ions (Volesky *et al*., 1995).

Experimental biosorption equilibrium isotherms used for investigate the biosorptive metal uptake. Uptake of species by the sorbent involves steps that transfer the solute from the bulk of the liquid phase to certain sites on the sorbents (Guibal, 2004). On contact between the sorbent and the sorbed species, equilibrium is established at a given temperature. Certain amount of the metal species sequestered by the sorbent is in equilibrium with the residue left free in the solution (Shetty, 2006).