ADDIS ABABA UNIVERSITY
INSTITUTE OF TECHNOLOGY (AAIT)
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMICAL ENGINEERING

HORIZONTAL SUBSURFACE CONSTRUCTED WETLAND FOR REMOVAL OF HEAVY METALS FROM LEACHATE USING *Phragmites australis*

(A Case of Addis Ababa Solid Waste Open Dump)

By

Mesele Bahre Abrha

A Thesis Submitted to the School of Graduate Studies of Addis Ababa University in Partial Fulfillment of the Requirements for the Degree of Masters of Science in Environmental Engineering

Advisor

Eng. Teshome Worku (Ass.Prof.)

April, 2013

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Acknowledgement

Firstly, I would like to thank my advisor Eng. Teshome Worku (Ass. Prof.) for his invaluable suggestions and comments, as well as consistent encouragement throughout this research. I would also like to thank him for his unlimited help in every step of this thesis work.

Secondly, I would like to thank my sponsor, Wollo University for sponsoring my study.

Thirdly, I would like to extend my gratitude to all members of the Chemical Engineering Department for their help and support.

I would also like to thank the Department of Chemical Engineering, Department of civil engineering, Addis Ababa Environmental Protection Authority and JIJE Laboratory Plc. for providing me with laboratory facilities and genuine support.

Last but not least, a heartfelt thanks goes to my mother and my brothers for their patience, understanding, encouragement and warm support throughout my study.

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List of Abbreviations

AAiT	Addis Ababa Institute of Technology
APHA	American Public Health Association
BOD	Biological oxygen demand
COD	Chemical oxygen demand
CWs	Constructed Wetlands
FDREPCC	Federal Democratic Republic of Ethiopia Population Census Commission
HLR	Hydraulic Loading Rate
HRT	Hydraulic retention time
HSSF	Horizontal Subsurface Flow
FWS	Free water surface
IWA	International Wetland Association
SF	Surface flow
USEPA	United States Environmental Protection Authority

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Abstract

Heavy metals were present at relatively high concentrations in the landfill leachate. The disposal of heavy metals into the environment is of great concern due to their serious effects on food chain and furthermore on animal and human health. Constructed wetlands have played a significant role in treatment of domestic, agricultural and industrial wastewater containing heavy metals effectively. This study focused on the efficiency of horizontal subsurface constructed wetland with Phragmites australis in the removal of heavy metals in landfill leachate. Where, it also determines the amount of heavy metals uptake by Phragmites australis and the amount of heavy metals retained in the soil media. In this work a laboratory-scale study was conducted on HSSF constructed wetland systems which comprises one planted and one control system. The systems operated identically at a flow rate of 22L /d and HRT 4 days for about 28 days treatment period. The result shows the heavy metals composition of the leachate of "reppi" open dump was significant in both season with more slightly higher in wet season. The experimental study shows higher removal of heavy metals by the planted compared to unplanted system. A removal efficiency of 99.33% Fe, 93.67% Mn, 89.24% Pb, 96.14% Cu and 98.33% Zn were achieved in the planted system at the 28th day. While removal efficiency of 98.43% Fe, 91.66% Mn, 85.01% Pb, 90.70% Cu and 85.19% Zn were observed in the control system at the 28th day of the treatment period. The plants uptake of Pb and Cu were also analyzed. The results show that uptake on roots for both heavy metals were high comparing the uptake on leaves and stems. The ability of soil to accumulate Pb and Cu was analyzed. Soil samples were taken from the inlet, middle and outlet of control and planted system. The result shows that accumulation of Pb was highest on inlet part of both systems while accumulation of Cu was highest on the outlet part of both systems. This study concludes that HSSF constructed wetland with Phragmite australis plant and red ash gravel can remove heavy metals from leachate.

Keywords: Landfill leachate, Constructed wetland, heavy metals removal, Plant uptake, Soil media

1. Introduction

1.1. Background

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 tons of solid waste generated per year. If all of the trashes are not managed properly, they will pose a major threat to human, animals and the environment.

Large amount of solid waste is produced in most of the industrialized countries. Developing countries also produce a solid waste of quantity that is depends up on their lifestyle and development. Most of this waste is deposited in controlled sanitary landfills or dumped simply in open dump (Tesfaye, 2007). Leachate disposal is considered as one of the most difficult tasks associated with the operation of landfills. Organic and inorganic matter present in crude refuse and the products of decomposition can be leached by water, either rainfall or groundwater, passing through the wastes. This is a potential cause of serious water pollution. The containment and treatment of leachate may therefore be necessary, to avoid or minimize contamination of adjacent ground or surface water resources.

Addis Ababa Region, with 2.7 million inhabitants represents nearly 4.7% of the Ethiopian population according to the 2007 census. The city produces 0.4 kg of garbage per capita daily. The annual amount of MSW produced in Addis Ababa in 2001 was about 242,874 metric tons (Shewit, 2005). Municipal authorities have used many methods in managing the waste like Composting, incineration, open dumping, reuse and recycling are some example in managing waste. However, open dump is the most common method to manage solid waste in Ethiopia.

The use of landfill and open dump 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 (Bagchi, 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.

Several technologies are applied for the removal of heavy metals from wastewaters. Since most of the convectional wastewater treatment system are very energy intensive and expensive for developing countries; effective but simple, cheap and reliable, wastewater treatment alternatives are needed (Vymazal *et al*., 1998).

Being low cost and low technology system, eco-technological system like constructed wetlands are now standing as the potential alternative or supplementary system for treatment of municipal, industrial, agricultural wastewater, as well as storm water (Vymazal *et al*.,1998). Since the 1950's constructed wetlands have been used effectively to treat different wastewater with different configuration, scale and designs throughout the world. This was because of their nutrient capturing capacity, simplicity, low construction/operation and maintenance cost, low energy demand, process stability, little excess sludge production, effectiveness and potential for creating biodiversity (USEPA, 2000). Constructed wetland technology is much more spread in industrialized countries due to more stringent discharge standards, finance availability, change in tendency to use natural and/ or decentralized wastewater treatment system and due to existing pool of experience and knowledge based on the science and practical work (Korkusuz, 2004).

Even though the potential for application of wetland technology in the developing world is enormous, the rate of adoption of wetlands technology for wastewater treatment in those countries has been slow (Korkusuz, 2004). Recently, a variety of application for constructed wetland technology for water quality improvement were initiated in developing countries as a result of the transfer of the knowledge, technical collaboration and co-operation by developed countries (Kivaisi, 2001).

However, Denny (1997) critically discussed the implementation of the constructed wetland technology in developing countries by developed world advisors. He found that aid programs from developed countries tend to favor the more overt technology that have commercial spin-off for the donors. Additionally, he asserted that most of these advisors were unable to transfer their conceptual thinking to the realities and cultures of developing countries. Thus, rather than assisting developing countries to improve their own constructed wetland technologies, the tendency has been to translocate “northern” designs to tropical environments. Moreover, Gopal (1999) has identified the current limitation to widespread adoption of constructed wetland technology for wastewater treatment in developing countries as they have limited knowledge and experience with constructed wetland design and management.

In this regard, developing countries should carefully consider if the constructed wetland technology is an appropriate option for water quality enhancement for their countries. Clearly, these countries interested in implementing wetland technology must identify their own specific research needs and develop appropriate strategies based on local parameters (Kivaisi, 2001). Clear understandings of the biological, hydraulic and chemical process involved are essential (Denny, 1997). Most importantly, careful economic analysis must be conducted to determine whether constructed wetland treatment technology can be feasibly developed for a given project location or not (Gopal, 1999). In order to assess the feasibility of utilizing sustainable wetland technologies in developing countries, coordinated and multidisciplinary approach that involving environmental and social scientists, engineers and policymakers are required (Kivaisi, 2001).

Compared to conventional treatment system, constructed wetland technology is cheaper, more easily operated and more efficient to maintain. As a result implementing low technology systems like constructed wetlands can be a proper solution for treatment of different types of wastewater in Ethiopia.

1.2. Statement of the Problem

Unlined sanitary landfills and open dumps are well known to release large amounts of hazardous and venomous chemicals to nearby ground water, surface water, soil and the air, via leachate and landfill gas. It is known that such releases contain a wide variety of potential carcinogens and potentially toxic chemicals that represent a threat to public health.

According to Tesfay Zewdie (2007) there is a high risks associated with ground water pollution and public health near the Reppi solid waste dumping site. He found high concentration of heavy metals in the grand water near the dumping site. Hunchew Beyene (2011) also found that high concentration of heavy metals in the soil of the dumping site vicinity. Though high levels of heavy metals were reported in the ground water and soil near the dumping site, there is no any treatment method being practiced at the specific disposal site.

1.3. Significance of the Study

Leachate poses a number of environmental problems. This is due to variable types of waste and its composition. Leachate can contain high concentration of organic matters, nutrients and heavy metals. In the recent years the interest is more on natural system treatment. In this way, constructed wetlands represent a viable choice, offering extremely positive characteristics for treatment of the landfill leachate, as a good removal of heavy metals; great capacity of nitrifying-denitrifying, with consequent lowering of high concentrations of ammonia typical of landfill leachate; sensible reduction of the volume of the leachate, due to high evapotranspiration bring by plants, and consequently sensible reduction of the costs of an eventual further treatment of the leachate. This treatment can be used and practice widely by municipal authorities in order to control and reduce pollution posed by leachate from the sanitary landfill or open dump.

2. Objectives of the Study

2.1. General Objective

The main objective of this work was to study the removal of heavy metals from leachate by HSSF constructed wetland using *Phragmites australis* plants and volcanic soil-gravel.

2.2. Specific Objectives

The specific objectives of this study were:

- To characterize the raw leachate in terms of heavy metals (Fe, Mn, Cu, Ni, Pb, Zn and Cd).
- To determine heavy metals removal efficiency of the HSSF microcosms constructed wetland.
- To determine the ability of *Phragmites australis* to uptake selected heavy metals (Cu and Pb).
- To determine the ability of volcanic soil to retain selected heavy metals (Cu and Pb).

3. Literature Review

3.1. The Source and Fate of Heavy Metals in Landfills

Many heavy metals are problematic environmental pollutants, with well-known toxic effects on living systems. Nevertheless, because of their useful physical and chemical properties, some heavy metals, including mercury, leads, and cadmium, are intentionally added to certain consumer and industrial products such as batteries, switches, circuit boards, and some pigments. Many products containing heavy metals are disposed in municipal solid waste or hazardous waste landfills. Recently, there has been an increase in the use and disposal of electronic devices such as cell phones, mp3 players, and computers, raising questions about the fate of these devices, and the metals they contain, in landfills. These products typically contain lead, cadmium, mercury, arsenic, copper, zinc and other heavy metals and rare earth metals (Aucott, 2008).

Metals in landfills can be found in many different forms, depending on the characteristics of the product that contains the metal and the landfill environment, except for mercury which is more volatile than the others. If heavy metals escape from a landfill, they are likely to do so primarily in the aqueous form, via landfill leachate or runoff which is not successfully captured by the leachate collection system. It can be expected that situations in landfills that favor the formation of oxidized compounds would lead to some, perhaps significant, dissolution of some heavy metal-containing compounds in leachate. However, the organic matter present in landfills is likely to have some capacity to absorb heavy metals and other cations (Aucott, 2008).

The landfill environment depends on the climate, drainage, and other characteristics. The environment also changes over the years as the waste decomposes. There are no measurements that provide conclusive information on the long-term fate of metals in landfills because data are available extending back in time no more than about 60 years. Thus, the knowledge is limited to experiments that try to mimic landfill conditions and models that predict changes that are likely to occur over decades or centuries in landfills and what these changes might mean to the fate and possible transport of metals. As time passes and organic matter decomposes, landfills may trap metals to a lesser degree or release previously bound metals. However, research suggests that there are other substances likely to be present in these later stages that would adsorb at least a portion of the metals (Aucott, 2008).

3.2. Characteristics of Selected Heavy Metals

Among the most common heavy metals detected in leachate are: lead (Pb), copper (Cu), chromium (Cr) and cadmium (Cd) (Aucott, 2008). Because of high toxicity of these metals, it is necessary to remove them from runoff before they reach the receiving water body, due to their high toxicity.

In order to apply appropriate treatment it is necessary to understand the nature of heavy metals in water and their environmental and health impact. This section gives insight of the chemistry, environment and health impacts of lead and copper.

3.2.1. Lead

Lead is a main element of group 14 with symbol Pb (Latin: plumbum) and atomic number 82. It is a bluish-white metal of bright luster, very soft, highly malleable, ductile, and poor conductor of electricity. Lead has the highest atomic number of all stable elements (West *et al*., 1987). Lead can be found in nature as: $PbCO_3$(s) (cerussite), PbS(s) (galena), and $PbSO_4$(s) (anlesite). Concentration of lead in natural waters may range from <1.0 to 890 μg/l (Faust and Aly, 1998). Physico-chemical speciation of lead indicates there is little or no free ionic lead present in drinking water. Depending on the composition of water a significant portion of lead is bound to colloids, either hydrous iron oxides or organic macromolecules. A substantial fraction is non-ion-exchangeable (Moore and Ramamoorthy, 1984).

It is well known that lead is very resistant to corrosion. It was already used in Roman Empire for making pipelines and it is still used today. Lead is usually used as metal or in its dioxide form (for the storage batteries). As metal it is also used for cable covering, plumbing, ammunition, and in the manufacture of lead tetraethyl, used as an antiknock compound in gasoline. In metal form it is very effective as a sound absorber; it is used as a radiation shield around X-ray equipment and nuclear reactors, and is used for vibration adsorption. For different purposes, lead is also used in building construction (West *et al*., 1987).

Environmental and Health Impacts

The sources of lead in urban storm-water runoff are numerous. Important sources for lead are building sites and atmospheric deposition (Davis *et al*., 2001). Close to the sources of lead, ecosystems show a wide range of harmful effects like losses in biodiversity, changes in community composition of plants and animals as well as neurological effects in vertebrates (Valavanidis and Vlachogianni, 2008). For centuries people are aware of the toxic properties of lead. People are exposed to lead in various quantities that can be found in food, air, and water. Care must be taken in handling lead, as it is a cumulative poison. The largest deposits of lead, once it is absorbed by the body, are in the bones followed by the kidneys and liver. Infants and young children are particularly sensitive to even low levels of lead (Sarkar, 2002). The Maximum Contaminant Level Goal (MCLG) for lead in drinking water is zero (Faust and Aly, 1998).

3.2.2. Copper

Copper is a chemical element with the symbol Cu (Latin: cuprum) and atomic number 29. Copper is reddish colored, takes on a bright metallic luster, and is malleable, ductile, and a good conductor of heat and electricity (second only to silver) (West *et al*., 1987).

In aquatic environments, copper can exist in three broad categories: particulate, colloidal and soluble form. The dissolved phase can contain both, the free ion as well as copper complexes with (in) organic ligands. The physico-chemical and hydro-dynamic characteristics, as well as the biological state of the water determine speciation of copper in natural waters (Moore and Ramamoorthy, 1984). In naturally occurring compounds copper is most often found with a valance of +2 (cupric). It can also be found in its pure metallic state (+0), as well as with +1 valence (cuprous). Less common, it is +3 charges in complexes. In aquatic solutions, Cu(II) ions are more stable than in other oxidation states (Cotton *et al*., 2000).

Environmental and Health Impacts

Important sources of copper identified in urban stormwater runoff are building sites, vehicle brake emission, and atmospheric deposition (Davis *et al*., 2001). Despite universal toxicity at high concentrations, the 2^+ copper ions at lower concentrations are an essential trace nutrient to all higher plant and animal life. In animals, as well as humans, it is found widely in tissues, with higher concentrations in liver, muscles, and bones (Aucott, 2008).

Copper is an essential nutrient for humans and animals, with an adult recommended daily allowance of 2 to 3mg/day. In ionic form copper is absorbed from the gastrointestinal tract and lungs, and to a lesser degree, through the skin. Following absorption, copper is distributed to all parts of the body, especially the liver. There is no clear relationship between chronic exposure to copper and copper toxicity in adult mammals probably because of homeostatic mechanisms. The purpose of these mechanisms is to maintain a baseline copper level in the body and protect mammals from the adverse effects of different copper levels (Aucott, 2008).

Copper ion exhibits high acute and high chronic toxicity to aquatic organisms, which can result in the death of the organism. The aquatic toxicity of copper ion is depends on water quality factors such as acidity, presence of organic substances, calcium, and carbonate. Toxicity decreases as water hardness (concentration of calcium carbonate), alkalinity or total organic carbon content increases. The MCLG for copper is 1.3 mg/l in drinking water (Faust and Aly, 1998).

3.3. Conventional Technologies for the Removal of Heavy Metals

There are several methods known for the removal of heavy metals from urban leachate. In continuation, review of literature on some of the methods and techniques recommended for the removal of heavy metals is presented (Rich and Cherry,1987).

Reverse Osmosis: It is a process in which heavy metals are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is expensive.

Electrodialysis: In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane.

Ultrafiltration: They are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge.

Ion-exchange: In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages include: high cost and partial removal of certain ions.

Chemical Precipitation: Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage.

Adsorption processes: involves an inter-phase accumulation or concentration of substances at a surface or interface. The process can occur at an interface between any two phases, such as liquid-liquid, gas-liquid, gas-solid, or liquid-solid interface. The material being concentrated or adsorbed is adsorbate and the adsorbing phase is termed as adsorbent. Adsorption from solution onto a solid occurs as the result of one of the two characteristic properties for a given solvent-solute-solid system, or a combination thereof.

- The primary driving force for adsorption may be a consequence of lyophobic (solvent-disliking) character of the solute relative to the particular solvent.
- A high affinity of the solute for the solid.

For the majority of water and wastewater treatment systems, adsorption results from a combined action of the two forces.

3.4. Wetland

Constructing a correct and complete definition for a constructed wetland is not an easy task. As a result there are many different terms for description of wetland systems, but the most widely accepted definition was developed by the International Union for the Conservation of Nature and Natural Resources (IUCN) in the Ramsar convection, in 1980. According to this convection, wetlands are defined as ‘’any areas of swamp, pond, peat or water, natural or artificial, permanent or temporary, stagnant or flowing water, including estuaries and marine water, the depth of which at low tide does not exceed six meters.” (Mitsch, 1986).

Wetlands, which exist in every climate from the tropics to the frozen tundra and on every continents except Antarctica and which comprise 7.7% of the Earth’s landscape, or in other wards a total surface of 11.65 million km^2 (Patten, 1990), mean different thing to different people with different backgrounds. To some, they are important habitats for numerous kinds of waterfowl and fish whereas to other they are the” kidney of the earth”. Sometimes they have been called as “biological supermarkets” for the extensive food chain and rich biodiversity they support (Mitsch, 1986).

3.4.1. Constructed Wetland

As a result of the exponentially increasing demands of human expansion and resource exploitation, it has been recognized that natural wetland ecosystems cannot always function efficiently for desired objectives and stringent water quality standards. These and many other factors have led to the rapid development of constructed wetlands for waste water treatments by scientists and engineers (Wetzel, 1993).

Constructed wetlands are engineered systems designed to simulate natural wetlands to exploit the water purification functional value for human use and benefits. Constructed wetlands consist of former upland environments that have been modified to create poorly drained soils and wetlands flora and fauna for the primary purpose of contaminant or pollutant removal from wastewaters or runoff. Constructed wetlands are essentially wastewater treatment systems and are designed and operated as such even though many systems do support other functional values (Hammer, 1992).

According to EPA Constructed wetlands may be used for primary, secondary and tertiary treatment of wastewaters from different origins. It has been demonstrated that CW can successfully improve the quality of municipal and domestic wastewater as well as agricultural and industrial wastewater like landfill leachate, petrochemicals, food waste, pulp and paper and mining if a typical adequate pre-treatment method is used (Kadlec, 2000).

3.4.1.1. Types of Constructed Wetland

A selection among different types of constructed wetlands should be done based on the required treatment (i.e. secondary or tertiary treatment), mass loading, the available land, climate conditions and accessible financial support.

Constructed wetlands have been classified based on the water flow regime, in two types of systems, which are distinguished by the location of the hydraulic grade line (USEPA, 2000).

3.4.1.1.1. Surface Flow Wetlands

This type of treatment system is composed of earthen (sand, stone, mud, clay) basins planted with emergent wetland vegetation (rooted). The basins are shallow, the water stream flows crosswise surface at a depth ranging from 15-50 cm. The depth of flow depends mainly upon the vegetation type but also other factors might play an important role. The bottom slope has to be flat from side to side (USEPA, 2000).

The treatment processes in those systems are based on the activities of micro-organisms like fungi and bacteria which bloom in this favorable environment. A big group of organisms attaches to submerged plant roots and stems while other turn out to be part of the soil/plant root matrix. There are also different microorganisms found in the water column (USEPA, 2000). This type of treatment system resembles wetlands which can be found in nature. In FWS flow velocities are lower and HRT is increased like in natural wetlands (Ran, 2004). The cross section of surface flow wetlands (also known as free water flow wetlands) is presented in Figure 3.1.

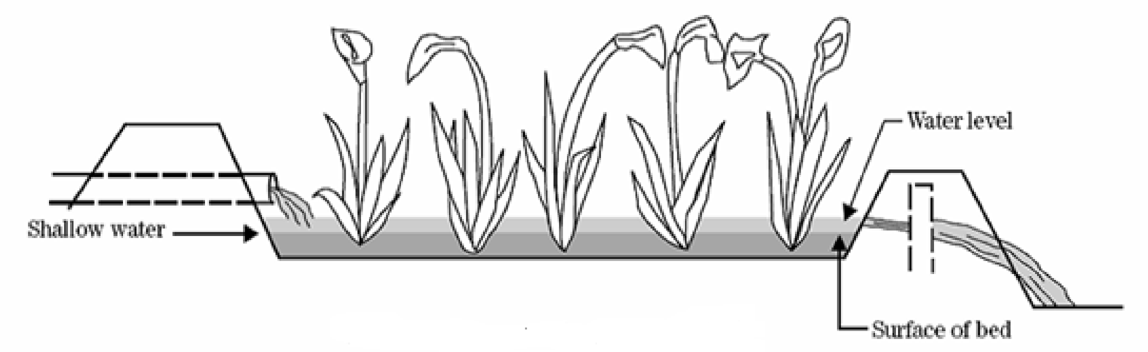

Figure 3.1 Surface flow wetland Source (USEPA, 2000)

3.4.1.1.2. Subsurface flow wetlands

The main part of a subsurface flow wetland is a bed of rock, gravel, soil or another type of media through which wastewater flows. The placement of the bed takes place below ground level so that the wastewater enters the bed at approximately mid-depth. The vegetation in this type of wetland consists of emergent, hydrophytic plants. The plants are planted at the surface of the wetted area but their roots become widespread also in the saturated bed. As bed material for implanting the root cuttings a thin layer of wood chips, pine straw or some other bedding may be used. In some cases there is a high risk of migration of wastewater from the subsurface wetland to adjacent soils or in to ground water, in those cases it is recommended to use impermeable fabricate linear. This can also prevent infiltration of ground water into the substrate matrix in case of seasonal fluctuations of the water table (USEPA, 1993).

The surface of water in those systems should be kept at a level just below the surface of the bed. An important factor for the proper functioning of subsurface systems is the hydraulic gradient of the wastewater passing through the substrate material. The hydraulic gradient depends on the daily average flow of wastewater, the bottom slope and the porosity of the filling material. A miscount of these factors may cause a drop of the water level below the roots or inversely an inundation and the ponding of water on the surface (USEPA, 2000).

There are mainly two types of flow direction in this system. These are Horizontal flow (HF) and Vertical flow (VF). Horizontal systems are more common and because of that there is a larger knowledge base. Vertical flow systems are commonly used in mining applications. Wetland systems are best suited for small to moderate sized applications and at larger systems where the risks of public contact, mosquitoes, or potential odors are major concerns. Their use for on-site systems provides a high quality effluent for in ground disposal, and in some States a significant reduction in the final disposal field area is allowed. SF wetlands will reliably remove BOD, COD, and TSS, and with sufficiently long detention times can also produce low levels of nitrogen and phosphorus. Metals are removed effectively and about a one log reduction in fecal coliforms can be expected in systems designed to produce secondary or advanced secondary effluents (USEPA, 2000).

The treatment processes in SSF wetland system is more efficient than in the SF wetland system; because the media provides a greater number of small surfaces, pores and crevices where treatment can occur. Waste consuming bacterial attach themselves to the various surfaces, and waste materials in the water become trapped in the pores and crevices on the media and in the spaces between media. Chemical treatments also takes place as certain waste particles contact and react with the media (USEPA, 1993).

The biological treatment in SSF wetlands is mostly anaerobic, because the layers of media and soil remain saturated and unexposed to the atmosphere (Sinclair, 2000). However, wetland plants are able to grow extensive roots even in these anaerobic conditions. The area where the roots grow is called root zone and usually includes the upper 0.15 to 0.40 meter of media. If cells are alternated or allowed to rest periodically, or if the water level is regularly cycled, the roots can reach throughout the media layer (Pottir and Korathonasis, 2001).

The SSF type of CW is thought to have several advantages over the SF type since the water surface is maintained below the media surface with little risk of odors, and insect vectors (Vymazal, 2002). In addition, it is believed that the media provide greater available surface area for treatment than the SF concept. Consequently, the treatment responses may be faster in SSF type, which is smaller in area than a SF system designed for the same wastewater conditions (USEPA, 1993).

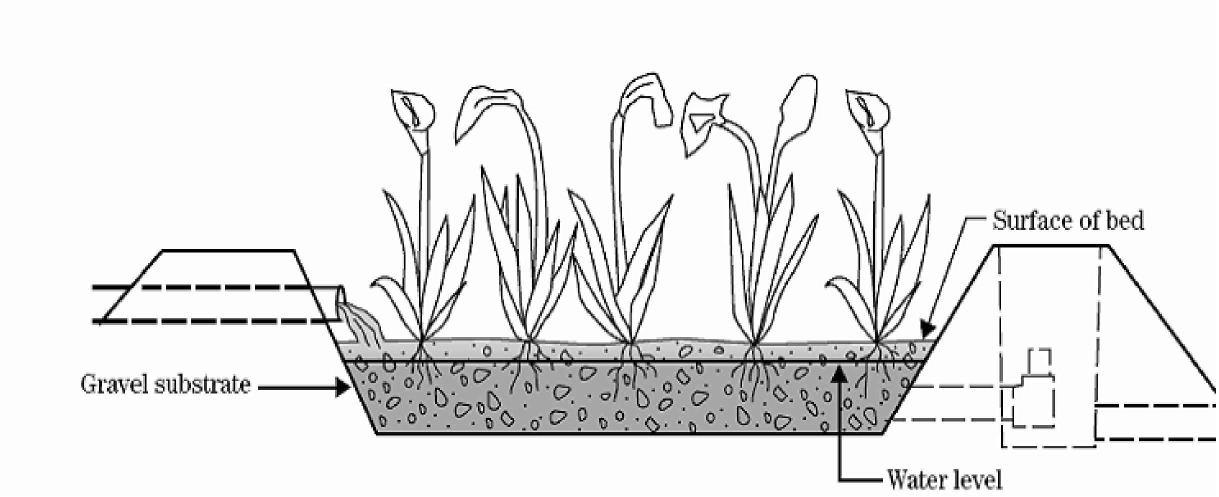

Figure 3.2 Subsurface Flow Wetland: Sources (USEPA, 2000)

3.4.1.2. Components of Constructed Wetland

Wetlands consist of basic components such as underlying strata, water, hydric soil, detritus and macrophytes (vegetation). However, other important components of wetlands such as the communities of microorganisms and aquatic invertebrates develop naturally. Water, soil and vegetation are basic components for the characterization of a wetland (IWA, 2000).

The understanding of the components is useful for the manipulation of constructed wetland. Constructed wetlands are wastewater treatment methods that mimic natural wetlands processes by utilizing the components to cleanse water. However, wetland processes are among the most complicated sets of soil and water chemistry, plant and hydrology interactions occurring within any ecosystem on earth. The underlying strata are unaltered organic, mineral or lithic strata which are usually saturated with or impervious to water and are below the active rooting zone of the wetland vegetation (Campbel and Ogden, 1999).

Water : Wetlands are areas where water is the primary factor controlling the environment and the associated plant and animal life. They occur where the water table is at or near the surface of the land, or where the land is covered by shallow water. A wetland can be built almost anywhere in the landscape by shaping the land surface to collect surface water and by sealing the basin to retain the water. All wetland soils must be hydric - saturated with water for at least part of the growing season. Hydrology is the most important design factor in constructed wetlands because it links all of the functions in a wetland and because it is often the primary factor in the success or failure of a constructed wetland (USEPA, 1993).

Small changes in hydrology have fairly significant effects on a wetland and its treatment effectiveness because of the large surface area of the water and its shallow depth, a wetland system interacts strongly with the atmosphere through rainfall and evapotranspiration. The density of vegetation of a wetland strongly affects its hydrology, first, by obstructing flow paths as the water finds its sinuous way through the network of stems, leaves, roots, and rhizomes and, second, by blocking exposure to wind and sun (USEPA, 2000).

Substrate: Substrates (also called aggregates or wetland media) used to construct wetlands include soil, sand, gravel, rock, and organic materials such as compost. Soil is the main supporting material for plant growth and microbial films in constructed wetlands. The soil matrix has a decisive influence on the hydraulic processes. Soils consist of unconsolidated, natural material that supports or is capable of supporting plant life. The upper limit contains air, and the lower limit is either bedrock or limit of biological activity. Soils are generally divided into two different types - mineral and organic. Soils can be further categorized based on the amount of moisture present. Under wetland conditions, soils are considered to be hydric, i.e., saturated, flooded, or ponded long enough during the growing season to develop anaerobic conditions in the upper portion of the soil (ITRCWT, 2003).

Hydric soils are developed under conditions sufficiently wet to support vegetation typical to wet areas (hydrophytic vegetation) (ITRCWT, 2003). The physical and chemical characteristics of soils and other substrates are altered when they are flooded. In a saturated substrate, water replaces the atmospheric gases in the pore spaces and microbial metabolism consumes the available oxygen. Since oxygen is consumed more rapidly than replaced by diffusion from the atmosphere, substrates become anoxic (without oxygen) (USEPA, 2000). A mixture of sand and gravel is recommended to improve hydraulic condition and the removal of contaminants (IWA, 2000).

Wetland plants: Wetland plants enhance the treatment process of wetlands in several ways such as filter wastes, regulate flow, provide surface area for microbiological treatment, provide shed and control algae growth, contribute oxygen to the cells, take up and store some of metals and nutrients from the wastewater (Sinclair, 2000).

Then the presence of wetland plants has been hypothesized to play a key role in wastewater remediation (IWA, 2000). In addition to their aesthetic roles, wetland plants exhibit several properties which enhance wastewater treatment processes and thus make them an essential component of the treatment wetland. These properties influence wastewater treatment through physical effects such filtration, adsorptions followed by sedimentation, provision of surface area for the growth and attachment of microorganisms and shed the water surface and regulating of the undesirable water temperature as well as surplus algal growth (Sinclair, 2000).

Metabolically, plants take up pollutants; produce organic carbon and oxygen thereby improving the quality of water. Plants in wetland systems have been viewed as storage compartments for nutrients where nutrient uptake is related to plant growth and production. Emergent plants utilize their roots to obtain sufficient nutrients from wastewater. Free floating species have roots with numerous root hairs and successfully obtain nutrients from both the water column and substrate (USEPA, 1988).

They often grow in gravel beds to stimulate uptake and create suitable conditions for the oxidation of the substrate, thereby improving the ability of the system to treat wastewater (Njanu and Mlay, 2000). This needs consideration of plant selection and management techniques that create rhizosphere surface area per volume of bed and bed design; optimal depth, HRT and media of constructed wetland (Muhammad, 2004).

If the wetland plant is intended as a major oxygen source for nitrification in the system, then the depth of the bed should not exceed the potential root penetration depth for the plant species to be used. This will ensure availability of some oxygen throughout the bed profile, but may require management practices which assure root penetration to these depths (Sinclair, 2000).

From the standpoint of wastewater treatment, certain plant species appear to be more efficient in CW treatment systems and others may be more tolerant of high pollutant concentrations. It appears that major contribution from the vegetation in SSF system is service of the root/rhizome structure as a substrate for microbial activity and is a limited oxygen source for nitrification (Vigneswaran*et al.*, 2004).

Plant species selection has impacts on sedimentation, plant nutrient accumulation and on the creation of favorable environment for microorganism that facilitates microbial degradation of contaminants. Furthermore, plant species selected for constructed wetland systems should be hydrophyte plants that are suitable for local climatic conditions and tolerant of the concentration of nutrients and other constituents in the wastewater stream and selected for their treatment potentials. Preference shall be given to native wetland plant materials collected or grown from materials adapted to local conditioning (USEPA, 1988). Some examples of macrophytes that are mostly used in constructed wetland systems are reeds, bulrushes, water hyacinths, cattails, duckweeds, Cyprus papyrus, Cyprus alternifolia and lilies (USEPA, 1993).

The root zone of aquatic plants is also primary site for pollutant uptake and transformation as it is a zone of oxygen transfer between the plant and sediment microbial activity and pollutant oxidation. This also will be depending on the potential root penetration depth and root mat structure of the plant species (USEPA, 1988).

Microorganisms: Microbes which live virtually ubiquitously in soils are the key player in wetlands. In any wetland, the ecological food web requires microbes, to function in all of its complex transformations of energy. In a constructed wetland, the food web is fueled by influent wastewater, which provides energy stored in organic molecules. Microbial activity is particularly important in the transformations of nutrients into varying biologically useful forms (USEPA, 2000).

Microorganisms that naturally live in water, soil, and on the roots of wetland plants feed on organic materials and/or nutrients thus reducing, breaking down or completely removing a wide variety of contaminants from the wastewater. Functions of wetlands are largely regulated by microorganisms and their metabolism (Wetzel, 1993). Microorganisms have a capability of destructing contaminants because they possess enzymes that allow them to use environmental contaminants as food and because they are so small that they are able to contact contaminants easily. The microbial community associated with the plant rhizosphere creates an environment, which enhances the degradation of many volatile organic compounds. Constructed wetlands depend on the indigenous microorganisms in presence of sufficient oxygen and nutrients to break down hydrocarbons and other organic contaminants (Hilton, 1993).

Microbial populations adjust to changes in the water delivered to them. Populations of microbes can expand quickly when presented with suitable environment and energy-containing materials. When environmental conditions are no longer suitable, many microorganisms become dormant and can remain dormant for years (Hilton, 1993). Microbial performs very important activities in wetlands such as; transforming a great number of organic and inorganic substances into innocuous or insoluble substances, alters the reduction-oxidation conditions of the substrate and thus affects the processing capacity of the wetland, and is involved in the recycling of nutrients (USEPA, 2000). Many microbes are capable of functioning under both aerobic and anaerobic conditions (facultative anaerobes) in response to changing environmental conditions. In aerobic respiration, microbes use O_2 to oxidize part of the carbon in the contaminant to carbon dioxide (CO_2), with the rest of the carbon used to produce new cell mass (USEPA, 2000). Transformation of organic contaminants by microorganism normally occurs because of the utilization of contaminants for their own growth and reproduction. Organic contaminants serve two purposes for the organisms: they provide a source of carbon, which is one of the basic building blocks of new cell constituents, and they provide electrons, which the organisms can extract to obtain energy (Stottmeister, 2003).

Microorganisms will gain energy for growth and reproduction by catalyzing energy-producing chemical reactions that involve breaking chemical bonds and transferring electrons away from the contaminant. The energy gained from these electron transfers is then "invested," along with some electrons and carbon from the contaminant; to product more cells (Pottir and Korathonasis, 2001).

However, microorganisms do not always gain energy from degradation of contaminants; instead, degradation may be an incidental reaction, commonly referred to as "secondary utilization" or "co-metabolism", where the presence of primary substrates to support microbial metabolism is required (Stottmeister, 2003).

3.4.1.3. Mechanism of Metals Removal in Constructed Wetlands

The removal of contaminated in constructed wetland is very complex phenomena, but the major physical, chemical and biological process of metal removal in constructed wetlands includes: sedimentation, filtration, adsorption, complexation, precipitation, cation-exchange, plant uptake, and microbial mediated reaction especially oxidation (Wattson*et al.*, 1989)

Metals occur in either soluble or particulate associated forms, with the former representing the most bioavialable form particularly when the metal is present as either an ionic or weakly complexed species. The distribution between particulate and dissolved phases is determined by physic-chemical process such as sorption, precipitation, complexation and sedimentation (Kadlec and Wallace, 2009).

Trace metals have a high affinity for adsorption and complexation with organic material and are accumulated in a wetland ecosystem (Kadlec and Wallace, 2009). Although some metals are required for plant and animal growth in trace quantities (such as barium, beryllium, boron, chromium, cobalt, copper, iron, magnesium, manganese, nickel, selenium, sulphur, molybdenum and zinc), these same metals can be toxic at higher concentrations. Other metals such as arsenic, cadmium, lead; mercury and silver have no known biological role, and can be toxic at even lower concentrations (Valavanidis and Vlachogianni, 2008).

Adsorption and Cation Exchange

Adsorption involves the binding of particles or dissolved substances in solution to sites on the plant or matrix surface. In a cation exchange reaction, positively charged metal ions in solution bind negatively charged sites on the surface of the adsorption material. The attractive force for cation exchange is electrostatic; the size of this force depends on a wide range of factors. A cation in solution will displace a cation bound to a site on the surface of a material if the electrostatic attraction of the site for the dissolved cation exceeds that of the bound cation. The cation exchange capacity (CEC) of a material is a measure of the number of binding sites per mass or volume.

The CEC value has been shown to be the same whether the plant is alive or dead. Wetlands sediments and soils also have large CEC values. The adsorption of metals in the surface of soils is therefore a significant process in treatment wetlands. The CEC of wetlands depends on the material of construction selected (Kadlec and Wallace, 2009).

Microbial Mediated Processes

The wetlands can be differentiated into two zones: aerobic and anaerobic. The presence of metal oxidizing bacteria in the aerobic zones and sulphate reducing bacteria in the anaerobic zones, which cause the precipitation of metal oxides and sulphates respectively, has been established by Batal*et al.*, (1987)(Cited in: kadlec and Wallace,2009). Generally the following equation by describe the biological oxidation of ferrous iron *Thiobacillus ferrooxidans,* followed by the subsequent precipitation of iron hydroxide, is considered the most important iron removal mechanism in wetlands treating metal rich mine wastewater. In balanced equation form:

$$4FeSO_4 + 2H_2SO_4 + O_2 \longrightarrow 2Fe_2\,(SO_4)_3 + H_2O \qquad 3.1$$

$$2Fe_2\,(SO4)_3 + 12H_2O \longrightarrow 4Fe\,(OH)_3 + 6\,H_2SO_4 \qquad 3.2$$

Similar chemistries and limited investigation suggest similar oxidations for many other metals including nickel, copper, lead, zinc, silver and gold.As a result, wetlands plants can potentially stimulate the growth of metal-oxidizing bacteria by oxygen transfer into the rhizosphere(Cooper and de Maeseneer, 1996).

Microbial mediated sulphate reduction consumes sulphate ions and produces hydrogen sulphide and alkalinity in the form of bicarbonate ion. In balanced equation form, where `CH_2O' represents a simple organic molecule:

$$SO_4^{2-} + CH_2O \longrightarrow H_2S + HCO_2 \qquad 3.3$$

The H_2Sdissolves and ionizes to give sulphide ions, which react with a range of metal ions to produce metal sulphide precipitates. Precipitation of metals assulphides rather than oxides has the following advantages: alkalinity produced by sulphate reduction helps to neutralize acidity; sulphate precipitates are denser than oxide precipitates; sulphides are precipitated within the origanic sediments and so are less vulnerable to disruption by sudden surges in flow (Kadlec and Wallace, 2009).

Filtration

Vegetation and the soil media can assist in metal removal by aiding the direct filtration of particulate matter. Macrophyte species with high plant surface areas have been shown to be very effective at retaining metal hydroxide particles that have precipitated out of solution (IWA, 2000).

Plant Uptake

Some wetlands species have a well-established ability for direct uptake of heavy metals. Unfortunately, accumulation can become sufficient to kill the plant within just one growing season. Fortunately, some species such as *Typhalatifolia* and *Phragmitesaustralis* have a species-wide constitutional tolerance for heavy metals and do not accumulatemetals to toxic levels. The presence of an iron plaque in plant root system decreases the uptake of metals by the root hairs, but it has been suggested plant forming an ionic plague has an advantage due to adsorption and immobilization of the metals by the iron plague (IWA, 2000). Numerous studies from natural as well as constructed wetland s have shown that the highest concentration of metals are found in the plant roots whereas the lower concentrations are found above ground parts i.e in stem and leaves (Vymazal, 1995).

It should be noted that direct uptake is an active process, requiring the plant to be alive. Plant matter liberates its metal content on decomposing. Harvesting of the foliage would only minimally assist metal in the above ground parts of the plants.It is preferable to allow litter to form, as this can provide new sites for metal removal and thermal insulation (Vymazal and Kropfelora, 2008).

3.4.1.4. Hydrology of Constructed Wetlands

The hydrology of constructed wetlands is the most important factor in their effectiveness. Hydrologic considerations include climate, hydroperiod, hydraulic residence time, hydraulic loading rate, groundwater exchanges (infiltration and exfiltration), losses to the atmosphere + (evapotranspiration) and overall water balance (Pfafflin and Ziegler, 2006). The hydroperiod is a result of the balance of inflow, outflow and storage in the system and depends further on seasonal differences in precipitation and evapotranspiration. Evapotransporation (ET) decreases the hydraulic loading and will not contribute to surfacing. Precipitation dilutes pollutants in the system, temporarily raises the water level and decreases the HRT while ET concentrates pollutants, temporarily lowers the water level and increases the HRT. The overall water balance for a constructed wetland is an account of the inflow, storage and outflow of water.

The wetland water balance is important for determining conformance with desired limits for HLR, HRT and mass balances during design and operation. A simple water balance equation for a constructed wetland is expressed as equation 3.5 (USEPA, 2000).

$$\frac{\mathrm{dV}}{\mathrm{dt}} = Q_i - Q_o + \mathrm{P} + \mathrm{I} - \mathrm{ET} \qquad 3.4$$

Where, $\mathrm{Q_i}$ = Influent wastewater flow rate,$\frac{\mathrm{m^3}}{\mathrm{d}}$

$\mathrm{Q_o}$ = Effluent wastewater flow rate,$\frac{\mathrm{m^3}}{\mathrm{d}}$

P = Precipitation, $\frac{\mathrm{m^3}}{\mathrm{d}}$

I =Net infiltration (infiltration less exfiltration)

ET =Evapotranspiration,$\frac{\mathrm{m^3}}{\mathrm{d}}$

V = Volume of water, $\mathrm{m^3}$

t = Time, d

The hydraulic residence time (HRT) is defined as the average residence time during which the water remains within the wetland system. In subsurface flow systems, the “reactive” volume is defined as the volume of water in the media in consideration of the void fraction that is defined as the fraction of the total media volume through which water can flow. The void fraction, also termed media porosity, ranges usually from 0.3 - 0.5 depending on the media material chosen

(Vymazal, 1998). If short circuiting occurs, the actual HRT can be less than the theoretical one which can result in lower removal efficiencies. To meet advanced treatment standards in surface flow as well as in subsurface flow wetlands, the HRT can be 3-8 days. A hydraulic retention time of at least 6 to 8 days recommended ensuring an adequate nitrification rate (Brovelli, 2010). It can be calculated from equation 3.6 (USEPA, 1993).

$$\mathrm{HRT} = \frac{\mathrm{L\ x\ W\ x\ n\ x\ d}}{\mathrm{Qav}} \qquad 3.5$$

Where, $\mathrm{L} =$ Length of wetland(m)

$\mathrm{W} =$Width of wetland (m)

$\mathrm{n} =$Media porosity

$\mathrm{d} =$Water depth (m)

$\mathrm{HRT} =$Hydraulic retention time(d)

$\mathrm{Q_{av}} =$Average flow rate,$\frac{\mathrm{m^3}}{\mathrm{d}}$

The hydraulic loading rate (HLR) refers to the loading on a water volume per unit area over a specified time interval. It is defined as the volumetric averaged flow rate divided by the wetland surface area. Typically, hydraulic loading rates are specified in cm/day or mm/day. It depends on media material, which is a critical parameter for subsurface flow wetlands, flow rate, area-size and the resulting hydraulic residence time. A hydraulic loading rate of 0.2$\mathrm{m^3/m^2}$/day provides for maximum treatment efficiency (Heers, 2006). Because high organic loading will cause anaerobic conditions, and plants die off. Therefore, the maximum organic loading rate for both type of systems (SF and SSF) should not exceed (1.12 mg $\mathrm{BOD_5/cm^2}$.d) (Pfafflin and Ziegler, 2006). Hydraulic loading rate (HLR) is calculated from equation (3.7).

$$\mathrm{HLT} = \frac{Q_{av}}{A_s} \qquad 3.6$$

Where, Q_{av} = Average flow rate ($\frac{\mathrm{m^3}}{\mathrm{d}}$)

$\mathrm{A_s}$ = Surface area of wetland ($\mathrm{m^2}$)

3.4.1.5. Heavy metals Treatment Performance of Constructed Wetland

Deferment research has been made to evaluate the performance of constructed wetland in removing heavy metals over the entire world by different researchers. The following are some summary of performance of constructed wetland in removing heavy metals which are sited in Hui, 2005.

- Muna Mohamed (2003) reported the metal removal efficiency SSF constructed wetland with S. *globulosus* and *E.sexangulare* in treating leachate. The removal efficiency of Zn, Ni, Cu, Cr and Pb were 89.81%, 81.33%, 86.57%. 88.35% and 94.19%, respectively for S.globulosus. While for E.sexangular were 86.91 %, 77.59%, 83.8787%, 86.11% and 95.88%, respectively.
- Peverly et al., (1995) reported the heavy metal accumulation of reeds in SSF constructed wetland. He found that heavy metals were not translocated to and accumulated by the shoots or rhizomes but exhibited elevated level in roots. The rhizosphere provided a particularly effective, locally oxidized environment for metal precipitation and adsorption outside the roots. Roots and /or their iron coatings acted as filters for metal movement into rhizomes and tops.
- Refidah B. H. (2002) reported the removal efficiency of heavy metals of SF constructed wetland with S.sumantrensisana S.mucronatus in treating leachate. He found, the removal efficiency of Fe, Zn and Mn were 89%, 90% and 89%, respectively for *S. sumantrensis*. While for *S.mucronatus* were 85%, 90% and 91%, respectively (cited in, Hui, 2005)
- El-gendy (2003) reported the removal efficiency total iron of FWS constructed wetland with water hyacinth and salvinia in treating landfill leachate were 84 % after 21 day treatment period.
- Krishnan (2002) found high concentration of zinc, iron and manganese in the roots of *Scrirpu smucronantus* in SF constructed wetland with *Scrirpu smucronantus* and *Sccleria sumantrensis Reth*. In treating leachated.
- Lee (2004) found that the uptake of *Typha angustifolia* for Chromium and cadmium were 91.7% and 81.8% in SSF constructed wetland with *Typha angustifolia* in treating leachate for about 27 days treatment period with three days retention time.

In addition to the above Kamarudzaman N.A. (2011) also studied Removal of Heavy Metals from Landfill Leachate Using Horizontal and Vertical Subsurface Flow Constructed Wetland Planted with *Limnocharis flava*. He reported that the highest removal efficiency of Fe and Mn were 99.2% and 99.8 %, respectively for the HF constructed wetland for 45 days treatment period with 3 day retention time.

3.4.1.6. Constructed Wetland as Leachate Treatment Technology

Treatment and disposal of liquid leachate is one of the most difficult problem associated with use of sanitary landfills for disposal of solid waste. The highly variable nature of solid waste, difference in age and decomposition, and the diversity of chemical and biological reactions that take place in the land fill result in wide range of chemical quality of the leahate. Wetland treatment of the leachate is an alternative method of water quality improvement. The volumetric flow of leachate is often fairly small, compared to other wastewaters such as domestic, industrial and urban or agricultural runoff. Thus, long detention times are possible for small wetland-land fill area ratios (Kadlec and Wallace, 2009).

Alternatives to wetlands are extremely costly by comparison, usually; the target pollutants can be more completely removed, but only with the expense of multistep processes involving chemical engineering technology. Those competing processes that have strong tendency to create large operations and maintenance requirement are onerous for remediation that is anticipated to last for many decades. The passive wetland alternative, with low or non-existent replacement costs better life cycle prospective (Vymazal and Kropfelora , 2008).

The use of constructed wetlands to treat landfill leachate is a rapidly developing technology, with both subsurface and flow wetland and surface flow wetlands. Subsequently, wetland treatment of landfill leachates has been successfully tested at the several locations. Extensive studies of a very wetlands receiving leachate in Florida demonstrated that the ecosystem could easily absorb all leachate constituents (Kadlec and Wallace, 2009).

4. Materials and Methods

4.1. Materials

Materials used during the study to achieve the overall objectives were: two sedimentation thanks (120L each) which served as pretreatment and storage of the leachate for the given retention time, Rectangular Wooden material used for the construction of wetland basin, Black plastic used as lining for the wetland to prevent infiltration, Two receiver tanks (30L each) used for receiving of the effluent from the each wetland basin, Sample collector of plastic bottles-used to collect sample for laboratory analysis, Galvanized pipes (1.27cm diameter) and plastic pipe (1.27 cm diameter) - used for the supply, distribution and collection of the leachate, Gravel (15-25mm diameter): used as soil media and *Phragmites australis* as wetland plant species.

Equipment used during the study are: Atomic Adsorption Spectrophotometer (AAS) both flame and graphite which was used for analysis of heavy metals, Aluminum weighing dishes, glass fiber filter disks, suction flask, Membrane filter funnel, crucible, filter paper (45um), measuring cylinder (50Mland100mL), Analytical balance (accuracy 0.001g), desiccators, beaker (100mL), pH meter (Wagtech N374,M128/03IM,USA) which was used for the measurement of pH of the raw as well as treated leachate. Oven (SRJX-5-13 model box resistance furnace control box)-used for drying soil and plant tissue , BUCHI Digest Automat K- 438- used for soli digestion,/ BUCHI wet Digester B- 440-used for plant tissue digestion.

4.2. Methods

4.2.1. Description of the Study Area

This study was conducted in Addis Ababa City (Figure 4.1) solid waste disposal site from May 8, 2012 to January 10, 2013. The city is the capital of Ethiopia which covers an area of 540 square kilometers and situated between 9^o North and 38^o East in a plateau ranging from 2200-2800 meters of altitude above sea level. The average annual relative humidity of the area is 60.7% with an average monthly rainfall of 1089 mm (Cecilia and Junestedt, 2008). In 2008 the population of the city was around 3 million with a population density of 5,165.1/km^2 (FDREPCC, 2008). The daily per capita solid waste generation was 0.4 kg, where 76% originated from households, 18% from institutions, commercial, factories, hotels and the remaining 6% from street sweeping, with a composition of 60% organic, 15 % recyclables and

25% (Tessema, 2010). The Repi Landfill site is located in the south-western part of Addis Ababa in Lafto- Nifas-Silk KifleKetema (Fig.4.1). In 1960s, the site was considered to fall outside of the city's master plan since it was inhabited by only a few Farmers. The municipal administration of Addis Ababa started to use the site in 1964 (Yirgalem, 2005). Currently the municipal administration of Addis Ababa selected new landfill out of the city which is known as Chebi-weregenu sanitary landfill which is located north-east of the city and can be accessed via Addis Ababa -Dessie road. This landfill site is located at downstream of Legedadi. The site is found in a flat land (table land) between 2400-2600m above sea level with a mean annual precipitation and temperature of 1186mm and 16.2^{o}c, respectively (MOMGSE, 2010).Currently the Repi open landfill is in the process of closure. The French company took a contract to collecting the leachate and producing biogas. During the study they were collecting the leachate to one point by burring perforated PVC pipe.

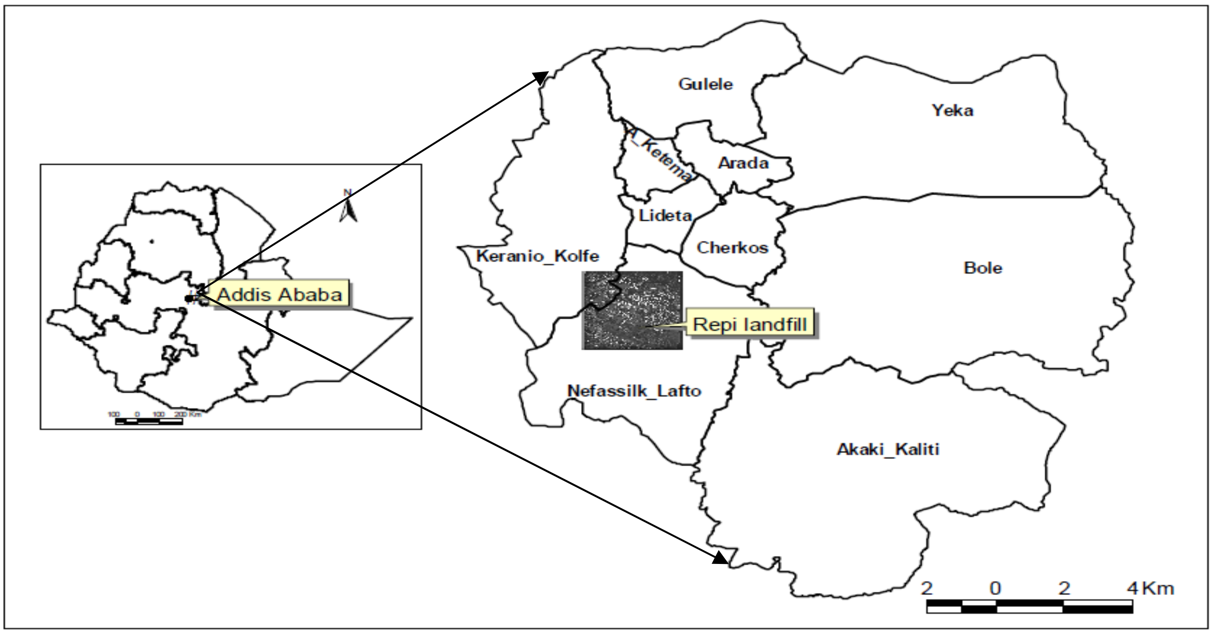

Figure 4.1: Location Map of the city of Addis Ababa and Repi landfill Site

Source: (Yirgalem, 2005)

4.2.3. Sample Collection

Before any experiment can be run in the constructed wetlands, leachate sample need to be collected. For this study, raw leachate sample was taken from 'Repi' open landfill using 10 containers (200 litter) every collection trips. Before run the experiments, sample was taken from the out let of the temporary pond which is excavated by the French company for production of biogas, during dry (May 8, 2012) and rain season (July18, 2012) in order to characterize the leachate in terms of metals. The grab samples were taken for selected heavy metals analysis every 4 days (HRT=4days) from one common inlet and outlet of the planted and unplanted basin for about 28 days. Putting in mind the assumption that wastewater fed at a given day will come out of the system after 4 days. The samples were collected using sterile plastic sampling bottles and transported to the laboratory for analysis.

Figure 4.2 Outlet of the temporary pond

Soil sample was taken before and after the experiment for analysis of selected heavy metals (Cu and Pb). Cu and Pb were selected based on environmental risk and standards for analysis in the sediment. This was conducted by taking a sample before the soil is used and after the soil is used from both the planted and unplanted wetland basin means at termination of the study to identify the initial and final heavy metals composition of the soil. At the termination of the experiment sample was taken from three points of planted basin (A1, A2 and A3) and from three point of control basin as shown in Figure 4.3.

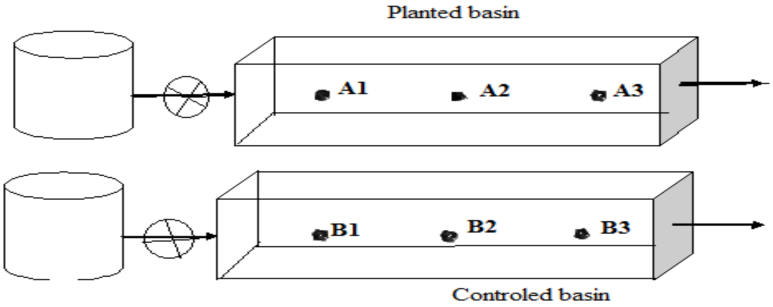

Figure 4.3 Soil Sampling Points

Plant tissue sample was taken before and after termination of the experiments by harvesting the plant’s leaves, stems and roots for Cu and Pb analysis. Then, washed with tap water and distilled water.

4.2.4. Experimental Set up

The experiments were conducted using two lab-scale HSSF Microcosms constructed wetland systems at Addis Ababa Institute of Technology Compound. One system was planted with *Phragmits species,* while the Control system is without plants. Each system consists of a wetland reactor, a feeding pipe, distribution pipe and settling tank, that are designed based on necessary information obtained: porosity (0.5), average flow rate (22 l/d), retention time (4 days) and width to length ratio (3:1).

The microcosms were constructed by wooden material with a dimension of 1.22 meter length, 0.4 meter width and 0.4 meter depth (surface area of 0.5m^2). Plastic liner was used as impermeable layer to avoid treated water infiltration in to the ground, it was mandatory to use impermeable materials which would block the flow of water out of the system other than the outlet. After lined by plastic the wetland basin was filled by red ash gravel and planted with *Phragmites australis* species aquatic plants.

In this study, the media used in the SSF constructed wetlands are red ash gravel with 15-25 mm diameter and porosity of 50%. After making sieve analysis to find the required size of the gravel, the gravels were cleaned first by washing with tap water before putting into the HSSF wetland basin to free from debris which can block the flow of leachate through the media. The water table in the bed was controlled and maintained 1cm under the media surface by an adjustable outflow pipe leading into a receiving tank.

Figure 4.4 Prepared Red Ash Gravel

In this study, *Phragmits australis* were used as aquatic plants. *Phragmits australis* were collected from Lake Ziway which is located in the southern region of Ethiopia (165 Km from Addis Ababa). The wetland is planted by hand. The planting densities were 8 plants of *phragmits australis. These* plants were selected as the wetland plants because of their local availability (available at nearest study area), easy to control and maintain, and have capability to survive with leachate constituents.

The hydraulic Retention Time (HRT) was selected to be four days. Two- seven days of HRT is recommended for horizontal subsurface wetland (USEPA, 2000). After selection of HRT the average flow rate (Q_{av}.) of the wetland was calculated by using Darcy’s formula (USEPA, 1993).

$$\mathrm{HRT} = \frac{\mathrm{L\ x\ W\ x\ n\ x\ d}}{\mathrm{Qav}} \qquad 4.1$$

Where, L = Length of wetland(1.22 m)
W =Width of wetland (0.40 m)
n =Media porosity (50 %)
d =Water depth (0.36 m)
HRT =Hydraulic retention time(d)

$$Q_{av} = \text{The average of the inflow and outflow } (Q_{av} = Q_{in} = Q_{out})\ (21.96 = 22\frac{L}{d})$$

The porosity of the media was measured to establish a nominal retention time for the wetland. The measurements were done on gravel size of 15-25mm which was used for horizontal sub-surface wetland. In a bucket 5 liters of water was added. The surface level was marked on the bucket wall and the water poured out. Then gravel was added up to the mark, and the bucket was shaken to make sure the carriers were packed as much as possible. Then water was added up to the mark, and the volume (2.5L) was registered as the water was being poured. The porosity was calculated by dividing the volume of water *with* the gravel, by the volume without them (5 liters) and it is 50%.

The valve installed at storage tank was adjusted to control the flow rate of the leachate and to make sure the entire tank were fed with leachate influent at a constant flow rate (21.96 L/d). The daily flow rate was adjusted and checked manually using a measuring cylinder and a stopwatch. The HSSF wetland was elevated to allow gravity follow.

After the transplantation, the wetland reactors were loaded with tap water to establish the emergent plant for about one month. The duration it takes for the acclimatization process depend on the readiness of the plant for the actual experimental procedure which is illustrated by the healthy leaves and stem and also by the growth of new leaves and inflorescence. After acclimatization the wetland basins were fed with different proportion of tape water to leachate (90:10, 75:25, 50:50, 25:75 and 10:90) for twenty days with four days duration for each proportion in order to prevent short shock.

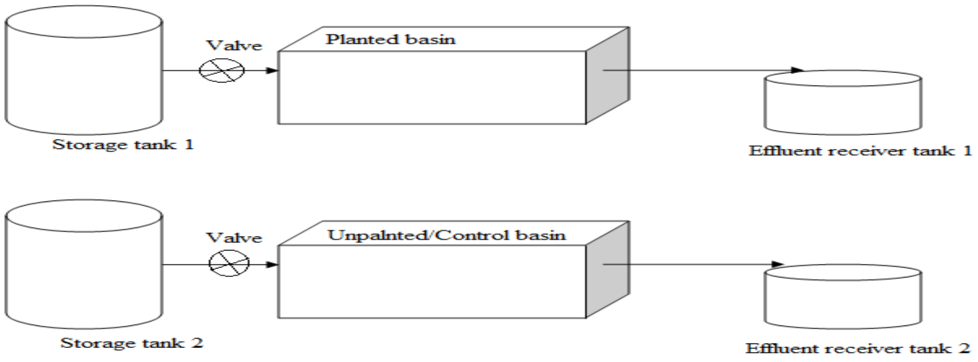

Figure 4.5 Setup of the experiment

Figure 4.6 Photo of the experimental setup

4.2.5. Sample Analysis

Analysis of heavy metals was done on plant tissue of *Phragmite australis*, red ash soil and leachate. All the laboratory analysis was done in Addis Ababa EPA laboratory, JIJE LABOGLASS Pvt. Limited Company and AAiT of chemical and civil engineering department's laboratories.

4.2.5.1. Analysis of Heavy Metals in Leachate

pH was determined using a pH Meter and total heavy metal concentrations were analyzed using AAS (Atomic Absorption Spectrometry). Before analysis, the sample was immediately preserved by acidifying with nitric acid (HNO3) to pH < 2. The sample was transferred to a volume of 100ml beaker then 5 ml concentrated HNO3 was added, and it was brought to a slow boil evaporate by putting on hot plate until it decreased to 20ml before precipitation occurred. The heating and adding of concentrated nitric acid was continued until digestion is completed. After digestion was completed, the sample was filtered through $0.45\mu m$ membrane paper and the filtrate was transferred to 100ml volumetric flask (APHA, 1998). The filtrate was then analyzed for total heavy metals using Atomic Absorption Spectrophotometer (AAS).

4.2.5.2. Analysis of Heavy Metals in Plant Tissues

Analysis of selected heavy metals (Cu and Pb) on the leaves stems and roots of *Phragmitesaustralis* harvested sample were made using wet digestion method. The plant samples were dried in oven at

105°C for 24 hour, and the dry weight of each component was measured. The samples were then ground with mortar and pestle to a fine powder. And 1 g of the ground plant sample was put inside the conical flask 250 ml and 50 ml of 2 M hydrochloric acid was added in for plant digestion. The sample mixture was then shaken overnight with orbital shaker. After that, the mixture was centrifuged for 20 minutes and filtered with cellulose acetate membrane 0.45 µm (Plank, 1992). The filtrate was then analyzed for heavy metal (total lead and copper).

4.2.5.3. Analysis of Heavy Metals in Soil Media

The analysis of heavy metals (Cu and Pb) on the soil composition was conducted to determine the ability of the soil to retain heavy metals. Prior to the AAS analysis, the soil samples were oven dried at 105°C overnight, grinded and sieved to obtain soil samples size of less than 70µm. 1g of soil samples were transferred in to Kjeldahl Digestion tube having model of BUCHI Digest Automat K- 438.To this 12ml of aquaregia (3:1 of HCl 37% to (70%) HNO_3) were added and the mixture was digested on a Kjeldahal Digestion apparatus fitting the flask to a reflux condenser by setting the temperature first to 180 degree Celsius for the first 30 minutes and then raised to 240 ^{o}c for next 30 minutes and finally raised to 270 ^{o}c for the remaining 2 hours (Wilson et al.,2005). After digestion was completed, the sample was filtered through $0.45\mu m$ membrane paper and the filtrate was transferred to 100ml volumetric flask then the samples were analyzed using Atomic Absorption Spectrophotometer (AAS).

4.2.6. Data Analysis

Statistical analysis was performed with SPSS version16.00 for windows. This included Mean, Standard Error, and one way t-test was done using this package. T-test has been used to reveal significant differences between planted and control constructed wetland. Statistical significance differences were tested at P<0.05 (95% levels of significance). P–value less than 0.05 were considered as statistically significant.

The removal efficiency of the HSSCW for each heavy metal was calculated using:

$$\text{Removal efficiency} = \frac{C_i - C_e}{C_i} \times 100 \qquad 4.2$$

Where: C_i: is the concentration of the heavy metal in the influent,C_e is the concentration of the heavy metal in the effluent.

5. Results and Discussion

5.1. Raw Leachate Heavy Metal composition

Raw leachate analysis for heavy metals and pH were undertaken during dry and wet seasons and the result are shown in Table5.1. It can be observed that the leachate sample exhibited high concentration of heavy metals in dry and wet seasons. Hence, the highest concentrations of iron, copper, lead, manganese, and zinc were found to be 29.433mg/l, 2.711mg/l, 0.480mg/l, 1.700mg/l and 1.503mg/l respectively in wet season. Moreover, the standard deviations were relatively small in both cases. This indicates that there is no significant variation of heavy metals concentration within the season.

Table 5.1 Heavy metals composition of leachate

Parameters	**Dry season**	**Wet season**
Fe (mg/l)	21.210 ± 1.65	29.433 ± 1.85
Mn (mg/l)	0.633 ± 0.08	1.700 ± 0.13
Pb (mg/l)	0.440 ± 0.10	0.480 ± 0.21
Cu (mg/l)	2.657 ± 0.01	2.711 ± 0.06
Ni (mg/l)	ND	ND
Zn (mg/l)	0.900 ± 0.60	1.503 ± 0.29
Cd (mg/l)	ND	ND
pH	7.850 ± 0.05	8.17 ± 0.24

Note: ND= Not detected

Leachate collected during wet period has shown higher concentrations of heavy metals particularly, for lead, iron, manganese, copper and zinc except for nickel and cadmium, which were not detected in both seasons. This could be attributed to surface water ingress into the landfill that promotes solubilization of heavy metals from actively decomposing waste mass into leachates emanating from the landfill site (Campbell, 1993). Similar result was observed in Nigeria by Aluko *et al*., (2003). High concentration variation of Fe was observed between dry and wet seasns compared to Cu and Pb. This indicates that Fe may found as water exchangeable and oxides that can easily washed out by the surface water ingress in to the soil waste while Cu and Pb may found as carbonate and sulfate fraction which are strongly bounded.

As lead is acutely hazardous substance, significant concentration was observed. The probable source of lead is industrial waste from companies that manufacture batteries and lead-based paints and from combustion of leaded petrol that results in lead collecting in surface water bodies. Lead-chloride batteries and household detergents rubble were evident in the landfill.

High mean concentration of copper (2.657 mg/l and 2.711 mg/l in dry and wet seasons, respectively) indicate that the existing practice of disposing electrical waste like copper contain wires and other electronic appliances. High mean concentrations of iron (21.21 mg/l and 29.433 mg/l in dry and rain wet seasons, respectively) in leachate indicate that scrap metal waste from foundry, machining, car breaking and heavy metalwork engineering firms and steel materials are dumped on the landfill. This result concurs with Al-Yaqout and Hamoda (2003) who reported that iron is a common metal in municipal landfill leachate and is responsible for the reddish-brown colour of leachate that may change the groundwater colour. The landfill soil is reddish-brown, indicating presence of ferric iron.

Table 5.1 also shows that the pH of the leachate ranges from 7.8 to 7.9 in dry season and from 7.83 to 8.41 in wet season. This is typical of samples from aged wastes. Alkaline pH (>7) is normally encountered at landfills 10 years after waste disposal (SWANA, 1997).

5.2. Heavy Metals Removal Efficiency

Heavy Metals are frequently associated with leachate (Aucott, 2008). The metals which are most commonly occured in landfill leachate are iron, copper, lead, zinc and manganese, which are the contaminant of concern in this study. Wetland system is often served as sinks for contaminants, and there are many cases in which wetland plants are utilized for removal of pollutants, including metals. The removal efficiency of the above heavy metals is discussed below separately.

5.2.1. Iron

Influent of iron (Fe) concentration ranges approximately 30.13mg/l to 32.23mg/l while the final effluent concentration in each system was 0.211mg/l for planted and 0.492mg/l for control system at the 28th day of the treatment period. Figure 5.1 illustrates the overall removal efficiency of Fe for planted and control systems. The removal efficiency ranges from 68.69% to 99.33% and from 55.91% to 98.43% in the planted and control system, respectively with in the 28 days of study period. This result complies with the finding of (Kamarudzaman *et al*., 2011).

In this study it can be observed that both systems show significant removal efficiency but planted was observed to have higher removal efficiency as compared to the control constructed wetland. One way t-test showed that there is a significant difference ($p<0.05$) in removal efficiency of Fe between Planted and control systems.

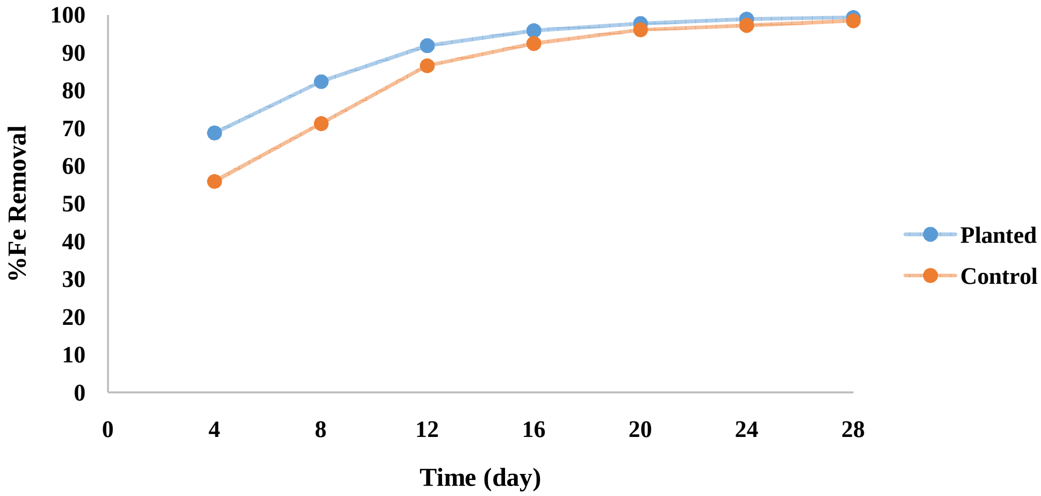

Figure 5.1 Removal efficiency of Fe in control and planted constructed wetland

From the results, it can be explained that Emergent plants can help in reducing heavy metals by retaining it in either their roots or in the leaves. Plants species have variety of capacity in accumulating and removing heavy metals. Uptake and accumulation of elements by plants may follow two different paths, i.e., the root system and foliar surface (Vymazal and Kropfelora , 2008). The results indicated that *Phragmites australis*could accumulate significant amount of Fe concentration. Wetland plants, however, can influence metals removal and storage indirectly through their effects on hydrology, sediment chemistry and microbial activity.

Both planted and control systems achieved high Fe removal percentage at the end of the 28th period. The significant heavy metals removal in the Control system probably, was due to the clogging of the substrate in soil sediment. So, the reduction of heavy metal concentration in the Planted and Control system were most likely attributed to the chemical precipitation and sorption on sediments.

Other possible removal processes include precipitation as metal hydroxides in the aerobic zone. It is also believed that an external aerobic microzone can be established around parts of the growing roots (Vymazal and Kropfelora, 2008). As a result, iron is precipitated.

5.2.2. Manganese

Influent of manganese (Mn) ranges approximately 1.643 to 1.670 mg/L while the effluents at the end of treatment period was 0.104 and 0.137mg/L for planted and control systems, respectively. As it has been demonstrated in Fig. 5.2, the highest removal efficiency was 93.67% for planted system and 91.66% for the control system at the end of treatment period.

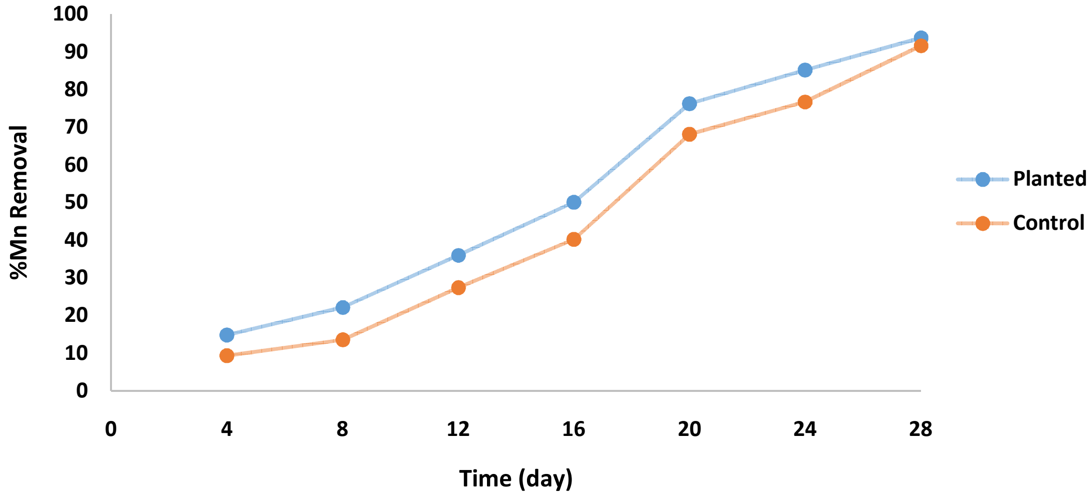

Figure 5.2 Removal efficiency of Mn in control and planted constructed wetland

In this study it can be observed that all wetland system managed to subsequently reduce the concentration of Mn to significantly low concentrations after 28 days of treatment period. The control system (unplanted) also demonstrated high reduction of heavy metals which is more than 90% removal. The reduction of heavy metals in the HSSF wetland system was may be due to settling and sedimentation, uptake by algae and bacteria, precipitation as insoluble salts, and binding to soil, sediments and particulate (Kadlec and Wallace, 2009).

However, the reduction of Mn in control system still showed lower removal as compared to the planted system. One way t-test showed that there is a significant difference ($p<0.05$) between planted and control systems.

Plants species have variety of capacity in accumulating and removing heavy metals. Several processes are envisioned as being effective in pollutant reduction; for example Mn are taken up by plants, and in many cases stored preferentially in the roots and rhizomes (Kadlec, 1999). Since it is vital to plant photosynthesis and is used as an enzyme cofactor for respiration and nitrogen metabolism by plants.

In wetland sediment, manganese can form soluble complexes with bicarbonate, sulfate, and organic compounds. Under reducing conditions, manganese forms insoluble complexes with carbonate, sulfide, and hydroxide, whereas, under anaerobic conditions, manganese is typically quite soluble. Manganese sulfide (mineral form alabandite) is stable only at very high pH and high concentrations of Mn(II). However, the carbonate has been postulated for anaerobic removal in some wetland systems ($MnCO_3$) (Wildeman *et al*., 1993).

5.2.3. Lead

Figure 5.3 shows the overall removal of Pb for both planted and control constructed wetland system within 28 days of treatment period. The influent concentration ranges from 0.523 mg/l to 0.567 mg/l. Effluent concentrations from constructed wetland system ranges from 0.0061 mg/l to 0.285 mg/l and 0.085 mg/l to 0.312 mg/l for planted and control system, respectively. The maximum removal efficiency has reached 93.55% and 85.61% for planted and control system, respectively at the end of treatment period. Removal of lead in HSSF systems is highly variable with removal efficiencies between -220% and 98% and the median removal of 25%. However, most data available from SSF constructed wetlands are from the systems treating municipal sewage where lead is not the target and the inflow concentrations are usually very low as compared to mine drainage waters (Kadlec and Wallace, 2009). According to Song *et al*., (2001) (Cited in Hui, 2005) higher removal efficiency (>90%) of Pb can be achieved by constructed wetland with retention time of 4.5 days.

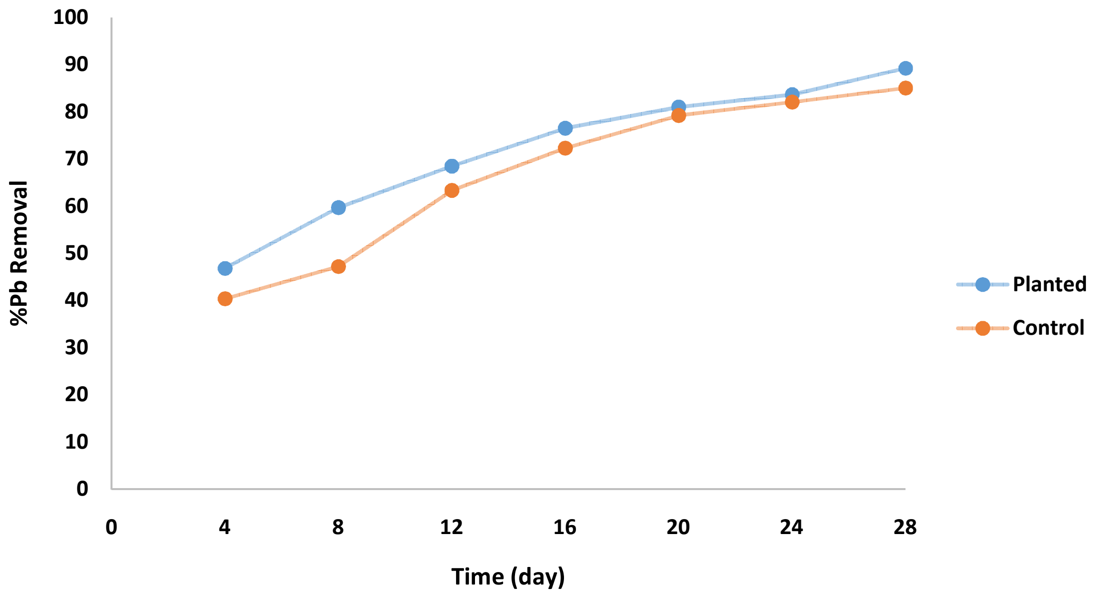

Figure 5.3 Removal efficiency of Pb in control and planted constructed wetland

As can be seen from figure 5.3 the trend in the removal of the lead analyzed increased with time in both planted and control system, but the planted system showed slightly higher removal of Pb than the control system. Simple t-tests indicated that there is significant difference ($p<0.05$) between planted and control system. A different researcher observed that removal of heavy metals is higher in planted than in control (Kadlec and Wallace, 2009).

Constructed wetlands have the potential to trap and remove lead contained in wastewater. Long-term removal is expected to occur by accumulation and burial in the sediments. Even though, the majority of total lead in wetland waters is usually bound to dissolve organic matter, but some fraction is associated with incoming particulate matter, as a result, particulate lead is subject to removal with total suspended solids, by processes of settling and trapping (Kadlec and Wallace, 2009).

Lead can also form very insoluble compounds with sulfide, sulfate, and carbonate, among others: Sulfide is formed by SRB in the anaerobic zones of treatment wetlands, while incoming sulfate persists in aerobic zones. If a source of sulfate is present in the incoming water, the wetland can be configured to provide a sustainable supply of sulfide. Carbonates are ubiquitous in wetlands environments. Lead may partition to organic constituents in the wetland sediments, ortoinorganic substrates, such as oxyhydroxides of iron and manganese (Kadlec and Wallace, 2009). Plants play important roles in constructed wetland for the removal of lead by accumulation in tissues and facilitate biological and chemical reaction by providing oxygen (IWA, 2000). However, these mechanisms are complex and not yet entirely understood.

5.2.4. Copper

Figure 5.4 shows the overall removal of Cu for both planted and control constructed wetland system within 28 days of treatment period. The influent concentration ranges from 2.640 mg/l to 2.667 mg/l while effluent concentrations from constructed wetland system ranges from 0.103 mg/l to 2.132 mg/l and 0.248 mg/l to 2.310 mg/l for planted and control system, respectively. The highest removal efficiency achieved was 96.14% and 90.70% in planted and control system respectively.

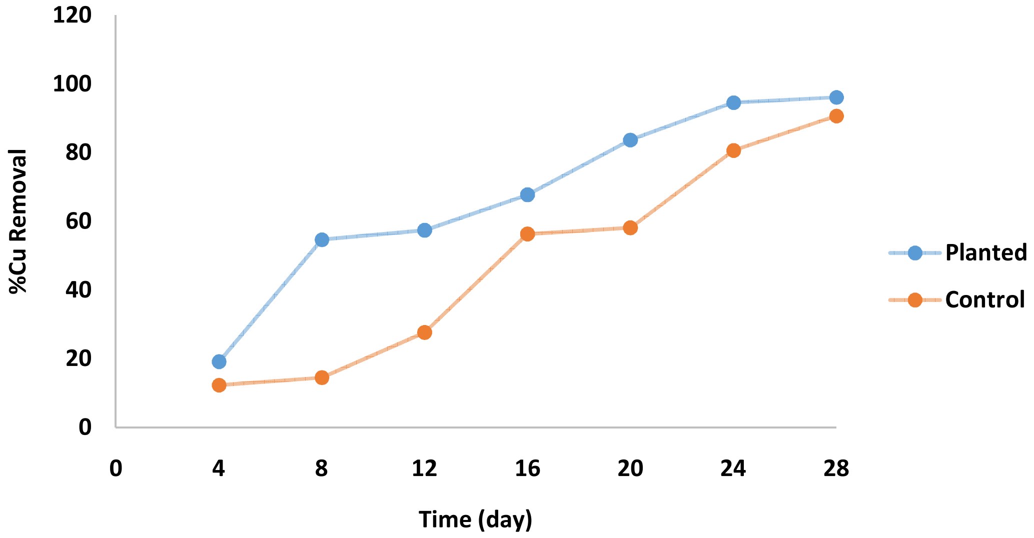

Figure 5.4 Removal efficiency of Cu in control and planted constructed wetland

The result indicates that the removal of lead increased with time in both planted and control systems, but the planted system showed greater removal of lead than the control one. One way t-test indicated that there is significant difference ($p<0.05$) in removal of Cu between planted and control system. This may be due to the role of *Phragmites australis* because Copper is an essential micronutrient for plants, plants require minimal amounts of this element (Wetzel, 1983). Additionally, *Phragmites australis* can transfer oxygen through their root and rhizome systems to the bottom of treatment basins. It also provides a medium beneath the water surface for attachment of microorganisms that perform most of biological treatment. Several processes are envisioned as being effective in pollutants reduction such as phytoextraction, phytoaccumulation and rhizofiltration ((IWA, 2000).

The result also showed that constructed wetlands have the potential to trap and remove Cu contained in wastewater. Long-term removal is expected to occur by accumulation and burial in the plant detritus in a manner similar to the removal of phosphorus. Copper forms very insoluble compounds with sulfur. Sulfide and bisulfide are formed by SRB in the anaerobic zones of treatment wetlands. If a source of sulfate is present in the incoming water, the wetland can be configured to provide a sustainable supply of sulfide (Cooper and de Maeseneer, 1996).

The removal of copper can also be taken place through coprecipitation with iron and manganese oxides. However, this mechanism is contingent on considerable supplies of iron, which are typically present only in a fraction of cases. Although iron and manganese oxides are generally excellent scavengers for other metals, they are unstable under anoxic conditions (Knox *et al.*, 2004).

5.2.5. Zinc

The influent concentration of zinc ranges from 1.438 mg/l to 1.443 mg/l while effluent concentrations from constructed wetland system ranges from 0.024 mg/l to 1.113 mg/l and 0.213 mg/l to 1.318 mg/l for planted and control systems, respectively. Figure 5.3 shows the overall removal efficiency of Cu for both planted and control constructed wetland systems within 28 days of treatment period. The removal efficiency ranges from 23.08% to 98.33% and 8.93% to 85.19% in planted and control system, respectively.

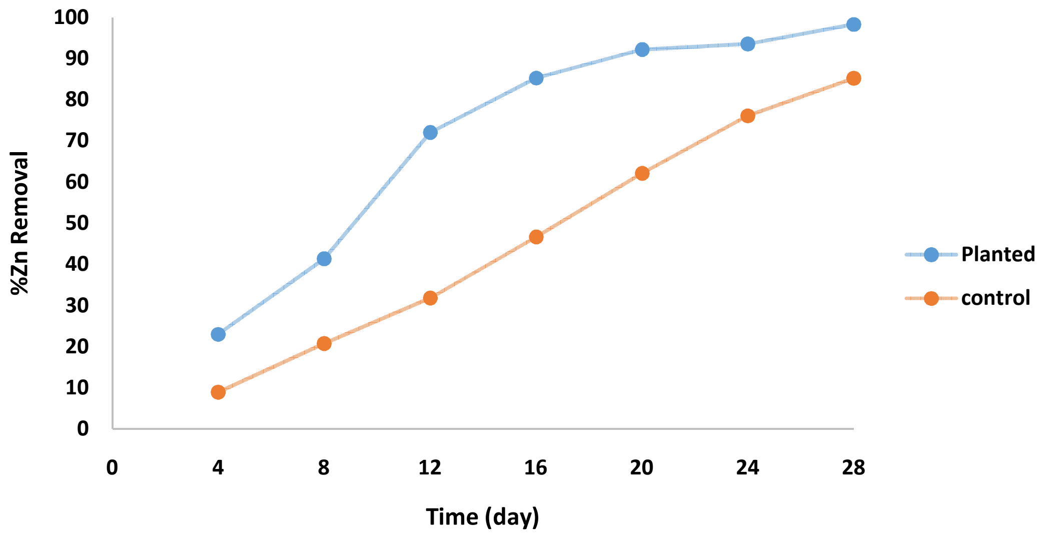

Figure 5.5 Removal efficiency of Zinc in control and planted constructed wetland

The result shown in figure 5.5 that the removal of zinc increased with time in both planted and control systems, but the planted system showed greater removal of zinc than the control one. One way t-test indicated that there is significant difference ($p<0.05$) in removal of zinc between planted and control system. This may be due to the fact that zinc is an essential element for both plants and animals. It activates some enzymatic reactions important in respiration and serves as a cofactor in plant photosynthesis and DNA synthesis.

There are a lot of mechanisms in removal of zinc in constructed wetland. Zinc can be removed by particulate settling and trapping, chemical precipitation and co-precipitation, partitioning to sediments, and to the least extent by plant uptake. Zinc forms very insoluble compounds with sulfide and carbonate, among others: Hydrated forms of the carbonate, such as hydrozincite, also have been identified on wetland plant roots, and zinc may substitute by calcium carbonates (Roberts *et al.*, 2003).

The removal of zinc can also be taken place through co-precipitation with iron, manganese, and aluminum oxyhydroxides (Roberts *et al.*, 2003). However, this mechanism is contingent on considerable supplies of the secondary metals, which may not be present. Besides, although iron and manganese oxides are generally excellent scavengers for other metals, they are unstable under anoxic conditions (Knox *et al.*, 2004).

It is likely that zinc sorption to organic sediments Roberts *et al.* (2003) determined that zinc partitioned very strongly to aluminum hydroxides and silica, with essentially 100% on the solids at pH > 7.5.

5.3. Heavy Metals in Plant's Tissue

Biological removal is perhaps the most important pathway for heavy metal removal in the wetlands. Probably the most widely recognized biological processes for metal removal in wetlands is plant uptake (Vymazal and Kropfelora , 2008). Therefore, analysis of the roots, stem and leaves for copper and lead were done at the beginning of experiment before the plants planted in the constructed wetland and at the end of the experiment.

Figure 5.6 Illustrates Lead concentrations in different part of *Phragmites australis.* The initial average concentration in leave, stems and roots were 0.08mg/kg, 0.07mg/kg and 0.56mg/kg in dry weight basis, respectively, while the final average concentration of Pb was significantly greater in roots followed by leaf and stem which were 12.9mg/kg, 7.3mg/kg and 4.6mg/kg on dry weigh basis, respectively.

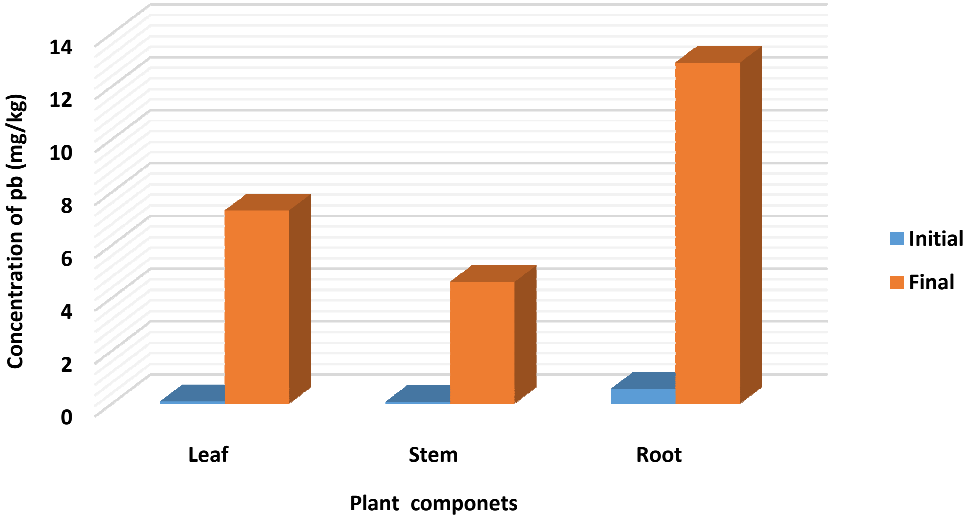

Figure 5.6 Lead accumulations by *Phragmites australis in* HSSF wetland systems

Figure 5.7 Illustrates Copper average concentrations in different part of *Phragmites australis.* The initial average concentration in leaves, stems and roots were 134.55mg/kg, 15.74mg/kg and

98.75mg/kg on dry weight basis, respectively. Figure 5.7 also shows that the final average concentration of Cu was significantly greater in root compared to stems and leaves, which were 343.37mg/kg, 232.5mg/kg and 294mg/kg dry weight, respectively.

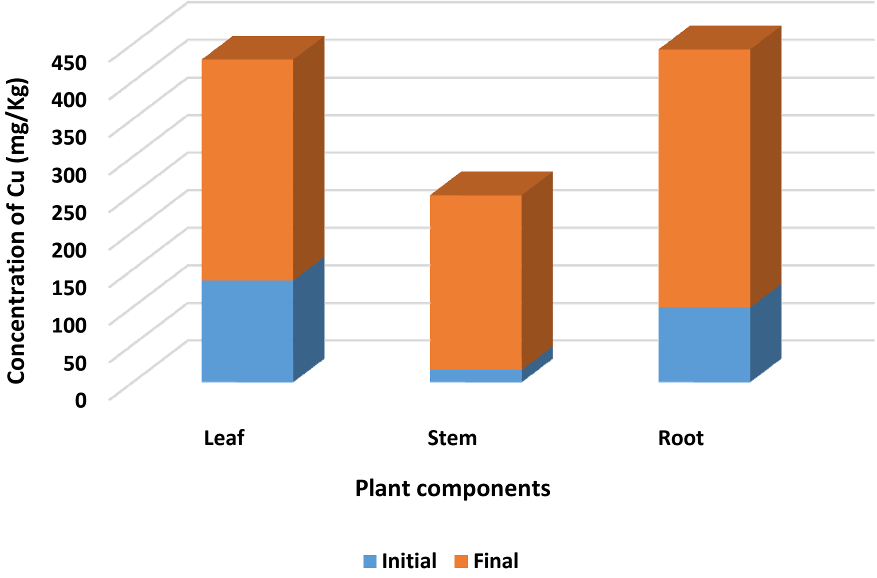

Figure 5.7 Copper accumulations by *Phragmites australis in* HSSF wetland systems

The ability of *Phragmites australis* to uptake Cu and Pb was proven in this study, which agrees with the finding by Bragato *et al*, (2006). The high accumulation of heavy metal in the *phragmites australis tissues* were probably due to the branched nature of the plant's roots and were able to create aeration zones for heavy metal uptake (Vymazal and Kropfelora , 2008).

Fig.5.6 and Fig.5.7 show that lead and copper accumulations were manifested mainly in the roots compared to stem and the shoots as such. *Phragmite ausstralis* accumulated 244.62 mg/kg of copper and 12.34 mg/Kg of lead within the 28 days study period in its root. As copper and lead are more localized in the aquatic plant roots, rhizolfiltration may be the predominant mechanism for accumulation of copper and lead (Zhu *et al.*, 1999). Plants may accumulate higher concentration of metals in the roots as roots are usually at the base of the plant and removed from the photo synthetic process for their own tolerance (Vymazal, 1995).

Many researchers have concluded that accumulation of metals occur mainly in the roots of plants, due to the slow mobility of metal transport from root to shoot (Kadlec and Wallace, 2009). Better accumulation of heavy metals in the roots is well explained by the studies of

(Skinner *et al.*, 2006). The studies indicate that the roots absorbed metal cations via the plasma membrane involving cationic channel such as calcium and restrict their translocation to the shoots. The roots retain the cations by binding them to the cell wall. The preference to store metals in the roots system was thought to be an exclusion strategy of the plant by avoiding the toxic metals from interacting more with other plants parts (Skinner *et al.*, 2006).

5.4. Heavy Metals in the Soil Media

In this study, soil analysis was conducted to determine the suitability of the media beds used, as it is indicated by the accumulation of the heavy metals within the soil media. Fig. 5.8 shows concentration of Pb in the soil media being collected at different points (Fig 4.3) of planted and control systems. Pb average initial concentrations of the soil were 4.92mg/kg dry weight. The final average concentration of Pb found in the soil media at the inlet (A1), middle (A2) and outlet (A3) (of the planted systems were 10.9mg/kg, 6.18mg/kg and 6.8mg/kg dry weight, respectively. While at the inlet (B1), middle (B2) and outlet (B3) of control system were 12.87mg/kg, 6.78mg/kg and 6.2mg/kg dry weight, respectively.

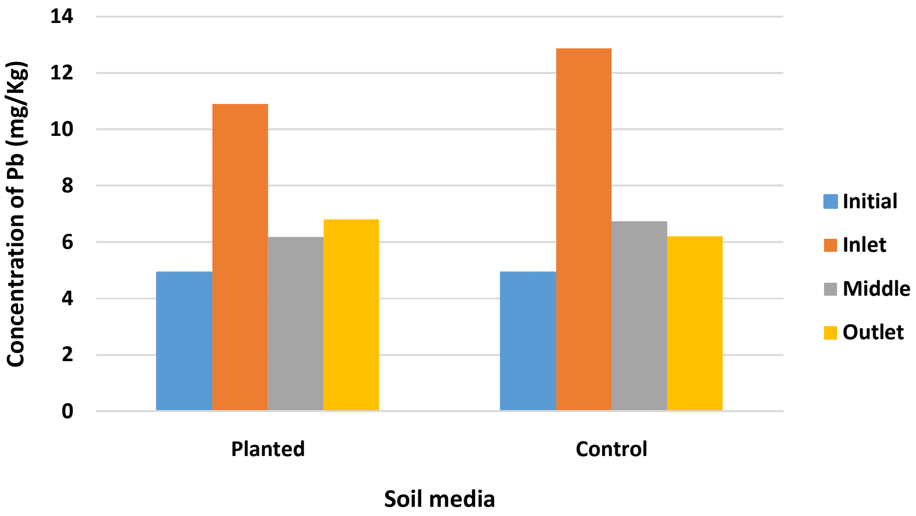

Figure 5.8 Concentration of Pb in soil at different points of planted and control systems

Fig. 5.8 shows concentration of Cu in the Soil media collected at different points (Fig.4.3) of planted and control system. The average initial concentration of copper in the soil was 44.35 mg/kg dry weight. The average concentration of Cu at the inlet (A1), middle (A2) and outlet

(A3) of the planted systems were 79.25mg/kg, 64mg/kg and 98mg/kg dry weight, respectively. While at the inlet (B1), middle (B2) and outlet (B3) of the control systems were 82mg/kg, 80.23mg/kg and 122.75mg/kg dry weight, respectively.

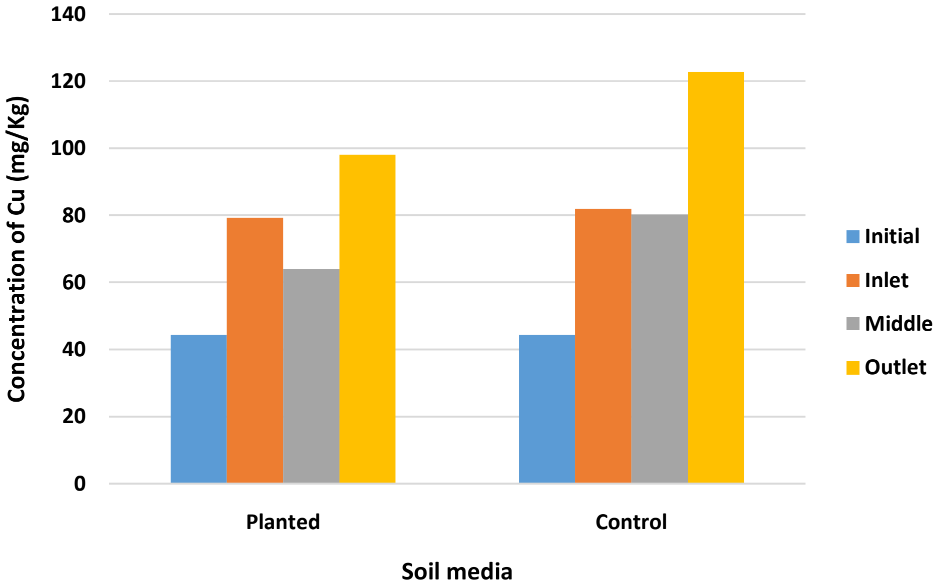

Figure 5.9 Concentration of Cu in soil at different points of planted and control systems

From the result, it has been observed that the control system exhibited higher concentration of Cu and Pb than planted system. This may be due to the effect of plant that the plant can uptake the heavy metals. The two systems exhibited a higher concentration of Pb in the soil samples collected at the inlet of the systems. Other researchers have found that metal concentrations, of lead in particular, are greater in constructed wetland sediments inlet (Debusk *et al*. 1996). Unlike other heavy metals such as Zn and Cd, which have been shown to have a stronger affinity for the dissolved phase, Pb tends to be predominantly particulate associated (Morrinson *et al*,1984) as a result it can be settled and trapped by the gravel or filter media immediately in the inlet part of the constructed wetland. If Pb is found in the form of soluble it will precipitate and stabilized through time and distance. This may be the reason that high concentration of lead was observed on the outlet next to the inlet part of the planted wetland.

It has also been observed that the two systems exhibited a higher concentration of Cu in the soil samples collected at outlet of the systems. Though the retention time and the type of soil media has effect on the treatment wetland Knox *et al.*, (2004) reported that the concentration of Cu is higher in wetland sediment outlet. In aquatic environments, copper can exist in three broad categories: particulate, colloidal and soluble form. In this case more Cu may found in the form of soluble as a result it cannot be settling out and trap by sediment at the inlet part rather than stabilized and predicated through time and distance.

There are a lot of mechanisms that heavy metals are retained by the soil media. The wetland media is one of the important components of constructed wetland, which provides a viable condition for maximum removal of pollutant, since the reduction is said to be accomplished by diverse treatment mechanisms including sedimentation, filtration, chemical precipitation and adsorption, microbial interactions and uptake by vegetation which governed by the accurate selection of media type (USEPA, 1993)

Wetland sediments are typically the major repository of stored lead in wetlands. Any of several compounds may precipitate, and there is strong partitioning to wetland organic sediments. Therefore, the lead removed by the wetland builds up in the sediments. DeBusk *et al.* (1996) hypothesized that the lead was bound as sulfides, based upon acid extractions with analyses for lead and sulfides. However, other lead precipitates were identified by DeVolder *et al.* (2003), namely carbonates and sulfates. Lead fate in wetlands is that removed lead is found in sediments and to a lesser extent in belowground plant parts. For instance, Vymazal and Krasa (2005) found over 97% of the stored lead in the sediment.

From the result, it has been proven that wetland sediments have the ability to store copper. According to Vymazal and krasa (2005) the majority of removed copper is associated with wetland sediment, in sorbet or chemically precipitated forms in HSSF wetland treating domestic wastewater.

6. Conclusions and Recommendations

6.1. Conclusions

From study done, heavy metals (Fe, Pb, Mn, Cu and Zn,) were found in substantial quantity in the samples of leachate of Addis Ababa solid waste open dump (Reppi) in both seasons; This may be due to the fact that the city does not have separate dumping site for hazardous waste generated from useless mobile batteries, computer peripherals and different electronic appliances (Tessema, 2005).

In this study, HSSF constructed wetland systems have shown higher removal efficiency of heavy metals from leachate. Furthermore, by comparing the planted and control system, both systems achieved high percentage of heavy metals removal at the end of treatment. High heavy metals removal efficiency was observed in the control system, this may be due to clogging of the substrate in the soil media. So it can be concluded that, reduction of heavy metals concentration in the planted and control systems were most likely due to chemical precipitation and sorption on sediment, and aided by the macrophytes.

The study also showed that the shorter treatment period is required in achieving optimum removal for planted system as compared to unplanted system. However, for a longer treatment period there were only slight differences in the effluent concentration of pollutants between the planted and control system.

It was shown that Pb and Cu uptake by *Phragmite australis* is more significant in roots as compared to leaves. The study also observed that *Phragmites australis planted* in the HSSF beds were notable less vigorous and healthy. So, it can be concluded that *Phragmites australis* had capability to survive with leachate constituents.

From the result observed, red ash gravel had ability to retain heavy metals specially lead and copper.

6.2. Recommendations

To further enhance the result obtained in this study, the following areas of investigation are recommended:

- Degradation by microorganism is among the important mechanisms in the removal of pollutants. However, this study does not quantify the development of microorganism within the wetland reactor. If the microorganism formation and development within the reactor could be measured, it would by far enhance the findings in this study.
- Further studies should be conducted by considering the variation of flow rates, retention time, types of plant and size of constructed wetlands system in order to determine the efficient of pollutants removal.
- Further studies should be conducted in the sediment analysis in order to know the mobility of heavy metals and their speciation in the sediment.
- Since, this study is found to have reduced various heavy metals to the desired levels. I recommend that Addis Ababa Solid waste Reuse and Disposal Project Office to use this treatment technology for the new landfill to be constructed especially in combination with other physicochemical methods which are proven to be viable and economical in keeping the environment safe.

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Appendices

Annex A

A. Initial concentration of the leachate or leachate characterstics (mg/l)

Parameter	Concentration(mg/l)					
	Dry season			Wet season		
	S_1	S_2	S_3	S_1	S_2	S_3
Fe	21.32	19.5	22.8	29.40	27.60	31.30
Mn	0.61	0.72	0.57	1.70	1.83	1.57
Pb	O.46	0.53	0.33	0.48	0.69	0.27
Cu	0.61	0.65	0.58	0.63	0.76	0.51
Ni	ND	ND	ND	0.15	0.10	0.21
Zn	0.90	0.84	0.96	1.83	1.43	1.25
Cd	ND	ND	ND	ND	ND	ND
pH	7.8	7.9	7.85	7.83	8.27	8.41

B. Heavy metal concentration on *Phragmites australis*

Plant component	Average Heavy metal concentration (mg/kg)		
		Pb	Cu
Root	Initial	0.56	98.75
	Final	12.90	343.37
Leaf	Initial	0.08	134.55
	Final	7.30	294.00
Stem	Initial	0.07	15.74
	Final	4.60	232.50

C. Heavy metal concentration in the soil

Sample	Average heavy metal Heavy metal concentration (mg/kg)				
		Control set		Planted set	
		Pb	Cu	Pb	Cu
Initial		4.92	44.35	4.92	44.35
Final	Inlet	8.55	82.00	6.90	79.25
	Middle	6.73	80.25	6.18	64.00
	Outlet	6.20	122.75	6.80	98.00

A. Quality of leachate

D1. Planted reactor

Days	***Run***	***Parameters (mg/l)***				
		Fe	*Mn*	*Pb*	*Cu*	*Zn*
4	*Influent*	*30.250*	*1.670*	*0.523*	*2.640*	*1.443*
	T1	*10.500*	1.423	*0.285*	*2.132*	*1.113*
	T2	*8.601*	1.424	*0.295*	*2.146*	*1.103*
	T3	*9.310*	1.422	*0.256*	*2.127*	*1.115*
	Mean	***9.470***	**1.423**	***0.278***	**2.135**	***1.110***
8	*Influent*	*30.250*	*1.670*	*0.523*	*2.640*	*1.443*
	T1	*5.213*	1.313	*0.205*	*1.199*	*0.845*
	T2	*5.372*	1.246	*0.212*	*1.201*	*0.834*
	T3	*5.457*	1.338	*0.216*	*1.189*	*0.859*
	Mean	***5.347***	**1.299**	***0.211***	***1.196***	***0.846***
12	*Influent*	*30.250*	*1.670*	*0.523*	*2.640*	*1.443*
	T1	*2.641*	1.101	*0.165*	*1.126*	*0.404*
	T2	*2.302*	1.103	*0.163*	*1.128*	*0.406*
	T3	*2.535*	1.00	*0.167*	*1.124*	*0.403*
	Mean	***2.493***	**1.068**	***0.165***	***1.126***	***0.404***
16	*Influent*	*30.250*	*1.670*	*0.523*	*2.640*	*1.443*
	T1	*1.312*	0.822	*0.124*	*0.874*	*0.212*
	T2	*1.204*	0.911	*0.126*	*0.901*	*0.213*
	T3	*1.323*	0.768	*0.128*	*0.784*	*0.211*
	Mean	***1.280***	**0.834**	***0.126***	***0.853***	***0.212***
20	*Influent*	*31.350*	1.643	*0.567*	*2.667*	*1.438*
	T1	*0.613*	0.431	*0.110*	*0.443*	*0.112*

	T2	*0.832*	0.387	*0.113*	*0.433*	*0.113*
	T3	*0.756*	0.476	*0.101*	*0.425*	*0.114*
	Mean	***0.734***	**0.391**	***0.108***	***0.434***	***0.113***
24	*Influent*	*31.350*	1.643	*0.567*	*2.667*	*1.438*
	T1	*0.367*	0.245	0.094	*0.148*	*0.092*
	T2	*0.454*	0.262	*0.087*	*0.146*	*0.093*
	T3	*0.323*	0.225	*0.098*	*0.138*	*0.094*
	Mean	***0.381***	**0.244**	***0.093***	***0.144***	***0.093***
28	*Influent*	*31.350*	1.643	*0.567*	*2.667*	*1.438*
	T1	*0.215*	0.111	*0.063*	*0.103*	*0.024*
	T2	*0.216*	0.101	*0.046*	*0.098*	*0.023*
	T3	*0.203*	0.100	*0.073*	*0.107*	*0.024*
	Mean	***0.211***	**0.104**	***0.061***	***0.103***	***0.024***

D2. Control reactor

Days	Run	Parameters (mg/l)				
		Fe	Mn	Pb	Cu	Zn
4	Influent	*30.250*	*1.670*	*0.523*	*2.640*	*1.443*
	T1	13.012	1.513	0.312	*2.310*	*1.318*
	T2	11.572	1.514	*0.315*	*2.315*	*1.298*
	T3	12.431	1.515	*0.308*	*2.317*	*1.327*
	Mean	**13.338**	**1.514**	***0.312***	***2.314***	***1.314***
8	Influent	*30.250*	*1.670*	*0.523*	*2.640*	*1.443*
	T1	8.749	1.452	0.278	*2.262*	*1.143*
	T2	8.436	1.389	*0.269*	*2.264*	*1.139*
	T3	9.014	1.487	*0.280*	*2.246*	*1.146*

	Mean	**8.733**	**1.443**	***0.276***	***2.257***	***1.143***
12	Influent	*30.250*	*1.670*	*0.523*	*2.640*	*1.443*
	T1	4.721	1.212	0.193	*1.864*	*0.981*
	T2	3.671	1.208	*0.195*	*1.745*	*0.978*
	T3	3.812	1.219	*0.189*	*2.120*	*0.992*
	Mean	**4.068**	**1.213**	***0.192***	***1.910***	***0.984***
16	Influent	*30.250*	*1.670*	*0.523*	*2.640*	*1.443*
	T1	2.213	0.892	0.164	*1.163*	*0.719*
	T2	2.645	1.000	*0.134*	*1.148*	*0.779*
	T3	2.054	1.102	*0.136*	*1.152*	*0.812*
	Mean	**2.304**	**0.998**	***0.145***	***1.154***	***0.770***
20	Influent	*31.350*	1.643	*0.567*	*2.667*	*1.438*
	T1	1.347	0.531	0.122	*1.119*	*0.565*
	T2	1.241	0.498	*0.124*	*1.120*	*0.498*
	T3	1.171	0.542	*0.109*	*1.116*	*0.573*
	Mean	**1.253**	**0.524**	***0.118***	***1.118***	***0.545***
24	Influent	*31.350*	1.643	*0.567*	*2.667*	*1.438*
	T1	0.913	0.384	0.104	*0.497*	*0.345*
	T2	0.865	0.367	*0.098*	*0.486*	*0.336*
	T3	0.907	0.396	*0.105*	*0.568*	*0.348*
	Mean	**0.895**	**0.382**	***0.102***	***0.517***	***0.343***
28	Influent	*31.350*	1.643	*0.567*	*2.667*	*1.438*
	T1	0.521	0.136	0.084	*0.247*	*0.215*
	T2	0.473	0.138	*0.078*	*0.245*	*0.205*
	T3	0.482	0.137	*0.094*	*0.253*	*0.219*
	Mean	**0.492**	**0.137**	***0.085***	***0.248***	***0.213***

Annex B

I. T-test for Iron

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Fe - Fec	-1.45238	.05555	.03207	-1.59038	-1.31439	-4.528E1	2	.000

II. T-test for Manganese

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Mn Mnc	-.11538	.03233	.01867	-.19570	-.03506	-6.181	2	.025

III. T-test for lead

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Pb - Pbc	-.02686	.00295	.00170	-.03418	-.01953	-1.577E1	2	.004

IV. T-test for Copper

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	Cu - Cuc	-.50405	.04487	.02591	-.61552	-.39258	-19.456	2	.003

V. T-test for Zinc

		Paired Differences					t	df	Sig. (2-tailed)
					95% Confidence Interval of the Difference				
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper			
Pair 1	Zn - Znc	-3.58713E-1	.01095	.00632	-.38591	-.33152	-5.676E1	2	.000

N.B. Fe, Mn, Pb, Cu,Zn and Fec, Mnc, Pbc, Cuc, Znc are designated for planted and control, respectively.

Annex C

Fig.C1 Sample digestion

Fig.C2 BUCHI wet Digester B- 440.

Fig. C3 pH meter

Fig.C4 Atomic adsorption Spector photometer

Annex D

I. Leachate

Fig.D1 Leachate transportation

Fig.D2 Leachate collection

Fig.D3 Leachate sample collection

Fig.D4 Effluent sample collection

II. Soil (gravel)

Fig.D5 Soil sample collection

Fig.D6 Soil sample labeling

III. Plant

Fig.7D Plant Collection from Lake Ziway

Fig.D8 Plant sample collection

Fig.D9 Phragmites *australis* plant above ground biomass

Annex E

Fig E1 Setup of the experiment before planted

Fig.E2 Setup of the experiment after planted


Fig.E3 Setup of the experiment at the end of the treatment period

Annex F

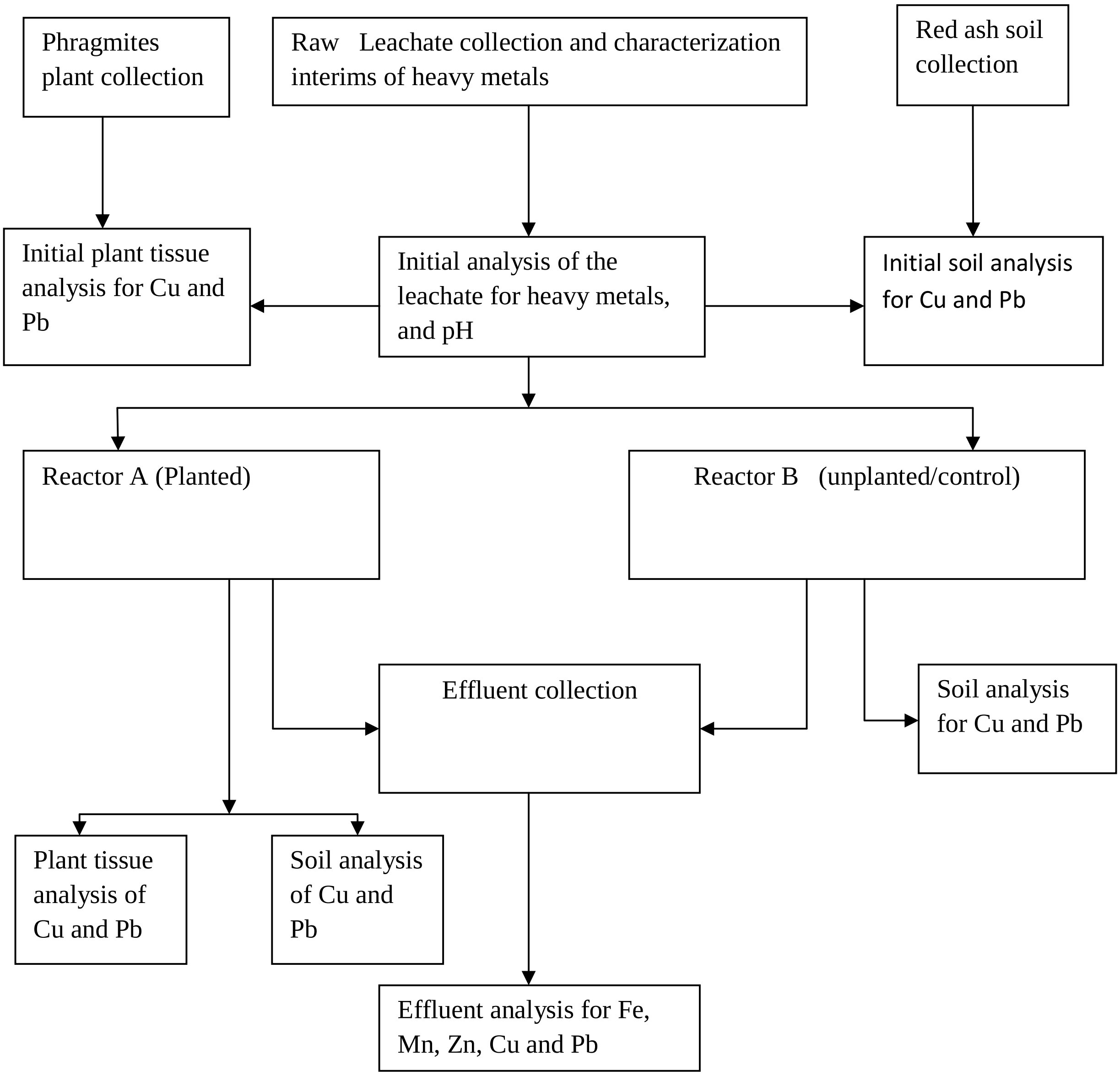

Figure E1. Overall frame work of the experiment

Declaration

I, the undersigned, hereby declare that the work contained in this thesis entitled " Horizontal Subsurface Constructed Wetland for Removal of Heavy Metals from Leachate using *Phragmites australis:* A Case of Addis Ababa Solid Waste Open Dump*”* is my own Original work and it has not previously in its entirety or in part submitted it at any other University for degree. And that all source of materials used for the thesis have been duly acknowledged.

Mesele Bahre ____________________ __________________

Name Signature Date