DEVELOPMENT OF A PERMEABLE REACTIVE BARRIER TO TREAT LEACHATE FROM MUNICIPAL SOLID WASTE DUMPSITES IN SRI LANKA: AN EFFECTIVE USE OF LOCALLY AVAILABLE MATERIALS FOR HEAVY METAL REMOVAL

（スリランカにおける廃棄物処分場浸出水処理のための浸透性浄化壁の開発：重金属除去を目的とした地域資材の有効活用）

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By

B. G. N. Sewwandi

Approved by

Prof. Ken Kawamoto, Academic supervisor and committee chairman

Prof. Norio Tanaka, committee member

Assoc. Prof. Masahiko Osada, committee member

Assoc. Prof. Shingo Asamoto, committee member

Prof. Per Møldrup, committee member (Aalborg University, Denmark)

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By

B. G. N. Sewwandi

B.Sc. (Hons.) Agriculture (Agric. Eng.), 2008

M.Phil. Integrated Water Resources Management, 2011

University of Peradeniya

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Chapter 1 GENERAL NTRODUCTION

Municipal solid waste management has become a serious environmental, social and economical issue due to the increased waste production with the enhanced lifestyle of people and the industrialization (Montusiewicz and Lebiocka, 2011). The common solid waste management method practiced in most of the countries around the globe is landfilling of municipal solid wastes as it is the simplest and the cost effective way of handling solid wastes over the other methods (Kjeldsen et al.,2002; Kurniawan et al., 2006; Hunce et al., 2012). Most of the developed countries also used landfilling as solid waste management technique for the most of the solid wastes generated. Moreover, almost all the wastes generated in developing countries are landfilled (Bhalla et al., 2012). The solid wastes dumped in a landfill composed of municipal solid wastes that collected from households, commercial wastes, non-hazardous industrial wastes, and construction and demolition wastes.

However, landfills in developing countries like Sri Lanka is often operated as uncontrolled and unmanaged open dumpsites creating several environmental, social and economical issues (Abenayaka and Werellagama, 2007). There is no application of cover soil on top of the waste layer or collection of landfill leachate from the dumpsites and treatment facility for the generated leachate. The common practice in Sri Lanka is that the solid wastes from urban areas are collected by tractors and brought into nearby open dumpsites and unloaded freely. The wastes consists of household wastes, street litter, commercial wastes, non-infectious hospital wastes as there is no segregation of wastes and all wastes dumped together without considering its origins or hazardous nature.

Many biological, chemical and physical reactions are taking place in landfills as degradation of solid wastes which results in production of landfill gasses and leachate. The leachate is formed when water is in contact with the wastes in landfills (Skulteryova, 2009; Ping, 2006). The water either from precipitation or natural moisture percolates through the wastes dissolving soluble organics and inorganics and leaching heavy metals from cans, batteries, pesticides, cleaning fluids, inks and paints.

Since household waste and non-hazardous industrial waste are disposed in open dumpsites, landfill leachate contains various types of pollutants (Baun et al., 2004). The major pollutants in landfill leachate are organic and inorganic compounds and hazardous substances such as xenobiotic organic compounds and heavy metals (Slack et al., 2005). The quality as well as the quantity of leachate is determined by the nature of the wastes, climatic condition, age of the landfill, moisture content, site hydrology, waste compaction, interaction of leachate with the environment and landfilling technology (Snow et al., 2008; Kulikowska and Klimiuk, 2008; Umar et al., 2010).

Since municipal landfill leachate contains large amount of organic and inorganic contaminants, it can cause severe environmental and health hazards if not properly treated (Asadi, 2008). The level of pollution by landfill leachate depends on the landfill age, technological structure of the landfill, climatic conditions and composition of wastes dumped in the landfill (Jaskelevicius and Lynikiene, 2009). Environmental hazards such as dissolved oxygen depletion, eutrophication and toxicity to aquatic life *etc.* are some of the problems which can be caused by contamination of water with leachate (Abbas *et al.,* 2009; Salem *et al.,* 2008). Groundwater and surface water can be contaminated by leaching landfill leachate in unlined landfills (Ageena, 2010).

Health hazards such as kidney damage, liver damage, mental retardation in children, cancers, gastrointestinal disorders can be caused by pathogens, toxins, carcinogenic or mutagenic compounds present in landfill leachate. Heavy metals present in leachate plays an important role as it is toxic in traces as well as detrimental to both flora and fauna (Alluri *et al.,* 2007; Das *et al.,* 2008).

Studies on landfill leachate characterization in Sri Lanka have proved that there is a risk of soil and water pollution by heavy metals in nearby areas of the dumpsites in Sri Lanka (Sewwandi et al., 2011; Wijesekara et al., 2014; Sewwandi et al., 2013). Onsite treatment facilities for generated leachate have to be operated and managed in open dumpsites to reduce the risk of polluting soil and groundwater by leachate flow.

Chemical, biological and Physical treatment methods used in wastewater treatment in general are recommended for landfill leachate treatment based on composition of leachate (Kilic *et al.,* 2007). Chemical treatment with coagulants has been widely used for removal of heavy metals from landfill leachate (Asadi, 2008). Hydrated Aluminum sulphate, lime and hydrated ferric chloride have been used to test the removal efficiency of Fe, Ni, Cd, Pb and Zn from leachate. They have concluded that hydrated aluminum sulphate is the best coagulant for heavy metal removal.

Maleki *et al.* (2009) studied the effect of chemical treatment i.e. coagulation and flocculation process on treatment of leachate from a composting plant. They have studied the removal of organic matter and heavy metal (Cu, Zn, Cd, Cr and Ni) by using two coagulants (alum and ferric chloride) with the variation in pH. They have found that at the higher pH levels, removal of organic matter is comparatively higher and at the low pH levels, heavy metal removal is higher than the removal of organic matter. Moreover, both coagulants gave the higher removal of heavy metals but for the removal of organic matter, $FeCl_3$ was better than the alum. The same results have been obtained by Zazouli and Yousef (2008) from a study with same coagulants.

Kilic *et al.*, (2007) have studied the physicochemical methods in combination with adsorption process for treatment of landfill leachate. Lime and the granular activated carbon have been tested for the adsorption of metals. They have found that leachate is treated by adsorption process followed by chemical coagulation to a level of pollutants which is suitable for direct discharge. Furthermore, the treatment with lime pretreatment and ammonia stripping is more applicable than the adsorption process though its pollutant removals are not up to the discharge standards.

Another study on landfill leachate treatment have been investigated the effect of ozone oxidation and moss on removal of organic matter and some heavy metals (Cu, Zn and Pb). The results of the study indicate that the use of both ozone oxidation and moss gives the better treatment than when uses only moss (Kobayashi *et al.*, 2009). When it is used moss only, it has removed only Zn but not the other pollutants.

A study has been conducted by Derco *et al.* (2002) have monitored the effectiveness of ozone treatment in improving biodegradability of organic compounds in landfill leachate. Biological pretreatment has done before the ozone treatment and the treatment efficiency was monitored with the removal of organic matter. The result of the study is that the highest removal of organic matter occurred during 10-11.5 h after ozonation of pretreated leachate.

Short rotation willow coppice plants have been used in landfills to study the effect of plants in leachate management. In addition to plants, soil is acted as a dilution medium for leachate and a buffer zone for the downstream to prevent from shock loadings (Alker *et al*, 2003). Further, the complete removal of ammonium can be achieved by both nitrification and plant uptake by willow coppice.

The effect of municipal landfill leachate on plant growth has been studied with a floating plant (*Eichhornia crassipus*) in different salinity levels, pH, nutrients and heavy metals under a greenhouse conditions (EI-Gendy *et al.*, 2005). The optimum concentrations for different nutrients have been investigated. Further, they have found that the heavy metal concentrations for which supported the plant growth as well as inhibited the plant growth. The conclusion of the study is that with higher plant growth, the removal efficiency is increased.

Constructed wetlands have been used by many researches for the treatment of landfill leachate worldwide (Demirezen and Aksoy, 2004; Lesage et al., 2007; Mohanty *et al.*, 2006; Schneider *et al.*, 2001; Kara, 2005; Maine *et al.*, 2004; Bajza and Vreek, 2001; Cheng *et al.*, 2002; Jayaweera *et al.*, 2008). Most of them have studied the heavy metal removals from the leachate with different plant types, flow rates, substrates *etc.* in constructed wetlands. Pendelton *et al.* (2005) studied the leachate treatment in sub surface flow constructed wetlands in a pilot study and found that especially for older landfills, constructed wetlands are a viable option in places where the other long term options are limited by the leachate disposal costs, space and environmental concerns.

The efficiency of an anaerobic digestion reactor have been studied by Trabelsi *et al.* (2009) for the treatment of landfill leachate in terms of removing organic matter (measured as BOD_5, COD, TOC), NH_4-N and TKN. The effluent from the anaerobic digestion reactor has been treated in three aerobic submerged biological reactors. They have found that the removal efficiencies of all the parameters are higher when both anaerobic and aerobic reactors were used in sequence than a single anaerobic or aerobic reactor.

It is common to use agricultural by products for leachate treatment either as raw material itself or with a little treatment. Oil palm shells and coconut husk have been used for leachate treatment after forming into activated carbon (Joseph *et al.*, 2006).

Filter materials have been tested for heavy metals removal (Modin and Persson, 2008). Granular activated carbon, CAP meal (fine powder derived from animal bones) and zero valent iron are the filter materials that have been tested in this study. However, they have faced some problems like no flow in leach columns with some filter materials (CAP meal). The conclusion of the study is that activated carbon has a good ability to remove heavy metals tested than the other two filter materials.

Waste derived filter media have been used for the treatment of compost leachate by Tyrrel *et al.*, (2008). Two grain sizes of compost and granite chips have been studied for the removal of nitrogenous and carbonaceous compounds by bioremediation process. The results of the study highlight that the compost granules more than 10 mm size is most effective as a filter medium for the treatment of compost leachate.

The use of above methods for leachate treatment is sometimes limited due to social, economical and environmental issues prevailing in local situations. In that case cost effective treatment technologies which are site specific, cost effective and suitable for the local conditions are needed to control the contaminant source and to manage contaminants along its pathway. Therefore, it is worth to investigate the use of new and innovative technologies which are developed to be suited the conditions at open dumpsites.

Permeable reactive barriers (PRB) are one such a new and innovative technology used in polluted groundwater treatment which gives a simple and inexpensive solution. It is a subsurface structure constructed across the contaminated water flow path downstream of the contaminant plume (Day et al., 1999; Blowes et al., 2000). Figure 1.1 shows the schematic diagram of a permeable reactive barrier. Accordingly, contaminant plume is treated by the precipitation, adsorption or degradation of pollutants while the contaminant plume passes through the barrier.

The concept of PRB has been first born at the University of Waterloo, North America focusing on funnel-and-gate system to remove chlorinates and recalcitrant compounds by elemental iron. Since then, research has been carried out and the research focusing on PRB designs, suitable reactive materials and target contaminants has been increased significantly in 1990s (Blowes et al., 2000).

There are two installation configurations of PRB as continuous walls, and Funnel-and-Gate barriers (Gavaskar, 1999; Vogan et al., 1999). Continuous walls are simplest to install which extends across the width and depth of the plume and give least effects to the existing groundwater flow pattern. On the other hand, Funnel-and-Gate barriers have permeable gates which contain reactive materials and contaminated plume is funneled through these gates.

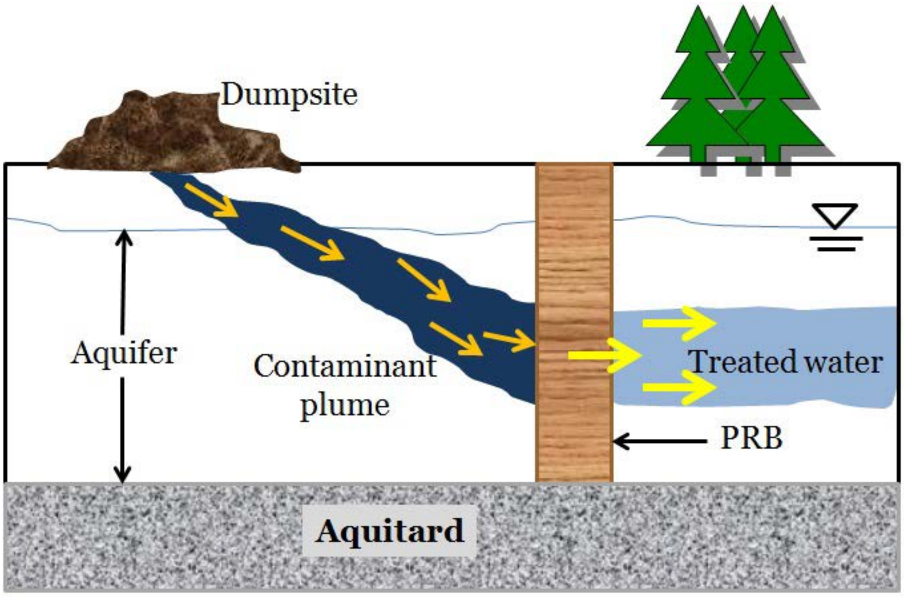

Figure 1.1: Schematic diagram of a permeable reactive barrier

Different kinds of reactive materials have been used in PRBs to treat contaminated groundwater. Activated carbon, zero valent iron, bentonite, soil-bentonite mixture are some of reactive materials used. The selection of a particular reactive material for a PRB depends on several factors i.e. reactivity, stability, availability and cost, environmental compatibility, hydraulic performance and safety.

Several mechanisms are involved in contaminant removal process by PRB which occurs collectively or as separate processes. Some of such mechanisms are degradation, precipitation and sorption of contaminants (Simon and Meggyes, 2000). The use of PRB is advantageous over the other treatment methods due to its low energy input, continued productive use of installation, and cleans up on only the area of contamination.

There is a plenty of research carried out on PRB to remove different pollutants in contaminated groundwater. Table 1.1 presents a summary of some of the studies conducted around the world. Accordingly, it is clear that most of the studies have been carried out in the developed countries using reactive materials with chemical origin. The pollutant of interest in most of these studies is radioactive wastes or organic halogenated hydrocarbons. Thus, there is a lack of studies on PRB to remove organic pollutants and heavy metals from wastewater and use of use of natural materials like soil or biomaterials.

Studies have shown that soils and biomaterials can effectively be used in treatment to remove different kinds of pollutants. Researchers have studied waste materials from agriculture, food and wood industry for adsorption (biosorption) of heavy metals and found that those can effectively be used as biosorbents to remove heavy metals (Das *et al.,* 2008; Vinodhini and Das, 2010, Bansal *et al.*, 2009, Gonzalez *et al.*, 2008). There are studies that soils or sand has been used as the adsorbent to remove heavy metals form contaminated water (Appel *et al.,* 2008; Gabaldon *et al.,* 2006; Altin *et al.,* 1999; Vithanage *et al.,* 2007; Vithanage *et al.,* 2009; DeBusk *et al.,* 1997). Table 1.2 summarizes the studies on natural materials to remove heavy metals in laboratory studies.

Table 1.1: Past studies conducted on permeable reactive barriers

Reactive material	Pollutant of interest	Scale	Variables	Country	Reference
Clinoptilolite (a natural zeolite)	Ammonium and heavy metals (Pb and Cu)	Lab scale (batch and column)	Concentration of metal Particle size	Korea	Park et al., 2002
Zeolite with high SiO_2/Al_2O_3	Methyl tert-butyl ether (MTBE) Chloroform, trichloroethylene	Lab scale	Pore size Ratio of SiO_2/Al_2O_3	USA	Anderson et al., 2000
Bone apatite material (Contain HAP)	Uranium	Lab scale	Concentration of U Effect of carbonate	USA	Fuller et al., 2003
Activated carbon	Cd	Lab and field scale (> 6 months)	Initial U concentration pH Time	Italy	Di Natalie et al., 2008
Amorphous ferric hydroxide	U(VI)	Lab scale	Initial U concentration Effect of CO_3^{2-} & SO_4^{2-} pH	USA	Morrison et al., 1995
Apetite	Cd, Pb, Zn, SO_4^{2-}, NO_3^-	Field scale (>2y)	Time	USA	Wright et al., 2003
Fly ash	Pb	Lab scale	Pore volume pH	USA	Brooks et al., 2010
Silica sand+Ca crushed limestone + readily available metal oxides	Phosphate	Lab scale (batch and column)	% of each material Contact time	Canada	Baker et al., 1998

Table 1.2: Past studies on biosorption of heavy metals

Biosorbent	Heavy metal	Type of wastewater	Reference
Activated carbon, Bengal gram (*Cicer arientinum*) husk, Potato peel waste, saw dust, rice husk, raw coconut coir	Cr	landfill leachate, chemical solutions, synthetic wastewater, sulphochromic waste	Ahalya *et al*., 2005, Abdullah and Prasad, 2009, Vinodhini and Das, 2010, Bansal *et al*., 2009, Gonzalez *et al*., 2008
Erythrina variegate orientalis leaf powder, activated carbon from peanut hulls and commercial granular activated carbon, saw dust, fly ash, treated saw dust, rice husk, Na2CO3 treated rice husk	Cd	chemical solutions, synthetic wastewater, chemical solutions, Cd contaminated wastewater	Prasad and Kumar, 2010, Periasamy and Namasivayam, 1994, Ulmanu *et al*., 2003, Sharma *et al*., 2009, Kumar and Bandyopadhyay, 2006
Pine (Pinus virginiana) fruit, coconut shell, coconut shell fibre, rice husk	Fe	chemical solutions, industrial wastewater,	Najim *et al*., 2009, Mohan *et al*., 2008,
Treated and untreated rice husk	Ni	synthetic wastewater	Ajmal *et al*., 2003
Pine (Pinus virginiana) fruit, saw dsut,	Cu	chemical solutions,	Najim *et al*., 2009, Ageena, 2010, Bajpai and Rohit, 2007

coconut shell, coconut shell fibre, rice husk, chemically treated saw dust, saw dust, rice husk ash, maize cobs	Pb	Industrial wastewater, chemical solutions, battery industry wastewater	Mohan *et al.*, 2008, Ansari and Raofie, 2006, Abdel-Ghani *et al.*, 2007, Sharma *et al.*, 2009,
coconut shell, coconut shell fibre, rice husk,	Zn	industrial wastewater,	Mohan *et al.*, 2008,

Only very few studies have been conducted on the use of plant materials and soils as the reactive material for PRB as shown in Table 1.1. The selection of a reactive material which is most effective, readily available, relatively inexpensive and compatible with subsurface conditions is a challenge in using PRB. Since agricultural waste materials and soils have shown good removal of heavy metals from wastewater, it will be worth to investigate the ability of using these materials as a reactive media for PRB.

This study focuses on using locally available materials in a PRB to remove heavy metals from leachate generated in open dumpsites in Sri Lanka. Agricultural waste materials and soils are two possible materials to be used in PRBs. Being an agricultural country, agricultural waste products like coconut husk, saw dust, rice husk etc. are freely available for any use (only transport cost incur) in Sri Lanka. Often these materials are dumped in open sites which cause environmental noises. Therefore, the use of these materials in PRB would be an advantage for reducing the risk of heavy metal contamination of water, and soil and also provide a solution to the solid waste generated from agricultural activities.

Different soils have also been tested for heavy metal removal in laboratory experiments (Appel *et al.*, 2008; Gabaldon *et al.*, 2006; Altin *et al.*, 1999; Vithanage *et al.*, 2007; Vithanage *et al.*, 2009; DeBusk *et al.*, 1997) and have found that the heavy metal removal by soils is satisfactory. There are many types of soils in different parts of Sri Lanka representing several soil orders.

Even though, PRBs have extensively been used in treating contaminated groundwater in different parts of the world, the use of PRB in landfill sites is limited. PRBs could be a better solution to be used as a site specific treatment system in open dumpsites in Sri Lanka to prevent soil and groundwater pollution by leachate generated. The main issue regarding the use of PRB in open dumpsites will be the selection of a proper reactive material which is suited to the local conditions of the dumpsite.

As mentioned earlier based on the previous studies, soil and groundwater pollution by heavy metals in the vicinity of open dumpsites is remarkable and therefore this study will be focused on removing heavy metals using PRB. It is economical to use a reactive material that is effective and readily available at local conditions. Thus, this study aims to find out the possibility of using locally available biomaterials and soils in treating leachate generated from open dumpsites with the aim of developing a reactive material to be used in PRB at low cost. This research aims to explore the biomaterials i.e. coconut husk and seven soils of different areas of Sri Lanka as these materials are readily available in Sri Lanka at no or low cost, to be used in PRB to treat leachate from municipal solid wastes dumpsites. The objectives of the study are to (1) characterize leachate from open dumpsites from different areas of Sri Lanka to identify the most critical pollutants in leachate (2) characterize agricultural waste materials (biomaterials) for pollutant removal and (3) characterize soils of Sri Lanka to identify the efficient metal sorbing soils.

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Chapter 2 CHARACTERIZATION AND EVALUATION OF LEACHATE CONTAMINATION POTENTIAL OF LEACHATE FROM MUNICIPAL SOLID WASTE DUMPSITES IN SRI LANKA

Abstract

Open dumping of municipal solid waste (MSW) is the most common way of handling solid waste in Sri Lanka due to high cost involved with advanced technologies for landfilling, lack of technical capacity, lack of know-how to manage landfill sites, and so on. Landfill leachate generated from the MSW open dump sites must be treated before dispose into the environment as it creates many social and environmental problems. Characterization of leachate is important to identify the most critical pollutants present in the leachate and thereby to introduce suitable and applicable treatment technologies such as *in-situ* permeable reactive barrier technologies for contaminant remediation. Moreover, quantification of contaminants present in leachate is important in deciding remediation technologies for a particular site as well as to compare the contaminant potential of dumpsites in a region. Some indices (eg: leachate pollution index) have been developed to quantify the leachate contaminant potential. Therefore, the objective of this study are to characterize leachate collected from several MSW open dumpsites in Sri Lanka and to evaluate contamination potentials of municipal solid waste dumpsites based on leachate pollution index (LPI) and quality rating scale (QRS). The leachate samples were collected from 12 landfill sites located in Matale, Hambantota, Kataragama, Bandaragama, Kolonnawa, Gampola, Gohagoda, Wennappuwa, Rathnapura, Negombo, Galle, and Matara. For the collected samples, general water quality parameters (pH, EC, DO, ORP, and SS), organic pollutants (BOD_5, COD, TOC, IC, TN, TP), typical anions and cations (Cl^-, SO_4^{2-}, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, etc), and heavy metals (Cr, Mn, Fe, Se, Pb, etc) were measured. The results showed that most of the pollutants (F^-, Cl^-, PO_4^{3-}, NH_4^+, Fe, Se, Pb, BOD_5, and COD) exceeded the maximum tolerance limits in Sri Lankan Standards. It was found that the BOD_5/COD ratio ranged from 0.01 to 0.6 for the most samples and the highest value of 0.6 was observed in the Kolonnawa sample. Measured EC values for all samples were high and varied ranging from 4.5 to 38.3 mS/cm, indicating the biological treatment system alone would not be effective in reducing the pollutants especially for heavy

metals. The highest LPI_{or} and LPI_{hm} of 91.5 and 10.12, respectively resulted from the Kolonnawa dumpsite. However, the highest LPI_{in} of 65.4 is resulted in leachate from Bandaragama. Further, the overall LPI is highest in leachate from Kolonnawa dumpsite followed by Bandaragama and Rathnapura sites. Accordingly, Kolonnawa landfill leachate is polluted with organic pollutants and heavy metals and it has the highest potential of environmental pollution by means of organic pollutants and heavy metals. The leachate from Bandaragama site has the highest pollution potential of inorganic pollutants. Even though, the concentrations of As, Cr, Cd and Pb are low, the impact of those metals is higher which is shown by QRS values. Most of the heavy metals studied showed a higher concentration in Kolonnawa leachate sample which could be a result of dumping industrial wastes in to the Kolonnawa dumpsite since it is located near to the industrial area. The results of this study will be used in developing site specific remediation technologies in landfill leachate treatment.

2.1 Introduction

Landfills are the most common way of disposing municipal solid wastes in developing countries due to the higher capacity of landfills at lower cost than other waste management techniques. In the case of Sri Lanka, almost all the landfills are operated as unmanaged and uncontrolled open dumpsites as a result of lack of technology, high cost of operation and maintenance, and running out of capacity etc.

There are several forms of landfill emissions as gaseous emissions of volatile organic compounds, airborne particulate matter and landfill leachate (Slack et al., 2005). Among them, landfill leachate generation is a serious environmental problem associated with open dumpsites since leachate is highly contaminated with different types of pollutants. The composition of landfill leachate varies from time to time and site to site due to the differences in waste composition, amount of precipitation, moisture content, climatic changes, site hydrology, waste compaction, interaction of leachate with the environment etc. (Kulikowska and Klimiuk, 2008; Umar et al., 2010).

Landfill leachate consists of organic matter (biodegradable and non-biodegradable), inorganic pollutants and hazardous substances (Slack et al., 2005; Umar et al., 2010). Hazardous substances in MSW are in the form of paints, mercury containing wastes, batteries, pharmaceuticals, vehicle maintenance products and many other diffuse products (Slack et al., 2005). Thus, the disposal of landfill leachate prior to the treatment is a source of hazard to receiving water bodies.

Landfill leachate characterization is necessary to have a proper treatment facility since the composition of landfill leachate is varied from site to site. This will facilitate the introduction of site specific technologies such as in-situ permeable reactive barriers for the treatment of landfill leachate. Mostly, studies have been conducted to assess pollution level by measuring the concentrations of different contaminants and/or comparing the concentration of each contaminant to the standards of the respective contaminant (Christensen et al., 1998; Kang et al., 2002; Tatsi and Zouboulis, 2002; Aziz et al., 2010). An index called leachate pollution index (LPI) has been developed and used to quantify the leachate contamination potential elsewhere (Kumar and Alappat, 2005a). LPI is a quantitative tool which measures the leachate pollution potential in a comparative and an increasing scale. Even though LPI gives an overview of the leachate contamination potential of landfill leachate, it does not provide the dominating pollutants in leachate. Therefore, sub-indices of LPI have been developed to describe the dominating pollutant and the impact from each pollutant type (Kumar and Alappat, 2005b).

Leachate pollution potential of a particular landfill in terms of overall LPI and its sub-indices are important in planning and designing of remedial measures for environmental pollution by landfill leachate and to compare the pollution potential of different landfill sites. The information on dominant pollutant in a particular landfill site may help to apply the treatment methods giving the priority for that.

Moreover, only few data are available on leachate characteristics for the open dumpsites in Sri Lanka. Therefore, the objectives of this study are to characterize landfill leachate collected from several MSW landfills and to evaluate and compare the contamination potential of landfill leachate from different sites in Sri Lanka, based on sub-indices of LPI and the overall LPI for a particular site.

2.2 Materials and Methods

2.2.1 Sampling of landfill leachate

Landfill leachate were collected from several open dumpsites located in different areas of Sri Lanka to represent Wet and Dry zones of Sri Lanka (Fig. 2.1). All the selected landfill sites are in active operation. Samples were collected in polypropylene bottles and leachate was collected as to minimize the headspaces in the bottles to prevent aeration of the samples. Landfill leachate sampling was carried out from November 2011 to August 2012. The collected samples were transported to the laboratory and stored at $4^{o}C$ until analysis of the samples.

2.2.2 Leachate characterization

Mainly, four groups of pollutants, general water quality parameters, anions and cations, organic pollutants and heavy metals were measured in collected leachate samples using standard methods. Dissolved oxygen (DO), pH, oxidation reductive potential (ORP), electrical conductivity (EC), suspended solids, total nitrogen (TN) and total phosphorous (TP) were measured as general water quality parameters. DO, pH, ORP and EC were analyzed using DO meter (DKK-TOA corporation, Japan), pH meter (DKK-TOA corporation, Japan), ORP meter (DKK-TOA corporation, Japan) and EC meter (DKK-TOA corporation, Japan), respectively. Suspended solids were measured by filtration followed by oven drying. TN and TP were analyzed using colorimetric method (UV mini 1240, Shimadzu, Japan).

Ion chromatography technique was used to measure the anions and cations in landfill leachate. Anions, F^-, Cl^-, NO_2-N, NO_3-N, SO_4^{2-} and PO_4^{3-} and cations, NH_4^+, Mg^{2+} and Ca^{2+} were analyzed in collected landfill leachate samples using CLASS-VP software (Shimadzu, Japan).

The amount of organic pollutants in landfill leachate was measured in terms of biochemical oxygen demand for five days (BOD_5), chemical oxygen demand (COD), total organic carbon (TOC), inorganic carbon (IC) and total carbon (TC). TOC analyzer (TOC-V CSH, Shimadzu, Japan) was used to measure the TOC and IC. TC was calculated from IC and TOC results for each sample. Standard methods were used to analyze BOD_5 (Water test kit, Kyoritsu chemical check lab, corp., Japan) and COD (HACH DRB 200, USA) in leachate samples.

Landfill leachate was characterized by total heavy metal availability. Total concentrations of Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sr, Cd, Sb and Pb were measured in inductively coupled plasma mass spectrometer (ICPM-8500, Shimadzu, Japan). Concentrations of pollutants were compared among landfill sites as well as with the maximum tolerance limit of each pollutant based on Sri Lankan Standards.

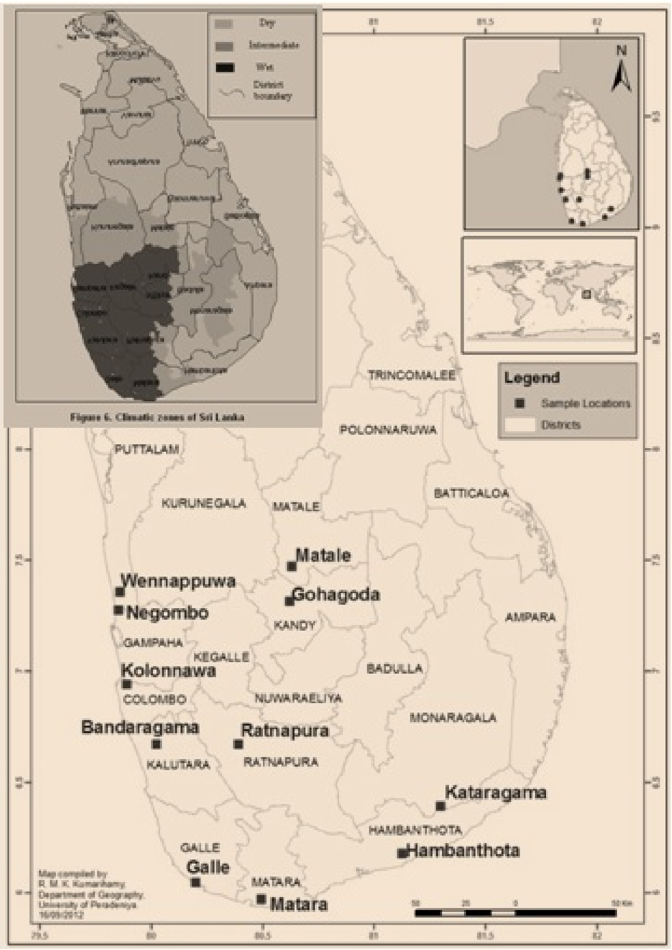

Figure 2.1: Landfill leachate sampling sites

Comparison of heavy metal concentrations in leachate to the maximum permissible levels was carried out by calculating quality rating scales as per the eq. 2.1 (Ramakrishnaiah et al., 2009).

$$q_i = \frac{C_i}{S_i} \times 100 \qquad (2.1)$$

Where,

q_i = Quality rating scale (%)

C_i = Concentration of heavy metal in leachate (mg L^{-1})

S_i =Tolerance limit/maximum permissible level of heavy metal (mg L^{-1})

Sub-indices of leachate pollution index (LPI) and the overall LPI were used to characterize landfill leachate from different sites. Sub-indices of LPI; LPI inorganic

(LPI_{in}), LPI organic (LPI_{or}) and LPI heavy metals (LPI_{hm}) were calculated as per the Equation 2.2 (Kumar and Alappat, 2005a). Finally, overall LPI for leachate samples was calculated using Equation 2.3.

$$LPI = \frac{\sum_{i=1}^{n} w_i p_i}{\sum_{i=1}^{n} w_i} \qquad (2.2)$$

Where LPI is the leachate pollution index, w_i is the weight factor for the ith pollutant variable, p_i is the sub index score of the ith pollutant variable and n is the number of leachate pollutant variables used in calculating LPI.

$$Overall\,LPI = 0.232LPI_{or} + 0.257LPI_{in} + 0.511LPI_{hm} \qquad (2.3)$$

Leachate quality of the studied open dumpsites were compared with the Sri Lankan standards for wastewater to be discharged into inland surface water and composition of landfill leachate as reported by Kjeldsen et al. (2002).

2.3 Results and Discussion

Leachate quality is affected by environmental factors (temperature, moisture content), climatic factors (precipitation, drought), and composition of wastes. Thus, the quality of leachate changes with time and the location of the dumpsite. Selected open dumpsites for leachate collection are located in different areas of Sri Lanka. Most of them are located in the Wet Zone (Matale, Bandaragama, Kolonnawa, Gampola, Gohagoda, Wennappuwa, Rathnapura, Negombo and Galle) of Sri Lanka while Hambantota and Kataragama are located in the Dry Zone. Open dumpsite located in Matara belongs to the Intermediate Zone of Sri Lanka.

2.3.1 Variation of general water quality parameters

General water quality parameters in landfill leachate are illustrated in Fig. 2.2. Almost all the leachate samples show a basic pH value ranging from 7.5 to 8.6 except for Rathnapura and Kolonnawa samples. The pH of leachate from Rathnapura and Kolonnawa dumpsites showed an acidic pH, 5.7 and 6.24, respectively. Generally, the fresh landfill leachate shows an acidic pH than matured leachate. Chen (1996) has observed the same variation in a study carried out to assess leachate characteristics. He has found that the pH of landfill leachate is increased with the age of the landfill due to the biological decomposition of organic N into ammonium N. The result in this study also shows the same tendency as that indicated by Chen (1996).

All the landfill leachate samples have a very low DO concentration which shows an anaerobic condition. This is also verified by the negative ORP values of the leachate samples. Electrical conductivity of all the samples ranged from 450 to 3830 mS m^{-1}. The highest EC was reported from Kolonnawa leachate sample which indicates that the dissolved ion content in landfill leachate from Kolonnawa site is higher over the other sites.

Total residue on evaporation represents the sum of both suspended and dissolved solids including colloidal materials in leachate. Kolonnawa leachate sample has the highest total residue among all the samples. Other samples had more or less similar concentration of total residue. However, approximately equal amount of suspended solids concentration were observed in all the samples. Therefore, the rest of the total residue is dissolved solids (DS) and the DS concentration is much higher in Kolonnawa sample than that in the other leachate samples.

2.3.2 Anions and cations in landfill leachate

Nitrogenous pollutants in landfill leachate

Fig. 2.3 shows NH_4-N, NO_2-N and NO_3-N concentrations variation in landfill leachate from different dumpsites. Landfill leachate samples from Hambantota and Kataragama show very low concentrations of nitrogenous pollutants compared to other samples. Moreover, almost all the samples show very low concentrations of NO_2^- and NO_3^- as well as a high concentration of NH_4^+. Nitrite and nitrate concentrations were varied from 0 to 58.29 mg L^{-1} and 2.19 to 132 mg L^{-1}, respectively. On the other hand, ammonium concentration in leachate samples studied varied from 34 to 2753 mg L^{-1}. The highest concentration of NO_2^- and NO_3^- were shown in landfill leachate from Gohagoda and Negombo open dumpsites, respectively. As shown in Fig. 2.3, the lowest and the highest NH_4^+ were shown in leachate from Kataragama and Matale dumpsites, respectively.

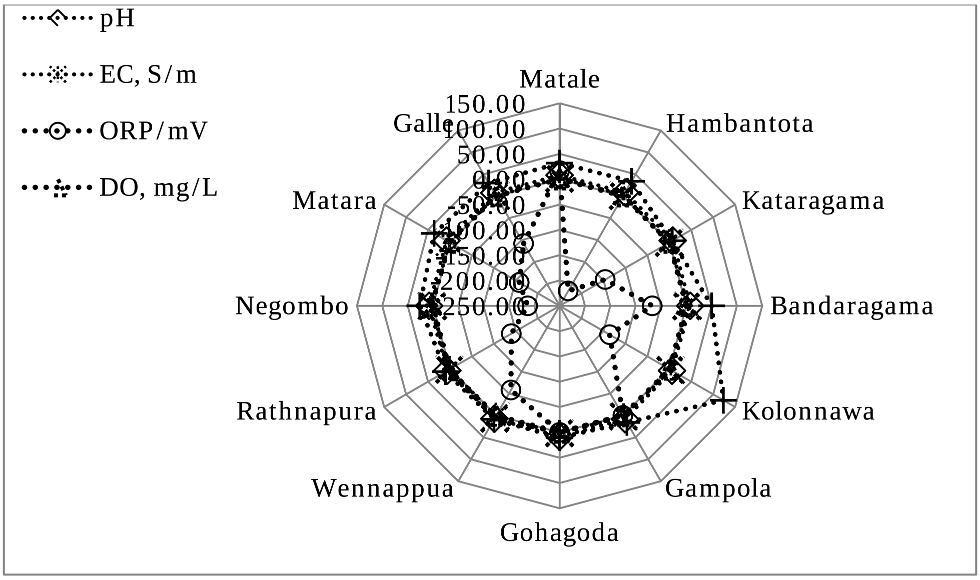

Figure 2.2: Variation of general water quality parameters in landfill leachates from different dumpsites

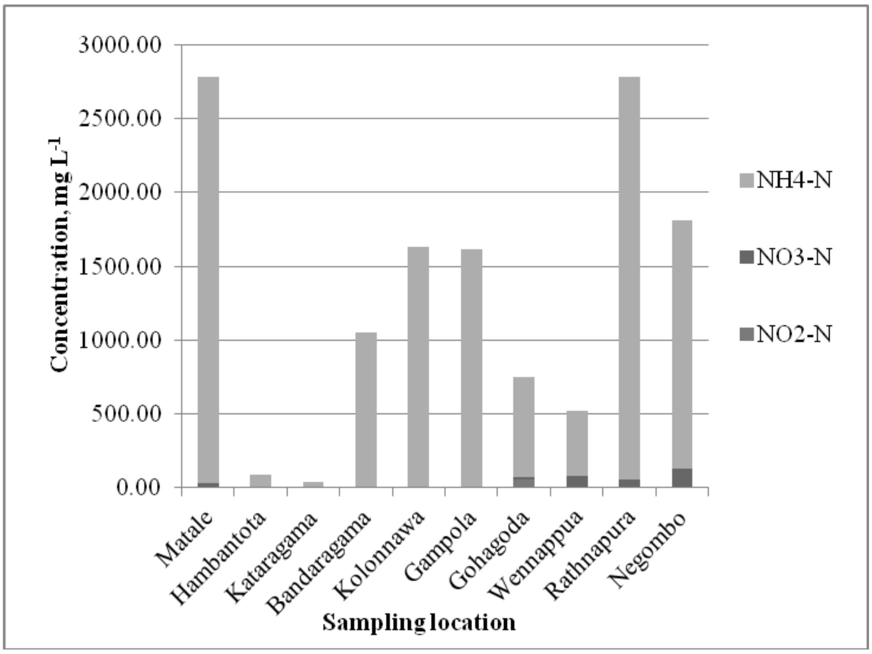

Figure 2.3: Nitrogenous pollutant variation in landfill leachate

In the case of nitrogenous pollutants, total ammonia, which has two forms as ammonium ion (NH_4^+) and free ammonia (NH_3), is important (Sri Shalini and Joseph, 2012). From the two forms, NH_3 is the active substrate and the most important N compound in surface water and other ecosystems. Ammonia concentration in landfill leachate varies with the age of the dumpsite ranging 100-

5500 mg L^{-1} (Renoui et al., 2008). Sri Shalini and Joseph (2012) have stated that four groups of NH_3 as, beneficial (50-200 mg L^{-1}), detrimental (200-1000 mg L^{-1}), inhibitory (1500-3000 mg L^{-1}) and toxic (>5000 mg L^{-1}). However, in this study ammonia was not estimated as free ammonia in leachate and it was measured as NH_4^+. Most of the samples show a high concentration (>1000 mg L^{-1}) of NH_4^+ which indicates that the leachate is from old landfills and the high concentrations are resulted from hydrolysis and fermentation of the nitrogenous fractions of biodegradable substrates (Carley and Mavinic, 1991). Only leachate from Hambantota and Kataragama sites showed very low concentrations of NH_4^+ and it further suggests that landfill leachate from new landfills has very low NH_4^+ concentration.

Other anions and cations in landfill leachate

Analysis of F^-, Cl^-, SO_4^{2-}, PO_4^{3-}, Mg^{2+} and Ca^{2+} in leachate was carried out. Fluoride concentration was not detectable in the leachate from Gampola and Gohagoda dumpsites. Very high concentrations compared to maximum permissible level (2 mg L^{-1}) of F^- in wastewater to discharge in to inland surface water were observed from other dumpsites. Among them, leachate from Kolonnawa dumpsite showed a very high concentration of F^- (117 times higher than max. permissible limit) than other sites.

Chloride concentration in leachate in sites except for Kataragama is ranged from 3 to 6 times higher than the maximum permissible level and the highest concentration was observed in Kolonnawa leachate sample. The high concentrations of F^- and Cl^- in Kolonnawa landfill leachate could be due to the dumping of specific type of solid waste that contains F^- and Cl^-.

Sri Lankan standards for portable water was used to compare PO_4^{3-}, SO_4^{2-}, Mg^{2+} and Ca^{2+} ions in landfill leachate. Based on that, maximum permissible levels of PO_4^{3-}, SO_4^{2-}, Mg^{2+} and Ca^{2+} are 2.0, 400, 150 and 240 mg L^{-1}, respectively. Even though, the other pollutants are higher in Kolonnawa leachate sample, PO_4^{3-} was not detectable. Some sites showed a higher concentration than maximum permissible level. Very low concentrations of SO_4^{2-} were shown in landfill leachate from Matale, Kataragama and Bandaragama dumpsites. It was varied from 1.4 to 5.3 times higher than the maximum permissible level (400 mg L^{-1}) in other sites studied.

Only three sites, Matale, Hambantota and Bandaragama showed higher concentrations of Mg^{2+} than maximum permissible level in leachate. On the other hand, very low concentrations of Ca^{2+} were observed in all the sites. These two cations, $Mg^{2+}$and Ca^{2+} are important in water quality as they cause hardness in water creating many problems such as formation of soap scum, galvanic corrosion etc.

2.3.3 Organic pollutants

Total organic and inorganic carbon in leachate

Total organic carbon and inorganic carbon content variation in landfill leachate are illustrated in Fig. 2.4. Total carbon content in leachate is illustrated together with TOC and IC (Fig. 2.4). Accordingly, TC content is very high in Kolonnawa leachate sample than the other samples. In addition, IC content is very low in Kolonnawa, Matara and Galle leachate samples than the other sites and those were 50, 80 and 49 mg L^{-1}, respectively. Thus, almost all the TC in that leachate is organic carbon. Therefore, the wastes disposed in these landfill sites could be organic in nature. On the other hand, IC content is higher than the TOC content in landfill leachate from Wennanppuwa, Rathnapura and Negombo sites.

Other organic pollutants in leachate

Maximum permissible levels of BOD_5 and COD are 30 and 250 mg L^{-1}, respectively based on Sri Lankan standards. Both lowest BOD_5 and COD have resulted from Gohagoda landfill leachate and the highest BOD_5 and COD have resulted from Kolonnawa landfill leachate (Table 2.1). Both BOD_5 and COD in Kolonnawa landfill leachate are extremely higher than the other leachate samples and the concentrations are 49600 and 82577 mg L^{-1}, respectively. Kolonnawa landfill site is located near the Capital of Sri Lanka and the disposal of industrial wastes near Colombo area could be the reason for the high concentration of BOD_5 and COD.

Biodegradability of wastes can be measured by the ratio of BOD_5/COD (Kulikowska and Klimiuk, 2008). In this study, the ratio of BOD_5/COD varies from 0.01- 0.6 which indicates that the amount of biodegradable wastes are different in dumpsites studied. The highest amount of biodegradable wastes is in Kolonnawa landfill leachate followed by Rathnapura leachate. The ratio of BOD_5/COD in Kolonnawa and Rathnapura landfill leachates are 0.6 and 0.27, respectively. All the other samples show very low values of BOD_5/COD ratio which indicates a considerable amount of biologically inert materials in leachates. Moreover, it has shown that the ratio of 0.1 or lower is resulted from old landfill leachate (Kurniawan et al., 2006).

In contrast, the TN showed a higher concentration in leachate from Matale and Gampola landfill sites and the TP concentrations were low in all the leachate samples.

2.3.4 Heavy metals in landfill leachate

Heavy metals in landfill leachate were determined as total metal concentration. Heavy metal concentrations were compared with the maximum permissible level of heavy metal in wastewater to be discharged in to inland surface water (CEA, 1990). Heavy metal concentrations and the respective quality rating scales (QRS) are listed in Table 2.2 and 2.3, respectively.

The impact of heavy metal is different from each other and accordingly the maximum permissible level is different. Therefore, it is important to consider a common factor like QRS to study the impact of heavy metals. Table 2.2 shows the maximum permissible level of heavy metals based on Sri Lankan standards for wastewater to be discharged in to inland surface waters (CEA, 1990). Accordingly, maximum permissible levels of As, Cr, Cd and Pb are lower than the other metals.

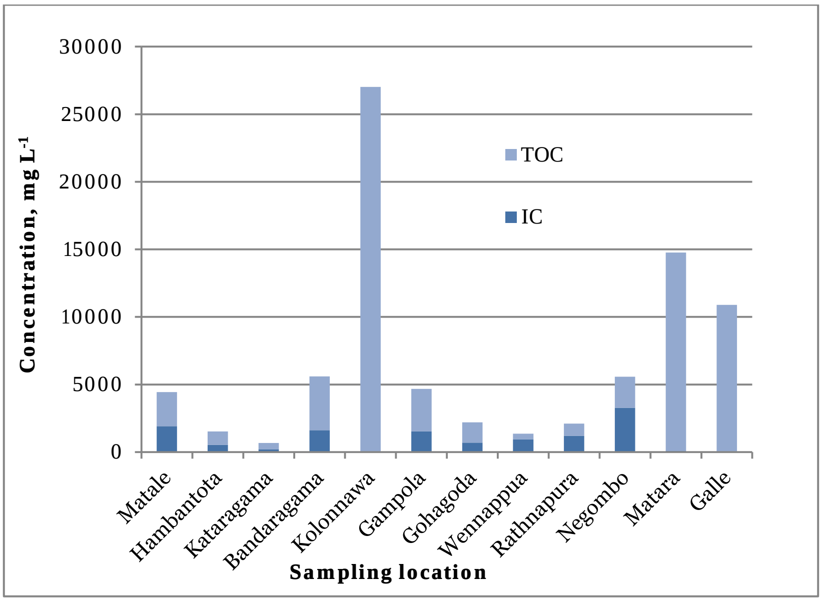

Figure 2.4: Variation of TOC and IC in landfill leachate

Even though, the concentrations of those metals are low, the impact of them is higher which is shown by the QRS (Table 2.3). Most of the heavy metals studied showed a higher concentration in Kolonnawa leachate sample which could be a result of dumping industrial wastes on to the Kolonnawa dumpsite since it is located near to an industrial area.

Table 2.1: Biochemical oxygen demand, chemical oxygen demand, total nitrogen and total phosphorous content in leachate

Sample	BOD_5	COD	BOD_5/COD	TN	TP
Matale	71	4236	0.02	1549	43
Hambantota	49	2475	0.02	224	12
Kataragama	38	1047	0.04	180	20
Bandargama	938	9279	0.10	305	24
Kolonnawa	49600	82577	0.60	664	11
Gampola	41	1249	0.03	1212	6
Gohagoda	19	714	0.03	684	8
Wennappuwa	86	2405	0.04	361	18
Rathnapura	3757	13951	0.27	558	35
Negombo	294	18328	0.02	703	86

Landfill leachate from Kataragama landfill shows only high concentration of Pb and the concentration of other metals are lower than the maximum permissible level. It was observed that most of the wastes dumped in the Kataragama landfill are food wastes from the nearby temple. It can be the reason for low levels of other pollutants also in Kataragama landfill leachate.

Even though, the concentrations of Ni and Cu are higher in most of the leachate samples, the impact is very low compared to other metals. The highest QRS for Ni (149%) was obtained for Kolonnawa leachate sample and none of the QRS values of Cu exceeded 100.

Among the heavy metals studied in this study, Cr, Fe, As, Se and Cd show higher QRS for most of the samples. However, some researchers have mentioned that Fe is not considered as a heavy metal and that falls onto the group called inorganic macro-components which occur at high concentrations (Slack et al., 2005).

Table 2.2: Heavy metal concentrations in landfill leachate and the maximum tolerance limits of heavy metals. Values are in µg L^{-1}

Sample	*Cr*	*Fe*	*Ni*	*Cu*	*Zn*	*As*	*Se*	*Cd*	*Pb*
Matale	*345*	*60762*	*115*	*573*	*6876*	*522*	*1935*	*100*	*1777*
Hambantota	*80*	*5341*	*226*	*166*	*19909*	*678*	*2522*	*172*	*492*
Kataragama	*11*	*1117*	*89*	*58*	*638*	*106*	*400*	*50*	*123*
Bandargama	*329*	*7167*	*912*	*227*	*5362*	*722*	*2607*	*90*	*479*
Kolonnawa	*1968*	*346930*	*4473*	*55*	*11759*	*705*	*2443*	*15*	*421*
Gampola	*220*	*5546*	*335*	*734*	*462*	*164*	*461*	*4*	*34*
Gohagoda	*139*	*3004*	*331*	*334*	*389*	*148*	*465*	*1*	*19*
Wennappuwa	*363*	*2501*	*399*	*431*	*409*	*939*	*2812*	*53*	*87*
Rathnapura	*439*	*56343*	*1311*	*627*	*1685*	*1551*	*4922*	*52*	*168*
Negombo	*330*	*20111*	*666*	*535*	*2062*	*846*	*2184*	*51*	*333*
Matara	*830*	*7528*	*571*	*464*	*500*	*1219*	*3705*	*48*	*60*
Galle	*486*	*15477*	*673*	*564*	*593*	*1796*	*5947*	*52*	*169*
Max. permissible level	***100***	***3000***	***3000***	***3000***	***5000***	***200***	***500***	***100***	***100***

Table 2.3: Quality rating scale values of heavy metals for leachate samples. Values are in percentages

Sample	QRS_{Cr}	QRS_{Fe}	QRS_{Ni}	QRS_{Cu}	QRS_{Zn}	QRS_{As}	QRS_{Se}	QRS_{Cd}	QRS_{Pb}
Matale	**345**	**2025**	38	19	**138**	**261**	**387**	**100**	**1777**
Hambantota	80	**178**	8	6	**398**	**339**	**504**	**172**	**492**
Kataragama	11	37	3	2	13	53	80	50	**123**
Bandargama	**329**	**239**	31	8	**107**	**361**	**521**	90	**479**
Kolonnawa	**1968**	**11564**	**149**	2	**235**	**352**	**488**	15	**421**
Gampola	**220**	**185**	11	24	9	82	92	4	34
Gohagoda	**139**	**100**	11	11	8	74	93	1	19
Wennappuwa	**363**	83	13	14	8	**469**	**562**	53	87
Rathnapura	**439**	**1878**	44	21	34	**775**	**984**	52	**168**
Negombo	**331**	**670**	22	18	42	**423**	**437**	51	**333**
Matara	**831**	**251**	19	16.	10	**609**	**741**	48	60
Galle	**486**	**516**	22	19	12	**898**	**1189**	52	**169**

2.3.5 Leachate Pollution Index

Leachate pollution index is a quantitative tool to evaluate the leachate contamination potential over time and to compare leachate contamination potential of different landfills in a given area (Rafizul et al., 2012). Even though, LPI has been developed using 18 pollutant parameters, it can be calculated from the less number of pollutant parameters (Equation 2.2). However, LPI fails to represent the effect of different pollutant groups present in landfill leachate. Therefore, Kumar and Alappat (2005b) have formulated sub-indices of LPI; LPI inorganic (LPI_{in}), LPI organic (LPI_{or}) and LPI heavy metals (LPI_{hm}).

Sub-indices of LPI and overall LPI calculated for Matale landfill leachate sample are shown in Table 2.4. Accordingly, pollution potential by inorganic pollutants is higher in leachate from Matale dumpsite over that of by organic pollutants and heavy metals. Similarly, sub-indices of LPI and overall LPI were calculated for leachates from other sites and for the standards levels of pollutants in wastewater to be discharged into inland surface waters. The calculated values for leachate samples along with the climatic zone and the precipitation data for each site are shown in Table 2.5. Sub-indices of LPI and the overall LPIs for the Sri Lankan standards for wastewater to be discharged into inland surface water and composition of landfill leachate reported in literature are also shown in Table 2.5.

Leachate from Kolonnawa, Rathnapura and Bandaragama showed higher LPI_{or} of 91.53, 62.61 and 51.17, respectively (Table 2.5). On the other hand, the highest values of LPI_{in}, 65.42 and 62.62 were resulted from leachates of Bandaragama and Kolonnawa sites, respectively. Therefore, it indicates that leachates from Kolonnawa, Bandaragama and Rathnapura sites are polluted with organic and inorganic pollutants over the other sites. Leachate from Kolonnawa dumpsite possesses the highest risk of heavy metals which is clearly indicated by the highest LPI_{hm} of 10.12. Moreover, leachates from Gohagoda and Matale sites also showed high risk of contaminant potential of heavy metals even though contaminant potentials of organic and inorganic pollutants are comparatively lower (Table 2.5). Overall LPI was higher in landfill leachate from Kolonnawa, Bandaragama and Rathnapura sites as 442.5, 31.31 and 25.93, respectively.

The results give detailed information about the composition of landfill leachate from each site. Accordingly, leachate of Kolonnawa site has the highest risk of environmental pollution with respect to the organic pollutants and heavy metals. It has found that heavy metal can form colloids or complexes, especially with organic matter in leachate (Christensen and Christensen, 1999; Jensen and Christensen, 1999). Therefore, heavy metals in leachte from Kolonnawa site may form the complexes with high amount of organic matter leading to a high concentration of heavy metals than the other sites. Moreover, Kolonnawa open dumpsite is located in Colombo, the capital of Sri Lanka and therefore the wastes dumped in the site can have all kinds of solid wastes including industrial, household, agricultural wastes (Esakku et al., 2007).

Comparison of LPI values of leachates in this study with the data reported in the literature shows that all the sub-indices of LPI and the overall LPI values for the sites studied are within the range of composition of landfill leachate except LPI_{in} of Kataragama site. The general leachate composition reported in Kjeldsen et al., (2002) are based on the data from newer landfills. Accordingly, it is clear that the leachate generated from the open dumpsites studied possesses characteristics similar to the leachate generated from new landfills.

Table 2.4: Sub-indices of LPI and overall LPI for leachate sample from Matale MSW dumpsite

Index	**Parameter**	**Pollutant concentration, mg L^{-1}**	**Sub-index value, p_i**	**Weight factor, w_i**	**$w_i p_i$**
LPI organic,	BOD_5	71.0	7.0	0.263	1.84
	COD	$4.23x10^3$	60.0	0.267	16.02
				0.530	17.86
LPI_{or}					**33.70**
LPI inorganic,	pH	8.0	5.0	0.214	1.07
	TDS	$3.01x10^4$	75.0	0.195	14.63
	NH_4-N	$2.75x10^3$	100.0	0.198	19.80
	Cl^-	$4.02x10^3$	33.0	0.187	6.17
LPI_{in}				0.794	41.67
					52.48
LPI heavy metal,	Total Fe	60.7	6.0	0.088	0.53
	Cu	0.6	6.0	0.098	0.59
	Ni	1.1	7.0	0.102	0.71
	Zn	6.9	6.0	0.110	0.66
	Pb	1.8	12.5	0.123	1.54
	Cr	0.3	5.3	0.125	0.67
	As	0.5	5.3	0.119	0.62
				0.765	5.31
LPI_{hm}					**6.94**
LPI	$0.232LPI_{or}+0.257LPI_{in}+0.511LPI_{hm}$				24.85

Comparison of sub-indices of LPI of leachate samples with the standards shows that the leachates from all dumpsites contain organic and inorganic pollutants exceeding the Sri Lankan standard limits for the discharge into inland surface waters. Even though, overall LPI value is greater than the reference value, only leachate from Kolonnawa and Gohagoda exceeds the standard limits for the heavy metals as per the LPI_{hm} values. This further confirms the importance of characterizing leachate based on sub-indices of LPI rather than overall LPI, for an effective remediation of pollutants. Therefore, the leachate treatment facility for Kolonnawa and Gohagoda should be focused on removal of heavy metals in addition to the inorganic and organic pollutants. All the other sites have to be implemented with a treatment facility for the removal of organic and inorganic pollutants. In addition, a care has to be taken to prevent increase of heavy metals in leachate from other sites which helps to maintain the LPI_{hm} below the reference LPI_{hm}.

Overall LPI for leachate from all the sites are within the range of LPI for the composition for landfill leachate. Moreover, LPI of leachate from all sites higher than the reference LPI, 7.4 which is based on Sri Lankan standards for wastewater to be discharged into inland surface water. This implies the need for the treatment of leachate from open dumpsites to protect the environment.

The results indicate that the leachate treatment methods to be used in Kolonnawa, Gohagoda and Matale sites should be given a more concern on removal of heavy metals. In addition, special care must be taken to prevent the leachate flow into the natural water bodies especially due to unlined landfills. In the cases of Gohagoda and Matale dumpsites, leachates directly flow into the ground contaminating soil and groundwater sources nearby. Therefore, site specific leachate treatment methods have to be used after characterizing the leachate.

In the cases of Rathnapura and Bandaragama dumpsites, special care must be taken focusing on organic and inorganic pollutants in leachate. Further, it is important to consider on organic matter and heavy metal removal in the leachate treatment facility for the Kolonnawa site. Similarly, sub-indices of LPI gives contaminant potential specific to a group of pollutants in which overall LPI fails to give. Thus, the information provided by sub-indices of LPI can be used in planning, designing and implementation of remediation measures for a particular site.

However, it is important to note that here; some error can be existed as all the 18 parameters were not available in calculating overall LPI as well as sub-indices of LPI. Some researchers have assumed that the concentration of the missing parameters based on the concentrations reported from the other landfills in the region. However, Kumar and Alappat (2005c) have found that the error will not be higher if the sub index values of the missing parameters are not too high or too low.

Table 2.5: Sub-indices of LPI and overall LPI for leachate from each site with climatic zone and precipitation data

Sampling site	**LPI_{or}**	**LPI_{in}**	**LPI_{hm}**	**Overall LPI**
Matale	33.70	52.48	6.94	24.85
Hambantota	29.17	34.96	6.08	18.86
Kataragama	24.65	7.71	5.02	10.26
Bandaragama	51.17	65.42	5.59	31.54
Kolonnawa	91.53	62.62	10.53	42.71
Gampola	22.62	44.77	5.17	19.40
Gohagoda	17.10	29.18	5.03	14.03
Wennappuwa	38.59	15.97	5.39	15.81
Rathnapura	62.61	32.35	5.75	25.78
Negombo	45.26	43.31	5.59	24.49
Landfill leachate[a]	7-94	11.6-61.1	5-62.9	7.2-69.7
Reference[b]	8.0	6.7	7.5	7.4

[a] based on the data reported in Kjeldsen et al. (2002).

[b] based on Sri Lankan standards for wastewater to be discharged into inland surface water

The pollution potential may be affected by the type of wastes dumped in the site. For example the major sources of organic pollutants are domestic and industrial origin (Holt, 2000). Further, high concentration of Fe in leachate indicates that the Fe and steel wastes have been placed on dumpsites (Mor et al., 2006).

2.4 Summary and Conclusions

The results of the study showed clearly the complex nature of landfill leachate from different sites due to the differences in waste composition, moisture content, climatic conditions etc. the effect of each pollutant was different from site to site as the concentration of each pollutant varies with the site. It was noted that the most of the pollutants, BOD_5, COD, TOC and some heavy metals are much higher in landfill leachate from Kolonnawa site while nitrogenous pollutants are higher in landfill leachate from Matale dumpsite. The highest concentrations of BOD_5, COD, and TOC are 49600, 82577 and 26970 mg L^{-1}, respectively.

Sub-indices of leachate pollution index (LPI) provide pollutant potential of landfill leachate specific to a type of pollutant group where overall LPI fails to give. Highest LPI_{or} and LPI_{hm} of 91.53 and 10.12 were shown by leachates from Kolonnawa site. However, the highest LPI_{in} of 65.4 is resulted in leachate from Bandaragama. Leachates from Kolonnawa site showed high risk of contaminant potential of heavy metals as shown by QRS and LPI values. It can be concluded that the leachate from Kolonnawa dumpsite possess the highest risk of environmental pollution. LPI of leachate from all sites shows a higher value than the reference LPI. This very clearly shows the importance of assessing pollution potential with respect to sub-indices of LPI and the results can be used in planning, designing and implementation of leachate treatment methods for each site.

Even though the quality rating values of most of the heavy metals are exceeding the value of 100, only leachate from Kolonnawa site exceeded the reference value of LPI_{hm}. Though the heavy metals are not shown as the critical pollutant, heavy metals are most difficult to clean and cause serious problems to the releasing bodies. On the other hand, there are many studies on inorganic and organic pollutants and thereby heavy metals were selected for further studies in this research.

Supporting papers

Sewwandi, B. G. N., Koide Takahiro, Ken Kawamoto, Shoichiro Hamamoto, Shingo Asamoto and Hiroyasu Sato.2012. Characterization of Landfill Leachate from Municipal Solid Waste Landfills in Sri Lanka. In Proc. 2nd International Conference on Sustainable Built Environment. 14-16 December 2012. Kandy, Sri Lanka. pp 21.

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Chapter 3 ADSORPTION OF Cd(II) AND Pb(II) ONTO HUMIC ACID–TREATED COCONUT (*Cocos nucifera*) HUSK

Abstract

This study was conducted to characterize the adsorption of Cd^{2+} and Pb^{2+} by raw coconut husk (RCH) and humic acid–treated coconut husk (HACH). Grounded and sieved coconut husk (CH) from Sri Lanka was treated with humic acid to use as the adsorbent in laboratory experiments. Capacities of HACH and RCH for adsorption of Cd^{2+} and Pb^{2+} at different pH, ionic strengths, initial metal concentrations, and contact times between adsorbent and adsorbate were measured. The effects of binary metal solution, anions, and cations on adsorptions of Cd^{2+} and Pb^{2+} by treated and non-treated CH in batch experiments were also examined. The surface characteristics of HACH and RCH were investigated by scanning electron micrography (SEM), X-ray energy dispersion analysis (EDAX), methylene blue (MB), and Brunauer, Emmett and Teller (BET) methods to explain the results. Results showed that adsorption of Cd^{2+} and Pb^{2+} ions by HACH was independent of pH and ionic strength. The maximum adsorption capacities of Cd^{2+} and Pb^{2+} of HACH were 47.28 and 66.26 mg g^{-1} and were greater than 24.24 and 21.21 mg g^{-1} for RCH. The adsorption of both Cd^{2+} and Pb^{2+} onto HACH was a chemical sorption, and Pb^{2+} adsorption needed a longer reaction time than Cd^{2+} adsorption. The adsorption reaction rates of Cd^{2+} and Pb^{2+} of HACH were 0.056 and 3.17 mg g^{-1} min^{-1}. Some anions and cations affected the adsorption of Cd^{2+} and Pb^{2+} onto HACH. Based on the results from adsorption tests under different conditions, RCH and HACH are effective for individual removal of Cd^{2+} and Pb^{2+} from aqueous solutions. However, humic acid treatment effectively removes metal ions from single metal solutions, although the removal of metal ions in the presence of co-existing ions and other anions and cations could be retarded.

3.1 Introduction

Industrial discharge of toxic substances like heavy metals and their accumulation in the environment causes degradation of the ecosystem (Xu et al., 2008; Bansal et al., 2009; Lesmana et al., 2009; Bulgariu and Bulgariu, 2012). At present, various sources of heavy metals are recognized: electroplating, batteries, metal surface coating treatments, and industries such as textile, pigments, plastics, and mining (Bulgariu and Bulgariu, 2012; Cheng et al., 2012). The removal of heavy metals from industrial wastewater is of great importance due to their impact on the environment. As a result, different treatment methods including chemical precipitation (Kornboonraksa et al., 2009; Fu et al., 2012), coagulation-flocculation (Amakrone et al., 1997), floatation and electrochemical processes (Raghu and Ahmed Basha, 2007; Belkacem et al., 2008), adsorption (El-Shafey, 2007; Ofomaja and Ho, 2007; Bansal et al., 2009; Najim et al., 2009), membrane filtration (Mavrov et al., 2003), and ion exchange (Dabrowski et al., 2004) have been used in removing heavy metals from wastewater. The use of advanced technologies for treating wastewater, however, has become limited, especially in developing countries, due to their high cost and low feasibility in small-scale industries (Pagnanelli et al., 2001; Liu et al., 2010; Mahmoud et al., 2010).

Among the different methods of removing heavy metals, on the other hand, biosorption has become popular recently due to the simplicity of the process, effectiveness, and low cost (Cheng et al., 2012). Different types of biosorbents from agricultural by-products and biowaste materials such as sawdust (Božić et al., 2009; Sewwandi et al., 2012), rice husk (Bansal et al., 2009), algal waste biomass (Bulgariu and Bulgariu, 2012), and oil extracts (Rao and Khan, 2009) have been used in heavy metal removal. Raw and modified sawdust (SD) have been used by Sewwandi et al. (2012) to remove Cd^{2+} and Pb^{2+} from aqueous solutions. They found that raw SD is more capable of removing mentioned metals than acid- or base-treated SD. Božić et al. (2009) studied the abilities of SD of three different trees to remove Cu^{2+} and Fe^{2+} from synthetic wastewater and reported that the initial concentration of the metals and adsorbent concentration strongly affected the removal process.

Rice husk (RH) has been used with pretreatments such as boiling and formaldehyde treatments to remove Cr^{6+} from synthetic wastewater (Bansal et al., 2009), and the two treatments were not found to be different. Boiled RH would be more prevalent in small-scale industries to remove Cr^{6+}. Green algae waste biomass has been used to remove Pb^{2+}, Cd^{2+}, and Co^{2+} from aqueous solutions. The best removal of heavy metals was obtained at pH 5 and a contact time of 60 s (Bulgariu and Bulgariu, 2012). Rao and Khan (2009) studied the capacity of Neem oil cake to remove Cu^{2+} and Cd^{2+}. The results showed that the maximum sorption of metals onto the biosorbent occurs in acidic medium and that it increases with an increase in the initial metal concentration.

Coconut husk (CH) is a byproduct of the coconut industry, and it is abundantly available in tropical countries such as India, Sri Lanka, and Thailand. CH is rich in short/medium length fibers with a typical diameter of hundreds of micrometers and powdered coir pith/dust with a particle size ranging from a few micrometers to a few millimeters (Nam et al., 2011). According to Abad et al. (2002), the coir dust obtained from Sri Lankan coconut (*Cocos nucifera L.*) averages 476 g kg^{-1} lignin, 329 g kg^{-1} cellulose, and 56 g kg^{-1} hemicellulose on dry weight basis. Raw and treated coir pith have also been used for wastewater treatment. Makehelwala et al. (2009) studied the mechanism of Cr^{6+} adsorption by coir pith and found that reductive adsorption of Cr^{6+} occurred. Moreover, they found that the adsorption is dependent on pH and ionic strength. Adsorptions of Co^{2+}, Cr^{3+}, and Ni^{2+} onto coir pith have been studied as single ions and a mixture of ions (Parab et al., 2006). The results of the study showed that coir pith is efficient as a low cost adsorbent to remove these metals. In addition, coir pith carbon (Kavitha and Namasivayam, 2007) and $ZnCl_2$-activated coir pith carbon (Namasivayam and Sangeetha, 2004) have been used to remove methylene blue and phosphate in laboratory experiments. However, while modification of different biomass types with chemical substances has given better removal of heavy metals from wastewater (Gode et al., 2008; Liu, et al., 2010; Wong et al., 2003), less attention has been paid to the treatment of CH to increase its metal removal efficiency.

Humic acid is a naturally occurring substance in soils, marine and lake sediments, natural waters, and peat that has a comparatively large molecule. It contains functional groups such as -COOH, -OH, -C=O, and $-NH_2$ that can affect the bonding distribution of cations of trace metals in the environment (Lubal et al., 1998; Coles and Yong, 2006). Therefore, the use of humic acid for modification of a biomass may enhance its metal uptake capacity. In addition, real wastewater contains various physical and chemical substances including heavy metals, anions, and cations that can interfere with the adsorption of heavy metals onto biosorbents. Thus, it is important to study the adsorption of heavy metals in binary metal solutions and the effect of anions and cations on adsorption. Certain anions (SO_4^{2-} and PO_4^{3-}) and cations ($Mg^{2+}$and Ca^{2+}) that are commonly found in natural environment can interfere the adsorption of heavy metals in actual field conditions. Therefore, the objectives of this study were (1) to determine the adsorption capacity of HACH for Cd^{2+} and Pb^{2+} adsorption at different pH, ionic strength, initial metal concentration, and contact time of adsorbent and adsorbate, (2) to study the effects of Cd^{2+} and Pb^{2+} on adsorption in a binary metal solution, and (3) to study the effects of anions and cations on adsorption.

3.2 Materials and Methods

3.2.1 Materials used

Coconut husk (CH) from the species *Cocos nucifera* is abundantly available in Sri Lanka as a byproduct of the coconut industry. CH was collected and sundried for several days after removal of the nut. Collected CH was ground and sieved to obtain the < 350 µm fraction for the experiments. Humic acid sodium salt (Sigma Aldrich, MO, USA), hereafter sodium humate, was used to treat CH. Sodium humate salts were dissolved in distilled water to obtain a 50 mg L^{-1} solution. The pH of the sodium humate solution was 6.85. Stock solutions of Cd^{2+} and Pb^{2+} (1000 mg L^{-1}) were prepared in distilled water using $CdCl_2$ and $PbCl_2$ (Sigma Aldrich), respectively. Stock solutions were diluted with distilled water as required to obtain the experimental solutions.

3.2.2 Treatment of CH with sodium humate

The biomaterial treatment method described by Gode et al. (2008) was adopted to treat the CH in this study. A portion of CH was treated with sodium humate to obtain humic acid–treated CH (HACH). The CH was stirred overnight with 50 mg L^{-1} sodium humate solution at a 1:25 mass:volume ratio at a rate of 400 rpm. Then, the suspension was filtered through a Whatman 42 filter, and the residue was washed with distilled water three times to remove the remaining sodium humate. Finally, the residue was dried at 50°C till the weight became constant.

3.2.3 Surface area and pore size distribution analysis

The surface area of CH was analyzed by methylene blue (MB) adsorption and N_2 adsorption techniques (Santamarina et al., 2002) for < 350 µm particles. A spectrophotometer (UV-160A, Shimadzu, Japan) was used for the MB adsorption technique, and the complete cation replacement determined by the titration curve was used to derive the surface area value. The chemical formula of MB is $C_{16}H_{18}ClN_3S$, and in aqueous solution, it is a cationic dye, $C_{16}H_{18}ClN_3S^+$, that can be adsorbed to negatively charged surfaces. The amount of adsorbed MB is used to determine the surface area of the particles (Chen et al., 1999). A TriStar II 3020 surface area and porosity analyzer (Micromeritics, GA, USA) was used in this study to analyze the surface area using the BET method. Surface area measurement by the N_2 adsorption technique was performed on a dry specimen obtained by heating and degassing. The measurement was carried out in triplicate. The pore size distribution of the material was determined using the adsorption isotherms obtained from the N_2 adsorption technique.

3.2.4 Scanning electron microscopy and X-ray energy dispersion analysis (EDAX)

Scanning electron microscopy (SEM) and EDAX analysis were carried out to study the surface microstructures of the CH particles and to obtain the elemental mapping on the surfaces of metal-adsorbed CH particles, respectively. A scanning electron microscope (Quanta 200 FEG, OR, USA) and EDAX analyzer (Oxford INCA Energy+, Cardiff, UK) were used in this study.

3.2.5 Surface charge characterization

The surface charge characterization of CH was done in terms of ξ potential as a function of pH. The pH of the solution was adjusted using 0.1 M HCl or 0.1 M NaOH. The experiment was conducted to determine the electrophoretic mobility of the CH particles at different pH values using a Zeta meter (Model 502, Nihon Rufuto, Japan). The ξ potential values were calculated at each and every pH using the Smoluchowski equation (Sze et al., 2003).

3.2.6 FT-IR analysis

The infrared spectra of RCH, HACH, and separately Cd^{2+}- and Pb^{2+}-treated HACH were analyzed by Fourier transform infrared spectroscopy (FT-IR) (Nicolet 6700 USA series, USA). Transmission spectra were obtained between 400 and 4000 cm^{-1}, with 4 cm^{-1} resolution and 128 scans. Sample pellets were prepared for FT-IR by mixing 20 mg of vacuum-dried samples (< 350 μm) with FT-IR grade 100 mg of KBr. Each pellet contained approximately 70 mg of the above mixture. Spectral analyses were performed using OMNIC (version 7.3) software.

3.2.7 Effect of pH and background ion concentration on adsorption

Adsorption experiments were conducted for HACH at 0.01, 0.005, and 0.001 M $NaNO_3$ ionic strength levels. In order to avoid the effect of precipitation on adsorption, it was decided to use the values measured pH range from 4 to 8. At the same time, the experiment was conducted using RCH at 0.001 M $NaNO_3$ concentration at the same pH range. The adsorbent concentration used was 2.5 g L^{-1}. The pH of solutions was adjusted using 0.1 M HNO_3 or 0.1 M NaOH, and 10 mL samples at each pH were withdrawn to polypropylene tubes and shaken in a water bath shaker for 24 h at 100 rpm (EYELA B603, Japan). After that, the samples were centrifuged (2500 rpm, 10 min), filtered with a membrane filter (Millipore 0.45 μm, MA, USA) after measuring the final pH of the samples, and used in data analysis. The filtrate was acidified for analysis by flame atomic absorption spectrometry (GBC 933; NSW, Australia). The initial concentrations of Cd^{2+} and Pb^{2+} used were 20 and 100 mg L^{-1}, respectively.

3.2.8 Effect of initial metal ion concentration on adsorption

Batch adsorption experiments were carried out for 2.5 g L^{-1} raw and modified coconut husk samples at pH ~7. Suspensions of RCH and HACH were stirred for 2 h at a speed of 300 rpm to hydrate the surfaces of the material. The 10 mL samples from each RCH and HACH suspension were transferred to capped polypropylene tubes. Initial Cd^{2+} and Pb^{2+} concentrations varied from 2.5 to 200 mg L^{-1} and 25 to 200 mg L^{-1}, respectively. The ionic strength of the solutions was maintained at 0.001 M $NaNO_3$ concentration. Tubes were equilibrated for 24 h at 100 rpm in a water bath shaker. After that, the supernatant was centrifuged (2500 rpm, 10 min) and filtered for metal analysis. Detection of Cd^{2+} and Pb^{2+} were carried out using the flame method of an atomic adsorption spectrophotometer (AAS).

The data of Cd^{2+} and Pb^{2+} adsorption onto adsorbents was fitted to the Langmuir isotherm model [Eq. (3.1)] and Freundlich isotherm model [Eq. (3.2)] (Demirbas, 2008; Sarı et al., 2011; Bulgariu and Bulgariu, 2012; Cheng et al., 2012). The essential characteristic and feasibility of the Langmuir isotherm model, which is known as separation factor, R_L [Eq. (3.3)], was determined (Bansal et al., 2009; Rao and Khan, 2009). Model fitting was done using Origin 7 software (Origin Lab Corporation, USA).

$$q_e = \frac{q_m b C_e}{\left(1 + b C_e\right)} \tag{3.1}$$

$$q_e = K_f C_e^{1/n} \tag{3.2}$$

where,

q_e = weight of metal ions adsorbed per gram of adsorbent at equilibrium (mg g^{-1})

C_e = equilibrium aqueous metal ion concentration (mg L^{-1})

q_m = maximum adsorption capacity (mg g^{-1})

b = Langmuir constant related to the energy of adsorption (L mg^{-1})

K_f = adsorption capacity (mg g^{-1})

n = adsorption intensity

$$R_L = \frac{1}{1+bC_i} \qquad (3.3)$$

Where,

C_i = initial metal concentration (mg L^{-1}).

R_L is a positive number, and the magnitude of R_L determines the feasibility of adsorption.

If, $R_L = 1$ – biosorption isotherm becomes linear,

R_L = 0-1 – favorable for biosorption,

$R_L > 1$ – unfavorable for biosorption,

$R_L = 0$ – biosorption is irreversible.

3.2.9 Effect of contact time on adsorption

In order to investigate the mechanism of adsorption of Cd^{2+} and Pb^{2+} onto HACH, the effect of contact time on adsorption was studied using a 2.5 g L^{-1} suspension of HACH at pH~7. The ionic strength was maintained at 0.001 M $NaNO_3$ for all experiments. The suspensions of HACH were hydrated by stirring at 300 rpm for 3 h. Then, the suspension was spiked with the required amount of metal solutions to maintain the initial concentrations of 20 mg L^{-1} and 100 mg L^{-1} for Cd^{2+} and Pb^{2+}, respectively. Samples of 10 mL were taken from the solution at known time intervals. After centrifugation, the supernatant was transferred by membrane filtration (0.45 µm) for metal analysis. Detections of Cd^{2+} and Pb^{2+} were carried out using the flame method of the AAS. The data from adsorption kinetic experiments were analyzed using pseudo-first order [Eqs. (3.4a) and (3.4b)] and pseudo-second order [Eq. (3.5)] models (Javed et al., 2007; Ofomaja and Ho, 2007; Jústiz-Smith et al., 2008). The pseudo-first order model assumes non-dissociating molecular adsorption while the pseudo-second order model assumes the chemisorptions of the adsorbate onto the adsorbent where exchange or sharing of electrons occurred between the adsorbate and active sites of the adsorbent (Rajapaksha et al., 2011).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3.4a)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (3.4b)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

Where,

q_t = amount adsorbed per g of adsorbent at time t (mg g^{-1})

q_e = amount adsorbed per g of adsorbent at equilibrium (mg g^{-1})

k_1 = Lagergren rate constant (min^{-1})

t = time (min)

k_2= pseudo-second order constant (g mg^{-1} min^{-1}).

Further, the initial adsorption rate, h (mg g^{-1} min^{-1}) as $t \to 0$ can be defined as [Eq. (6)].

$$h = k_2 q_e^2 \qquad (6)$$

The best fitting model was selected based on the correlation coefficient, fitting, and measured amount of metals adsorbed onto the HACH at the equilibrium.

3.2.10 Desorption experiments

Desorption experiments were conducted to study the effect of water on leaching of adsorbed metals from HACH. After the adsorption of metals in batch tests, the adsorbent was washed with distilled water twice, mixed with distilled water, and filtered in a Büchner funnel. Then, the adsorbent was shaken with 10 mL of distilled water at 300 rpm for 3 h. After that, suspension was filtered and analyzed for heavy metals using the flame method on the AAS.

3.2.11 Effect of competitive ion on adsorption

Adsorption experiments were conducted to study the effect of competitive ions on adsorption onto HACH as described by Sewwandi et al. (2012). The effect of Cd^{2+} on Pb^{2+} adsorption onto HACH and the effect of Pb^{2+} on Cd^{2+} adsorption onto HACH were studied. Initial concentrations of Cd^{2+} and Pb^{2+} used for the experiments were 20 and 100 mg L^{-1}, respectively. In addition, the effects of other ions commonly found in wastewater (Ca^{2+}, Mg^{2+}, SO_4^{2-}, and PO_4^{3-}) were studied. The concentrations of these ions were the same as those Sewwandi et al. (2012) used. Concentrations of anions and cations were selected based on World Health Organization standard values of the respective ion (Ramakrishnaiah et al., 2009).

3.3 Results and Discussion

3.3.1 Characterization of coconut husk

CH surface areas determined by the MB adsorption and N_2 adsorption techniques were 270.49 and 1.83 m^2 g^{-1}, respectively. The difference in experimental conditions used by the two methods could be the reason for the difference in surface area. The MB adsorption technique is performed under wet conditions, whereas the N_2 adsorption technique is performed on a dry sample, which is accomplished by heating and degassing the sample (Santamarina et al., 2002). Since the adsorbate can reach the interlayer surfaces under wet conditions, the surface area determined by the MB adsorption technique is higher than in the N_2 adsorption technique, in which gas cannot cover the interlayer surfaces. Similar variations from the two methods have been observed by Chen et al. (1999) for montmorillonite soil and Santamarina et al. (2002) for soils. In addition, the results from the N_2 adsorption showed that more than 60% of the total volume was occupied by <10 nm size pores.

Zeta potential analysis of RCH and HACH with pH shows that both materials were negatively charged in the pH range of 3–11(not shown). The ξ potential values varied from -8 to -12 mV within the pH range studied.

3.3.2 SEM and EDAX analysis

Scanning electron micrographs (SEM) of RCH and HACH are shown in Figures. 3.1a and 3.1b, respectively, with a magnification of x400. Surface texture and porosity can reveal the morphological features and surface characteristics of biosorbents. It is clear from the SEM images that both RCH and HACH have numerous voids with an irregular structure and are rich in fine pores. Figures 3.2 and 3.3 showed the SEM images and SEM-EDAX spectrum of Cd^{2+}- and Pb^{2+}-adsorbed HACH, respectively. The SEM-EDAX spectra for Cd^{2+} and Pb^{2+} indicate the adsorption of the respective metal onto the active sites of HACH. Accordingly, the weight percentage of Cd^{2+} and Pb^{2+} adsorbed onto HACH are 1.3% and 4.36%, respectively.

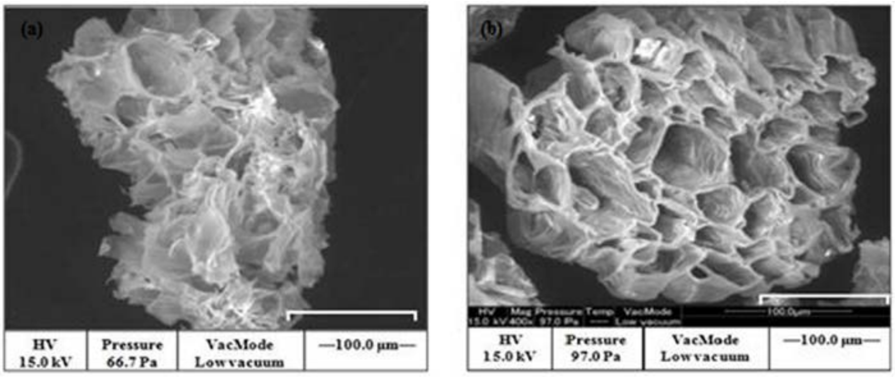
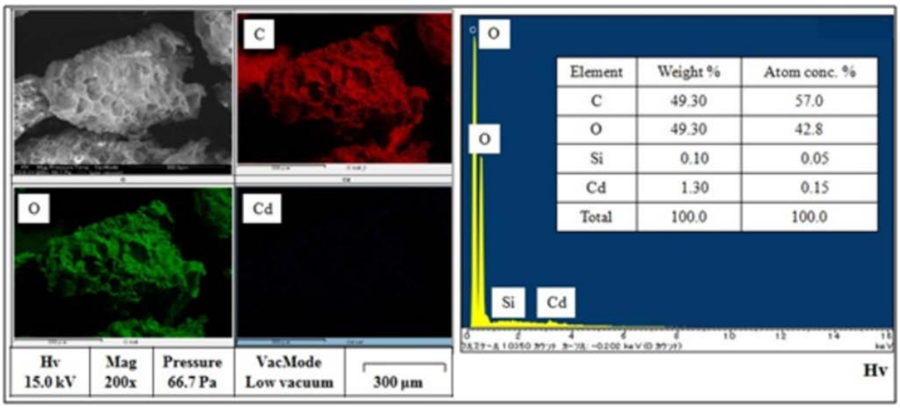


Figure 3.1: Scanning electron micrograph of (a) RCH and (b) HACH



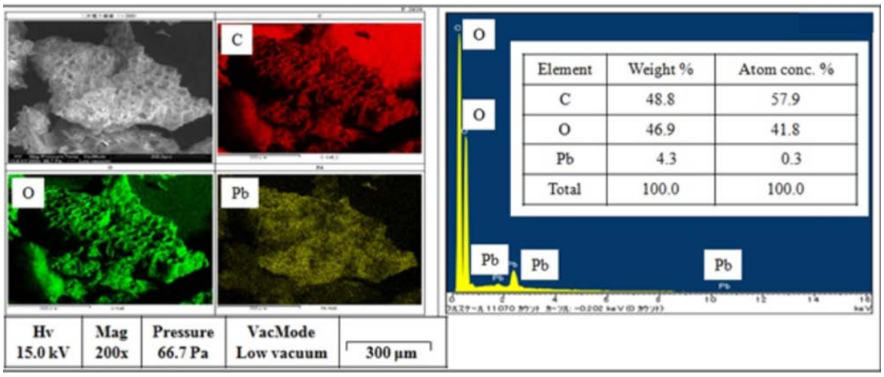
Element	Weight %	Atom conc. %
C	49.30	57.0
O	49.30	42.8
Si	0.10	0.05
Cd	1.30	0.15
Total	100.0	100.0

Figure 3.2: Scanning electron micrograph and SEM-EDAX spectrum of Cd2+ adsorbed HACH

3.3.3 FT-IR analysis

FT-IR spectrums of RCH, HACH, and Cd^{2+}- and Pb^{2+}-adsorbed HACH are shown in Figure 3.4. Only slight differences were observed between RCH and HACH. The characteristic peak at around 1637 cm^{-1} can be observed as the -OH bending of adsorbed water and -OH groups (Oh, 2005). The bands observed at 1514 cm^{-1} are due to C=C stretching vibrations of aromatic bonds (Makehelwala et al., 2009). Peaks at 1525-1460 cm^{-1} can be assigned to $-CH_3$ and $-CH_2$ deformations (Pretsch, 1989). Symmetric stretching vibrations at around 1412 cm^{-1} are assigned to $-COO^-$ groups

(Kitadai et al., 2009). The C-H deformation vibration and O-H deformation modes of alcohol and phenolic groups of cellulose appeared around 1375 cm^{-1} (Pretsch, 1989).



Element	Weight %	Atom conc. %
C	48.8	57.9
O	46.9	41.8
Pb	4.3	0.3
Total	100.0	100.0

Hv	Mag	Pressure	VacMode	
15.0 kV	200x	66.7 Pa	Low vacuum	300 µm

Figure 3.3: Scanning electron micrograph and SEM-EDAX spectrum of Pb^{2+} adsorbed HACH

Disappearance of C-H deformation vibration and O-H deformation modes of alcohol and phenolic groups of cellulose at 1375 cm^{-1} (Pretsch, 1989) were observed in HACH. Bands between 1250–1550 cm^{-1} shifted to low wave numbers after humic acid treatment. However, several changes in IR spectra can be identified between HACH before and after metal adsorption. The board band intensity at around 1730 cm^{-1}, which is assigned to stretching modes of the carbonyl (C=O) bond in the -COOH groups (Anirudhan et al., 2010), has shifted to low wave numbers after both Cd^{2+} and Pb^{2+} adsorption (Figure 3.4).

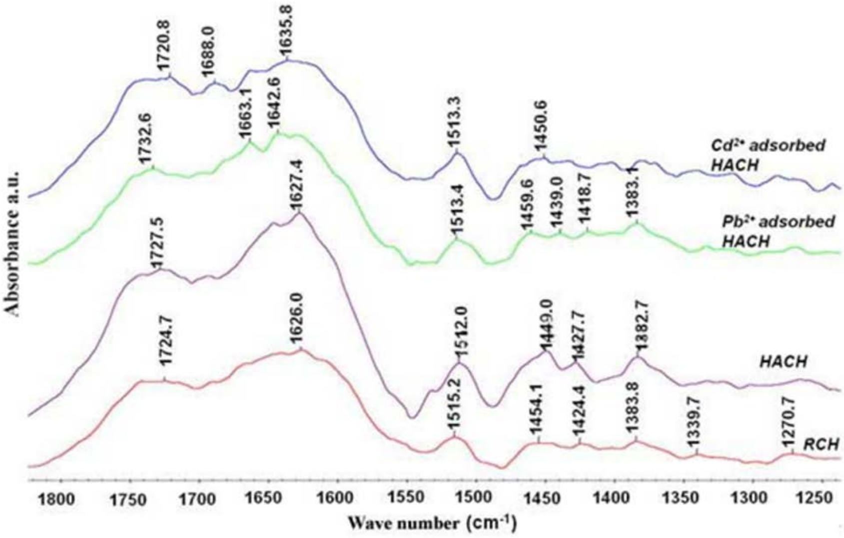


Figure 3.4: FT-IR spectra of RCH, HACH, and Cd^{2+} and Pb^{2+} adsorbed HACH

The wave numbers that have been shifted to lower values in C=O stretching for metal-adsorbed HACH strongly indicate that the interaction between -COOH groups and metal ions. Therefore, this results suggest that the adsorption of metal ions to -COOH groups through the C-O-M bond (M= Cd^{2+} or Pb^{2+}) via monodentate adsorption (Hug and Bahnemann, 2006).

3.3.4 Effect of pH and ionic strength on adsorption

The adsorption process is affected by pH because it affects the surface charge of the adsorbent, species of adsorbate, and the degree of ionization (Naiya et al., 2009a). The variations of Cd^{2+} and Pb^{2+} adsorption onto HACH with final pH at different ionic strength levels are given in Figure 3.5. According to it, the adsorption process is independent of the pH range studied in this study. Because of the reactions that have taken place in the adsorption of metal ions to the adsorbent, the pH of the solution is changed. However, Naiya et al. (2009a) found that when the pH of the solution is higher (pH > 6), total Pb^{2+} removal is increased due to the formation of $Pb(OH)_2$ precipitate, though there is a decrease in adsorption.

The mechanism of adsorption of metals onto the biosorbents can be determined by examining the ionic strength dependency of the process. Thus, if the adsorption process shows an ionic strength dependency, the mechanism of adsorption is binding to the outer sphere of surface complexes. In contrast, in the inner sphere bonding mechanism, the effect of ionic strength on adsorption is not observed (Bansal et al., 2009; Tang et al., 2009). The results shown in Figure 3.5 indicate that adsorption of Cd^{2+} and Pb^{2+} onto CH shows no dependence on ionic strength of the solution, which indicates that an inner sphere bonding mechanism is involved in adsorption. Since the adsorption capacities are independent of ionic strength of the solutions, 0.001 M $NaNO_3$ was used in later experiments.

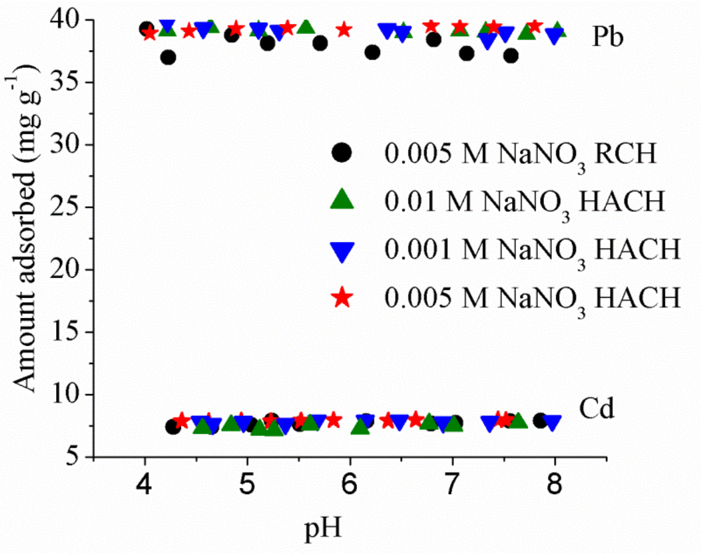


Figure 3.5: Variation of Cd^{2+} and Pb^{2+} adsorption with pH and ionic strength

3.3.5 Effect of initial metal concentration on adsorption

Langmuir and Freundlich isotherm models were used to analyze the data. Langmuir isotherm model fitting curves for the data obtained along with the fitted equation from the isotherm experiments are given in Fig. 6. Adsorption of Cd^{2+} onto RCH was higher than HACH up to the initial concentration of ~100 mg L^{-1} (equilibrium concentration~10 mg L^{-1}), and after that the reverse occurred (Figure 3.6a). The Pb^{2+} adsorption was significantly higher onto HACH than onto RCH for the entire range of the initial concentration (Figure 3.6b). Adsorption of both Cd^{2+} and Pb^{2+} was well fitted to the Langmuir isotherm model, which indicates that monolayer adsorption is predominant. In monolayer adsorption, metal ions are adsorbed onto the homogenous surfaces of the adsorbent without interaction between adsorbed molecules (Sarı et al., 2011; Cheng et al., 2012). Langmuir model fitting parameters are shown in Table 3.1. Higher correlation coefficient values may indicate that the heavy metal ions utilize their single molecular forms to adsorb metal ions onto both RCH and HACH within the concentration range used in this study (Rao and Khan, 2009; Sarı et al., 2011; Cheng et al., 2012).

The adsorption capacities of Cd^{2+} and Pb^{2+} onto HACH were 47 and 66 mg g^{-1}, and those onto RCH were 24 and 21 mg g^{-1}, respectively. The higher adsorption of Pb^{2+} than Cd^{2+} by HACH is clearly shown by SEM-EDAX elemental mapping (Figures 3.2 and 3.3). Similar results were observed by Chen et al. (2012), and they found that the smaller hydration radius, low free energy of hydration, and higher reactivity of Pb^{2+} than Cd^{2+} were the reasons for higher adsorption of Pb^{2+} than Cd^{2+}.

Table 3.1: Langmuir adsorption parameters for adsorption of Cd^{2+} and Pb^{2+}

Metal	Adsorbent	b (L mg^{-1})	q_m (mg g^{-1})	r^2	R_L
Cd^{2+}	RCH	0.953	24.2	0.89	0.005-0.290
	HACH	0.092	47.3	0.92	0.005-0.010
Pb^{2+}	RCH	3.680	21.2	0.95	0.001-0.010
	HACH	0.989	66.1	0.85	0.060-0.080

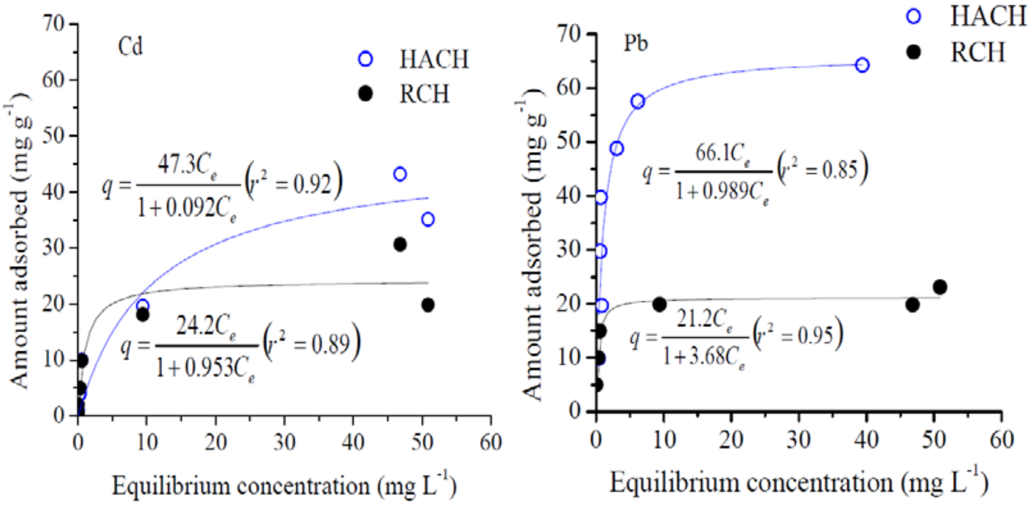


Figure 3.6: Langmuir isotherm model fitted curves

The R_L values respective to the maximum adsorptions of Cd^{2+} and Pb^{2+} given in Table 3.1 indicate that the adsorption of Cd^{2+} and Pb^{2+} onto CH is favorable and that the metal ion binding to the surfaces of CH is strong. Moreover, the values of R_L became very close to zero, indicating that the process was closer to the irreversible adsorption (El-Shafey, 2007). However, isotherm data was not fitted to the Freundlich isotherm model (data not shown).

3.3.6 Effect of contact time on adsorption

Table 3.2 shows pseudo-first order kinetic parameters and correlation coefficient values obtained from the plot of log (q_e-q_t) with time. The correlation coefficient values and/or measured and fitted values of equilibrium adsorption capacities are not correlated, indicating that the kinetic data do not fit the pseudo-first order model. Therefore, the rate of occupation of biosorption sites is not likely to be proportional to the number of occupied sites (Najim et al., 2009; Vinodhini and Das, 2010).

On the other hand, adsorption kinetic data was well fitted to the pseudo-second order model (Table 3.3). This suggests that the rate-limiting factor in adsorption of

Cd^{2+} and Pb^{2+} onto HACH is a chemical sorption that involves valence forces through sharing or exchange of electrons between metal ions and the functional groups of HACH, as shown in previous studies (Ho and McKay, 1999; Naiya et al., 2009b; Najim et al., 2009). As indicated by the reaction rate constant values, Cd^{2+} adsorption onto HACH reached in equilibrium faster than Pb^{2+} adsorption.

3.3.7 Desorption experiment

Desorption studies were conducted to study the regeneration of used biomaterials for repeated biosorption. The results of the experiments showed that desorption of the metals adsorbed onto CH is very low (not detectable) in the pH range studied with water. Therefore, this confirms that the main process of adsorption is a chemisorption process (Kavitha and Namasivayam, 2007).

Table 3.2: Pseudo first order kinetic model parameters and correlation coefficient values for adsorption of Cd^{2+} and Pb^{2+} onto HACH

Metal	$q_{e, measured}$ $(mg\ g^{-1})$	$q_{e, fitted}$ $(mg\ g^{-1})$	k_1 (min^{-1})	r^2
Cd^{2+}	7.88	4.31	0.059	0.91
Pb^{2+}	38.5	0.362	0.002	0.14

Table 3.3: Pseudo second order kinetic model parameters and correlation coefficient values for adsorption of Cd^{2+} and Pb^{2+} onto HACH

Metal	$q_{e,measured}$ $(mg\ g^{-1})$	k_2 $(g\ mg^{-1}\ min^{-1})$	h $(mg\ g^{-1}\ min^{-1})$	r^2
Cd^{2+}	7.93	3.17	200	0.99
Pb^{2+}	38.46	0.056	83.3	0.99

3.3.8 Effect of competitive ions on adsorption

Figures 3.7a and 3.7b show the adsorption variations of Cd^{2+} and Pb^{2+} in the presence of different concentrations of the other metal ion, respectively. As shown in Figure 3.7a, almost 100% adsorption of Cd^{2+} was observed when there was no Pb^{2+} in the solution. However, when the Pb^{2+} concentration in the aqueous solution increased, the adsorption of Cd^{2+} decreased drastically. Similarly, 96% removal of Pb^{2+} was observed when there was no Cd^{2+} present in the aqueous solution. Removal of Pb^{2+} decreased from 95% to 80% when the Cd^{2+} concentration was the same as the

Pb^{2+} concentration in the solution. However, a further increase in Cd^{2+} in the solution did not affect further reduction of Pb^{2+} removal from the aqueous solution.

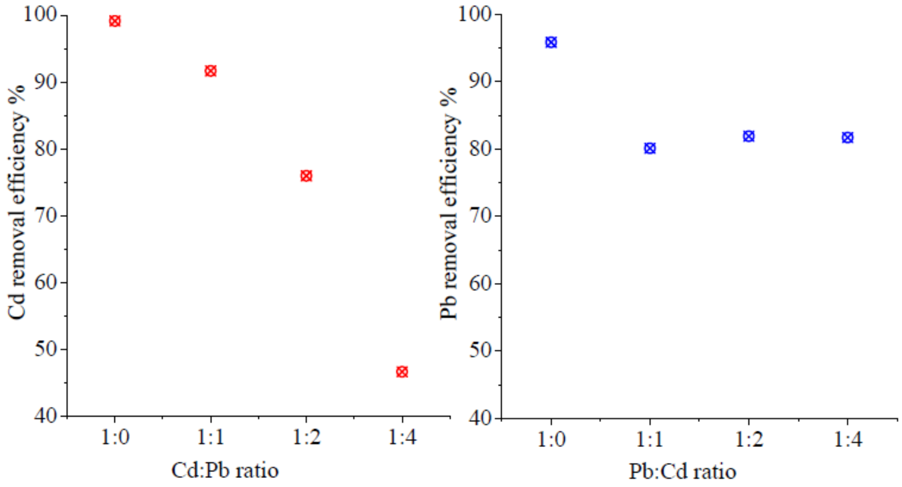


Figure 3.7: (a) Cd^{2+} and (b) Pb^{2+} adsorption variation in binary metal solutions

Competitive adsorption of metal ions could be due to the differences in radius of the hydrated ions, free energy of adsorption, and activity of metal ions (Cheng et al., 2012). Srivastava et al. (2009) studied the competitive adsorption of Cd^{2+} and Ni^{2+} onto rice husk ash (RHA) and found that the affinity of RHA for Ni^{2+} is greater than that of Cd^{2+} in binary metal mixtures. The competitive effects of different metals on adsorption of other metals are different (Qin et al., 2006). Qin et al. (2006) studied the mechanisms of competitive adsorption of Cd^{2+}, Pb^{2+}, and Cu^{2+} onto peat and found that the competitive adsorptions of the studied metals are in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$, similar to the results observed in the present study.

The impact of cations (Ca^{2+} and Mg^{2+}) and anions ($SO_4^{2-}$and $PO4^{3-}$) on the adsorption of Cd^{2+} and Pb^{2+} when their availability in the environment was higher and their effect on the adsorption of metals onto adsorbents were studied. The results of the experiment are shown in Table 3.4. Adsorption of Cd^{2+} onto HACH was decreased in the presence of Ca^{2+} and Mg^{2+} ions in the aqueous solution. It was observed that the adsorption of Cd^{2+} was decreased from 86% to 21% when the Ca^{2+} concentration in the solution increased from 10 to 75 mg L^{-1}. Moreover, Cd^{2+} adsorption was decreased from 76% to 24% when the Mg^{2+} ions are present in the aqueous solution (Table 3.4). However, only a few changes in the adsorption of Pb^{2+} were observed at the presence of Ca^{2+} and Mg^{2+}.

Neither Cd^{2+} nor Pb^{2+} adsorption was affected much by the availability of SO_4^{2-} in the solution. Similarly, Cd^{2+} adsorption did not show a change due to PO_4^{3-} ions in the solution, whereas Pb^{2+} adsorption was affected by PO_4^{3-} ions. Thus, removal of Pb^{2+} decreased from 89% to 9% when the PO_4^{3-} concentration increased from 1 to 10 mg L^{-1}. The differences in the adsorption of the two metals by HACH could be due to differences in the chemistry of Cd^{2+} and Pb^{2+} ions. Wang and Xing (2002) found that presence of phosphate enhanced the Cd^{2+} adsorption process. Both Cd^{2+} and Pb^{2+} ions forms complexes with phosphate, and the forms of the complexes are different and their solubility is also different in aqueous solution (Ayati and Lundager Madsen, 2000). Therefore, it shows the importance of using a pre-treatment to remove inorganic contaminants that can affect the adsorption of heavy metals in wastewater.

Table 3.4: Adsorption of Cd^{2+} and Pb^{2+} in the presence of anions and cations

Ion added	**Concentration of ion (mg L^{-1})**	**% adsorption**	
		Cd^{2+}	**Pb^{2+}**
Ca^{2+}	10	85.7	89.8
	25	61.5	85.5
	50	34.4	80.0
	75	21.4	73.4
Mg^{2+}	25	75.9	95.8
	50	51.5	89.0
	75	31.5	82.9
	100	29.8	80.3
	125	23.9	76.2
SO_4^{2-}	50	97.7	96.9
	100	95.5	90.8
	250	94.9	80.9
	400	84.4	84.8
PO_4^{3-}	1.0	99.7	88.8
	2.5	91.8	64.0
	5.0	99.0	33.6
	10.0	98.8	8.8

3.3.9 Comparison of Cd^{2+} and Pb^{2+} adsorption onto biosorbents

The Cd^{2+} and/or Pb^{2+} adsorption capacities of HACH with the other biosorbents in batch experiments are compared in Table 3.5. The adsorption capacity of raw coconut husk is similar to most of the biosorbents that other researchers studied (Table 3.5). However, humic acid-treated coconut husk shows higher adsorption capacity than untreated biosorbents. Similar results were obtained by Igwe and Abia (2007) and Wong et al. (2003) for modified maize husk and rice husk, respectively.

Table 3.5: Comparison of adsorption capacity of HACH with other adsorbents

Adsorbent	**Max. adsorption (mg g^{-1})**		**Reference**
	Cd^{2+}	**Pb^{2+}**	
RCH	24.24	21.21	Present study
HACH	47.28	66.06	Present study
Grape bagasse	53.84	42.27	Farinella et al., 2007
Neem oil cake	11.80	-	Rao and Khan, 2009
Sawdust of deciduous trees	3.50	-	Božić et al., 2009
Sugar beet pulp	0.13	0.37	Pehlivan et al., 2008
Rose waste biomass	-	151.15	Javed et al., 2007
Green algae waste biomass	39.20	74.30	Bulguriu and Bulguriu, 2012
Lemon peel	52.20	180.00	Arslanoglu et al., 2009
Tea waste	-	65.00	Amarasingha and Williams, 2007
Coconut copra meal	4.92	-	Ho and Ofomaja, 2006
Rice husk ash	-	91.74	Naiya et al., 2009b
Rice husk (tartaric acid modified)		108.0	Wong et al., 2003
Maize husk (unmodified)	-151.5	-217.4	Igwe and Abia, 2007
Maize husk (EDTA modified)	833.3	714.3	Igwe and Abia, 2007
Zeo;ite	1.2	55	Hamidpour et al., 2010
Bentonite	5.1	63	

3.4 Conclusions

The results of this study indicate that HACH can be used effectively for removal of Cd^{2+} and Pb^{2+} from single-metal ion solutions and that adsorption could be retarded by the presence of co-existing metal ions and other cations and anions. Adsorption of Cd^{2+} and Pb^{2+} ions onto HACH is independent of the pH and ionic strength used in this study. Adsorption by HACH is higher than RCH of Cd^{2+} and Pb^{2+} over the range of initial concentrations studied and shows a monolayer adsorption onto the adsorbent. The maximum adsorption capacities of Cd^{2+} and Pb^{2+} onto HACH were 47.28 and 66.26 mg g^{-1}, respectively, and 24.24 and 21.21 mg g^{-1}, respectively, for

RCH. The metal ion adsorption process by CH tends more towards an irreversible process that is endothermic in nature. Moreover, the Cd^{2+} and Pb^{2+} adsorption mechanism of CH involves the formation of inner-sphere complexes by metal ions with the active sites of CH. Since the adsorption process is irreversible, regeneration of the biomaterial with water is difficult, and therefore desorption methods with chemical solutions need to be studied.

Adsorption of Cd^{2+} and Pb^{2+} onto HACH is a chemical sorption in which Pb^{2+} adsorption needs a longer reaction time while Cd^{2+} adsorption reaches equilibrium faster. The adsorption reaction rates of Cd^{2+} and Pb^{2+} onto HACH are 0.056 and 3.17 mg g^{-1} min^{-1}, respectively. The presence of several anions and cations affected the adsorption of Cd^{2+} and Pb^{2+} by HACH, and therefore it is important to have a pretreatment unit to remove other ions and suspended solids in wastewater when HACH is used for actual wastewater treatment.

Supporting papers

Sewwandi, B. G. N., Meththika Vithanage, S.S.R.M.D.H.R. Wijesekara, M.I.M. Mowjood, Shoichiro Hamamoto and Ken Kawamoto. 2014. Adsorption of Cd(II) and Pb(II) onto Humic Acid Treated Coconut (*Cocos nucifera*) Husk. *J. Hazard. Toxic Radioact. Waste,* 18 (2): 1-10. DOI: 10.1061/(ASCE)HZ.2153-5515.0000196.

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Chapter 4 CHARACTERIZATION OF SOILS OF SRI LANKA TO BE USED AS A REACTIVE MATERIAL IN PERMEABLE REACTIVE BARRIER

Abstract

Exploration of locally available filter materials to use as a reactive media for permeable reactive barriers to be installed in municipal solid wastes dumpsites is important as they provide an inexpensive treatment method. A study was carried out to characterize soils of Sri Lanka aiming selection of suitable soils as a reactive media. Seven soils were sampled from different locations of Sri Lanka and analyzed for surface area, particle density, C/N ratio, mineral composition by XRD and particle size distribution by standard methods. Surface area of Anuradhapura, Ukuwela and Bangadeniya are 35, 31 and 28 m^2 g^{-1}, respectively, which are higher than the other soils. Most of the soils are categorized to the taxonomic group of sandy loam while soils from Ukuwela and Maharagama classified as Clay soils. Sandy clay loamy texture is shown by the soils of Katugastota and Bangadeniya. Highest C/N and SOM result from soils of Ukuwela followed by Iranamadu and Maharagama. Montmorillonite, Kaolinite and halloysite are the main minerals of studied soils. Three soils seems to be suitable for PRB applications based on physicochemical characteristics and further studies are needed to study the pollutant removal behavior of soils.

4.1 Introduction

Soil and groundwater contamination by leachate originating from the nearby landfill sites has become a global environmental issue at present (Mor et al., 2006; Nagarajan et al., 2012). The main solid waste management techniques practiced in Sri Lanka is dumping of collected solid wastes in nearby open dumpsites regardless of its origin or hazardous nature. Therefore, there is a high risk of contaminating soil and water resources in nearby areas. However, the treatment of contaminated soil and water sources by conventional methods such as pump and treat method cannot be used due to financial, technical and social issues. Thus, investigation of new and innovative technologies which are site specific at low cost would be the best solution to manage this burning issue.

Permeable reactive barrier (PRB) is a new technology which uses a wide variety of reactive materials to remove different contaminants from polluted water. It is used as a sub-surface structure across the contaminant plume. Activated carbon, zero valent iron, bentonite, soil-bentonite mixture are some of reactive materials used. The selection of a particular reactive material for a PRB depends on several factors i.e. reactivity, stability, availability and cost, environmental compatibility, hydraulic performance and safety.

Zeolites have been used as a reactive material in a PRB under a coastal refinery to remove petroleum hydrocarbons and gasoline additives and found that zeolites are more suitable for adsorption of light hydrocarbons (Vignola et al., 2011). Another study has been carried out by McMahon et al., (1999) using zero valent Fe to remove chlorinated aliphatic hydrocarbons (CAH) in a funnel-and-gate PRB system. The resuls of the study showed that effective removal of CAH can be achieved by zero valent Fe.

Di Natale et al., (2008) have studied the activated carbon for Cd removal in a laboratory study. The results of the study have been analyzed by a 2D numerical model and the model has been applied to a case study. The model simulation showed that activated C has a long term efficiency to prevent river pollution.

Han et al., (2011) have conducted a study on natural silica sand coated with FeS to remove As(III) under anoxic conditions. The study focuses on development of a material by coating natural silica sand with FeS. They have concluded that FeS coated silica sand with iron oxide coating is suitable for removing As(III) under anoxic conditions.

Organic carbon based PRB has been used to treat heavy metals by sulphate reduction and metal sulphide precipitation in a contaminated groundwater plume (Ludwig et al., 2002). The finding of the study is that the organic C barrier is effective in treating groundwater contaminated by dissolved metals. Gibert et al., (2008) have found that some organic substrates (softwood) is applicable for PRB filling from a study conducted on natural organic substrates to remove nitrate nitrogen.

It is common to use reactive materials with chemical in nature for PRB installations to remediate contaminated groundwater. However, the use of these materials is limited in developing countries due to high cost of these materials, need special care to handle and lack of know-how of using these materials. Therefore, it is useful to find out possible reactive materials that are locally available at low cost to be used in PRBs to treat leachate generated from open dumpsites in Sri Lanka.

Sri Lanka is a country where different types of soils are available with a unique soil profile. The predominant soil in a particular area depends on climate, parent material, plants and animals, slope or topography of the land, and to time needed for soil formation. Figure 4.1 shows the distribution of great soil groups of Sri Lanka.

Some studies have been carried out to characterize soils for some elements' availability (Loganathan et al., 1982), to study the spatial variability of soil properties (Nayanaka et al., 2010), to study the occurrence of organo-mineral complexes in relation to clay mineralogy (*Indraratne*, 2005). However, limited attention has been given to the soils' ability to remove heavy metals and to be used as a reactive material in PRB. Therefore, this study aims to characterize physico-chemical properties of soils of Sri Lanka and to find out soils that are suitable to be used in PRBs as a reactive material to remove heavy metals.

4.2 Materials and Methods

4.2.1 Sampling of soils in Sri Lanka

Seven soil types (great soil groups) were selected from six soil orders (USDA soil classification) based on climatic zone, availability of a soil in an area and the distribution of soils. Table 4.1 shows the soil order, great soil group, location and the climatic zone for each sampled soil. The collected soils are the predominant soil type available in the particular area. As given in Table 4.1, soils were collected from all climatic zones of Sri Lanka so that it represents the major soils in each zone. Figure 4.1 shows the distribution of great soil groups in Sri Lanka.

The selected soils were sampled at a depth of 0-20 cm depth and transported to the laboratory for the analysis of physical and chemical properties. Figure 4.2 shows a photograph of the collected soil samples after air drying.

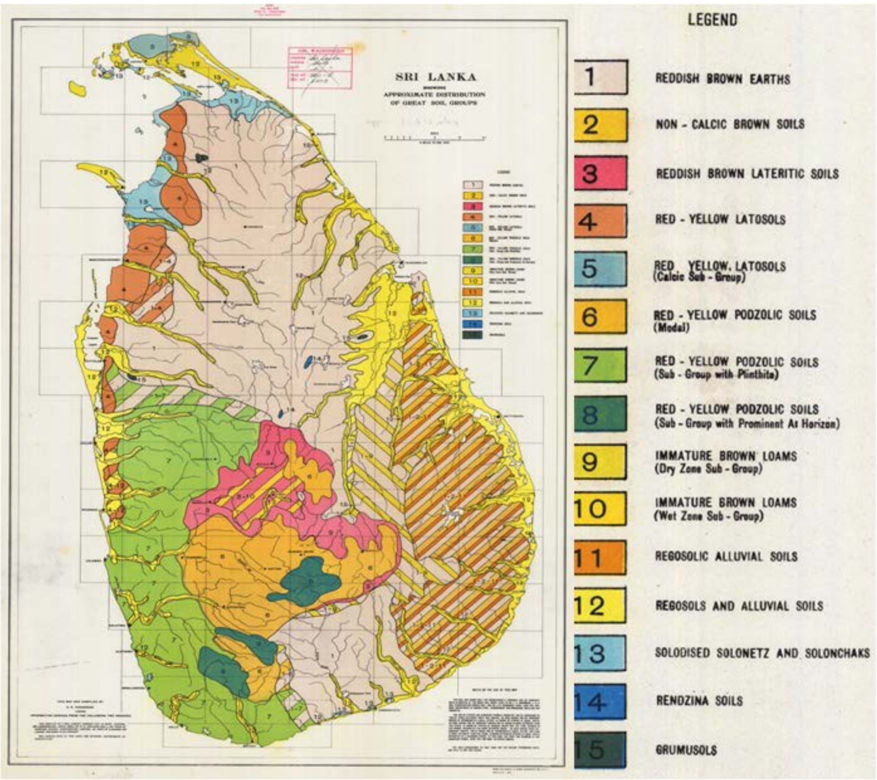

Figure 4.1: Distribution of great soil groups in Sri Lanka

(Source:http://eusoils.jrc.ec.europa.eu/esdb_archive/eudasm/asia/maps/LK3000_SO.htm)

4.2.3 Analysis of soil

Collected soil samples were transported to the laboratory and air dried for the analysis. The analyzed parameters and the standard analytical methods used are presented in Table 4.2. Organic composition was determined by measuring C, H and N content of soils by CHN analyzer. Soil organic matter content were estimated from soil organic C and soil organic N content.

Soil samples were tested for mineralogical compositions and elemental compositions by X-Ray Diffraction (XRD-7000, Shimadzu Corp., Japan) and energy dispersive X-Ray Fluorescence (EDX-700HS2, Shimadzu Corp., Japan) techniques, respectively after removing organic matter by hydrogen peroxide method. Dry and wet sieving methods were performed to determine the clay content of soils.

Table 4.1: Information on soil type, location and climatic zone of the area of collected soils

Soil sample	Soil order	Soil type (Great soil group)	Climatic zone
Anuradhapura	Alfisols	Reddish brown earth	DZ
Maharagama	Ultisols	Reddish brown latasolic	WZ
Ukuwela		Red yellow podsolic	
Iranamadu	Oxisols	Red yellow latasolic	DZ
Katugastota	Inceptisols	Immature brown loams	WZ
Bangadeniya	Entisols	Alluvials	IZ
Kilinochchi	Vertisols	Grumusols	DZ

Figure 4.2: Soils collected from Sri Lanka

Table 4.2: Analytical methods used in soil analysis

Physical/chemical property	Analytical methods
pH	pH meter
CHN content	CHN analyzer
Mineralogical and elemental composition	XRD/XRF_EDX
Particle size distribution	Sieve analysis/sedimentation

4.3 Results and Discussion

Soils in Sri Lanka have a vast diversity and therefore there is a spatial variation of soil properties. In addition, properties of the same soil can be varied from place to place due to the effects of environmental and climatic factors. Therefore, it is important to characterize soils collected to select best soils to be used as a reactive material for PRBs in municipal solid waste open dumpsites.

4.3.1 Physico-chemical properties of soils

Table 4.2 shows the results of CHN analysis, i.e. soil organic N and soil organic C and the respective C/N ratios. Highest C/N and SOM have been resulted in soils from Ukuwela followed by Iranamadu and Maharagama. C/N ratio and the SOM are important indicators with regard to pollutant removal as organic compounds such as humic matters can bind heavy metals from wastewater (Violante et al., 2010). Therefore, it is important to select a soil with high C/N ratio and SOM to use as a reactive material in PRB.

Table 4.3 shows the physico-chemical properties of studied soils of Sri Lanka. pH of soils varied from 21-81 µS cm^{-1} and 4.6-5.6, respectively. Accordingly, all soils revealed an acidic pH within the range of typical values of Sri Lankan soils (Mapa et al., 2010). All soils showed clay content of >30% and the dominant metal oxide in all soils was Al_2O_3. Organic matter content in all soils was very low.

Table 4.3: Organic composition of soils

Sample location	SON%	SOC%	C/N
Katuotagasta	0.03	0.37	12.33
Ukuwela	0.11	2.07	18.82
Kilinochchi	0.05	0.5	10.00
Iranamadu	0.07	1.24	17.71
Anuradhapura	0.07	0.71	10.14
Bangadeniya	0.06	0.63	10.50
Maharagamama	0.06	0.8	13.33

Table 4.4: Physicochemical properties of soils

Soil sample	pH	Clay%	Metal oxides%			SOM%
			Al	Fe	Mn	
Maharagama (RBL)	5.6	57.9	36.76	9.30	0.04	1.36
Katugastota (Immature brown loams)	5.3	30.7	25.83	15.08	0.32	0.63
Ukuwela (RYP)	4.6	55.2	28.49	19.75	0.23	3.52
Bangadeniya (Alluvials)	4.7	31.2	21.27	13.48	0.27	1.07
Anuradhapura (RBE)	4.7	48.5	27.26	17.99	0.28	1.21
Iranamadu (RYL)	5.2	37.6	29.47	18.63	0.16	2.11
Kilinochchi (Grumusols)	5.2	35.1	31.04	5.99	0.11	0.85

4.3.2 Mineralogical and elemental composition of soils

The qualitative results of the mineralogical and elemental (metal oxides) analysis of soils are shown in Table 4.5. mineralogy of a soil is important as it explained the environment where the soil was formed (Fontes and Gomes, 2003). Clay minerals can adsorb metal ions through cations replacement or by forming surface functional groups (de Pablo et al., 2011). Main mineral of most of the soils studied is Kaolinite and it is Ca-montmorillonite in Bangadeniya soil. Anuradhapura and Bangadeniya soil have Halloysite as the main mineral. Kaolinite is a non-expanding mineral due to its high molecular stability and limited or nonexistent isomorphous substitution. It is a clay with lowest reactivity which has a high pH dependency (Miranda-Trevino and Coles, 2003). On the other hand, Montmorillonite is a smectite mineral with a negative charge in both basal surfaces (de Pablo et al., 2011; Sakiewicz et al., 2011). Halloysite is a mineral which belongs to the Kaolinite sub group and has a high affinity for monovalent cations like K^+, Na^+, Li^+ and Cs^+. Opposite to the montmorillonite, halloysite has a net negative charge on one side of the surface and a positive charge on the other side (Sakiewicz et al., 2011).

Table 4.3: Mineralogical and elemental composition of soils

Sampling site	**Major minerals**	**Minor minerals**	**Major elements**
Katugastota	Kaolinite	Beidellite, quartz, Albite, seraphainite, geothite, gibbsite	TiO2, CaO, K2O, BaO
Ukuwela	Kaolinite	quartz, seraphainite, geothite, gibbsite	TiO2, BaO, CaO, MgO
Kilinochchi	Kaolinite, quartz	montmorillonite-Na, anorthite, illite	TiO2, MgO, BaO, K2O, CaO,ZrO2,MnO
Iranamadu	Kaolinite	montmorillonite - Na,quartz, geothite, gibbsite	MgO,TiO2, BaO, CaO,MnO, K2O
Anurdhapura	Halloysite	montmorillonite- Ca,quartz, geothite, hematite	MgO, CaO,TiO2, MnO,K2O,BaO
Bangadeniya	Ca-Montmorillonite, Halloysite,	quartz, $CaAl_2Si_2O_8$, geothite	K2O,MgO, CaO,TiO2,BaO, MnO
Maharagama	Kaolinite, quartz	montmorillonite - Na, illite, geothite, gibbsite	TiO2, MgO, BaO, K2O, CaO

4.3.3 Prediction of Pb and Cd adsorption onto soils

Soil composition i.e. soil organic matter, clay content and metal oxides affect the adsorption of metal ions onto soils (Lee et al., 1996; Shi et al., 2013). Different models have been used to predict the adsorption of Pb (Shi et al., 2013) and Cd (Lee et al., 1996) and developed curves to predict the adsorption based on soil properties. The curves developed by other researchers used in this study to predict the Pb and Cd by soils and thereby to find out best soils for Pb and Cd adsorption.

Prediction of Pb adsorption onto soils

The effect of soil organic matter, metal oxides and clay content on Pb adsorption has been studied by Shi et al. (2013) and developed curves to predict Pb adsorption by soils (Figure 4.3).

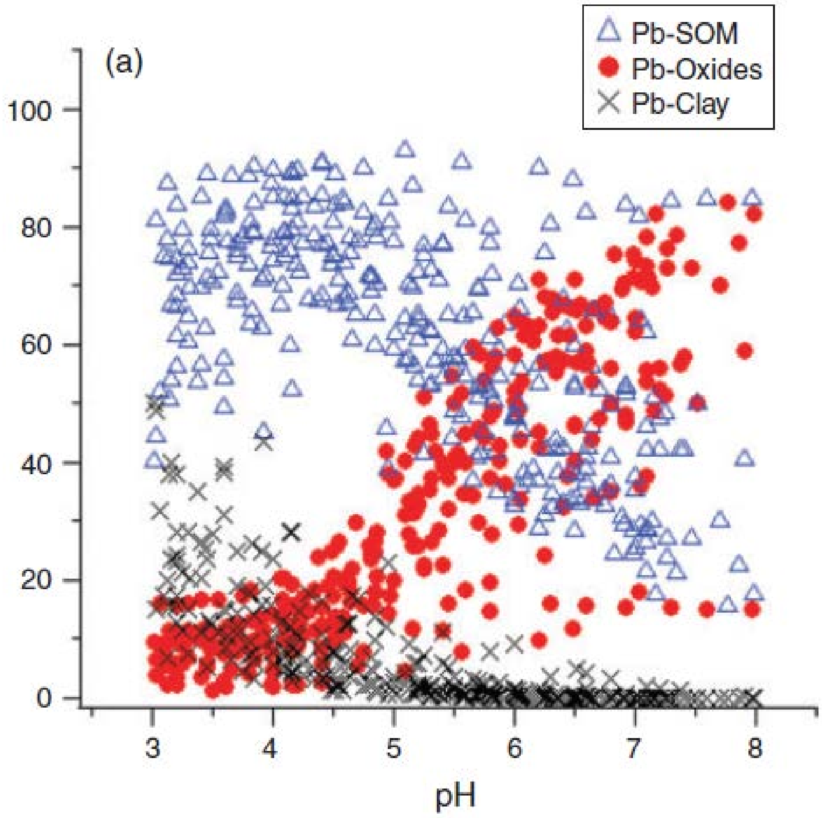

Figure 4.3: Relative contributions of soil organic matter (SOM), metal oxides and clay minerals to Pb adsorption: (a) at various reaction pHs for Pb adsorption from Shi et al., (2013)

As illustrated in the Figure 4.3, soil organic matter is the dominant adsorbent at pH from 3-5, than metal oxides and clay content. On the other hand, Pb adsorption onto metal oxides increased with increase in pH of the soil. Further, Shi et al. (2013) have found that the P adsorption by Aluminum hydroxides is minor compared with that of Iron hydroxides. The Pb adsorption by clay minerals is decreased with increase in pH and become lowest after pH 5. Accordingly, soils from Ukuwela show the best characteristics for adsorption of Pb by soil organic matter and clay minerals due to low pH, high content of organic matter and clay. In contrast, Pb adsorption by metal oxides could be higher in soils from Katugastota due to its high Fe oxide content and high pH.

Prediction of Cd adsorption onto soils

Figure 4.4 shows the variation of log Kd with pH for Cd adsorption onto soils, developed by Anderson and Christensen (1988). Accordingly, Cd adsorption is increased with increase in pH. The soils from Sri Lanka showed a pH varied from 4.6 to 5.6. Thus, the soils from Maharagama and Katugastota could be the best for Cd adsorption. Although the pH is the major factor controlling Cd adsorption, there are other factors that control the process. Therefore, it is important to consider other factors such as organic matter, clay content and metal oxides etc. on adsorption of Cd by soils.

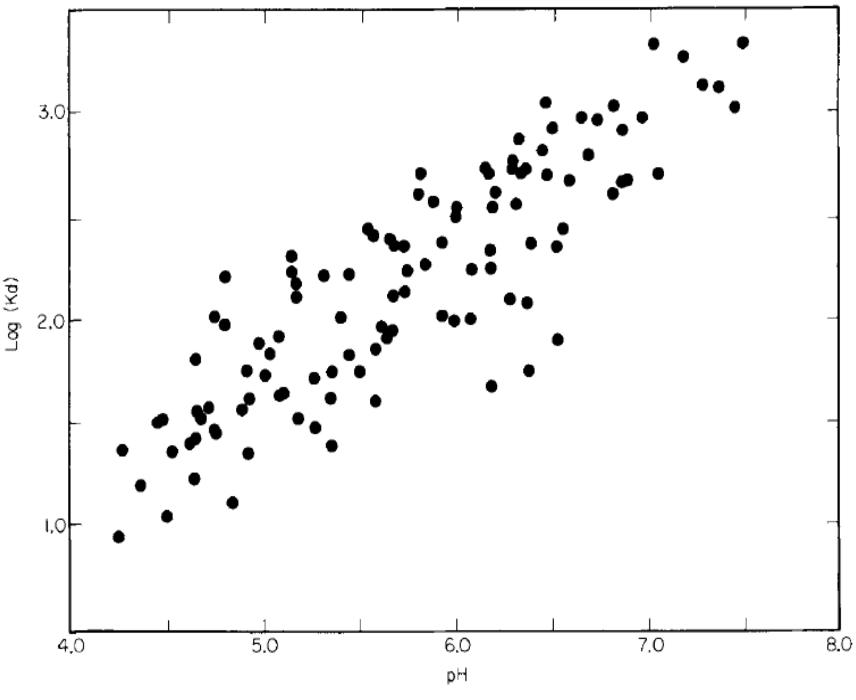

Figure 4.4: Log K_d for Cd as a function of pH from Anderson and Christensen (1988)

4.4 Conclusions

In this study, physico-chemical properties of soils were analyzed with the aim of finding suitable soils to be used as a reactive media for PRBs to treat leachate from municipal solid waste dumpsites in Sri Lanka. The best soils for Pb and Cd adsorption were predicted by dfferent models developed by other researchers. Accordingly, soils from Ukuwela and Katugastota are the best soils for Pb adsorption while soils from Maharagama and Katugastota are best for Cd adsorption. Further, the adsorption experiments have to be carried out to find best performed soils for Pb and Cd adsorption.

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Chapter 5 SUMMARY, CONCLUSIONS AND PERSPECTIVES

5.1 Characterization and evaluation of leachate contamination potential of leachate from municipal solid waste dumpsites in Sri Lanka

Composition of leachate from different open dumpsites from Sri Lanka was measured in order to characterize and evaluate the pollution potential by leachate. Pollutant parameters such as BOD_5, COD, heavy metals etc. were measured by standard methods. Pollution indices i.e. quality rating scales (QRS) and leachate pollution index (LPI) was calculated to evaluate the effect of leachate on environment. Quality rating scale was calculated for heavy metals and LPI was calculated for all pollutant groups, inorganic, organic and heavy metals. The results showed that most of the pollutants (F^-, Cl^-, PO_4^{3-}, NH_4^+, Fe, Se, Pb, BOD_5, and COD) exceeded the maximum tolerance limits in Sri Lankan Standards. The BOD_5/COD ratio ranged from 0.01 to 0.6 for most of the samples and the highest value of 0.6 observed in the Kolonnawa sample. The highest LPI_{or} and LPI_{hm} of 91.5 and 10.53, respectively resulted from Kolonnawa dumpsite and the highest LPI_{in} of 65.4 is resulted in leachate from Bandaragama. It was found that leachate from Kolonnawa dumpsite is polluted with organic pollutants and heavy metals and it has the highest potential of environmental pollution by means of organic pollutants and heavy metals. The leachate from Bandaragama site has the highest pollution potential of inorganic pollutants. Quality rating scales values show that most of leachate are loaded with heavy metals in most sites. LPI of leachate from all sites shows a higher value than the reference LPI which shows the impact of leachate on environment.

5.2 Adsorption of Cd(II) and Pb(II) onto humic acid–treated coconut (Cocos nucifera) husk

Coconut husk (CH), an agricultural by product available in Sri Lanka was studied for its capacity to remove heavy metals from wastewater aiming to study the possibility of using it as a reactive material in PRB. Raw CH (RCH) and humic acid treated CH (HACH) were studied for Cd and Pb adsorption with varying pH, ionic strength, contact time and initial metal ion concentration. Further, experiments were conducted to study the metal adsorption at the presence of competitive ions. The results of the study were evaluated with adsorption isotherm and kinetic models. The maximum adsorption capacities of Cd^{2+} and Pb^{2+} onto HACH were 47.28 and 66.26 mg g^{-1}, respectively, and 24.24 and 21.21 mg g^{-1}, respectively, for RCH. It was found that the adsorption of Cd^{2+} and Pb^{2+} onto HACH is a chemical sorption in which Pb^{2+} adsorption needs a longer reaction time while Cd^{2+} adsorption reaches equilibrium faster. Isotherm model fitting showed that the adsorption of Cd and Pb involves a monolayer adsorption. It was found that adsorption is affected by the some ions present in the wastewater. Humic acid treatment enhances the adsorption of Cd and Pb and it will be important in leachate treatment as leachate has humic substances resulted from waste materials.

5.3 Characterization of soils of Sri Lanka to be used as a reactive material in permeable reactive barrier

Chapter 4 presents the characterization of soils of Sri Lanka to use as a reactive material in PRB. Seven soils from were selected and collected from different locations of Sri Lanka. Soils were collected from Katugastota, Ukuwela, Anuradhapura, Kilinochchi, Iranamadu, Bangadeniya and Maharagama. The best soils for Pb and Cd adsorption were predicted by dfferent models developed by other researchers. Accordingly, soils from Ukuwela and Katugastota are the best soils for Pb adsorption while soils from Maharagama and Katugastota are best for Cd adsorption.

5.4 Conclusions and perspectives

The aim of this research was to find out suitable, low cost, locally available materials for the treatment of leachate generated from municipal solid wastes open dumpsites in Sri Lanka. Beforehand leachate characterization was done to identify the pollutants with great impact on environment. Then coconut husk and soils were studied for pollutant removal performances.

It was clear that the complex nature of leachate from different sites due to the differences in waste composition, moisture content, climatic conditions etc. The effect of each pollutant was different from site to site as the concentration of each pollutant varies with the site. Heavy metals were found to be the pollutant which has a high risk of environmental pollution in most of the open dumpsites studied. Thus, biomaterials and soils were studied for heavy metals, Cd and Pb removal from wastewater.

Biomaterial, coconut husk removed Cd and Pb well when it is modified with humic acid. Humic acid is an organic acid in leachate and humic substances are commonly found in soils with organic matter. Metal removal by humic acid treated coconut husk (HACH) was affected by some cations and anions. This may be overcome by installing a pretreatment unit to remove other ions and suspended solids in wastewater when HACH is used for actual wastewater treatment.

Seven soils from different areas of Sri Lanka were characterized for physico-chemical properties suitable for PRB. Best soils for Pb adsorption are soils from Ukuwela and Katugastota while soils of Maharagama and Katugastota best suited for Cd adsorption.

In perspective, adsorption capacities of metals by soils have to analyze in order to select best soils to be used in PRBs. Batch experiments need to be carried out at different conditions as used for the Coconut husk (Chapter 3). Best performed materials in the batch experiments have to be evaluated in a continuous system followed by a field evaluation (Figure 5.1).

Further, it is important to study the pollutant removal capacities by the mixtures of coconut husk and soils. This will facilitate the combination of mechanisms to remove metals form wastewater. Similarly, it is important to study the permeability of the materials and their variations with the time.

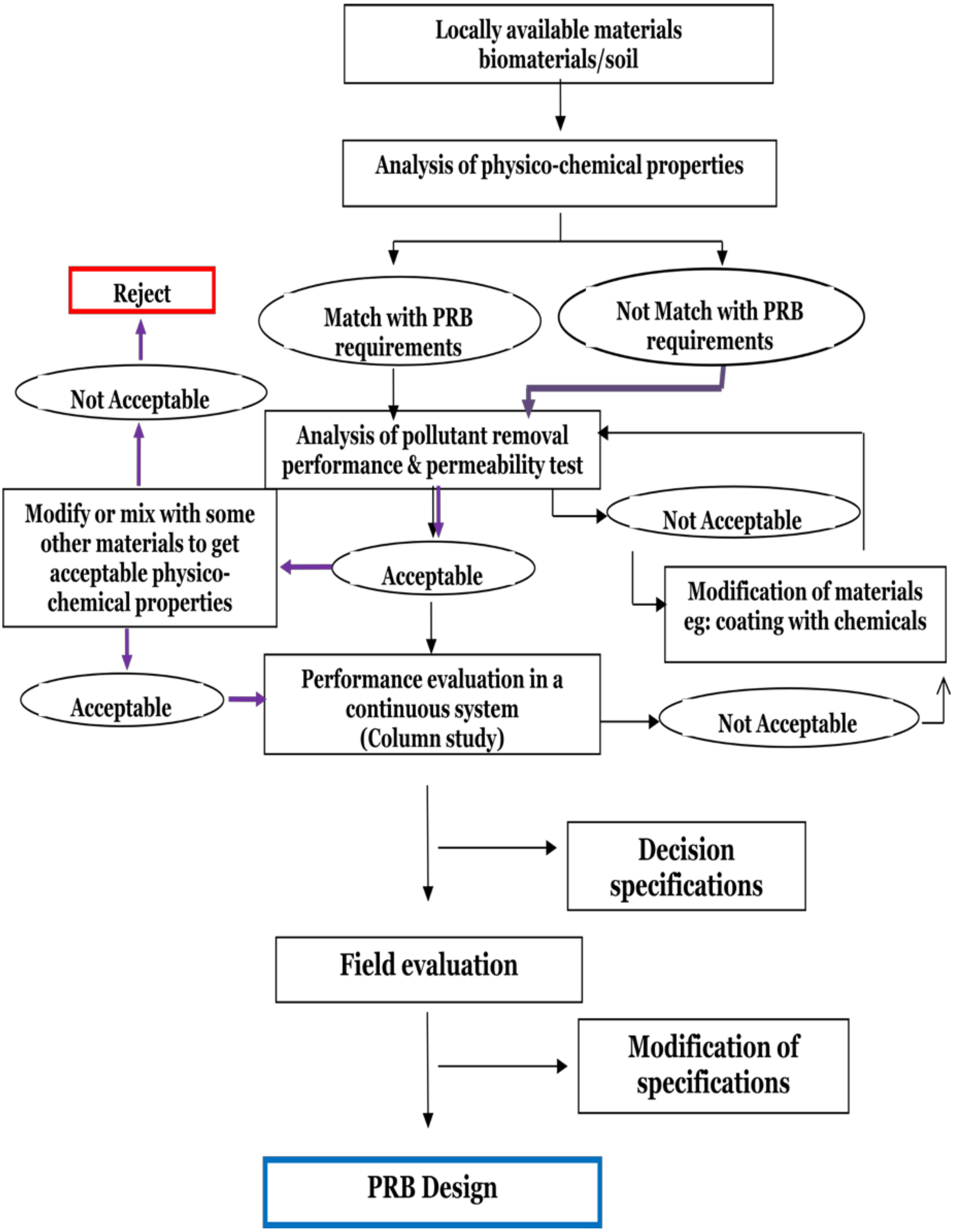

Figure 5.1: Steps of designing a permeable reactive barrier

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Journal publications

Sewwandi, B. G. N., Meththika Vithanage, S.S.R.M.D.H.R. Wijesekara, M.I.M. Mowjood, Shoichiro Hamamoto and Ken Kawamoto. 2014. Adsorption of Cd(II) and Pb(II) onto Humic Acid Treated Coconut (*Cocos nucifera*) Husk. *J. Hazard. Toxic Radioact. Waste*, 18 (2): 1-10. DOI: 10.1061/(ASCE)HZ.2153-5515.0000196.

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Paranavithana, G.N., B. G. N. Sewwandi, Takahashi Saito and Ken Kawamoto. 2014. Adsorption Characteristics of Cd(II) and Pb(II) onto Coconut Shell Biochar and Coconut Shell Activated Carbon as Media for Permeable Reactive Barriers in Sri Lanka. In proc. of 5th International symposium on Energy from Biomass and waste, Venice 2014. 17th to 20th November 2014. Accepted.

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