REMOVAL OF HEAVY METALS IONS FROM MUNICIPAL SOLID WASTE LEACHATE BY USING NATURAL ABSORBENTS

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CERTIFICATE OF APPROVAL

This dissertation submitted by **Mr. Nadeem Hussain** is accepted in its present form, by the Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Sciences and Technology (NUST), Islamabad as satisfying the partial requirement for the degree of Master of Science in Environmental Science.

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Dedicated to my parents and teachers

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List of Abbreviations

COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
TN	Total Nitrogen
TSS	Total Suspended Solids
XRF	X-Ray Fluorescence
AAS	Atomic Absorption Spectroscopy
USEPA	United States Environmental Protection Agency
Pb	Lead
Cd	Cadmium
Cr	Chromium
Ni	Nickel
Cu	Copper
Zn	Zinc
Co	Cobalt
Mn	Manganese

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ABSTRACT

Municipal solid waste leachate contains many contaminants like organic pollutants and toxic metals which cause serious effect on human health and environment. In this study, concentrations of organic compounds (COD, BOD5), and heavy metals were investigated and further the removal efficiency of toxic metals including Pb, Cd, Cr, Ni, Cu, Zn, Co and Mn by using agriculture waste including rice husk, peanut hull, wheat straw and corn cob were studied under batch sorption techniques. The effect of contact time, dosage of adsorbents and pH on equilibrium adsorption was examined. The concentration of metals was determined by using atomic adsorption spectroscopy and it was observed that various adsorbents exhibited differently at various pH levels, contact time and dosage of adsorbents. Peanut hull showed maximum adsorption efficiency 95 % to 99 % at pH 2, wheat straw showed maximum adsorption 98 % at basic pH range 9 to 11, rice husk exhibited better adsorption 86 % to 97.8 % at pH range 2 to 7, corn cob showed 90 % at neutral pH 7 and using 4 g / 100 ml dosage and 4 hours contact time for all adsorbents. Our results revealed that removal of heavy metals using locally available agriculture waste is cheaper and environmental friendly.

Chapter # 1

INTRODUCTION

1.1 Overview

Landfill leachate is generally known as wastewater generated, when the moisture content of a landfilled solid waste is higher than its field capacity (Robinson, 2004). The organic compounds (e.g. BOD, COD), inorganic compounds, metal ions and pathogens are significant main pollutants in landfill leachate (Aziz et al., 2004a). The quality and quantity of leachate differs from landfill to landfill and with the passage of time the leachate become complex wastewater and it is very problematic to design a landfill leachate treatment system.

Landfill leachate often contains various toxic metals like Barium, Calcium, Copper, Nickel, Cadmium, Mercury, Chromium, Zinc and Cobalt (Baun and Christensen, 2004). Varieties of industrial activities become cause of these heavy metals origination and waste sources and some are well known toxic and carcinogenic. The environment is threated by residual metals on the one hand and on the other hand theses metals cause serious detrimental effects on aquatic ecosystems (Papageorgiou et al., 2006). Sometimes landfill leachate permeates through landfill liners and becomes cause of contamination of the ground water. So we can say that the it is very important to develop best, cost effective and environment friendly system for the removal of toxic metals from landfill leachate.

1.2 Management of Leachate

The awareness and skills for environmental pollution control have become modernized and expensive, there has been increasing interest in techniques for waste management including the landfill leachate handling and treatment techniques. In the developed countries there are comparatively matured pollution prevention approaches for eliminating people exposure to health risks especially the solid was management. A research study revealed that biological processes as aerated ponds or activated sludge plants are the most common practice for leachate treatment. However, physical and / or chemical treatment is alternative treatment methods (Heyer et al., 2001).

1.3 National Perspective

In Pakistan, there are extensive unexplored agriculture wastes, which are following the hierarchy of waste management strategies i.e. Reduce, Reuse and Recycle. These agriculture wastes possess high efficiency of adsorption and can be utilized for the management of wastewater. The scope of research depends on the parameters of the experimental work and one of the parameter is modification of agriculture waste prepared by either chemical or physico chemical method. Other parameters are contact time of adsorption, dosage of adsorbents and pH of leachate. It leads to increase the adsorption capacity of adsorbents for the removal of metallic ions. By treating wastewater, a huge number of biotic factors can be saved from different diseases.

1.3 Hypothesis and Objectives of the Study

The crucial groundwater pollution by leachate is the most damaging environmental impact (Li et al., 2012). The leachate contains toxic heavy metals. The main objective of this research was to investigate heavy metal removal from municipal waste leachate using various adsorbent materials in a series of batch method studies under various experimental conditions.

Chapter # 2

LITERATURE REVIEW

The objective of this literature review is to point out and precise some of the literature concerning the removal of toxic metals ions from wastewaters and aqueous solutions including landfill leachate by using low-cost natural adsorbents. Pollutant concentrations in landfill leachate, alternatives for landfill leachate treatment and heavy metal mitigation using adsorption were reviewed, with a primary focus on adsorption approaches for heavy metal removal. Adsorption fundamentals, adsorption mechanisms, adsorbent materials for heavy metal removal, as well as a number of research investigations are reviewed and discussed.

2.1 Landfill Problems

There are two following main environmental problems due to landfills:

i. Air pollution

ii. Ground water pollution

2.1.1 Air Pollution

Landfills leachate create a robust harmful risk to human health and environment from the toxic contaminated air releases from the landfill biodegradation (El-Fadel et al., 1997). Landfills emitted more than 10 toxic gases including Methane, which is one of the most serious. The Methane is produced naturally during the decay of organic matter and is a more powerful greenhouse gas as compare to carbon dioxide.

There are several studies wherein the health effects of toxic gases emitted from landfills leachate have been reported. A study conducted near Love Canal, Niagara Falls, NY, showed that children live near the vicinity of chemical waste dump are seriously ill (Paigen et al., 1987). A review report of multisite studies has been examined adverse health effects like birth defects, low birth weight and certain types of cancers especially in children living in the vicinity of landfills (Vrijheid, 2000).

2.1.2 Ground Water Pollution

landfills groundwater pollution from leachates is a significant environmental and human health problem. The pollutants from landfill leachate have grasping consequence on the ecology system and food chains, which further leading to serious health effects like carcinogenic effects, genotoxicity, and acute toxicity among human beings (Mukherjee et al., 2015).

2.2 Leachate Generation

The landfill leachate is generated by the precipitation infiltrating through waste dropped in a landfill and once flows out of the waste material it is generally known as leachate. The decomposition in a municipal landfill can last for many years, as long as organic materials are available and sufficient to sustain bacterial activity. The main factors affecting the decomposition of the waste in a landfill include water movement, pH, temperature, degree of compaction, age of the landfill, and composition of the solid waste (Irene, 1996). Leachate can be collected through various collection system, using pipes system at the base of the landfill is famous system. The leachate could be collected in the storage are and directly pumped into the treatment plant for recycling. The characteristics of the landfill leachate have been represented by basic parameters such as color, smell, alkalinity, ammonium nitrogen, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and their ratio (NH_3-N) (Linde et al., 1995).

2.3 Pollutants in Landfill Leachates

The quality of landfill leachate is highly variable from landfill to landfill. Reliable methods to forecast the exact composition of a particular leachate at a particular time have yet to be developed (Ontario, 1995). Organic carbon compounds (BOD and COD), nitrogenous compounds, and metal or heavy metal ions are generally recognized as the main pollutants in landfill leachate (VanGulck and Rowe, 2004).

To measure the level of carbon compounds in the leachate, COD is used most often. Chemical oxygen demand is a simple test which allows for results to be obtained in a relatively shorter period of time than required for a five-day biochemical oxygen demand (BOD) determination. This parameter also gives an indication of the treatability of the leachate. The relationship between the landfill age and organic compound concentrations can be correlated through the COD concentration and the ratio of BOD5 to COD, as shown in Table 1.

Table 1: Leachate characteristics vs landfill age

Time	**Less than 5 years**	**5 to 10 years**	**More than 10 years**
COD(mg/L)	Less than 10000	500 to 10000	Less than 500
BOD/COD	Less than 0.5	0.1 to 0.5	Less than 0.1

Source: Morelli, (1992)

A verity of compounds like Ammonia-nitrogen (NH_3-N) and ammonium (NH_4^+-N) referred to as total Ammonia-N, are commonly found in leachate. Nitrogenous compounds in leachate can be analyzed using various parameters like Total Nitrogen (TN) and Total Kjeldahl Nitrogen (TKN). Total Kjeldahl Nitrogen and TN analyses can indicate the level of stabilization and the age of the landfill **(**Metcalf and Eddy, 2003).

Landfill leachate can contain various heavy metal ions present in significant concentrations. These heavy metal ions can include barium, calcium, cadmium, chromium, copper, nickel, lead, zinc, mercury and cobalt ions (Baun and Christensen, 2004). Some other metal ions such as iron, magnesium and calcium ions could exist at higher concentrations (Sletten et al., 1995) compiled average concentrations of heavy metals in landfill leachate from countries around the world. In general, cadmium, manganese, nickel and cobalt ions have been reported to be extensively present in landfill leachate from US landfills.

2.4 Treatment of Landfill Leachate

Traditionally, conventional landfill leachate treatment processes have been similar to those that have been used for regular wastewater. The main approaches include: biological, physical and chemical treatment processes. Biological treatment processes primarily remove high concentrations of organic compounds. However, to date, there is no evidence indicating that biological leachate treatment processes can provide the adequate microbial transformations of heavy metals through the selection of suitable microorganism (Enzminger et al., 1987; Norberg and Persson, 1984). Besides most chemical and physical treatment processes prove costly when removal of heavy metals considered (Wiszniowski et al., 2006).It has been identified by several researchers that adsorption is the most appropriate process for heavy metals removal (Wiszniowski et al., 2006).

Activated carbon is used as the main adsorption medium in traditional adsorption processes, but it is not so cheap and effective for heavy metals. Many investigations have been shown that natural agriculture adsorbents are substitute to activated carbon for the treatment of toxic metals from solution and wastewater. These natural low cost adsorbents are like chitin and chitosan (Auta and Hameed, 2014), macroalgae (Daneshvar et al., 2015), crab shell particles

(Akhtar et al., 2016), peat (Ohtsubo et al., 2012), activated and waste sludge (Ulmanu et al., 2003), fly ash (Asmaly et al., 2015), lignite (Mahmoudi et al., 2015), kaolinite (Wang et al., 2015), limestone (Aziz et al., 2004), diatomite (Ulmanu et al., 2003) and bentonite (Elkhalifah et al., 2015). In this study, wheat straw, rice husk, peanut husk and corn cobs were tested as potential natural adsorbents for the removal of heavy metals from leachate.

Moreover, it is frequently hard to get satisfactory treatment efficiency using a single treatment approach because of complex composition of landfill leachate. That is why, combining systems of chemical, physical and biological processes are frequently use for landfill leachate treatment (Aziz et al., 2004b). There is limited information in the literature regarding the comparison of the adsorption behaviors of different adsorbents, particularly natural adsorbents, for heavy metal removal from leachate. A series of experiments were conducted to identify appropriate and relatively inexpensive natural adsorbents for heavy metals removal from leachate.

In recent years, leachate treatment has received significant attention. Many in-situ or ex-situ treatment methods have been investigated and applied. This review will concentrate on ex–situ methodologies. It has to be noted that if leachate is sent to an off-site sewage treatment plant, pre-treatment is often required to avoid sewer use surcharges for high-strength wastes and to meet discharge criteria.

Leachate is essentially a type of wastewater that has an elevated concentration of contaminants. Thus, leachate treatment processes are generally similar to those designed and selected for municipal wastewaters. However, for more complex leachate compositions, a combination of physical, chemical and biological approaches are typically employed for its treatment. Satisfactory treatment efficiencies often cannot be achieved by simply using one of these approaches alone.

2.4.1 Biological Processes

Biological treatment processes play a critical role in the mitigation of leachate. By optimizing the growth of microorganisms, biodegradable organics can be treated efficiently. In a research study it is revealed that in biological processes the inorganic elements like phosphorus, sulphur, potassium, nitrogen, magnesium, calcium and organic matter can be converted into cell tissue and / or into various gases as a result of metabolism (Wiszniowski et al., 2006). Typically, biological treatment processes comprise of aerobic lagoons, activated sludge systems, rotating biological contactors, and some anaerobic treatment systems.

The underlying principle of activated sludge systems is that aerobic micro-organisms can be used for the biodegradation of organic matter. The leachate is mixed with recirculated sludge biomass and aerated in an open tank by diffusers or mechanical aerators. Activated sludge systems have demonstrated significant organic compound reductions in landfill leachate for influent BOD concentrations below 10,000 mg/L.

Aerobic lagoons, sometimes referred to as aerated ponds, are very shallow basins that treat wastewater with the use of algae and bacteria. The microbiology of aerated lagoon processes is essentially the same as for activated sludge processes. Temperature can significantly affect lagoons due to the large surface area. In general, aerated lagoons can only treat low strength leachate and are, therefore, best suited as a polishing step used in conjunction with other treatment approaches. Recommended loadings for aerated lagoons are less than 0.05kg BOD/m^3/d and the process yields approximately 0.5 kg sludge per kg BOD removed.

The Rotating Biological Contactors (RBC) normally contain a series of light weight plastic discs, these discs are fixed on a horizontal shaft and submerged in a semicircular or trapezoidal wastewater tank which slowly rotate. Microorganisms from the wastewater adhere to the plastic disc surfaces and then form biofilms (Wiszniowski et al., 2006). RBC treatment was commercialized during the early 1960's for municipal and industrial wastewater treatment (Wiszniowski et al., 2006), and was tested for landfill leachate in the mid-1980's in US (Howard, 1991).

Anaerobic biological treatment processes have also been demonstrated to be effective in reducing organic loadings from landfill leachate (Alkalay et al., 1998). These anaerobic processes use microorganisms in the absence of oxygen to convert organic compounds in the leachate to methane gas. A number of studies have reported its application at the laboratory-scale and at full-scale. Lin et al. (1998) obtained 86 % COD removal with an influent concentration of 315 g COD/m^3/day and a solids retention time of 20 days for landfill leachate treatment using anaerobic treatment. Kennedy et al. (2000) used an up-flow anaerobic sludge blanket (UASB) system and achieved between 77 % and 91 % COD removal efficiencies at hydraulic retention times of 24, 18, and 12 hrs at organic loading rates ranging between 0.6-19.7 g COD/l-d. Based on the reports, it was noted that the treatment efficiencies of anaerobic processes depend on the influent concentrations, reactor style, and hydraulic retention time.

Leachate biodegradation using biological treatment processes can primarily reduce high concentrations of organic compounds present in the leachate. However, many organic compounds or other constituents such as metals cannot be mitigated using biological processes. Physical and chemical approaches are used along with the biological processes mainly to make the treatment effective when biological oxidation processes are negatively affected by the presence of bio-refractory compounds such as heavy metals (Wiszniowski et al., 2006). Hence, a combination of physical, chemical and biological methodologies are often necessary for the successful treatment of landfill leachate (Kargi and Pamukoglu, 2003a).

2.4.2 Physical and Chemical Processes

Physical and chemical processes consist of chemical precipitation, chemical coagulation / flocculation, ion exchange adsorption, oxidation and membrane processes.

Chemical precipitation method has been practiced since many years for the removal of dissolved and suspended solids from a wastewater, this includes sedimentation and addition of chemicals e.g., alums. This is an oldest method and different chemical substances have been used as precipitants, among all these the commonly used inorganic chemicals are ferric chloride lime (calcium hydroxide) and the most popular is the alum (aluminum chloride) (Metcalf and Eddy, 2003). A latest study investigated that chemical precipitation can reduce the levels of COD, BOD, and heavy metals in wastewater (Singh et al., 2015).

Chemical coagulation/flocculation is a process in which colloidal particles in wastewater are chemically destabilized to bring about their aggregation during flocculation. The coagulants are the chemical substances which added in the wastewater to destabilize the colloidal particles such that floc formation and flocculants are those organic chemical which can improve the flocculation process (Metcalf and Eddy, 2003). Coagulation with alum or ferric chloride can remove iron and color, however, has very low effect in removing COD, chloride, hardness and dissolved solids. A study conducted by Amokrane et al., (1997) indicated that the coagulation and precipitation were not suitable for the treatment of high strength leachate and treatment efficiency was generally limited to a 50 % to 60 % for COD removal from a stabilized landfill leachate using a coagulation/flocculation process.

Chemical oxidation in wastewater treatment typically involves the use of oxidizing agents (oxidants) to oxidize the organic contaminants. Ozone (O_3), hydrogen peroxide (H_2O_2), permanganate (MnO_4), chloride dioxide (ClO_2), chlorine (Cl_2 or HOCl), and oxygen (O_2) are typical oxidants. A research report suggested that chemical oxidation is an effective method for the treatment of wastewaters containing soluble organics which cannot be removed by physical separation, as well as for non-biodegradable and/or toxic substances (Wiszniowski et al., 2006). In general, efficient treatment via chemical oxidation has been shown to be very cost effective for reducing COD in leachate.

Membrane processes usually consist of microfiltration, ultrafiltration, nano-filtration and reverse osmosis. The basis of these processes is that higher molecular weight organics cannot pass through when pressured wastewater is forced through the membrane. Reverse osmosis systems are the most widely used membrane process for leachate treatment (Robinson, 2004). The drawback of membrane processes is that the membranes are susceptible to fouling due to the formation of biological slimes. Their construction and operation are very costly compared to traditional biological treatment processes.

Ion exchange processes involve the displacement of a given ion from an insoluble exchange material by other ionic species in solution. The most common use of this process is in domestic water softening. Prior to ion exchange, the leachate needs to be clarified by coagulation/flocculation/precipitation to remove suspended solids and non-aqueous liquids.

Ion exchange is generally not recommended for any leachate containing over 2500 mg/L of dissolved solids.

2.4.3 Adsorption

Adsorption is the process of accumulation of substances present in solution on a suitable interface (Metcalf and Eddy, 2003). Hence, this method is known as a refining process for water which has already received normal biological treatment. Carbon adsorption is one of the most extensively applied physical-chemical processes for the removal of pollutants from leachate (Enzminger et al., 1987).

2.5 Heavy Metal Removal by Adsorption from Leachate

Heavy metals are widely used in industrial activities and are often found in industrial and municipal waste streams. A number of heavy metal ions, such as Cd, Hg, and Pb have been reported to have toxic and/or carcinogenic effects on human health (Kargi and Pamukoglu, 2003b). Thus, heavy metal removal is an important concern in landfill leachate treatment. As previously discussed, biological leachate treatment cannot effectively treat and remove all organic and inorganic compounds, particularly heavy metal ions. Many physical-chemical treatment processes can be very costly, because large quantities of chemicals are required. Heavy metals removal from landfill leachate by using locally available low cost agriculture waste adsorbents is cheapest and famous technique (Umar et al., 2015).

2.5.1 Fundamentals of Adsorption Processes

Adsorption is process in which ingredients in the liquid phase are transferred to the solid phase, hence resulted in the increase of a surface layer of solute molecules on the adsorbent. The adsorbate is the substance which is being removed from the liquid phase at the interface, while the adsorbent is the solid, liquid, or gas phase onto which the adsorbate accumulates (Ruthven, 1984).

Adsorption results as a consequence of an unbalance of surface forces or surface energy (Eckenfelder, 2000), and includes both physical and chemical mechanisms. Physical adsorption occurs as a result of molecular condensation in the capillaries of the solid, while chemical adsorption is generally through the formation of ionic complexes and chemical bonds between the adsorbate and the adsorbent (Eckenfelder, 2000). In a bulk material, all the bonding requirements of the constituent atoms of the material are filled. Some atoms on the adsorbent surface experience a bond deficiency and conditions are favorable to bond with other atoms in the solutions, however, nature of the bonding is normally depending upon the atomic species involved in the process.

Ruthven (1984) studies that the adsorption mechanism is takes place in through the following three steps;

a) Bulk solution transport
b) Diffusive transport
c) Bounding processes

In general, substances with higher molecular weights are most easily adsorbed. The rate of adsorption is systematized by the rate of diffusion of the solute molecules within the capillary pores of the adsorbent particles. The rate increases with the adsorbate concentration and temperature as well as the molecular weight of the solute (Eckenfelder, 2000)

2.5.2 Adsorbents for Heavy Metal Removal

Adsorption by activated carbon is a well-established technology employed extensively in the treatment of wastewaters from various industrial and municipal sources. Activated carbon can be prepared by making char from waste organic materials such as wood and coal, almonds, coconuts and walnut hulls. The char is then activated by exposing at a high temperature on oxidizing gas. Activated carbons are classified by the average diameter of the carbon. Generally, the diameter of granular activated carbon is greater than 0.1 mm and the diameter of powdered activated carbon diameter is less than 0.074 mm (Metcalf and Eddy, 2003).

A study exposed that activated carbon is the best and widely used adsorbent for the removal heavy metals and non-biodegradable organic compound (Rodrigue et al., 2004). A research examined that the activated carbon of almond husks showed 98 % removal efficiency for nickel (Hasar, 2003). A study conducted by Rodrigue et al. (2004) comparing the treatment efficiency of Granular Activated Carbon (GAC) with other adsorbents and revealed that GAC yielded the greatest reductions in effluent COD concentrations from landfill leachate.

Although activated carbon is widely applied for pollutant removal, natural low-cost materials have also successfully been employed as adsorbents for heavy metal removal from aqueous solutions and wastewaters. These have been considered and researched as alternatives to activated carbon. Peat has been shown to be a readily available, simple, effective and low cost adsorbent for the treatment of wastewater. For example, it has been reported to reach over 90% removal efficiencies in cadmium and nickel adsorption (Brown et al., 2000). Shells and natural chitin, are plentiful, inexpensive, and effective adsorbents for cobalt, copper, nickel, lead and cadmium removal from aqueous solutions and landfill leachate (Zhou et al., 2004).

As peat and mollusk shells are useful in adsorption applications, the feasibility and economics of using these natural adsorbent will be discussed further in the following subsections.

2.5.3. Bio Sorbents

The bio sorption process consists of a solid phase e.g., biological material and a liquid phase e.g., normally water, which containing a dissolved species to be sorbed e.g., metal ions. Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound with them by different mechanisms. The process continues till equilibrium is established between the amount solid bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its capability of distribution between the solid and liquid phases.

According to different surveys, it is investigated that agricultural products and by products has widely been used for the removal of toxic metals from water and wastewater. A research suggested that agricultural materials can be effectively used as a low cost adsorbent (Kumar, 2006). In a research, a number of low cost bio materials like rice husk, saw dust and eucalyptus bark were tested for removal of chromium and Euclyptus Bark found the most effective adsorbent for adsorption of chromium (VI) (Logeswari et, al., 2013).

Abia et al (2006) studied chemically modified and unmodified agricultural adsorbents for the removal of Lead and Nickel from the aqueous solution of metal, the results showed that oil palm fruit fibers are good adsorbents for the removal of Lead and Nickel. The percentage removal of each of these metals is increased by using chemically modified adsorbents.

Banana peel is helpful for the treatment of Cr (III) from wastewater. A study investigated that banana peel is efficiently removed the metal ion chromium from industrial waste water and absorption capacity is dependent on contact time, pH, initial concentration and temperature (Memon et al., 2008)

Activated carbon was prepared from low cost adsorbents such as rice husk, saw dust which have been utilized for the removal of dyes. It is helpful for the removal of dyes. Rice husk has been also activated by treating with phosphoric acid and then used for the removal of heavy metals from solution. Phosphoric acid modified rice was enhanced the efficiency of the rice husk for the removal of toxic metals like Cr (VI) (Kennedy et al., 2004).

The agriculture waste is widely used for the treatment of heavy metals. A comparative study for different bio sorbents is shown in the table 2.

Table 2: Low cost adsorbents and their adsorption capacity

Materials	Adsorbates	Adsorption capacity	Contact Time	Reference
Peanut Hull	Pb, Cu, Cd, Zn	30, 10, 6, 9 mg / g	4 hours	Brown et al 2000a
Hazelnut shell	Cd, Zn, Cr	5.42, 1.78, 3.08, 3.99 g / Kg	5 hours	Cimino et al 2000
Rice Husk	Pb(II)	19.86 mmol / g	10 min	Khalid et al, 1998
Maize (Zea mays) cob, hardwood sawdust	Cr(VI)	1.667 mg / L	3 hours	Ibrahim, 2011
Pomegranate peel	Pb(II), Cu(II)	5.6, 5.8 mg / g	2 hours	El-Ashtoukhy, et al 2008
Saw dust, and coirpith	Cr(VI)	1482 mg / kg 159 mg / kg	2 hours	Sumathi et al 2005
Banana peel	Cr(VI)	95 %	10 min	Memon, et al 2009

2.5.3.1 Removal of Heavy Metals by using Peanut Hull

Peanut is commercially produced in Pakistan since 1950 and peanut shell/hull is a waste product of industry as the peanut is the main ingredient of food industry. A research study revealed that it is a good renewable resource (Brown et al., 2000b) and has been also frequently used in the removal of heavy metals. The chemical structure of peanut hull contains cellulose, hemicellulose, pectin, lignin, and protein (Kumar, 2006) and many functional groups such as carboxyl, carbonyl, hydroxyl and amino (Tarley et al., 2004).

2.5.3.2 Removal of Heavy Metals by using Rice Husk

Pakistan is major producer of rice husk. There are several studies indicated that rice husk is widely used as a sorbent for the removal of heavy metals (Agrafioti et al., 2014; Lata and Samadder, 2014; Dai et al., 2015; Galletti et al., 2015). The chemical structurally of rice husks consist of cellulose (35 %), hemicellulose (25 %), lignin (20 %), ash (including silica 17 %) and crude protein (3 %), hence it is very suitable for metallic cations removal (Sobhanardakani et al., 2013).

2.5.3.3 Removal of Heavy Metals by using Wheat Straw

Pakistan is major grower of wheat and wheat straw is a by-product of wheat processing industries. The Chemical composition of wheat straw consist of cellulose (40 %), hemicellulose (26 %), lignin (22 %) and ash (9 %), hence it is very suitable for metallic cations removal (Yasin et al., 2010). There are several studies indicated that wheat straw is being widely used as a sorbent for the removal of heavy metals (Chun et al., 2004, Dang et al., 2009 and Krishnani, 2015).

2.5.3.4 Removal of Heavy Metals by using Corn Cob

Corns are widely growing in Pakistan. The Chemical composition of Corncobs contain approximately cellulose 939.1%), hemicellulose (42.1%), lignin (9.1%), protein (1.7%), and ash (1.2%), hence it is very suitable for metallic cations removal (Barl et al., 1991). There are several studies indicated that treated and untreated corn cob is being widely used as a sorbent for the removal of heavy metals (Vafakhah et al., 2014, Lin et al., 2015).

Chapter # 3

Material and Methods

Figure 1: Flow sheet diagram for removal of toxic metals by using low cost adsorbent

3.1. Sampling

Sampling is the most important pre-requisite technique used for the detailed study of physical and chemical characteristics of municipal solid waste leachate. There are some specific rules.

- The samples must represent the conditions existing at the point taken.
- The sample must be sufficient volume and must be taken frequently enough to permit reproducibility of testing requisite for the desired objective as conditioned by the method of analysis to be employed.
- The sample must be collected, packed and manipulated prior to analysis in a manner that protects against changes in the particular constituent or properties to be examined.

3.1.1. Sample Volume

A total 20-liter sample was collected.

3.1.2. Sample Location

Leachate was collected from Losar Dumpsite (an official dumpsite of Rawalpindi city), Pakistan. Per day municipal solid waste is dumped in Losar is about 1,200 metric tons. Most of the waste which is dumped is organic.

3.1.3. Time of Collection and Transportation of Sample

A period of 4 to 6 hours only consumed between the collection of sample and transportation to the laboratory.

Figure 2: Sampling location map of Losar dump site Rawat, Rawalpindi

3.1.4. Labelling

The following information was labeled on sample container,

- Date and time of sampling
- Source of sampling
- Temperature of sample

3.1.5. Preparation of Sample Bottle

A high quality plastic air tight bottle whose capacity 20 liter was taken from local market. It was washed with hot cleaning water by using soap. The bottle was rinsed with nitric acid to remove any metal contamination. Finally, bottle was rinsed with distilled water.

3.2. Preparation of Adsorbents

Four adsorbents have been selected for this research work i.e. rice husk, peanut hull, wheat straw and corn cob.

3.2.1. Rice Husk

Rice husk was collected from Usman Rice Mill Sahiwal. After collecting, it was grinded to convert into small particles by using grinder. After grinding passed through the sieve whose pore size was 0.2 mm to obtain small and uniform particles. Then it was washed with distilled water and dried at room temperature for four hours and then put in oven for 24 hours at temperature 105 ^{0}C.

3.2.2. Peanut Hull

Peanut Hull was collected from local market Attock. After collecting, 1st it was cutting into small parts then it was grinded to convert into small particles by using grinder. After grinding passed through the sieve whose pore size was 0.2mm to obtain small and uniform particles.

Then it was washed with distilled water and dried at room temperature for four hours and then put in oven for 24 hours at temperature 105 ^{0}C.

3.2.3. Wheat Straw

Wheat straw was collected from local Village of Sahiwal. After collecting, it was grinded to convert into small particles by using grinder. After grinding passed through the sieve whose pore size was 0.2 mm to obtain small and uniform particles. Then it was washed with distilled water and dried at room temperature for four hours and then put in oven for 24 hours at temperature 105 ^{0}C.

3.2.4. Corn Cob

Corn Cob was collected from local Village of Sahiwal. After collecting, 1st it was cutting then it was grinded to convert into small particles by using grinder. After grinding passed through the sieve whose pore size was 0.2 mm to obtain small and uniform particles. Then it was washed with distilled water and dried at room temperature for four hours and then put in oven for 24 hours at temperature 105 ^{0}C.

3.3. Leachate Characterization

3.3.1. pH

pH of leachate was measured with the help of pH meter before and after filtration. A small variation occurred in pH before and after filtration.

3.3.2. Electrical Conductivity

Electrical conductivity of leachate was measured by using EC meter (inoLab pH/Cond 720).

3.3.3. Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) was calculated using standard Open Flux method which involved followed steps. 1.5 ml of $K_2Cr_2O_7$ (99.5%) & 3.5 ml of H_2SO_4 reagents were added to 2.5 ml of leachate sample. The samples in the PTFE vial were heated in COD reactor (HACH) at 120°C for 2 hrs. Ferrous Ammonium Sulfate (FAS) was used as titrant in the presence of fermion indicator (5220 B. Open Reflux Method). COD was calculated using the following formula:

$$COD = \frac{(A - B) \times M \times 8000}{Volume\ of\ sample\ (mL)}$$

A = Volume of FAS used to titrate the blank in mL, B= Volume of FAS used to titrate the sample

M = Molarity of FAS solution which is 0.1

3.3.4. Qualitative Analysis of Heavy Metals

The presence of heavy metals in leachate were analyzed by X-Ray Fluorescence (XRF) Elemental Analyzer JEOL JSX 3202 M Elemental Analysis (Na-U). This was only qualitative analysis which was used for identification of elements present in leachate.

3.3.5. Quantitative Analysis of Heavy Metals

The concentration of selective metals was measured by Flame Atomic Absorption Spectrometer (A Analyst 800).

3.4. Removal of Heavy Metals

3.4.1 Methods for Removal of Toxic Metals

Many researchers were made a great effort for the removal of heavy metals from waste water. Most of the researchers used fixed bed column method (Brown et al., 2000b), or batch and column method (Agrawal et al., 2006) for the removal of toxic metals from aqueous solution (Sud et al., 2008) as well as waste water (Kumar, 2006). In this study batch method was used to remove heavy metals from municipal solid waste leachate by using four different low-cost natural adsorbents i.e. rice husk peanut hull, wheat straw and corn cob. Orbital shaker was used for removal of heavy metals.

Figure 3: Orbital shaker used during the experimental work for shaking the adsorbent and leachate solution for different contact times.

3.4.2 Experimental Work

A series of experiments for different adsorbents by using 50 ml leachate volume at pH 7.5 with constant temperature 18 ^{o}C and shaking time of 150 r.p.m were performed to study the removal efficiency of low cost agriculture adsorbents which are shown in the table 3.

Table 3: A series of experiments for different adsorbents

Contact Time (hours)	**Dosage (g)**				**pH**
	Rice Husk	Peanut Hull	Wheat Straw	Corn Cob	
1	1	1	1	1	2, 5, 9, 11
2	2	2	2	2	
3	3	3	3	3	
4	4	4	4	4	

3.4.3 Removal Efficiency

To calculate the removal efficiency, the following equation has been used:

$$\% \, Removal \, Efficency = \frac{Co - Ce}{Co} \, x \, 100$$

Where,

C_0= Initial Concentration of metal ions in leachate

C_e= Final Concentration of Metal ions in leachate

Chapter # 4

RESULTS AND DISCUSSIONS

The study was carried out with objectives to evaluate the contamination of heavy metals in municipal solid waste leachate collected from Rawalpindi and their treatment with low cost natural adsorbents. The assessments of trace elements were performed by using different analytical techniques including XRF analysis, atomic adsorption spectrometer. Batch method was employed in order to check the removal of heavy metals by using locally available low cast agriculture waste i.e., Rice Husk, Wheat Straw, Peanut Hull, Corn Cob.

4.1. Leachate Characterization

4.1.1 XRF-Analysis

The qualitative analysis of leachate samples was carried out by XRF in order to analyze the presence of selected heavy metals (Pb, Cd, Cr, Ni, Cu, Zn, Co and Mn). All samples were analyzed and results showed the presence of toxic trace elements. The XRF spectrum of one such is shown in figure 3.

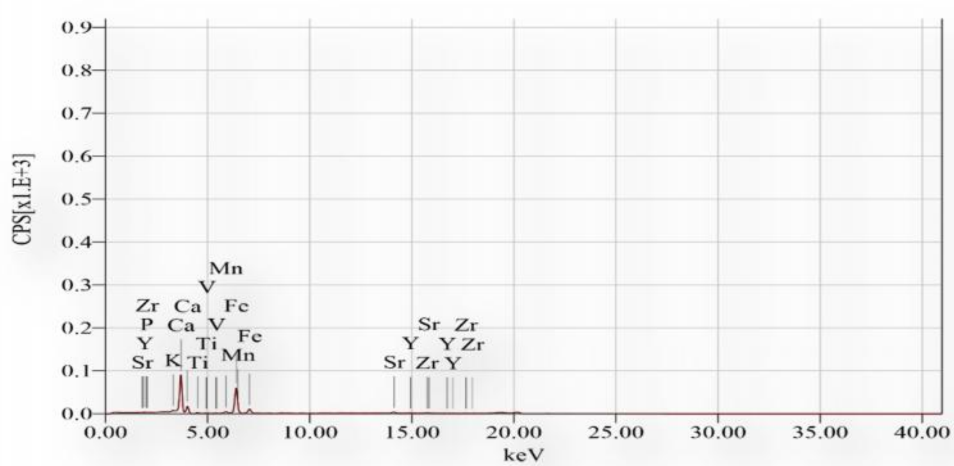

Figure 4: XRF of leachate solution

4.1.2. Concentration of Metals

The concentration of selective eight metals i.e. Cu, Zn, Co, Ni, Mn, Cr, Cd and Pb was measured by AAS.

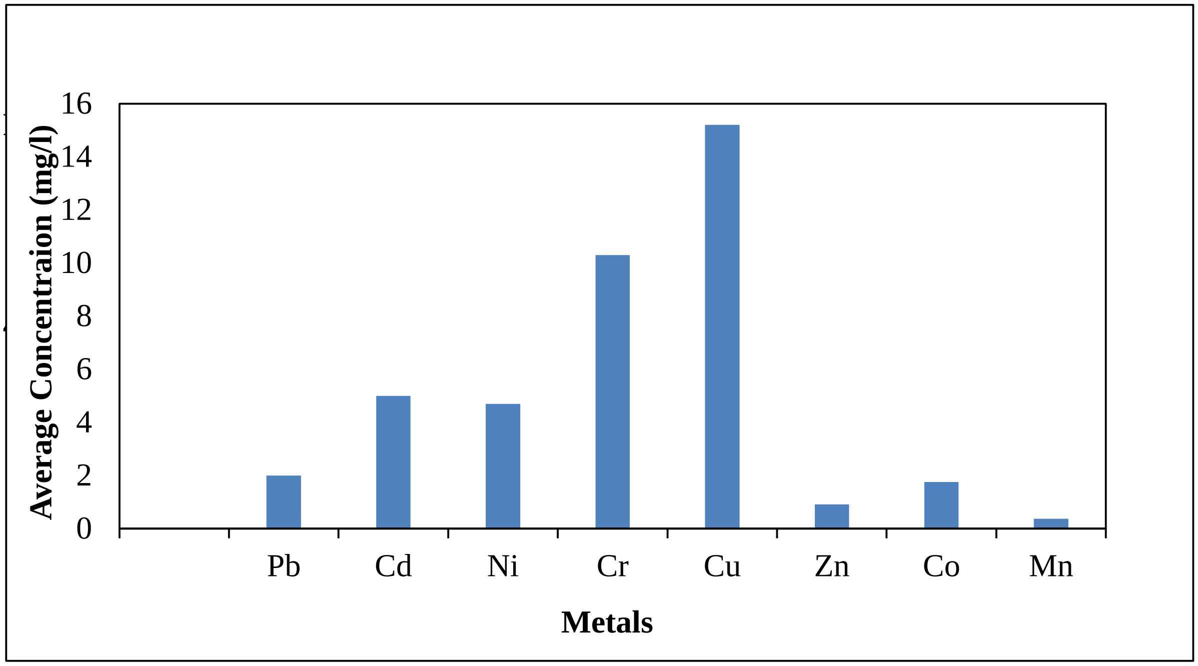

Figure 5: Concentration of metals in Leachate

4.2 Batch Sorption Studies

Batch sorption studies were conducted to identify the efficiency of Rice Husk, Peanut Hul, Wheat straw and corn straw at different pH, contact time and adsorbent dosage at constant temperature 18 $^{O}C \pm 3$ ^{O}C and 150 r.p.m. The adsorption capacity of adsorbent was studied for different metals i.e. Ni, Co, Mn, Pb, Zn, Cr, Cd and Cu. Under Batch sorption experiment the parameters including contact time, dosage of adsorbents and pH were studied. Above tables and graphs showed that peanut hull adsorption capacity changed by changing the parameters. The effects of various parameters discussed below.

4.2.1 Effect of pH

4.2.1.1 Rice Husk

It is reported by several scientist that adsorption is pH dependent (Yadav et al., 2015). When optimum contact time and dosage of adsorbent was identified then further to verify the pH effect as one of important factors on the *heavy metals (Pb, Cd, Cr, Ni, Cu, Zn, Co and Mn)* removal using rice husk, different experiments were performed by changing pH of leachate i.e. 2, 5, 9,11 and at original pH 7.5. Our results showed in figure 6, the maximum adsorption efficiency obtained at pH 2 for all metals. Zn showed 97.8 % adsorption at pH 2 and Pb, Cd, Ni showed 95% adsorption and Cr and Cu showed 93 % but Mn showed 86 % at that pH. It is also observed that rice husk showed maximum adsorption (86 % to 97.8 %) at pH range 2 to 7 but the adsorption capacity of rice husk was decreased in basic pH, in basic medium its efficiency was 7 % to 40 % as shown in figure 6. The concurrent results were reported by (Singh, 2015)

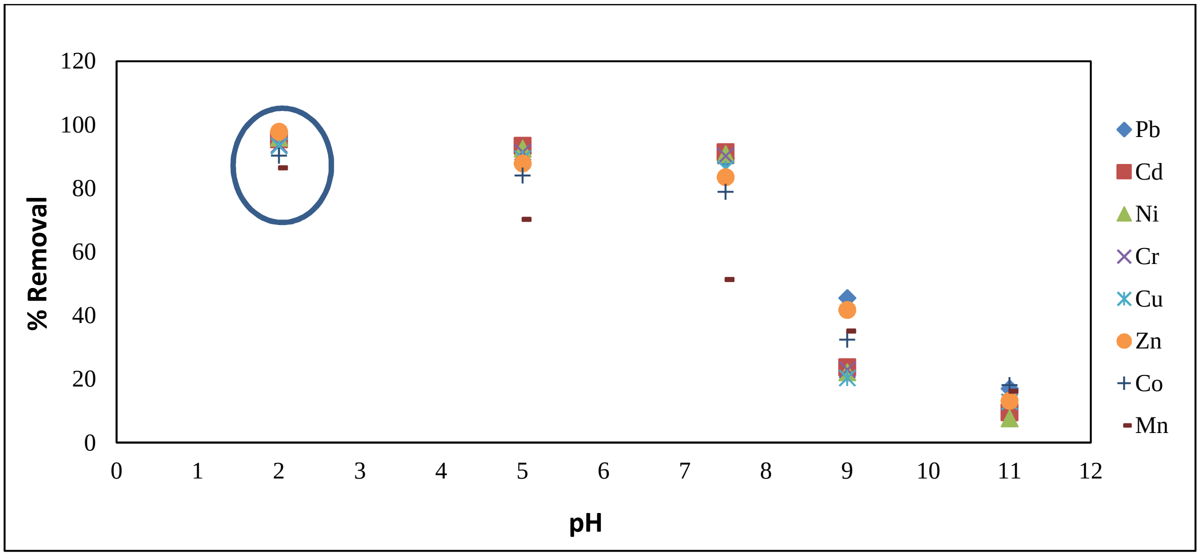

Figure 6: The removal of heavy metals in % studied at various pH using rice husk

4.2.1.2 Peanut Hull

It is reported by several scientist that adsorption is pH dependent (Georgieva et al., 2015;). When optimum contact time and dosage of adsorbent was identified then further to verify the pH effect as one of important factors on the *heavy metals (Pb, Cd, Cr, Ni, Cu, Zn, Co and Mn)* removal using peanut hull, different experiments were performed by changing pH of leachate i.e. 2, 5, 9,11 and at original pH 7.5. Our results showed in figure 7, the maximum adsorption efficiency obtained at pH 2 for all metals. Zn, Pb and Mn showed 99 % adsorption at pH 2 while Cd, Ni, Cu and cobalt showed 99 % adsorption. It is also observed that peanut hull showed maximum adsorption (80 – 99 %) at pH range 2 to 7 except manganese but the adsorption capacity of peanut hull was decreased in basic pH, in basic medium its efficiency was 3 % to 50 % as shown in figure 7.

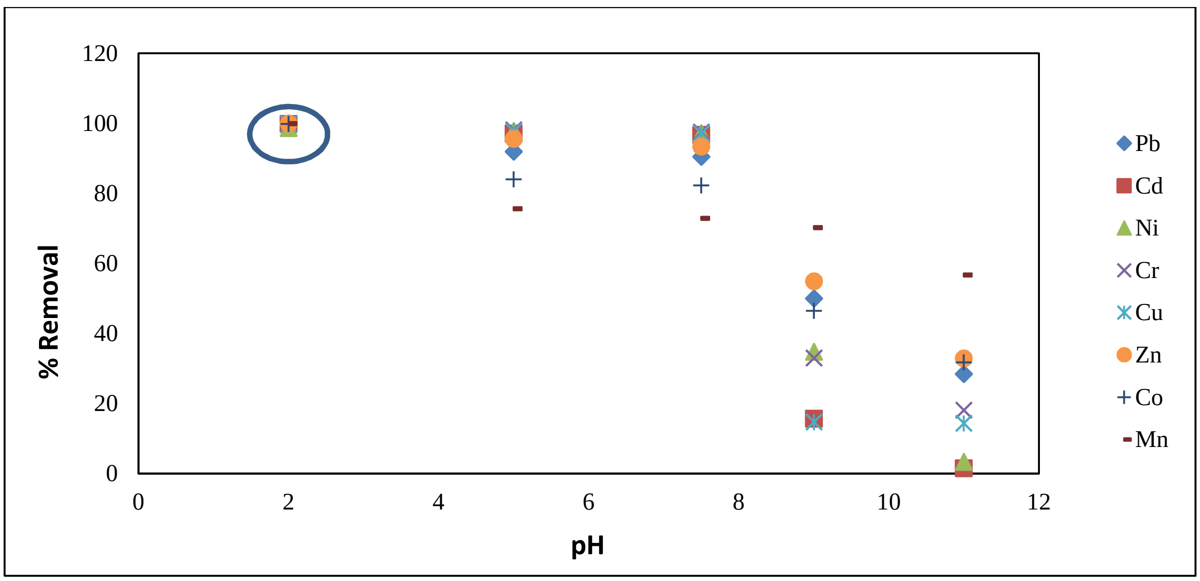

Figure 7: The removal of heavy metals in % studied at various pH using peanut hull

4.2.1.3 Wheat Straw

It is reported by several scientists that adsorption is pH dependent. When optimum contact time and dosage of adsorbent was identified then further to verify the pH effect as one of important factors on the *heavy metals (Pb, Cd, Cr, Ni, Cu, Zn, Co and Mn)* removal using wheat straw, different experiments were performed by changing pH of leachate i.e. 2, 5, 9, 11 and at original pH 7.5. The adsorption process by wheat straw is highly depended on pH (Yang et al., 2004) Our results showed in figure 8, the maximum adsorption efficiency obtained at pH 9 for mostly metals. Zn and Mn showed 98 % adsorption at pH 9 while Pb, Cr and cobalt showed more than 80 % adsorption. It is also observed that wheat straw showed maximum adsorption (70 % - 98 %) at pH range 9 to 11 but the adsorption capacity of wheat straw was decreased in acidic pH, in acidic medium its efficiency was 7 % to 60 % except Cd, Cr and Ni which showed 71.20 %, 76.12 % and 72.98 % respectively as shown in figure 8.

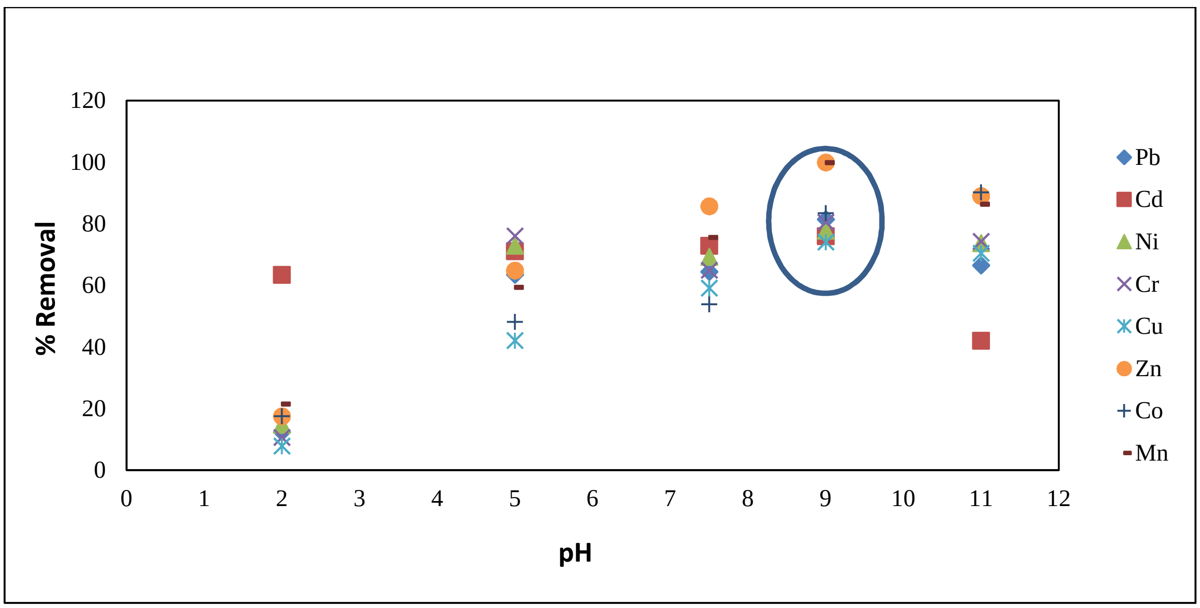

Figure 8: The removal of heavy metals in % studied at various pH using wheat straw

4.2.1.4 Corn Cob

When optimum contact time and dosage of adsorbent was identified then further to verify the pH effect as one of important factors on the *heavy metals (Pb, Cd, Cr, Ni, Cu, Zn, Co and Mn)* removal using Corn cob, different experiments were performed by changing pH of leachate i.e. 2, 5, 9, 11 and at original pH 7.5. Our results showed in figure 9, in above mentioned result it was observed that no significant change occurred by changing pH of leachate. It is also found that adsorption efficiency of corn cob was decreased in both cases either pH increased or decreased. It is concluded that the corn cob showed maximum absorption (90 %) at neutral pH 7, shown in the figure 9.

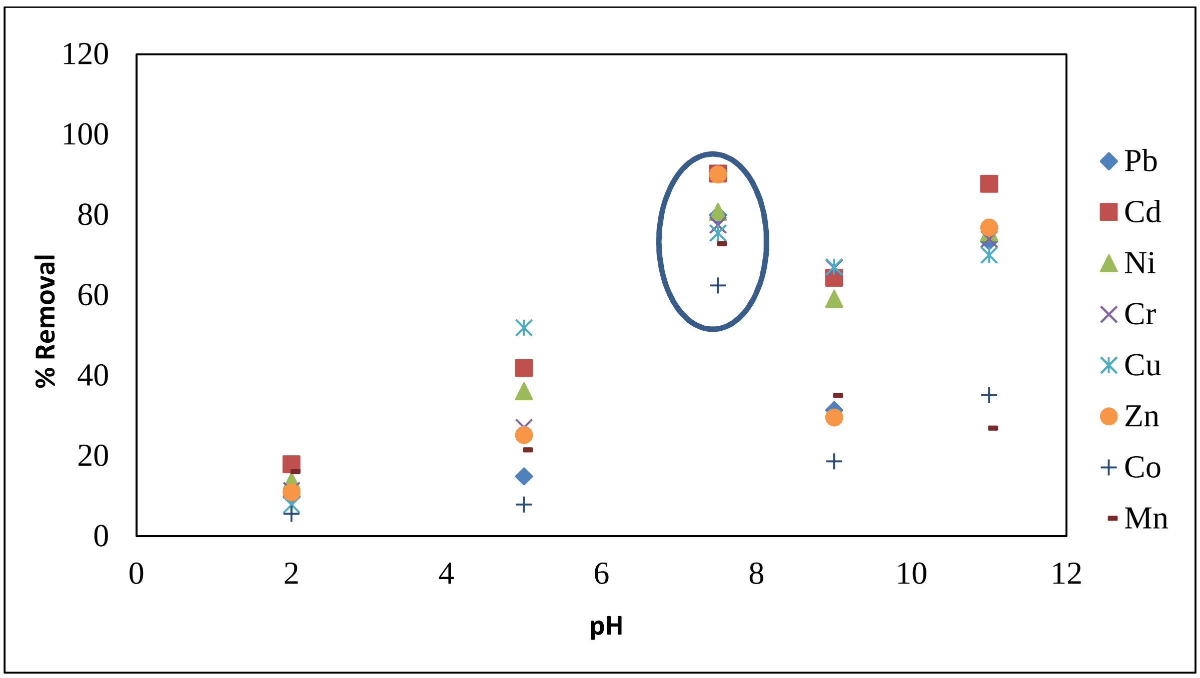

Figure 9: The removal of heavy metals in % studied at various pH using corn cob

4.2.2 Effect of Dosage and Contact Time

4.2.2.1 Rice Husk

Several experiments were performed to check the effect of dose of the rice husk and contact time, which are presented in Figure 10. Our results revealed that the adsorption capacity was changed by changing dosage of adsorbent and shaking time. The experiments were conducted by using 1 g, 2 g, 3 g, and 4 g amount of rice husk at different shaking.

g time 1hr, 2hrs, 3hrs, and 4hrs keeping all other parameters constant. The removal efficiency was observed different for different metals, Zn and Co was adsorbed 9.8 % and 15 % respectively by using 1g of adsorbent at shaking time for one hour, and other metals were not significantly adsorbed at that time. It is also observed that the adsorption capacity was increased by increasing shaking time i.e. 2 hours, 3 hours and 4 hours. Ni and Cd was maximum adsorbed 77.6 % and 76.8 % respectively for shaking 4 hours. It was also found that the adsorption capacity of most of the metals increased by using 2 g dosage of adsorbent at 4 hours contact time, except cobalt other metals showed more than 70 % adsorption and cadmium and zinc showed up to 90 % adsorption.

Similarly the adsorption of metals by further increasing the dose of rice husk i.e. 3 g and 4 g. Our experiments concluded that most of the metals showed maximum adsorption up to 90 % at 4 g dosage of adsorbent and at 4 hours shaking time, except Manganese, which showed only 51 % adsorption. Our results revealed that adsorption is dependent on contact time and increase with increase in adsorbent dosage and contact time till the equilibrium is attained. The similar results were reported by (Ajmal et al., 2003).

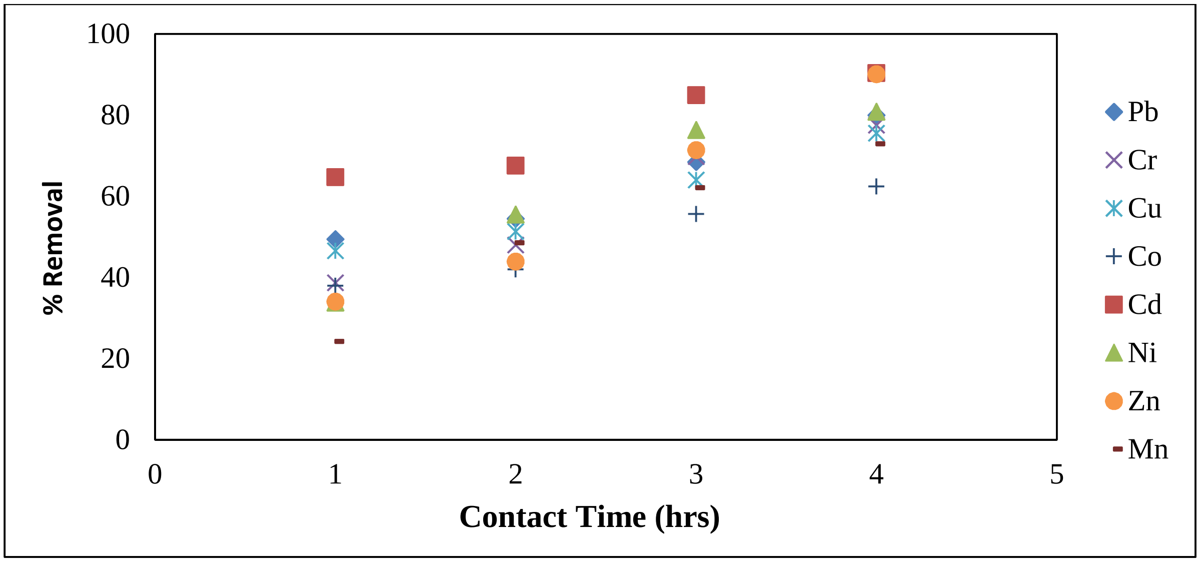

Figure 10: Effect of contact time using 4 g sorbent dose of rice husk

4.2.2.2 Peanut Hull

A number of experiments were executed to check the effect of dose of the peanut hull and contact time presented in Figure 11. Our results revealed that the adsorption capacity was changed by changing dosage of adsorbent and shaking time. The experiments were conducted by using 1g, 2g, 3g, and 4g amount of peanut hull at different shaking time 1hr, 2hrs, 3hrs, and 4hrs keeping all other parameters constant. The removal efficiency was observed different for different metals, Zn, Mn, Cr and Co was adsorbed 20.88%, 16.2%, 11.5% and 18.75% respectively by using 1g of adsorbent at shaking time for one hour, and other metals were not significantly adsorbed at that time. It is also observed that the adsorption capacity was increased by increasing shaking time i.e. 2 hours, 3 hours and 4 hours. Zn and Cd was maximum adsorbed 68.13% and 69.8% respectively for shaking 4 hours. It was also found that the adsorption capacity of most of the metals increased by using 2g dosage of adsorbent at 4 hours contact time, except cobalt and manganese other metals showed more than 70 % adsorption and chromium showed up to 87.18% adsorption.

Our experiments concluded that most of the metals showed maximum adsorption up to 97% at 4g dosage of adsorbent and at 4 hours shaking time, except Manganese, which showed only 72% adsorption. Our results exposed that adsorption is dependent on contact time and increase with increase in adsorbent dosage and contact time till equilibrium is attained. The similar results were reported by (Han et al., 2011).

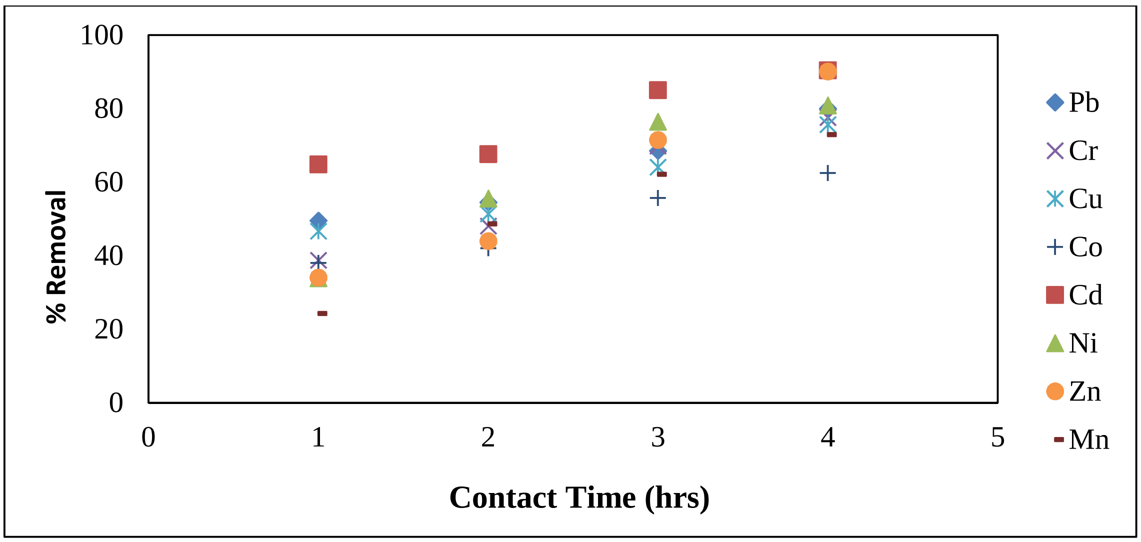

Figure 11: Effect of contact time using 4 g sorbent dose of peanut hull

4.2.2.3 Wheat Straw

The experiments to identify the influence of dosage and shaking time on sorption efficiency were carried using wheat straw, which are presented in Figure 12. Our results revealed that the adsorption capacity was changed by changing dosage of adsorbent and shaking time. The experiments were conducted by using 1g, 2g, 3g, and 4g amount of wheat straw at different shaking time 1hr, 2hrs, 3hrs, and 4hrs keeping all other parameters constant. The removal efficiency was observed different for different metals, Zn, Mn and Co was adsorbed 13.19%, 5.41% and 16.48% respectively by using 1g of adsorbent at shaking time for one hour, and other metals were not significantly adsorbed at that time. It is also observed that the adsorption capacity was increased by increasing shaking time i.e. 2 hours, 3 hours and 4 hours. Zn and Pb was maximum adsorbed 54.95% and 50% respectively for shaking 4 hours. It was also found that the adsorption capacity of most of the metals increased by using 2g dosage of adsorbent at 4 hours contact time, adsorption efficiency of Zn increased up to 68.13%. Our experiments concluded that most of the metals showed maximum adsorption 60% to 85.71% at 4g dosage of adsorbent and at 4 hours shaking time, except Cobalt, which showed only 53% adsorption. Our experimental data showed that adsorption is dependent on contact time and dosage of adsorbent till equilibrium is attained.

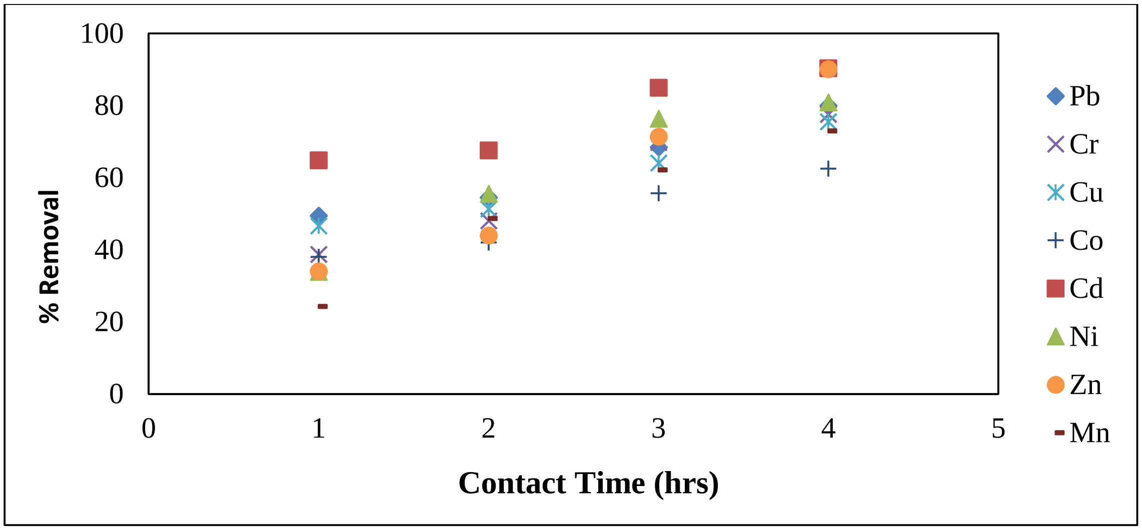

Figure 12: Effect of contact time using 4 g sorbent dose of wheat straw

4.2.2.4 Corn Cob

The experiments to check the effect of dose of the Corn cob and contact time were performed and presented in Figure 13. Our results revealed that the adsorption capacity was changed by changing dosage of adsorbent and shaking time. The experiments were conducted by using 1g, 2g, 3g, and 4g amount of Corn cob at different shaking time 1hr, 2hrs, 3hrs, and 4hrs keeping all other parameters constant. The removal efficiency was observed different for different metals, Zn, Mn, Cr, Cu, Ni and Co was adsorbed 21.98%, 16.2%, 16.89%, 11.78%, 12.55% and 25.57% respectively by using 1g of adsorbent at shaking time for one hour, and other metals were not significantly adsorbed at that time. It is also observed that the adsorption capacity was increased by increasing shaking time i.e. 2 hours, 3 hours and 4 hours. Zn and Ni was maximum adsorbed 62.64% and 56.8% respectively for shaking 4 hours. It was also found that the adsorption capacity of most the metals increased by using 2g dosage of adsorbent at 4 hours contact time, except cobalt, copper and manganese other metals showed more than 70% adsorption and cadmium showed up to 81.4% adsorption. Our experiments concluded that most of the metals showed maximum adsorption 70 – 90 % at 4g dosage of adsorbent and at 4 hours shaking time, except Cobalt which showed only 62% adsorption. The adsorption is dependent on contact time and adsorbent dosage till equilibrium is attained. Corn cob is considered an excellent absorbent (Karr, 1956).

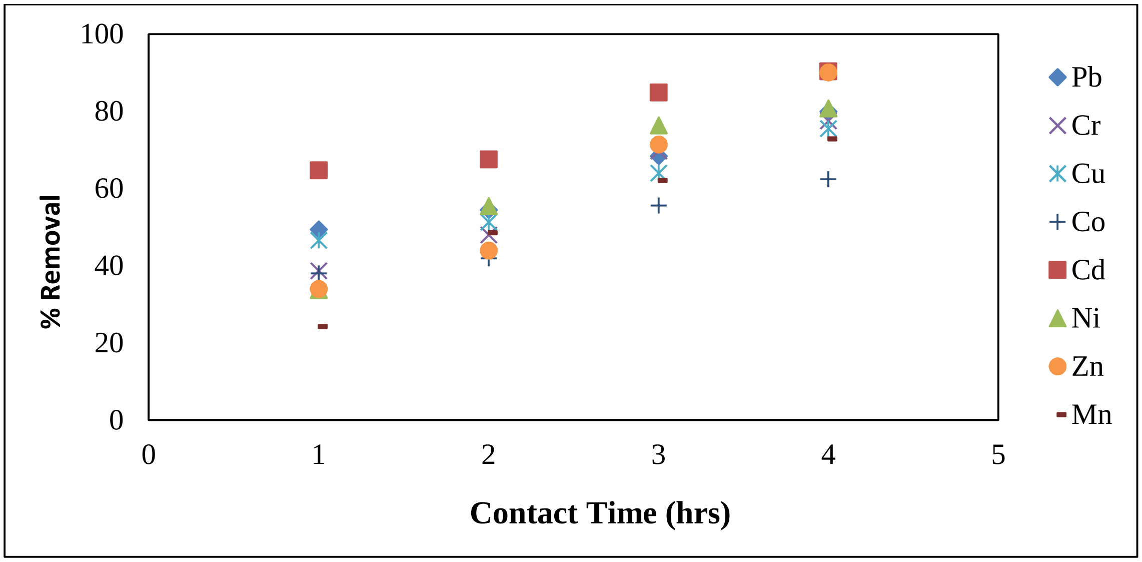

Figure 13: Effect of contact time using 4 g sorbent dose of corn cob

Chapter # 5

CONCLUSIONS

Based on the observations put forward in the forgoing sections, the following salient findings emerged from the present study.

i. Maximum removal was observed for all adsorbents namely peanut hull, rice husk, wheat straw and corn cob at following optimal conditions,

- Dosage of adsorbents 4 gm
- Contact time 4 hrs

ii. The maximum removal efficiency of four agriculture wastes was observed as;

Peanut hull (99 %) > Wheat Straw (98 %) > Rice husk (97.8 %) > Corn Cob (90 %)

Chapter # 6

RECOMMENDATIONS

a) Other agriculture wastes must be explored.

b) Agriculture adsorbents can be tested at commercial scale for treatment of landfill leachate

c) Cost benefit analysis may be conducted based on this study by comparing other methods.

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