ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMICAL ENGINEERING
ENVIRONMENTAL ENGINEERING STREAM

Heavy Metal Removal from Paint Industries Wastewater Using Wood Ash as an Adsorbent

(A Case of Zemilli Paint Factory)

By
Biruk Tsegaye

A thesis submitted to the school of Graduate Studies of Addis Ababa University in Partial fulfillment of the requirements of the Degree of Masters of Science in Chemical Engineering (Environmental Engineering Stream).

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ACRONYMS AND NOTATIONS

AAS	Atomic Absorption Spectrometer
Abs	Absorbance
AAEPA	Addis Ababa Environmental Protection Authority
ANOVA	Analysis Of Variance
ASTM	American society for testing and materials
APHA	American public health association
BAT	Best Available Technology
COD	Chemical Oxygen Demand
CWA	Clean Water Act
CU	Color Unit
EDTA	Ethylenediamine-tetraacetic acid
EPA	Environmental Protection Authority of Ethiopia
EU	European Union
MCL	Maximum Contaminant Level
SG	Specific Gravity
USA	United States of America

NOMENCLATURE

ºC	degree Celsius
mg/g	milligram per gram
kg	kilogram
mg	milligram
ml	milliliter
%	percentage
min	minute
l	litre
gm	gram
T	time
pH	negative logarithm of the concentration of hydrogen ions
Pb	lead
Co	cobalt
Cr	chromium
Hg	mercury
Cu	copper
Zn	zinc
Cd	cadmium
Ni	nickel

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ABSTRACT

Wastewater generated from Zemilli Paint Factory creates a wastewater that has a potential hazard to the environment by introducing various contaminants such as heavy metals into soil and water resources. The adsorption characteristics of Co^{2+} and Pb^{2+} ions found in waste water onto a wood ash surfaces were investigated with respect to changes in the pH of solution, adsorbent dose and contact time. The aim of this work was to evaluate the fundamental aspects of sorption of Pb (II) and Co (II) metal species using wood ash. Batch adsorption experiments were carried out in order to evaluate the metal uptake and to optimize condition of the adsorption. The optimized value of pH, adsorbent dosage and contact time were obtained. The results revealed that removal of 94% for cobalt at a pH of 8, 20gm/l adsorbent dose and 90 minute contact time was obtained; and 97% removal of lead is obtained at a PH of 10, 20 gm/l adsorbent dose and 90minute contact time. pH of Sample is adjusted to the required level by using 1M HCl and NaOH solution. Pb uptake increases with an increased with pH and became maximum at a pH of 10. But, uptake of Co best achieved at pH 8. Adsorbent dose affect uptake of both metal ions positively; and contact time gets equilibrium at 90 min of contact (shaking) time. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of lead and cobalt on to wood ash. Based on the result the pseudo second-order kinetic model provided the best correlation of the experimental data. In the desorption study the cationic forms of heavy metals were first complexes with a Na_2EDTA in order to recover water-soluble polymers and to obtain a heavy metal complexes with EDTA. This desorption study revealed that, the higher desorption efficiencies of up to 90% for Co^{2+} and up to 78% for Pb^{2+} was achieved by using the solution of Na_2EDTA at Temperature of 30 ^{O}C, 2 hour mixing time, solid to liquid ratio of 5 and 2M Na_2EDTA as Desorption solution. The adsorption column was designed using different parameters for Zemilli Paint Factory waste water and on the basis of the results obtained from the experiment, by using such necessary data; also size the dimensions of the adsorption column. Wood ash is an abundant resource in every part of the country; it is recommended that, wood ash can effectively be applied as an absorbent for the removal of Co (II) and Pb (II) ions from paint waste water.

Key words: lead, cobalt, heavy metal, wood ash, atomic adsorption spectrometer, paint, paint waste water, Adsorption.

1. INTRODUCTION

1.1 General

From different environmental issues, pollution by heavy metals of surface water, ground water and soil in urban areas are the major environmental problems. Increased industrialization and human activities have impacted on the environment through the disposal of waste containing heavy metals. Paint manufacturing, leather industries, etc. contribute such a kind of waste. In this context the problem could be significant in the Premises of the waste water in Zemilli paint factory. Particularly the nearby surface water, ground water and soil are at risk to contamination with heavy metals.

As water discharged through these areas, it dissolves organic and inorganic components and decomposition products, giving rise to a polluted liquid. Therefore, treatment of this polluted liquid is recognized as one of the most burning issues. The paint waste waters contains several toxic substances including heavy metals; which is a potential cause of serious water pollution that simultaneously cause health hazard. The containment and treatment of paint industries waste water may therefore be necessary, to avoid or minimize contamination of adjacent soil, ground and surface water resources. It is known that, the presence of heavy metals such as chromium (III, VI), cobalt (II), lead (II), cadmium (II), and zinc (II) in water and soil is hazardous to the biological environment and human health and their discharge into surface waters is a concern worldwide. Many processes for the removal of heavy metals from water and wastewaters have been proposed. Amongst these removal methods, chemical precipitation, physical treatment such as ion exchange and adsorption are some of the processes that have been reported to be the most effective [1]. However, these processes involve the use of chemicals and synthetic polymers whose impact on the environment has not been fully studied. As a result, interest in the subject of adsorbent for heavy metal remediation of waste waters has grown. Among these which have metal-binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost like natural zeolite, ash, rice husk, vermicompost, peat, volcanic stones, bentonite and clinoptilolite for adsorption of heavy metal ions [1, 3].

1.2 Background Information

1.2.1 General Description of the Study Area

Zemilli Paint Factory is a private owned factory that was established in July 1999 in Addis Ababa, around gergii area, for the production of high performance paints having the property of decorating, preserving and protecting the life of an object on which to be applied. The factory is mainly engaged in the production of a wide range of industrial and architectural paints like water based paints (plastic), solvent based paints (synthetic),varnishes, antirust, textured effect paints, wood and paper glue etc. These can be used as interior & exterior paints, primers, undercoats & clear finishes. The factory produces maximum of 36,000 liters of paint per day and as a result it generates about 500 liters of liquid waste on average per day.

This massive quantity of untreated effluent is disposed to the river side and cause considerable load on the water courses leading to widespread damage to aquatic life and to the environment. Paint waste is one of the most complexes, troublesome and strong industrial effluent, having high chemical oxygen demand (COD), total suspended solids (TSS) and heavy metals values. The high chemical oxygen demand (COD), total suspended solids (TSS) and heavy metal amount of the paint effluent typically ranged between 3,000 – 3,500 mg/l and 6,000 - 6,500 mg/l and 0.1 – 15.5 mg/l respectively [2].

1.3 Study Rationale and statement of the problem

Zemilli paint factory is among the paint factories which produce 36000 liters of paint per day and discharges its 500 liters waste directly on the river basin without treating.

The waste water from Zemilli paint factory is a highly concentrated, so that small amounts of waste water can pollute large amounts of groundwater rendering it unsuitable for use for domestic water supply. In addition to potential carcinogens and highly toxic chemicals, the paint factory wastewater contains a variety of conventional pollutants that render a waste water contaminated ground and surface water unusable. These paint waste water has been implicated as environmental pollutant of air, soil, surface water and groundwater pollution. The knowledge of the quantity and quality of paint waste water usually gives an insight into appropriate, effective and sustainable treatment approach [3].

There is an extensive recognition that the presence of heavy metals such as chromium (III, VI), copper (II), cadmium (II), Zinc (II), cobalt (II) and lead (II) in water and waste water are hazardous to the environment [3]. Many processes for the removal of heavy metals from water and wastewaters have been proposed. Chemical precipitation, physical treatment such as ion exchange and adsorption are some of the processes that have been reported to be the most effective ones in the removal of heavy metals [3]. However, these processes involve use of chemicals and synthetic polymers whose impact on the environment has not been entirely studied. Materials which have metal-binding capacities are able to remove unwanted heavy metals from contaminated water at low cost. Like natural zeolite, ash, rice husk, vermicompost, peat, volcanic stones, bentonite and clinoptilolite for adsorption of heavy metal ions. This has led to an increased interest in the subject of adsorption of heavy metal from wastewaters [3].

Besides the waste waters discharged from zemilli paint factory are at high level of hazardous heavy metal which is above the Ethiopian environment protection agency standard, Due to high environmental polluting effect the factory has targeted for environmental enforcement measure by Ethiopia Environmental Protection Authority with five years grace periods since 2006 [2]. Therefore the research conducted for treating and recovery valuable heavy metals.

1.4 General Objective of the research

The main objective of this project is to remove heavy metals from Zemilli Paint Factory waste water by adsorption using wood ash at the optimum value.

1.4.1 Specific objectives

- ✓ To assess and characterize paint factory wastewater.
- ✓ To optimize wood ash to remove heavy metal from paint wastewater.
- ✓ To recover heavy metals, after separation from its chelating agents.
- ✓ To design and Sizing of the adsorption column for the optimized condition.

2. LITERATURE REVIEW

2.1 Paints

Paints and coatings occupy a prominent place in the cultural history of mankind. People have always been fascinated with colors and used paints to decorate and beautify themselves and their environment. The ancient paints consisted of animal fat and colored earth or natural pigments such as ochre. Hence, they were based on the same principle as the paints that are used today - a binder and a coloring agent. However, that the production of modern house-paints began. Over the decades, formulations of paints and coatings have become more and more sophisticated. Today, coatings not only protect and beautify the substrate. They also have functional properties: they are used as anti-skid surfaces, they can insulate or act as an electrical conductor, they can reflect or absorb light, etc. Paints and coatings play an indispensable role in our modern world and cover virtually everything we use from household appliances, buildings, cars, and ships, airplanes to computers, microchips or printed circuit boards [4].

A modern paint is a complex mixture of components, synthetic (oil based) paint, the oldest form of modern paint, uses a binder that is derived from a vegetable oil, such as obtained from linseed or soya bean. In alkyd paint, the binder is a synthetic resin, which is called an alkyd resin. Hence, in a chemical sense the terms alkyd and polyester are synonymous. Commonly, the term “Alkyd” is limited to polyesters modified with oils or fatty acids. A typical alkyd resin is prepared by heating for example linseed oil, phthalic acid anhydride and glycerol to obtain fatty-acid containing polyester. Paints based on alkyd resin binders are usually solvent-borne paints, common solvents being white spirit (a mixture of saturated aliphatic and alicyclic C_7-C_{12} hydrocarbons with a content of 15-20% (by weight) of aromatic C_7-C_{12} hydrocarbons), or xylene [4]. Water-borne paints used water as solvent; the binder is a copolymerized acetate resin. Solvent borne paints often show a number of advantages over water-borne paints. Examples are: easier application properties, wider application and drying tolerance under adverse conditions (low temperature, high humidity) and a higher level of performance on difficult substrates, such as heavily stained or powdery substrates [4].

Table 2.1 Typical solvent based paint compositions

component	Weight (%)
binder	30
pigments	19
extenders	12
organic solvent	27
water	10
additives	2

2.1.1Main Components of Paint

Pigment:-Pigments are granular solids incorporated into the paint to contribute color, toughness, texture or simply to reduce the cost of the paint. Alternatively, some paints contain dyes instead of pigments. Pigments can be classified as either natural or synthetic types. Natural pigments include various clays, calcium carbonate, mica, silica, and talc. Synthetics would include engineered molecules, white lead, calcined clays, blank fix, precipitated calcium carbonate, and synthetic silica. Hiding pigments, in making paint opaque, also protect the substrate from the harmful effects of ultraviolet light. Hiding pigments include inorganic colored pigments like zinc oxide, zinc sulphide pigment, copper phatalocynine blue and green, iron oxide red, yellow, black and brown, chromium green and blue, cadmium pigments, cobalt blue and many others, and organic pigments like insoluble AZO class, carbon blacks, metallic pigments (aluminum, bronze and zinc powder), flushed pigments and many others. Fillers are a special type of pigment that serves to thicken the film, support its structure and simply increase the volume of the paint. Fillers are usually made of cheap and inert materials, such as diatomaceous earth, talc, lime, dolomite, baryte, clay, etc. Floor paints that will be subjected to abrasion may even contain fine quartz sand as filler. Not all paints include fillers. On the other hand some paints contain very large proportions of pigment/filler and binder [2, 4].

Binder or vehicle:-The binder, commonly referred to as the vehicle, is the actual film-forming component of paint. It is the only component that must be present; other components listed below are included optionally, depending on the desired properties of the cured film. The binder imparts adhesion, binds the pigments together, and strongly influences such properties as gloss potential, exterior durability, flexibility, and toughness. Such main types of binders in paint technology are alkyd and polyurethane resins for synthetic paints and copolymerized resins for plastic emulsion paints [4].

Solvent:-The main purposes of the solvent are to adjust the curing properties and viscosity of the paint. It is volatile and does not become part of the paint film. [5] It also controls flow and application properties, and affects the stability of the paint while in liquid state. Its main function is as the carrier for the non-volatile components. In order to spread heavier oils (i.e. linseed) as in oil-based interior house paint, thinner oil is required. These volatile substances impart their properties temporarily once the solvent has evaporated or disintegrated, the remaining paint is fixed to the surface.

Additives:-Besides the three main categories of ingredients, paint can have a wide variety of miscellaneous additives, which are usually added in very small amounts and yet give a very significant effect on the product.[4] Some examples include additives to modify surface tension, improve flow properties, improve the finished appearance, increase wet edge, improve pigment stability, impart antifreeze properties, control foaming, control skinning, etc. Other types of additives include catalysts, thickeners, stabilizers, emulsifiers, adhesion promoters, UV stabilizers, flatteners (de-glossing agents), biocides to fight bacterial growth, and the like. Additive used for facilitating drying purpose of the paint film are metals such as cobalt octet, lead octets, barium and calcium octet the main which used for drying using oxidation the paint film easily. Driers are metal soaps or coordination compounds which accelerate paint drying, thus shortening the total drying time. Without driers, the drying time of alkyd paint would be over 24 hours, which is clearly undesirable for most applications. Driers catalyse the uptake of dioxygen and decomposition of hydroperoxides to free radicals, resulting in hardened cross-linked polymer networks that bind the pigment to the painted surface of the treated object. Common driers are metal soaps of carboxylic acids. The reason for using branched carboxylic acids is to achieve a high solubility in the apolar environment that is the oil-paint binder system and to prevent precipitation of the complex [5].

The metals that have been used in drier compounds can be grouped in three categories: primary driers (also called active or oxidation driers), secondary driers (also called through-driers) and auxiliary driers [5]. The metals used for the driers in each category are listed in the Table 2.2 below.

Table 2.2 Metals that are used in paint formulation, in each drier category

primary driers	secondary driers	auxiliary driers
cobalt	lead	calcium
manganese	zirconium	zinc
iron	bismuth	lithium
cerium	barium	potassium
vanadium	aluminum	
	strontium	

2.2 Paint industries wastewater

Paint industries are among those industries that discharge effluent containing heavy metals. Paint components are pigments, solvents, binders and additives. Heavy metals are mainly used as pigments and additives in the paint. As additives used for facilitate the drying of the film by oxidation. The presences of these heavy metals are directly and indirectly hazardous for human and other beings [3].

The recently arising environmental drawback of the paint industry is the high generation of waste water. This main effluent or discharge in paint factory is generated from the cleaning of mixing equipments after the production of each batch. Depending on the type of paint produced; the mixing vessel is washed by either organic solvent (mostly kerosene) or water. This generates an effluent containing washing solvent, suspended solids & some hazardous chemicals like heavy metals which requires treatment before disposal. As Zemilli paint factory is one of the main paint factories in our country it has an effluent having enormous amount of this constituents, and this discharged amount of liquid waste which is hazardous is released to the nearby river with out treatment [2].

2.2.1 Wastewater management in Zemilli Paint Factory

Most Ethiopian paint industries don’t treat their waste before they discharge it out [6]. As the cost of implementing and running the treatment plant is high, most industries do not bother about the environment. Zemilli Paint Factory is one of the main paint factories in our country, which is a potentially pollution-intensive industry. Environmental concerns in this factory include solid waste, wastewater, air pollution, soil protection and health and safety aspects. The Factory releases its waste waters and it has an effluent having enormous amount of this constituents, this discharged amount of liquid waste which is hazardous is released directly to the nearby river without any pretreatment .The releases potentially contain toxic, persistent or otherwise harmful substances, which can directly affect the aquatic environment & even the surroundings.

2.2.2 Sources of heavy metals in paint wastewater

The final destiny of heavy metal used by human is environment in the form of either solid or liquid waste. Sources of heavy metals in paint wastewater are pigments and driers in the paint. The content of heavy metals in paint waste is primarily a consequence of the intended use of heavy metals. At the end of each batch the wastewater composed of heavy metal generated as a waste for cleaning of the equipments and machines. Heavy metals may, however, also be lost to waste during production and use phases. Losses in the manufacturing process are often disposed of as manufacturing waste [3].

2.2.3 Effects of paint wastewater heavy metals on health and environment

The release of heavy metals into the environment through industrial effluents is a major concern, worldwide and removal of such pollutants has been a great concern during last decades. Heavy metals can pose health hazards to man and aquatic lives if their concentrations exceed allowable limits. Concentrations of heavy metals below these limits even have potential for long-term contamination, because heavy metals are known to be accumulative within biological systems.

Pb (II) and Co (II) are particularly common heavy metals found in paint industries' wastewater. Heavy metals are not biodegradable and tend to be accumulated in organisms and cause numerous diseases and disorders. Chronic exposure to high amount of lead and cobalt can result in various and considerable damages to systems of the body, including nervous and reproductive systems and kidneys. Moreover, high blood pressure, anemia, lead poisoning, coma and death can be considered among the most substantial consequences.

The main threats to human health from heavy metal**s** are associated with exposure to lead, cadmium, mercury and arsenic. These metal**s** have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Heavy metal**s** have been used by humans for thousands of years. Although several adverse health effect**s** of heavy metal**s** have been known for a long time, exposure to heavy metal**s** continues, and is even increasing in some parts of the world, in particular in less developed countries, though emissions have declined in most developed countries over the last 100 years [5].

The release of industrial wastewaters to the environment causes several adverse effects. These wastewaters commonly include Cd, Pb, Cu, Cr, Zn and Co. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants and human beings [3].

Now days, since the waste discharged to the nearby rivers are causing environmental and socio-economic damage, waste minimization and treatment become the main issue of the time for the government, industry and the society as well. From this point of view, currently, the government sets some standard for the effluent discharged from the factories, and applying it by forcing the factories to reduce or treat the waste they generate in order to meet the standard. So it is important to treat the waste generated rather than discharging in order to get legal compliance, improve the life of the society & the environment [3, 5].

2.2.4 Ground water pollution effects of paint wastewater

The presence of chemicals in groundwater and drinking water is an important factor in determining the risk posed by the sites. There are studies of adverse health effects prompted by the contamination of well water used for drinking water and other domestic uses by hazardous substances from waste disposal sites mainly sites where chemical waste drums were buried. Paint industries may differ enormously in the conditions that render them hazardous, and conditions that determine the exposure to and resulting health risks posed by any waste site are likely to be unique to that particular site. Such conditions may include the types, quantities, and age of the waste present; hydro geological and meteorological factors; and site management and engineering practices [1]. Migration of hazardous substances into groundwater is often an important environmental concern in relation to paint factory sites operation. For people living in the vicinity of these sites, many routes of exposure are exists. Other possible routes of exposure include contamination of soil, ground, and surface water, which may lead to direct contact or pollution of indoor air in the case of evaporation of Volatile Organic compounds (VOCs) into basements of nearby houses. Contamination via the food chain may sometimes be of concern for nearby residents in the case of consumption of homegrown vegetables. Drinking water is a possible route of exposure only if water for domestic use is locally extracted. If this is the case, other domestic water uses (bathing, washing) may also lead to exposure via inhalation of evaporated VOCs and/or direct contact [3].

2.3 Heavy Metals toxicity

Heavy metals are perhaps the most common of all metabolic poisons. Metal toxicity can affect enzymes, the cellular proteins that regulate many important chemical reactions. Heavy metals are toxic primarily because they react with and inhibit sulfhydryl (SH) enzyme systems, such as those involved in the production of cellular energy.

A disturbance in enzymatic activity can seriously alter the functioning of the organ or tissue. As examples, mercury and arsenic both bind to certain enzymes, thereby blocking their activity. Lead binds to the thiol (SH^-) chemical group in the enzymes and consequently reduces the body's ability to synthesize enzymes necessary for respiration. The addition of chelating agents is used to eliminate such metal poisoning. For example, an effective chelating agent for removing lead from the human body is ethylenediamine-tetraacetic acid (EDTA) [6]. Because heavy metals are elements, they cannot be broken down, either chemically or by decomposer organisms. The only ways to dispose of them are to dilute them to levels at which they are no longer toxic or to treat them with chemicals that convert them into less toxic compounds [6].

2.3.1 Toxic effects of heavy metals

Mainly related to the heavy metals lead, mercury, cobalt, copper, cadmium and chromium as well extensive documentation of the potential harmful or toxic effects to humans and the environment is available. Generally heavy metals have each their story. Commonly used in paint industry lead, and cobalt are neither has any known useful function in biological organisms.

- **Toxic effect of lead (Pb)**

Lead contamination of the environment is primarily due to anthropogenic activities making it the most ubiquitous toxic metal in the environment. Research on Pb has become a dominant topic for environmental and medical scientists for two obvious reasons: It has no known biological use and it is toxic to most living things. Lead readily bioaccumulates in the human-rich surface layer of the soils due to its complexation with organic matter. It is the least mobile heavy metal in soils under reducing or non-acidic conditions. Furthermore, it is one of the most common trace metal contaminants in urban soils due to atmospheric deposition from industries and automobile emission. When Pb is ingested, there is rapid uptake into red blood cells forming PbB, then into soft tissues (kidney, bone marrow, liver and Brain) and followed by a slower distribution to mineralizing tissues (bones and teeth) [6].

The general population is exposed to lead from air and food in roughly equal proportions. During the last century, lead emissions to ambient air have caused considerable pollution, mainly due to lead emissions from petrol and leaded car batteries. Not only leaded gasoline causes lead concentrations in the environment to rise. Other human activities, such as fuel combustion, industrial processes, from land filling leaded car batteries and solid waste combustion, also contribute.

Lead cannot be broken down; it can only convert to other forms. Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present. Soil organisms can suffer from lead poisoning, too. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains [3].

Recent data indicating that there may be neurotoxin affects of lead at lower levels of exposure than previously anticipated .Too much lead can affect the nervous system and cause headaches, dizziness, irritability, memory problems, and disturbance in sleep. It can affect the digestive system and cause nausea, vomiting, constipation, appetite loss, and abdominal pain.

Lead also affects formation of blood and can result in anemia. Over time, the nervous and muscle systems can be damaged; this causes muscle weakness, decreased feeling in hands and feet, and a metallic taste in the mouth. Damage to the kidneys may lead to high blood pressure. Too much lead can also cause miscarriages and still births when pregnant women are exposed to lead. In men, the sperm can be affected and this may result in infertility. When copper ends up in soil it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water copper can travel great distances, either suspended on sludge particles or as free ions [1, 6].

- **Toxic effect of cobalt (Co)**

Cobalt is needed for good health, and at low levels it has a beneficial effect, but in high concentration it is toxic. Cobalt poses both an internal and external hazard, and the main health concern is associated with the increased likelihood of cancer. External exposure is a concern because of the strong external gamma radiation, and shielding is often needed to handle wastes and other materials with high concentrations of this isotope. Inside the body, cobalt presents a hazard from both beta and gamma radiation.

Cobalt is widely dispersed in the environment in low concentrations [3]. We may be exposed to small amounts of cobalt by breathing air, drinking water, and eating food containing it. Children may also be exposed to cobalt by eating dirt. We may also be exposed by skin contact with soil, water, cobalt alloys, or other substances that contain cobalt. Analytical methods used by scientists to determine the levels of cobalt in the environment generally do not determine the specific chemical form of cobalt present. Therefore, we do not always know the chemical form of cobalt to which a person may be exposed. Being exposed to radioactive cobalt may be very dangerous to your health. If you come near radioactive cobalt, cells in your body can become damaged from gamma rays that can penetrate your entire body, even if you do not touch the radioactive cobalt. Radiation from radioactive cobalt can also damage cells in your body if you eat, drink, breathe, or touch anything that contains radioactive cobalt. The amount of damage depends on the amount of radiation to which you are exposed, which is related to the amount of activity in the radioactive material and the length of time that you are exposed. Most of the information regarding health effects from exposure to radiation comes from exposures for only short time periods. The risk of damage from exposure to very low levels of radiation for long time periods is not known. If you are exposed to enough radiation, you might experience a reduction in white blood cell number, which could lower your resistance to infections. Your skin might blister or burn and you may lose hair from the exposed areas. This happens to cancer patients treated with large amounts of radiation to kill cancer. Cells in your reproductive system could become damaged and cause temporary sterility. Exposure to lower levels of radiation might cause nausea, and higher levels can cause vomiting, diarrhea, bleeding, coma, and even death. Exposure to radiation can also cause changes in the genetic materials within cells and may result in the development of some types of cancer [6].

2.4 Environmental Principles, Policy and Standards in Ethiopia

2.4.1 Environmental principles in Ethiopia

Pollution is a growing urban environmental challenge in Ethiopia. Developmental activities that likely cause pollution or other environmental hazard shall have an obligation to install sound technologies or adopt practices that minimize or avoid the generation of waste and to promote the reuse of waste. EPA or regional environmental agencies are empowered to require any person causing pollution to clean up or pay the cost of cleaning, and to prevent any harm including closure or relocation of operation that cause imminent danger to health and environment. This in line with the polluter pay principle is accepted as one of the environmental principle in Ethiopia [9, 13].

2.4.2 Environmental policy and standards

Draft pollution control legislation, Article 7 provides, formulation of environmental standards regarding discharge limit of effluent to water bodies and sewage system, air quality, specifying the allowable degree of emission both for stationary and mobile air pollution sources, soil quality, and noise and waste management is the responsibility of EPA in collaboration with other agencies. EPA may prescribe different environmental standards for different area of the country as necessary to rehabilitate or protect the environment. Based on their specific situation, national regional state may adopt environmental standard that are not stringent as the federal ones [9].

2.4.2.1 Policy on Control of Hazardous Materials

- To adhere to the precautionary principle of minimizing and where possible preventing discharges of substances, biological materials or their fragments from industrial plants and personal or communal appliances or any other external sources that could be harmful, and to disallow the discharge when they are likely to be hazardous;
- To adopt the "polluter pays" principle while endorsing the precautionary principle since pollution is likely to occur, and ensure that polluting enterprises and municipalities and wereda councils provide their own appropriate pollution control facilities;
- To establish clear linkages between the control of pollution and other policy areas including water resources, agriculture, human settlements, health and disaster prevention and preparedness;
- To ensure that pollution control is commensurate with the potency, longevity and potential to increase or reproduce of the pollutant;
- To establish safe limits for the location of sanitary landfill sites in the vicinity of wells, bore holes and dams, and issue regulations to enforce them;
- To review and develop guidelines for waste disposal, public and industrial hygiene and techniques to enable the cost-effective implementation of defined standards of control, and to issue regulations to enforce them;
- To formulate and implement a country-wide strategy and guidelines on the management of wastes from the medical, agriculture and other sectors that may use potentially hazardous biological organisms, their fragments or chemicals, and to issue the necessary regulations to enforce them;

- To establish a system for monitoring compliance with land, air and water pollution control standards and regulations, the handling and storage of hazardous and dangerous materials, mining operations, public and industrial hygiene, waste disposal, and water quality;
- To promote waste minimization processes, including the efficient recycling of materials wherever possible;
- To create by law an effective system of control, distribution, utilization and disposal after use or expiry of chemicals, biological organisms or fragments of organisms that could be hazardous but are required for use;
- To foster better understanding of the dangerous effects of chemicals and organisms and their fragments through the provision of information in a form understandable to users, and provide or enforce the provision of information on the appropriate methods and technologies for the treatment and disposal of wastes [10].

2.4.2.2 Ethiopian Water Resources Management Policy

The Federal Government of the Democratic republic of Ethiopia issued a comprehensive and integrated water resources management policy in 1998. The policy document outlines the following as the general policy objectives:

- ❖ Allocation and apportionment of water based on comprehensive and integrated plans and optimum allocation principles that incorporate efficiency of use, equity of access, and sustainability of the resource.
- ❖ Development of, the water resources of the country for economic and social benefits of the people on equitable and sustainable basis.
- ❖ Managing and combating drought as well as other associated slow on-set disasters through, inter-alia, efficient allocation, redistribution, transfer, storage and efficient use of water.
- ❖ Combating and regulating floods through sustainable mitigation, prevention, rehabilitation and other practical measures.
- ❖ Conserving, protecting and enhancing water resources and the overall aquatic environment on sustainable basis [12].

2.4.3 Water Quality Standard

The Ethiopian standard and quality authority is the appropriate government body which should have set quality standards for various use of water. However, the 1990 quality standards regulation No-12 only provides for desirable and permissible level that are required for chemical and physical as well as safety of drinking water and the testing method to be used. To a large extent the water quality standard incorporated in the said regulation are based on the international standard seated by WHO and do not necessarily reflect the particular condition of Ethiopia [11].

Substantive law of Ethiopia such as the penal and civil cods are very restricts on water contamination issues. In actual fact, contaminating drinking water serving for human or animal need by means of substances harmful to health is punishable with simple imprisonment not less than one month. With some serious cases with rigorous imprisonment not exceeds five years. In case of international poisoning of wells or cisterns, springs, water holes, river or lakes, rigorous imprisonment shall be up to 15years [Article 506 of the penal code] [14].

The World Health Organization (WHO), a U.N. agency dedicated to public health, first issued Guidelines for Water Quality in 1984–1985 as a basis for developing standards that, if properly implemented, would ensure the safety of drinking water supplies. Although the main purpose of these guidelines is to provide a basis for developing standards, the guidelines are also useful to countries in implementing alternative control procedures where the implementation of drinking water standards is not feasible. Table 2.3 presents the drinking water quality standard prepared by WHO [14].

Table 2.3: water quality standard [14]

Characteristics	***Action level (mg/l)***	***Characteristics***	***Action level (mg/l)***
Arsenic	0.05	Sodium	200
Aluminum	0.2	Zinc	5
Cadmium	0.005	Chloride	250
Chromium	0.05	Fluoride	1.5
Cobalt	0.1 (WHO,2001)	Sulphate	400
Copper	1.0 (WHO, 2004)	TDS	1000
Cyanide	0.1	pH	6.5-8.5
Lead	0.05	Hardness	500
Mercury	0.001	Chloroform	30
Iron	0.3		

2.4.4 Heavy metals Rule

This rule is prepared by America and it defines the action level for every heavy metal which is seen in table 2.4, establishing monitoring requirements for corrosion control, selecting sampling sites, issuing deadlines for public-education information, requiring monitoring data to be reported to the state, and clarifying which certified laboratories must be used.

Under the rule, the maximum contaminant level (MCL) for lead is 0.015mg/l, and the action level is 0.05 mg/l. For cobalt, both the maximum contaminant level (MCL) and action level is 0.1mg/l [6].

Table 2.4 Maximum contamination level of drinking water [6]

Parameters	***MCL (mg/l)***	***Parameters***	***MCL (mg/l)***
Arsenic	0.05	Aluminum	0.20
Barium	2.00	Chloride	250
Cadmium	0.005	Cobalt	0.10
Copper	1.00	Iron	0.30
Chromium	0.10	Manganese	0.05
Cyanide	0.20	Silver	0.10
Fluoride	4.0	Beryllium	0.004
Lead	0.015	Thallium	0.002
Mercury	0.002	Sulphate	250
Nickel	0.10	Zinc	5.0
Nitrate nitrogen	10.0	Color	15CU
Nitrite nitrogen	1.0	Odor	3TON
Selenium	0.05	pH	6.5-8.5
Sodium	160	TSS	500
Antimony	0.006	Foaming agent	0.50

MCL=maximum contamination level, CU=color unit, TON=threshold odor number

2.5 Method of heavy metals removal from waste water

2.5.1 Overview of previous investigations

Such methods may be useful for removing heavy metal ions from aqueous solution. Many researchers have explored the feasibility of this approach. An overview of previous investigations is provided below:

For environmental protection, waste solutions containing heavy metal elements need treatment systems that can remove these contaminants effectively. A number of technologies for treating contaminated municipal and industrial waters and waste waters have been developed over the years. Among different heavy metal removal methods, chemical precipitation, membrane filtration (reverse osmosis and electro dialysis), electrolytic processes, adsorption and biological sorption could be mentioned. Adsorption techniques for wastewater treatment have become more popular in recent years with regard to their efficiency in the removal of pollutants, especially heavy metal ions, color, odor and organic pollution. Adsorption has advantages over other methods for remediation of heavy metals from wastewater because its design is simple; it is sludge-free and can be of low capital intensive. Except that it's manufacturing cost is quite high [16].

Traditionally employed methods for heavy metal remediation consist of heavy metal removal by chemical coagulation using aluminum and ferric salts and cationic surfactants; physical precipitation using ion exchange and sorbents; and phytoremediation that include rhizofiltration, phytostabilisation, and phytoextraction. However, because of the high costs and unknown environmental effect associated with some of these methods, it is necessary to develop a more cost effective and environmentally friendly remediation system particularly in developing countries like Ethiopia. Moreover, research findings clearly report the serious drawbacks such as Alzheimer’s disease, carcinogenic effects and health problems associated with aluminum] sulphate, polyaluminum chloride, polyaluminum sulphate, iron hydroxide, iron chloride, soda ash and synthetic polymers used in water treatment , which strengthen the need for environmentally friendly and cost effective methods. Therefore, the use of natural coagulants that does not have adverse environmental effect, for treatment of water and wastewater to remove heavy metals, in developing countries is a research area where it becomes a growing interest [15].

2.5.2 Conventional technologies available for the removal of heavy metals

The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. The process description of each method is described below.

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

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

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

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

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

Phytoremediation: Phytoremediation is the use of certain plants to clean up soil, sediment, and water contaminated with metals. The disadvantages include that it takes long time for removal of metals and the regeneration of the plant for further sorption is difficult. Hence the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative for a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents.[15]

Alternative process is adsorption, which utilizes various natural materials of having high metal uptake capacity including ash, peat, zeolite, sand, etc, [1] these adsorbents possess metal sequestering properties and can decrease the concentration of heavy metal ions in solution from ppm to ppb level. They can effectively sequester dissolved metal ions out of dilute complex solutions with high efficiency and quickly. Therefore adsorption is an ideal candidate for the treatment of high volume and low concentration complex wastewaters [16].

Table 2.5: Treatment processes for removal of heavy metals [16]

Treatment Process	**Description**	**Economics**	**Types of Wastes**	**Example Applications**
Ion-Exchange	Waste stream pass through resin bed where ionic materials are selectivelyremoved	Relatively high costs	Heavy metal aqueous solutions	Metal plating solutions
Ultrafiltration	Separation of molecules by size using membranes	Relatively high costs	Heavy metal aqueous solutions	Metal coating applications
Reverse Osmosis	Separation of dissolved materials from liquid through a membrane	Relatively high costs	Heavy metals; organics, inorganic aqueoussolutions	Seldom used industrially
Electrolysis	Separation of positively charged materials by application of electric curren	Dependent on concentrations	Heavy metals; ions from aqueous solutions; copper recovery	Metal plating
Precipitation	Chemical reaction caused formation of solids which settle	Relatively high costs	Lime slurries	Metal plating, wastewater treatment
Evaporation	Solvent recovery by boiling off the solvent	Energy intensive	Organic/Inorganic aqueous streams	Rinse waters from metal plating waste
Electro dialysis	Separation based on differential rates of diffusion through membranes	Moderately expensive	Separation/concentration of ions from aqueous streams	Separation of acids and metallic solutions
Reduction	Oxidative state of chemical changed through chemical reaction	Inexpensive	Metals, mercury in dilute streams	Chrome plating solutions and tanning operations
Flocculation	Agent added to aggregate solids together to facilitate separation	Relatively inexpensive Aqueous solutions with	Aqueous solutions with finely divided solids	Refinery oil/water mixtures, paper wastes; mineral industry

2.6 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

- Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behavior of real gases.
- Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption [17].

2.6.1 Kinetics of adsorption

Kinetics studies and, offering information on the rate of metal uptake, together with the hydrodynamic parameters, are very important for adsorption process design. However, adsorption kinetics studies are insufficient according to the references published so far [18, 20].

2.6.2 Process of metal uptake

Generally speaking, the metal adsorption process by adsorbent is regarded one or two step process. In one step process, metal ions are adsorbed to the surface of adsorbent surface by interactions between metal–functional groups displayed on the surface of adsorbent. The first step, also called passive adsorption. In two step process, by keeping the passive adsorption, in addition it uses metabolism independent and proceeds rapidly within several minutes by any one or a combination of the following metal binding mechanisms: coordination, complexation, ion exchange, physical adsorption (e.g. electrostatic) or inorganic microprecipitation [19].Passive adsorption is a dynamic equilibrium of reversible adsorption–desorption. Metal ions bound on the surface can be eluted by other ions, chelating agent or acid. The two step process, metal ions penetrate the surface and enter into the adsorbent media, also called active adsorption. Metal uptake by non-living material such as wood ash is mainly in the passive mode.

2.6.3 Factors affecting adsorption capacity

2.6.3.1 pH

For adsorption of heavy metal ions, pH is one of the most important environmental factors. The pH value of solution strongly influences not only the site dissociation of the biomass' surface, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation, the speciation and the adsorption availability of the heavy metals. The adsorptive capacity of metal cations increases with increasing pH of the sorption system, but not in a linear relationship. On the other hand, too high pH value can cause precipitation of metal complexes, so it should be avoided during experiments. For different adsorption system of metal ions, the optimal pH is different. It is reported that the optimal pH value is 5–9 for copper adsorption by wood ash and 4–5 for uranium (Volesky, 1990b: 156). Mapolelo and Torto (2004) proved that the adsorption capacity of Cd^{2+}, Cr^{3+}, Cr^{6+}, Cu^{2+}, Pb^{2+} and Zn^{2+} is dependent on pH. For all metal ions they studied, the optimal pH values are all greater than 5. The optimal pH for Cd and Pb adsorption is 5.8, while for Cr (III) and Pb is 5.2. As the pH further increased, the adsorption capacity subsequently decreased. The reason may be that at low pH, the affinity with the proton at the binding site of the ash is much greater than that of the metal ion (H^+, M^{2+}), compared with that at higher pH, where M^{2+}, H^+. Vianna et al. (2000) obtained a similar conclusion. They found that the adsorption capacity of metal cations strongly depends on pH value. For Cu, Cd and Zn, the adsorption capacity at pH 4.5 is far higher than that at pH 2.5 and pH 3.5. Electrostatic attraction to negatively charged functional groups may be one of the specific adsorption mechanisms. At pH 4.5, the most important group is phosphate, and the other two main active molecular groups are carboxyl and sulphate. Marques et al. (2000) studied the pH effects (i.e. initial pH value and the pH shift and control) on the removal of Cu^{2+},Cd^{2+} and Pb^{2+} from unbuffered aqueous solution by non-viable wood ash. Özer and Özer (2003), it is found that optimal pH value for Pb (II) and Co (II) ion uptake is 5.0. However, metal anions, such as chromium (VI), exhibit different PH features from metal cations. Generally speaking, neutral pH value is favorable for adsorption [15].

2.6.3.2 Temperature

Temperature has also an influence on the adsorption of metal ions, but to a limited extent under a certain range of temperature, which indicates that ion exchange mechanism exists in adsorption to some extent. Adsorption process is usually not operated at high temperature because it will increase the operational cost . Brady and Duncan (1994) found that temperature (5–40 °C) had minor effect on the accumulation level of Cu^{2+}, Co^{2+} or Cd^{2+} by surface of wood ash in suspension. Adsorption reactions are normally exothermic, so adsorption capacity increases with decrease of temperature [15]. In the range of 15– 40 °C, the maximum equilibrium adsorption capacity for Pb(II), Ni(II), Co(II) and Cr(VI) ions by the wood ash was reached at temperature of 25 °C. The decrease in capacity at higher temperature between 25 and 40 °C revealed that the processes of adsorption for these metal ions by ash are exothermic. The decrease of adsorption capacity at higher temperature may be due to the damage of active binding sites in the biomass [15].

2.6.3.3 Contact time

The adsorption process of heavy metal by wood ash usually completes rapidly. The adsorption of metals such as copper, zinc, lead and uranium by wood ash is a rapid process and often reaches equilibrium within several hours. Generally speaking, the adsorption capacity and the removal efficiency of metal ions by wood ash became higher with prolonging the contact time [24]. However, in practice, it is necessary to optimize the contact time, considering the efficiency of desorption and regeneration of the biomass. Ferraz et al. (2004) optimized the sorption time for Cr (III) by wood ash from a brewery company in the sorption– desorption process, the result showed that a 30 min sorption period was the best option to ensure the metal removal from solution and good recovery from adsorbent.

2.6.3.4 Competing ions/co-ions

Real industrial effluent usually contains various ionic components, including metal cations and anions. Some studies indicated that cations and anions additional to the ions of interest have a generally detrimental impact on metal accumulation (Suh and Kim, 2000). Usually, the adsorption capacity of one metal ion is interfered and reduced by co-ions, including other metal ions and anions presenting in solution, however the gross uptake capacity of all metals in solutions remains almost unchangeable. Competitive effect occurred in a mixed solution containing lead and chromium during the adsorption process by flocculating ash (Ferraz and Teixeira, 1999). The ash of wood seems to have more affinity, higher selectivity and adsorption capacity to Pb (II) than to Cr (III) in aqueous solutions. The decrease of metal uptake in competitive conditions was thought to be a response to increased competition between same charged species for binding sites of the ash [15, 25].

2.6.3.5 Pretreatment

The chemical and physical conditions may also show very different properties for metal accumulation, compared with the original ash [15]. Now various pretreatment methods are reported to deal with the wood ash [28]. Physical methods include vacuum and freeze-drying, ashing, and mechanical disruption (grinding). Chemical methods include treatment with various organic and inorganic reagents, such as acid and caustic, etc. Those methods are found to improve metal adsorption to some extent. Because of the important role of the surface area of the ash in the metal adsorption by wood ash, metal adsorption may be enhanced by heat or chemical sterilization or by crushing. Thus degraded ash would offer a larger available surface area and expose the interaction components and more surface binding sites due to the destruction of the ash [27].

2.6.4 Adsorption Isotherms Models

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration [22].Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration.

Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been formulated in terms of three fundamental approaches. Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal. Whereas, thermodynamics, being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models, and potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters [17].

Two of the more common mathematical formulations used in establishing adsorption isotherms are the two parameter isotherms Langmuir and Freundlich equations [22] .

i) Langmuir isotherm model

One particular mathematical form of an isotherm which is often found to fit experimental data is the so-called Langmuir isotherm, which was derived in 1916 by Irving Langmuir.

Langmuir adsorption isotherm, originally developed to describe gas–solid-phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different bio-sorbents. In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate), with no transmigration of the adsorbate in the plane of the surface [18].

The Langmuir equation applicable to adsorption is described as:

$$\mathbf{Ce / qe = 1 / Qo^{*}b + Ce / Qo \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1)}$$

Where Ce = the equilibrium concentration of the adsorbate (mg/liter) in solution.

qe = the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g).

Qo and b = Langmuir constants related to the adsorption capacity and energy of adsorption, respectively.

When Ce/qe is plotted versus Ce, the slope is equal to 1/Qo and the intercept is equal to 1/Qob.

ii) Freundlich isotherm model

Non-ideal systems can sometimes be fitted to an empirical adsorption isotherm developed by the German physical chemist Herbert Max Finlay Freundlich.

Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. In this perspective, the amount adsorbed is the summation of adsorption on all sites (each having bond energy), with the stronger binding sites are occupied first, until adsorption energy are exponentially decreased upon the completion of adsorption process.

The Freundlich equation applicable to adsorption is described as:

$$\mathbf{Log\ qe = log\ K_f + 1/n\ log\ Ce} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \mathbf{(2)}$$

Where Ce = the equilibrium concentration of the adsorbate (mg/liter) in solution.

qe = the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g).

Kf and n = constants incorporating all factors affecting the adsorption such as adsorption capacity and intensity, respectively. Values of Kf and n may be calculated by plotting log (qe) versus log (Ce). The slope is equal to 1/n and the intercept is equal to log (Kf).

Both of these are “two- parameter” equations. That is, other than the variables qe and Ce, there appear only two parameters in the equations. The two parameters are evaluated by “fitting” the data to the equations. These two equations are used more than 99% of the time to describe the equilibrium adsorption of solutes onto solid particles. The reason is simple: in almost every case, one of these two equations fits the data quite well. Thus, there is no need for more elaborate isotherm equations, particularly those involving three or more parameters.

The Langmuir model assumes the surface of the sorbent to be homogeneous and the sorption energies to be equivalent for each sorption site. Immobilisation of metal ions occurs without mutual interactions between the molecules ions sorbed on the surface. The Freundlich model is based on an exponential distribution of sorption sites and energies. Moreover, molecules adsorbed on the surface can interact [26].

Adsorption of heavy metals is an attractive option due to the proven efficiency of this process in the treatment of wastewater and removal of a large number of different contaminants. It is a cost competitive operation that can contribute effectively to the removal of pollutants remaining in solution [22].

2.7 Adsorbents

2.7.1 Commercial Activated Carbons

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. However, amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater. In particular, the effectiveness of adsorption on commercial activated carbons (CAC) for removal of a wide variety of heavy metals from wastewaters has made it an ideal alternative to other expensive treatment options. Because of their great capacity to adsorb metals, CAC are the most effective adsorbents. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties.

However, activated carbon presents several disadvantages. It is quite expensive, the higher the quality, the greater the cost and non-selective. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications. This has led many workers to search for more economic adsorbents [19].

2.7.2 Low-cost Adsorbents

Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials.

According to Bailey et al. (1999), a sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for heavy metal removal [19].

Commercially available activated carbons (AC) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents, because of its availability and cheapness.

Plentiful agricultural and wood by-products may also offer an inexpensive and renewable additional source of AC. These waste materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low-cost by-products.

So, their conversion into AC would add economic value, many other factors can also affect the adsorption capacity in the same sorption conditions such as surface chemistry (hetero atom content), surface charge and pore structure. A suitable carbon should possess not only a porous texture, but also high surface area. The acid and base character of a carbon influences the nature of the heavy metal isotherms. The adsorption capacity depends also on the accessibility of the pollutants to the inner surface of the adsorbent, which depends on their size. The specific sorption mechanisms by which the adsorption of heavy metals takes place on these adsorbents are still not clear. This is because adsorption is a complicated process depending on several interactions such as electrostatic and non-electrostatic (hydrophobic) interactions.

Raw agricultural solid wastes and waste materials from forest industries such as sawdust and bark have been used as adsorbents. These materials are available in large quantities and may have potential as sorbents due to their physico-chemical characteristics and low cost. Because of their low cost and local availability, industrial solid wastes such as metal hydroxide sludge, fly ash and red mud are classified as low-cost materials and can be used as adsorbents for heavy metals removal.

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong candidates as adsorbents.[19]

The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials is termed biosorption. In this instance, biological materials, such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass, are used as chelating and complexing sorbents in order to concentrate and to remove heavy metals from solutions. The biosorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons, and can reduce heavy metal concentration to micro gram levels. Biosorption is a novel approach, competitive, effective and cheap [23].

2.8 Wood ash

Wood ash is a by-product waste which remains after incineration of wood residues. It can be found essentially without change its property [30]. Ashes are generally formed by highly selective open pit methods using excavated, underground, draglines lands. The wood ash is processed using either a dry (air flotation) or a wet carbonization process with a high temperature. The wet process produces a higher cost and higher quality product than the dry process. The ashes are mostly disposed in landfills; only a small part of it is recycled as forest fertilizer. Disposal of large amounts of ashes per year will be more difficult due to increasing land cost and other constraints to build up new landfill [30].

2.8.1 Physical and chemical properties of wood ash

Some physical and chemical properties of clay are listed below [16].

Physical properties – structurally complex

- Colloidal - sub-microscopic and held in suspension in solution.
- When wet - viscous and gelatinous, sticky; when dry – hard, packed and cohesive.
- Composed of micelles - flat, sheet-like plates laminated into stacks.
- Very large internal and external surface area.
- Average particle size - 230 μm.
- Color - white, grey
- Transparency - translucent
- Luster - dull
- Specific Gravity - 2.1 - 2.3
- Hardness - soft
- Crystal symmetry - monoclinic (and orthorhombic)
- Habit - lath-shaped, elongated, in bundles
- Pore Size - Very small internal and external pores, many μ long (60-100Å wide)
- Structure - silica tetrahedrons in double chains linked through oxygens at their longitudinal edges; the tips of the tetrahedrons of successive chains point in opposition directions. [16]

Chemical – very complex; negatively charged

- Very high cation exchange capacity (CEC): 10-100 meq/100g.
- Charge allows flocculation or de-flocculation.

Such literatures reported the following elements in wood ash: carbon (5% to 30%), calcium (5% to 30%), carbon (7% to 33%), potassium (3% to 4%), magnesium (1% to 2%), phosphorus (0.3% to 1.4%) and sodium (0.2% to 0.5%). The following compound composition limits were also reported: SiO_2 (4% to 60%), Al_2O_3 (5% to 20%), $Fe_2 O_3$ (10% to 90%), CaO (2% to 37%), MgO (0.7% to 5%), TiO_2 (0% to 1.5%), K_2O (0.4% to 14%), SO_3 (0.1% to 15%), LOI (0.1% to 33%), moisture content (0.1% to 22%), and available alkalis (0.4% to 20%) [30].

2.8.2 Uses of wood ash

The role of wood ash minerals is also fundamental in agriculture, fruit growing and forestry. The ash minerals in soils are important sources of nutrients and water. As negatively charged colloidal bridges, they encourage a long-term proton exchange from plant roots for necessary cations released from weathering primary minerals. Wood ash is the most common carriers of pesticides, insecticides and herbicides and sometimes also special fertilizers (Konta, 1995:284). In the building industries, the numerous manufacturers of structural materials and the knowledge of ground soils are closely connected with ash science. A simple but important fact underscoring the significance of Wood ash science in the building industries is that most of the buildings of the home kitchen textures [15, 27].

Wood ash, also an abundant biomaterial, is capable of removing heavy metals and can be considered as an efficient and low-cost adsorbent for heavy metals. The earlier studies on wood ash have also been reported to be effective in removing heavy metals, such as rice wood ash. Wood ash has been chosen as the adsorbing material because of its excellent sorptive properties. Wood ash’s porous structure and high surface area provide benefits in the absorption of liquids and the adsorption of heavy metals (J:\G&W Library Folder\Product Information\Attapulgite 06.2001.doc). It is well known that the use of ash particles derived from the combustion of agriculture wastes or coal as metal adsorbents would be most ideal, since these materials are inexpensive and available in abundance. In recent years, there has been an increase in the use of agricultural and industrial solid wastes as adsorbents for the removal of heavy metals (Periasamy and Namasivayam, 1996). The advantage of using solid wastes is that it saves disposal costs while alleviating potential environmental problems. Numerous studies have shown that different ashes and sludges may effectively immobilize heavy metals from aqueous solutions (Calace *et al*., 2002; Garcia-Sanchez and Alvarez-Ayuso 2002; Hassett and Eylands, 1999; Ferrero *et al*., 1986). Utilization of solid wastes for the treatment of wastewater from another industry could be helpful not only to the environment in solving the solid waste disposal problem, but also to the economy [30].

2.8.3 Adsorption capacity of wood ash

2.8.3.1 Metal ion uptake

A number of references have proved that wood ash can remove toxic metals, recover precious metals and clean radionuclides from aqueous solutions to various extents. Schott and Gardner (1997) reported the recovery of light metals, such as aluminum by wood ash. Brady et al. (1994) proved that the wood ash with hot alkali were capable of accumulating a wide range of heavy metal cations (Fe^{3+}, Cu^{2+}, Cr^{3+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Ag^{+}, Ni^{2+}, and Fe^{2+}). Lead, cadmium, copper, zinc, chromium, nickel, silver and uranium, etc. have been studied much more than molybdenum, iron, manganese, radium, selenium, lanthanide, precious metals, etc [15].

2.8.3.2. Adsorption capacity

The determination of the metal uptake rate by the adsorbent is often based on the equilibrium state of sorption system. The sorption uptake rate, q, is usually expressed in milligrams of metal sorbed per gram of the (dry) sorbent (the basis for engineering process—mass balance calculations), or mmol/g or meq/g (when stoichiometry and/or mechanism are considered) (Kratochvil and Volesky, 1998). Metal ion uptake by wood ash has been reported in a substantial number of references. The magnitude of metal uptake by wood ash can be estimated as follows: for lead, in the order of 2–3, above 10 and less than 300 mg Pb/g dry weight biomass; for copper, in the order of 1–2, less than 20 mg Cu/g dry weight yeast; for zinc, in the order of 1–2, usually less than 30 mg Zn/g dry weight; for cadmium, in the order of 2–3, usually above 10 but less than 100 mg Cd/g dry mass; for mercury, in the order of 2; for chromium and nickel, usually in the order of 1; for seldom, more than 40 mg/g dry mass; for precious metals , such as Ag, Pt, Pd, in the order of 2, around 50 mg/g dry weight ash. Adsorptive capacity of radionuclide uranium by wood ash is usually between 150 and 300 mg U/g dry weight biomass.

In particular, there is no standard measurement of dry weight of biomass, i.e. no standard of dry temperature and dry hours when drying biomass. Park et al. (2003) obtained the dry-ash weight by drying ashes at 70 °C until the weight of the ash became constant. Liu et al. (2002a) measured the dry weight of wood ash after drying in a stove for 2h at 100–120 °C to calculate the adsorption capacities. Özer and Özer (2003) dried the ash at 100 °C for 24h. Rapoport and\

Muter (1995) determined dry weight by drying the sample at 105 °C until the constant weight was achieved. In this particular research work, drying temperature of 60°C and drying time of 24h has been employed and the constancy of the terminal weight of dried wood ash biomass has been checked [28].

2.8.3.3 Comparison with other materials

Bakkaloglu et al. (1998) investigated various types of waste biomass including ashes (charcoal based and fly ash), sands, biomaterials (fungi, bacteria etc...), activated sludge as well as marine algae (F. vesiculosus and A. nodosum) for adsorption of metals. They compared the removal efficiency for zinc, copper and nickel ions at the stage of the adsorption, sedimentation and desorption. The results showed that wood ash has a mediocre efficiency for one or multi-metal adsorption systems. By comparing the index q_{max} of Langmiur equation with seven types of waste biomass for the removal of lead ion, Kogej and Pavko (2001) indicated that lead uptake capacity by wood ash is in the middle, in comparison with the other six materials they used in their study. Vianna et al. (2000) studied the adsorption capability for Cu, Cd and Zn, using three kinds of waste biomass from paint industries, that is, leca sand, zeolite and wood ash. The results showed that leca sand had the highest sorption capacity for Cu and Cd, followed by zeolite and wood ash. Wood ash was higher in comparison with other adsorbents such as aluminum oxide, activated carbon, and activated charcoal. Comparing with other materials, in spite of the mediocre metal adsorption capacity, wood ash is a unique material in adsorption research and practical application [27].

2.8.4 Properties of metal ions in solution

Adsorption of metal ions by ash was linearly influenced by the ionic radius, but independent of the ionic charge or electrostatic strength [27]. Pearson classified metallic ions based on a “hardness scale” defined by their binding strength with F^- and I^- under the consideration of the thermodynamics but not the kinetics. Nierboer and Ruchardson proposed a refined classification of metals for biological systems in determining their relativeness, considering the electronegativity, charge and ionic radius of metals. Hard metals, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, are usually nontoxic and often are essential macronutrients for microbial growth, they bind preferentially to oxygen-containing (hard) ligands, such as OH^-, HPO_4^{2-}, CO_3^{2-}, R– COO^-, and -C-O, whereas soft metals, such as Hg^{2+}, Cd^{2+} and Pb^{2+}, which often display greater toxicity, form stable bonds with nitrogen- or sulfur-containing (soft) ligands, such as CN^-, R–S^-, –SH^-,

NH_2-, and imidazol. Borderline or intermediate metals are less toxic and can even be detected in certain molecules where they assist in mediating specific chemical reactions, e.g., Zn^{2+}, Cu^{2+} and Co^{2+}. Based on the hard-and-soft principle of acids and bases, investigated the metal adsorption characteristics for metabolism independent uptake of the metal ions, including Sr^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ti^{2+} by wood ash[30] . The results showed that the complex characteristics of microbial metal uptake conformed well to the hard-and-soft principle. adsorption of metals ions such as Sr^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} by freeze-dried ash is observed to be related to covalent index (X_m, r), where X_m is electronegativity and r is the ionic radius. The greater the covalent index value of metal ion is, the greater is the potential to form covalent bonds with biological ligands [15, 28].

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals and reagents

A wood ash sample, grey in color, less than 80 µm particle size was used as adsorbent. The adsorbent was used directly for the experiments without any treatment. Chemicals used were of analytical/laboratory grade, The chemicals used for the study were Analytical grade Pb (II) NO_3, Co(II) $NO_3.6H_2O$, for standard metal ion sample preparation, Nitric acid for preservation of the samples, Hydrochloric acid and Sodium hydroxide for PH adjustment. Fresh dilutions and metal solutions were used in each sorption study. All experiments used distilled water.

3.1.2 Instruments

- Excella E 24 incubator shaker: as shown in Figure 3.1 was used to agitate the ash / aqueous metal ion mixtures.
- Precisa model 900 pH meter combined with a glass electrode and Universal-Indicator paper model Macherey-Nagel: to measure the pH of the solution.
- Filter paper (Advantec, 45µ): to filter the content of the flasks.
- Analytical balance model Mettler Toledo (PB 602-S): to weigh the samples.
- Perkin Elmer model 3110 Atomic Absorption Spectrometer (AAS) operating with air acetylene flame: as shown in Figure 3.2 is used to measure residual metal ion concentrations. The analysis on the AAS on each sample was carried out in duplicate.

Other most important materials used in the analysis procedure are described in the annex.

Figure3.1: Incubator shaker used for experimental setup.

Figure3.2: Atomic adsorption spectrometer used during the test run.

3.2 Methods

3.2.1 Assessment and characterization of paint waste water sample

3.2.1.1 Source of data

Primary data was obtained from Zemilli Paint Factory and its surrounding. Waste water sampling is made on the site, which is shown in figure 3.3, by applying stratified random sampling technique. The waste water sample collected is analyzed for the presence and amount of heavy metal concentration at Ethiopian environmental protection authority central Laboratory and JIJA laboglass Pvt.Ltd.Co central laboratory. After the heavy metal amount that is present in the waste water found to exceed the world standard sated above maximum contaminated standard level of heavy metals, further investigation which is evaluating the capacity of wood ash to remove heavy metal is done. During this study, preparation of adsorbent and adsorption process is made at Addis Ababa University, institute of technology, chemical engineering department laboratory and final determination of trace heavy metal is made at JIJA Laboglass Pvt.Ltd.Co central laboratory.

Figure3.3: Waste water collection site.

3.2.1.2 Samples collection, transportation and storage

3.2.1.2.1 Sample collection

Waste water samples were collected at several point of the waste water generated site for both high and Low rate of solvent based paints with location of the sampling point, indicated in the table 3.1 and 3.2.

Table 3.1: position of sampling points

Sample point	description
1	At initial output
2	At the middle point
3	At final out put

Table3.2: composition of paint waste water sample taken for characterization

No	date of sample taken	composition of waste water	No of samples
1	20/12/10	[0% -25%, synthetic paint]	3
2	28/01/11	[25% -50%, synthetic paint]	3
3	08/03/11	[50% -75%, synthetic paint]	3
4	10/01/11	[75% -100%, synthetic paint]	3
5	23/02/11	[almost 100% synthetic paint]	3

3.2.1.2.2 Waste water sample collection equipment

The equipments used to withdraw waste water sample from equalization tank were selected to keep physical or chemical alterations of the sample to a minimum and to preserve sample integrity.

Devices used for collecting waste water samples for metals analysis were made of plastic as shown in figure 3.4. Care was taken not to introduce errors during sampling and storage where contamination resulting from improperly cleaned sampling devices and sample containers. Loss of metals by absorption or precipitation in sample containers was avoided by acidifying the sample properly using HNO_3.

Sample Preservation is made by adding 1.5 ml of concentrated HNO_3 per liter of sample as stated in environmental sampling and analysis for metals. Sampling Equipments were cleaned before sampling and at the end of sampling, sampling equipment labeled referring to the sampling point and date of sampling. Deionized water is used for rinsing and adsorbent preparation. [40]

In waste water sampling, every attempt was made to minimize changes in the chemistry of the samples. To assist in maintaining the natural chemistry of the samples, preservation methods such as pH control, refrigeration and protecting from light was performed.

Figure3.4: The collected paint waste water.

3.2.1.2.3 Sample transportation and Storage

Storage and shipment of samples were performed in manners that maintain sample quality. Transportation arrangement was maintain proper storage conditions and provide for effective sample pickup and delivery to the laboratory. Sampling plan was coordinated with the Ethiopian Environmental Protection Authority so that appropriate sample receipt, storage, analysis and arrangements were provided.

3.2.1.3 Waste water sample characterization

Standard method was used for heavy metal analysis for Waste water samples. Sample collection, transport, storage and analysis were conducted in the study period. Samples were collected based on standard procedures to detect significant changes. These data quality objectives were addressed:

O Accuracy and precision of methods used in the analysis of samples, including measurements.

O Quality control and quality assurance procedures used to ensure the validity of the result. For example, use of blank samples, record keeping and data validation.[40]

3.2.1.4 Study variables

Cobalt and lead were selected from the available heavy metal in paint waste water as study variable for this study.

3.2.2 Experimental procedures on optimized wood ash to remove heavy metals of paint waste water

3.2.2.1 Preparation and characterization of adsorbent

- The ash biomass procured (collected) from five representative residences in Addis Ababa different places by checking their sources is wood of any type of tree. This is shown in figure 3.5.

Figure 3.5: The collected wood ash used for adsorption.

The following procedure was followed while preparing the adsorbent:

- The wood ash has been pretreated first by hand sorting .then,
- The material was dried in an electric drying oven at 60°C for 24 h and this dried material was pulverized to convert it into fine powder using attrition mill and sieved and retained at geometrical mean size gm between 50 µm - 80 µm for use in the experiments as adsorbent.

The detail procedure of preparing of wood ash for adsorption purpose is described in the annex.

The following wood ash characteristics were done in accordance to ASTM standard, to characterize the adsorbent.

I. Particle size

An ASTM standard (D1102-56) procedure was followed to determine the ash content of the wood ash.

- ✓ to weigh the known amount wood ash, and put on the sieve shaker with different sieve size.
- ✓ after shaking or vibrating the sieve , collect the ash which remain on the range of usable.
- ✓ after that weighing the usable range wood ash and preserve it for adsorption purpose.

II. Ash content

An ASTM standard (D1102-56) procedure was followed to determine the ash content of the wood ash.

- ✓ to ignite the empty crucible and cover over a burner or in the muffle at 600°c, cool in desiccators, and weight to the nearest 0.1 mg.
- ✓ to place the 2-g test specimen in the crucible, determine the weight of crucible plus specimen, and place the drying oven at 100 to 105 °c with the crucible cover removed.
- ✓ after 1 h, to replace the cover on the crucible, cool in desiccators, and weigh.
- ✓ to repeat the drying and weighting until the weight is constant to within 0.1 mg.
- ✓ to record the weight (crucible plus specimen minus weight of crucible) as the weight of the oven dry test specimen.
- ✓ to place the crucible and contents, with the cover removed, in the muffle furnace and ignite until all the carbon is eliminate.
- ✓ to heat slowly at the start to avoid mechanical loss of test specimen (temperature of final ignition is 580 to 600).

- ✓ to remove the crucible with its contents to desiccators, replace the cover loosely, cool, and weight accurately.
- ✓ to repeat the heating for 30-min periods until the weight after cooling is constant to within 0.2 mg.

III. Solid density

The following procedure was followed while determining the solid density of the sawdust.

- ✓ The pycnometer was cleaned using acetone and dried. And the mass of the pycnometer weighted using digital balance.
- ✓ unknown amount wood ash is added into the pycnometer and weighted.
- ✓ The pycnometer with a certain amount of wood ash is filled with insoluble liquid, distilled water,
- ✓ The volume of the distilled water and wood ash was determined and the solid density was calculated accordingly.

IV. Moisture content

The moisture content of the wood ash was determined based on ASTM standard (D 2016-65) by electric moisture analyzer.

Three samples, weighting 2 g each, were used to determine the moisture content with the use of the digital moisture analyzer. The temperature and the time were set at 105 °c and 30 min respectively so as to get reliable value. The mean value of the three results is reported. The moisture was also analyzed with the use of oven drying method and reveals the same result.

V. Porosity

The porosity of the wood ash was determined based on the particle size of the ash; the porosity of the ash is used for this method by simply read from the data graph by using particle size range. The porosity of the wood ash also shows the active surface area of the ash.

Vi. Chemical composition

The chemical composition of the wood ash was determined based on Flame Atomic Absorption, APHA 3111C. Extraction/Air-Acetylene Flame Method.

The results of chemical analysis of wood ash are shown the mineral content in the ash .for adsorption capacity the chemical content of the adsorbent is significant.

Vii) Surface area

The surface area of the wood ash is computed compared to its porosity and particle size, the surface area is the surface per volume ratio of one wood ash particle, it is the basic physical parameter for the adsorption capacity of the adsorbent.

The surface area of the ash particle is calculated by using

$$\mathbf{S = Ss*Sqrt\ T/Sqrt*Ts} \ldots\ldots \mathbf{(3.1)}$$

Where: Ss =surface volume of the bed, constant value for ash = 3774 cm^3.

T = time determined for weighting the particle absorbs the fluid.

Ts = time determined for dropping the fluid, constant value for ash =58.3 sec.

S = surface area of the particle.

3.2.2.2 Method of Adsorption studies

Atomic Absorption Spectrophotometer was used to determine the concentration of trace heavy metal because of its availability and reliability of the result. Procedure and operating conditions for analysis by an Atomic Absorption Spectrometer are described in the annex.

All experiments were carried out at room temperature in batch mode. Batch mode was selected because of its simplicity and reliability (Ćurković *et al.*, 2001:3437). The batch experiments were run in different Erlenmeyer glass flasks of 250 ml capacity. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The stirring was kept constant for each run throughout the experiment to ensure equal mixing. The desired pH was maintained using dilute NaOH/HCl solutions. Each flask was filled with a known volume of sample having desired pH before commencing stirring. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered through Advantech 5A filter paper (gravitational filtration). The experiments were carried out under different experimental conditions.

Experiments were carried out at pH 6.8 (when the shaking time effect was studied). The solutions were shaken vigorously for a given time period to reach equilibrium. The agitation speed was kept constant for each run to ensure equal mixing. After completion of a pre-selected shaking time, the suspensions were filtered using filter paper, and then the supernatant solution in each flask was analyzed by atomic absorption spectrometer (AAS) for residual metal content.

Langmuir and Freundlich isotherm models were fitted to the adsorption data and their constants were evaluated. Satisfactory conformity between experimental data and the model-predicted values was expressed by the correlation coefficient (R^2).

3.2.2.2.1 Studies of Factors influencing the adsorption Process

- **Effect of PH**

Experiments were conducted to study the effect of solution pH on lead (II) and cobalt (II) ion adsorption by contacting 2 g of sorbent with 100 ml of 5.4 mg/liter of lead (II) and 3.7 mg/liter of cobalt (II) ion solution. The mixture was agitated using an incubator shaker at 200 rpm and 25^0c for 120 min. The pH of the solution was adjusted by the addition of 0.1M NaOH or 0.1M HCl as needed, and studies were conducted at pH 4, 6, 8 and10. The adsorbent was then removed from the solution by centrifugation. The residual lead (II) and cobalt (II) ion concentration in solution was analyzed in Atomic Absorption Spectrophotometer as described above. All experiments were conducted two times.

- **Effect of Contact Time**

Batch adsorption tests were done at different contact time at the initial concentration of 3.7mg/l of Co (II) and5.4 mg/l of Pb (II) and wood ash dose concentration is 2 gm in 100mL solution. The samples were shaken in the rotary shaker at 200 rpm with the temperature controlled at 25^0c at PH is 6.8(raw waste water pH). The Samples were then taken at different time intervals (20, 60, 90 and120 minutes) and were centrifuged. The concentration of metal ions in the supernatant solutions was analyzed using flame atomic absorption spectrometry. Each determination was performed twice.

- **Effect of wood ash Concentration**

Kinetic studies on the effect of wood ash doses on lead (II) and cobalt (II) ion sorption were carried out at an initial concentration of 5.4 mg/liter and 3.7 mg/liter at pH 4, 6, 8 and 10 for lead and cobalt respectively, and at an agitation speed of 200 rpm and temperature of 25^0c. A series of kinetic experiments were conducted for four different wood ash doses varying between 5-20gm/l. Samples were withdrawn at pre-determined time intervals (30, 60, 90, 120 minutes), Centrifuged and analyzed for residual lead (II) and cobalt (II) ion concentration using flame atomic absorption spectrophotometer. Each determination was performed twice.

- **Equilibrium Study**

Equilibrium sorption experiments were carried out at a pH of 4, 6, 8 and 10 for lead (II) and cobalt (II) ion respectively by contacting 2 gm of sorbent with 100 ml of lead (II) and cobalt (II) ion solution at the concentrations 5.4 mg/l and 3.7 mg/l respectively. The pH was adjusted using 0.1M NaOH and 0.1M HCl. The adsorbent was separated from the solutions after 24h. The residual metal ion in the solutions was estimated. All experiments were conducted in duplicates at a temperature of 25^0c. The maximum variation in metal sorption data between duplicate experiments was 5%.

Adsorption isotherms show the distribution of solute between the liquid and solid phase's equilibrium conditions. Many different isotherm models have been proposed for the adsorption of solutes in a liquid solution onto a solid surface. Langmuir model is probably the most popular isotherm models due to its simplicity and its good agreement with experimental data. The Langmuir model, the saturated monolayer isotherm, can be described by the linear form:

$$1/q_e = (1/C_e * 1/bq_{max}) + 1/q_{max} \ldots\ldots\ldots\ldots(3.2)$$

Where: C_e is the equilibrium metals concentration in aqueous phase (mg/l); q_{max} is the q_e for a complete monolayer (mg/g), a constant related to sorption capacity (the maximum amount of metal ion per unit weight of adsorbent); and b is a constant related to the affinity of the binding sites and energy of adsorption (l/mg). By plotting $1/q_e$ versus $1/c_e$, q_{max} and b can be determined. The linearized plot of Langmuir (plot of $1/q_e$ and $1/C_e$) isotherm was given for both metals ion. The Langmuir constant q_{max}, defined as the amount of adsorbate per unit weight of adsorbent to form a complete monolayer on the sorbent surface and b which reflects quantitatively the affinity between the adsorbent and adsorbate were calculated for both metals.

The equilibrium established between the adsorbed metal ions (q_e) and that remained free in the solution (C_e) was also represented by the Freunlich adsorption isotherm, by the linear equation as follows.

$$\ln q_e = \ln K_f + 1/n * \ln C_e \ldots\ldots\ldots\ldots(3.3)$$

Where: K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively.

3.2.3 Experiment on adsorbent Recovery

The experiment on adsorbent recovery was conducted by eluting the adsorbed metal ions using 2M Na_2EDTA both for Lead (II) and cobalt (II) ions .where the adsorption was initially conducted at conditions expressed in the above sections. recovery test was conducted on ash residue centrifuged after sorption test at pH from 4 to 10 , both lead and cobalt recovery test was performed on wood ash residue from sorption test at Pb(II) 5.4mg/l and Co(II) 3.7mg/l initial metal concentrations . The Elution (recovery) tests were done for contact time of 120 minutes, after that metal ion concentrations and metal ion recovery was calculated.

$$\textbf{Recovery} = (C_{fel} * V_{el}/m)/q * 100\% \text{...} (3.4)$$

Where: q is the metal uptake (mg/g); m is the adsorbent dry weight (g); C_{fel} the Co (II) or pb (II) final concentration in effluent (mg/L); V_{el} the effluent volume (L).

3.3 Experimental design

3.3.1 Full factorial design

Factorial design is used to test the effect of each factor. In factorial experiment, all possible combination of factor levels was tested. And it was determined the effects of individual factors and assessed the effect of change of variables at a time for each metals.

- **Independent factors (f)**: Three; pH, contact time and dose of wood ash.
- **Factor levels (L)**: 4, for all factors.
- **Number of runs**: $Lf = 4^3 = 64$ for each heavy metals.
- **Replicate**: two times = 2×64 = 128
- **Center points**: 3*2
- **Dependent/ response variable**: percentage of metal removal (%E)

$$\%E = \frac{(Ci - Cf)}{Ci} \times 100\ \% \text{..} (3.5)$$

Where, R is % metal removal

Ci is initial concentration of metal

Cf is concentration of metal after treatment

- **The three independent factors and their levels**
    - i. pH: 4, 6, 8, 10
    - ii. Contact time: 30, 60, 90, 120 min.
    - iii. Dose of wood ash: 5, 10, 15, 20 gm/lit

3.3.2 Statistical analysis

Parametric analyses of variables (Co & Pb) were followed by comparative procedures to identify statistically significant result using JMPIN 5.0 Software, The method was used in estimating and testing of Waste water sample for each metal (Pb &Co).

The statistical performance standards were used to provide a means to limit the possibility of making false conclusion from the sample analysis data. The specified error level of 0.01 for individual sample compression for probability of false positive essentially means that the analysis is expected to be predicted with 99% confidence that significantly increase.

After the determination of the concentration of metals and treating with wood ash, linear regression analysis was applied to investigate the relationship between a dependent variable (removal of metal) and the independent variable pH, contact time and Dose of the ash. Regression analysis is used in such cases for determining unknown coefficients in a theoretical equation from available experimental data. And Analysis of variance (ANOVA) was carried out to sort out effect as a result of using different conditions, and to understand the main and the interaction effects.

4. RESULT AND DISCUSSION

The following chapter provides result of laboratory analysis made for wood ash characterization, paint waste water characterization; study of effects of parameters such as pH, dose of wood ash and contact time on heavy metal removal capacity of wood ash from Zemilli Paint Factory waste water and findings of other scientific data generated from this study.

Five wood ash samples were collected at different residences of Addis Ababa which has a base of wood source, the ash then analyzed for physical and chemical tests. Fifteen paint waste water samples were collected at different point of Zemilli Paint Factory waste water for two months. The paint waste water is then analyzed for the type of heavy metal they contain and their concentration. Heavy metals which exceeded the permissible limit of heavy metal in drinking water sated by WHO and EU and; those which have hazardous effect on human health were selected as study variable.

The paint waste water loaded with heavy metal is then treated with wood ash and the performance of the wood ash is measured by varying the parameters to optimize those factors which affect the performance of Wood ash for specific metal ion.

4.1. Characterization and Analysis of paint waste water sample

During sampling at the first time, it seems difficult to obtain reliable paint waste water sample because, the Zemilli Paint Factory waste water generation site is not properly designed to collect the paint waste water produced in the site.

The paint waste water produced in the site percolates in to the peripheral soil and to the ground water without any barrier. The paint waste water samples obtained from these points were more localized than representing the paint waste water of the site. An initial paint waste water sample taken on 20/12/10 at three surface of the site showed that at the initial output, at equalization tank and at the final output, heavy metals analyzed are present in amount on the range of 0.001 mg/l - 5.4 mg/l. However, subsequent samples taken for depending of the production plan because of when more of the synthetic (solvent based) paint produced, there is more concentration of heavy metal present, since enamel paints are forced drying which takes more metal driers to dry the film easily. After sampling, during the period of synthetic paints produced, fluctuating results were still encountered due to quantity of waste water and rapid infiltration rates of rainfall. The results given in Table 4.1 shows, the summary of analysis of paint waste water samples taken on the site during the period between December 20, 2010 and march 08, 2011 on a fifteen day programme. They show large fluctuations in the key determinant heavy metals. This is partially due to the changing character of the paint waste water due to generation rate, topography and paint type produced; it also reflects different infiltration rates and generation rates.

The following table shows some of the laboratory results of paint waste water analyzed for heavy metal. Paint waste water samples are taken at different three sampling point on the site at different days of the study time.

Table 4.1: Result of paint waste water characterized for heavy metal in mg/l.

COMPOSITION	**SAMPLE NO**	**COPPER**	**MERCURY**	**LEAD**	**CHROMIUM**	**ZINC**	**CADMIUM**	**COBALT**
[0% -25%, synthetic paint]	**1**	**0.072**	**0.0012**	**0.968**	**0.085**	**1.23**	**0.05**	**0.26**
	2	**0.025**	**0.03**	**0.692**	**0.003**	**3.24**	**0.006**	**0.09**
	3	**0.027**	**0.002**	**0.521**	**0.26**	**2.35**	**0.012**	**0.042**
[25% -50%, synthetic paint]	**1**	**0.89**	**0.09**	**1.33**	**0.64**	**1.98**	**0.06**	**1.14**
	2	**0.26**	**0.03**	**1.21**	**0.38**	**1.99**	**0.08**	**0.64**
	3	**0.19**	**0.02**	**0.96**	**0.74**	**2.60**	**0.09**	**0.37**
[50% -75%, synthetic paint]	**1**	**0.36**	**0.002**	**3.11**	**1.62**	**1.22**	**0.08**	**2.12**
	2	**0.33**	**0.0064**	**2.60**	**2.10**	**2.99**	**0.50**	**2.67**
	3	**0.34**	**0.028**	**2.92**	**1.69**	**3.22**	**0.06**	**1.55**
[75% -100%, synthetic paint]	1	**0.12**	**0.02**	**3.69**	**0.9**	**3.22**	**0.02**	**2.69**
	2	**0.28**	**0.03**	**3.53**	**1.2**	**2.96**	**0.03**	**1.99**
	3	**0.33**	**0.02**	**3.29**	**1.33**	**1.07**	**0.04**	**1.36**
[almost100% synthetic paint]	**1**	**2.15**	**0.20**	**5.40**	**2.50**	**2.02**	**0.15**	**3.65**
	2	**1.34**	**0.50**	**5.12**	**1.90**	**2.33**	**0.17**	**3.70**
	3	**1.23**	**0.60**	**4.69**	**2.30**	**3.44**	**0.11**	**2.99**

4.1.1 Discussion on paint waste water analyzed for heavy metal

The analysis made on samples taken from the equalization tank which have a composition of (75% - 100%) synthetic paints shows, the presence of heavy metal such as cobalt 2.69mg/l, copper 0.33, lead 3.69, chromium 1.33 mg/l, and zinc 3.22mg/l, mercury and cadmium less than 0.1mg/l.

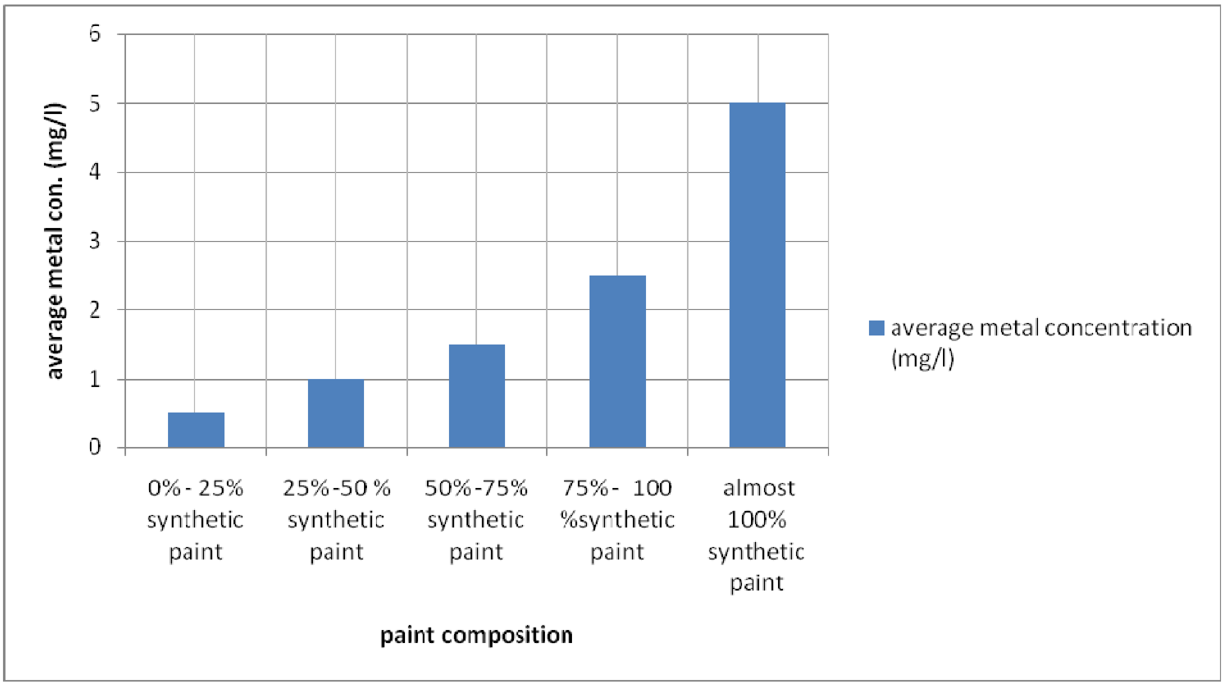


Figure 4.1: composition of synthetic paints versus average concentration of heavy metal in paint waste water analyzed

Attention is given to the two heavy metal cobalt and lead which appears to be in higher concentration than those heavy metals analyzed. In addition to exceeding the permissible limit of heavy metal for drinking water sated by WHO, these two heavy metals also exhibit adverse environmental and health hazards.

Additional sample collection and analysis is made to determine the amount of the selected two Heavy metals lead and cobalt those are present in the paint waste water Therefore, paint waste water samples which have composition of almost 100%synhetic paint and analyzed for these two heavy metals. As can be seen from table 4.1 a cobalt content varying from 2.69mg/l to 3.7mg/l and lead content from 3.69mg/l to 5.4mg/l was found from three samples taken on the site.

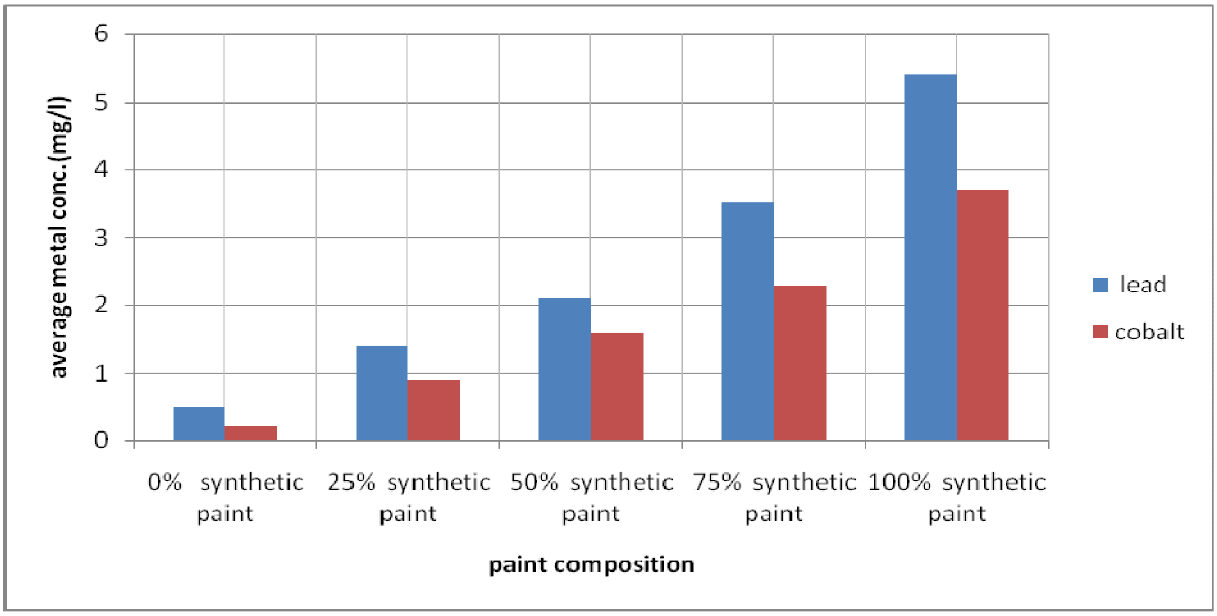


Figure 4.2: composition of paints versus average metal concentration for cobalt and lead

The result can be explained regarding amount of waste generated, substance transport and characteristics of Paint type which is produced. Taking in to consideration these three parameters conclusion is made as follows. As synthetic paint production rate increase, the amount of dissolved heavy metal that can be wasted from the factory is increase simultaneously. Substance transport and the amount of waste water generated are the other factor contributed to the results of paint waste water sample was almost all plastic (water based) paints production program, concentration of heavy metal is minimum at this sampling period. The paint waste water sample was almost all synthetic (solvent based) paints production program shows greater amount of heavy metal compared to the other days. These phenomena can be explained as; the production programs as these days are more of synthetic paints, because of these the concentration or amount of heavy metal in this waste water is maximum.

4.2 Optimizing wood ash to remove heavy metals

4.2.1 Adsorbent characterization result

i) Ash content

In accordance to ASTM D 1102-56, the percentage of ash was calculated based on the weight of the moisture-free wood ash as:

Ash, percent = $(W_1/W_2)*100$ ……………………………………………………………….4.1

where:

W_1=weight of ash, and

W_2=weight of oven-dry sample

Accordingly the ash content of the wood ash,

Ash, percent = (0.79/2)*100

=89.5%

ii) Solid density

As per the stated method in the methodology section, the solid density characteristic is calculated in the following manner:

- ✓ weight of pycnometer =28.828g
- ✓ weight of pycnometer plus sample weight=36.8926g
- ✓ filling with distilled water and weighting yield 77.6285g

Therefore the mass of the sample will be 8.0646 g. And based on density to mass and volume relationship, the density of the wood ash was calculated to be 0.986g/cm^3.

iii) Moisture content

The moisture content of the sawdust was calculated by using digital moisture analyzer at 105 °c and for 30 min. And the average moisture of wood ash was found to be 1.85%.

iv) Particle size

The average particle size of raw wood ash used fall below 500 µm. but used for adsorbent purpose is milled by crusher, sieved and then the average particle used is on the range between 50µm - 80 µm.

v) Porosity

The porosity of the wood ash was found by using porosity against particle size graph of the indicated type of material. And the average porosity of wood ash was read to be 0.5.

vi) Chemical composition

The chemical analysis of wood ash, total percentage composition of Iron oxide (MgO = 19.32%), aluminium oxide (CaO = 28.0%) and silicon dioxide (SiO_2 = 31.80%) was found to be 79.12%. The result of chemical composition of wood ash is given in Table 4.2.

Table 4.2: Chemical composition of the analysed wood ash

Constituent	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**NaO**	**L.O.I**
Composition [%]	31.8	2.34	8.2	28.53	19.32	10.38	6.5	17

Vii) Surface area

The surface area of the wood ash was calculated by using calculation to determine the surface area per weight. And the average surface area of wood ash was found to be 65.5 m^2 /gm.

Table 4.3: The result of Characterised wood ash

Characteristics	**Unit**	**Value**
Ash content	%	89.5
Solid density	g/cm^3	0.986
Moisture content	%	1.85
Porosity	-	0.5
Particle size	µm	50 - 80
surface area	m^2/gm	65.5
color	-	grey
pH	-	8.5

4.2.2 Adsorption studies results and discussions

4.2.2.1 The effects of contact time, pH and dose of wood ash

4.2.2.1.1 Effect of pH

Four Raw paint waste water samples have been adjusted to pH 4, 6, 8, and 10. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were added gradually to the raw paint waste water in order to adjust its pH. As can be seen from figure 4.3, the effect of pH to remove cobalt (II) and lead (II) from paint waste water using wood ash as a natural adsorbent, is very high. Best lead removals that were accomplished by the effective wood ash dosages were 97% with the dosage of 20ml at a pH of 10. The binding of Cobalt and lead by wood ash was interesting. In all cases some binding occurred at pH 4 and pH 6 and then the binding with wood ash increased to over 96% then after the rate of binding drop out when the pH further increased after 10. The result for the study of effect of pH on Co^{2+} and Pb^{2+} sorption capacity of wood ash revealed that, the sorbability of lead tends to increase as pH value increases up to 10. The maximum sorbability was found to be 97% at pH 10. The trend for sorbability of cobalt is different. The maximum sorption is achieved at a PH of 8 which is 94 % and decrease beyond this pH value. Therefore, these values was chosen as optimum pH and kept constant for all experiments.

Table 4.4: Effect of pH to remove cobalt and lead from paint waste water sample

Initial Conc. Of* Co (II) *(mg/l)	***Initial conc. Of* Pb(II) *(mg/l)***	***pH***	***Final conc. Of* Co (II)**	***Final conc. Of* Pb(II)**	***% removal of* Co (II)**	***%removal of* Pb(II)**
3.7	5.4	4	1.0	1.18	68	61
3.7	5.4	6	0.55	0.75	79	83
3.7	5.4	8	0.19	0.48	94	90
3.7	5.4	10	0.37	0.16	90	97
3.7	5.4	12	0.53	0.26	85	95

When pH value is lower than 6, sorption of Co^{2+} and Pb^{2+} ions may be slowed down by the effect of density of H^+ ions that make the interaction of metal cations with the binding site of the biomass difficult because of the repulsive force, as a result of the competition for possible binding sites between Co^{2+} & H^+ and Pb^{2+} & H^+ ions. As the pH value increases, protonation of functional groups (such as carboxylate and carboxyl) by H^+ ions may decrease and the interaction between metal ions and the binding sites may increase. When pH value is higher than 10, soluble Co^{2+} and Pb^{2+} ions begin to precipitate as metal hydroxides because of the increasing concentration of OH^- ions.

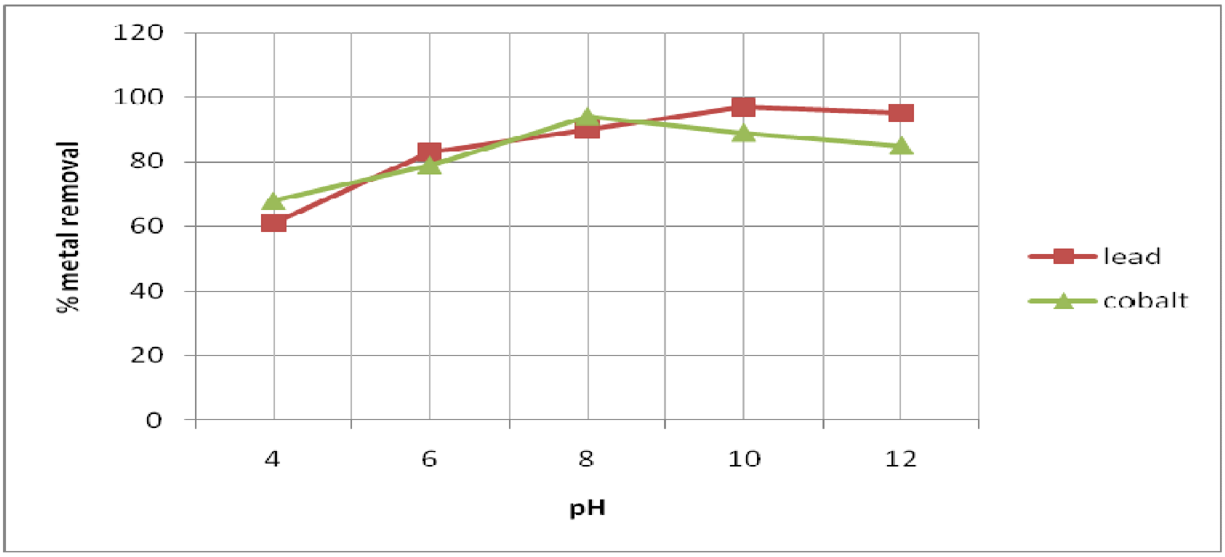


Figure4.3: Data plot of effect of pH for % removal of cobalt (II) and lead (II)

4.2.2.1.2 Contact time

Optimum shaking conceded to determine the optimum contact time of wood ash with cobalt (II) and lead (II) exist in Zemilli paint factory paint waste water sample. As can be seen from table 4.5 and figure 4.5, the experiment is made at 30 minute time interval for two hours, for constant initial concentration of cobalt 3.7mg/l and lead 5.4mg/l and 20 gm/l dose of wood ash for 50ml paint waste water sample.

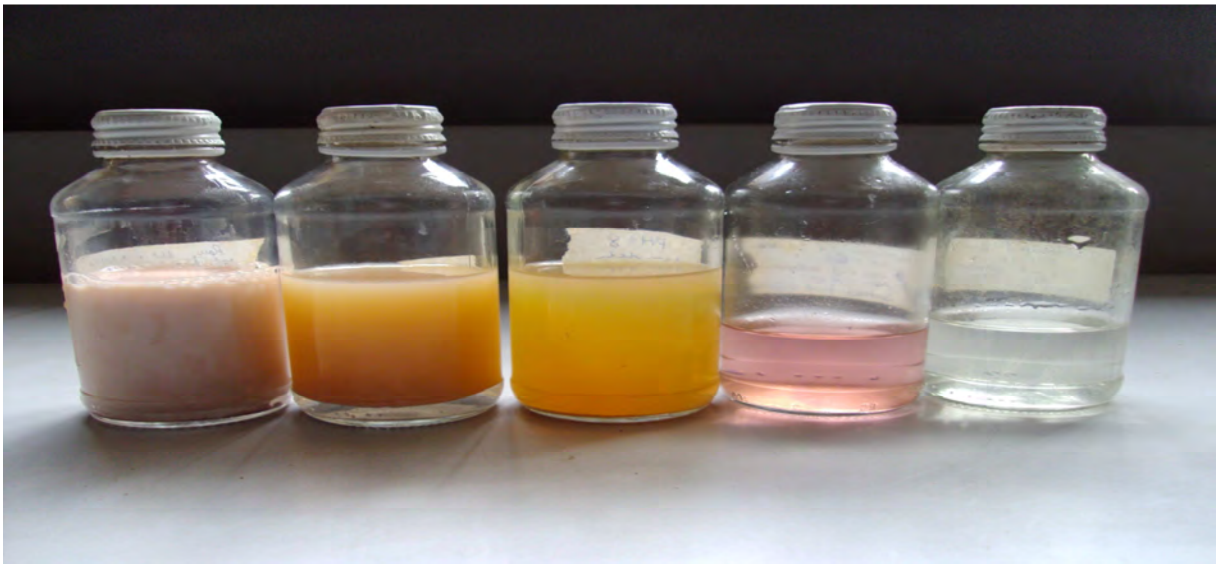


Figure 4.4: Waste water sample after treatment with wood ash.

Lead removal rate is progressed with time from 30, 60, 90, 120 minute at removal of 65%, 81%, 95% and 93% simultaneously. As can be seen from figure 4.6 and table 4.5, Lead removal rate decreases after the nineteenth minutes. Similarly, percentage removal of Cobalt with respect to time is 70%, 84%, 93% and 90% for the time lap of 30, 60, 90 and 120 minute.

As can be seen from figure 4.4, the color of paint waste water after treated with the wood ash, is changed from reddish to clear, from left to right. This change is due to the fact that, most of the pollutant including suspended and dissolved organic and inorganic materials present in the paint waste water adsorbed and settle out when the adsorbent is added for the given time interval.

Table 4.5: varying time used in jar tests for the optimization of contact time to remove cobalt and lead at pH of 6.8.

Time (minute)	**Dose wood ash (gm/ml)**	**Conc. Of Pb(II) in 50ml paint waste water sample (mg/l)**	**Conc. Of Cobalt in 50ml paint waste water sample (mg/l)**	**% Pb(II) removal**	**% Co (II) removal**
30	20	5.4	3.7	65	70
60	20	5.4	3.7	81	84
90	20	5.4	3.7	95	93
120	20	5.4	3.7	93	90

The rate of cobalt and lead removal decreases after the 90th minutes as shown in the experimental results presented in table 4.5 and figure 4.5. Therefore, the optimum contact time for lead and cobalt were taken as 90 minutes.

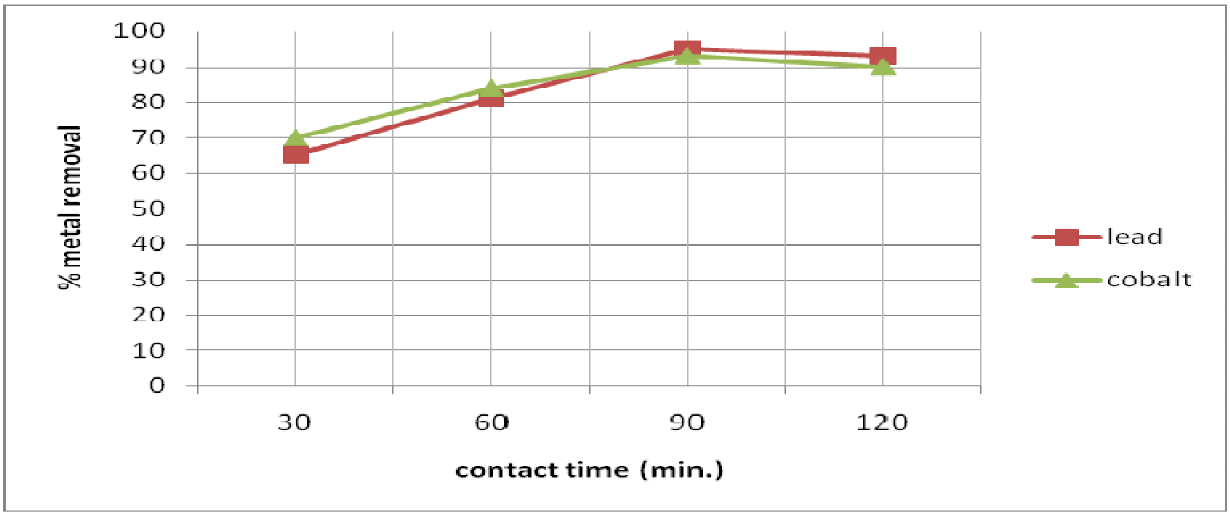


Figure 4.5: Time required by wood ash to remove cobalt (II) and lead (II) from paint waste water

4.2.2.1.3 The effect of Dose of wood ash

In the same way as time of contact, jar test was undertaken to determine the optimum dosage of Wood ash to remove the cobalt (II) and lead (II) available in Zemilli Paint Factory paint waste water. Different dose range of wood ash was added as shown in table 4.6, in a 50ml paint waste water sample at pH 6.8 and shaken for 90minutes contact time for lead and 90minute contact time for cobalt.

Table 4.6: Dose of wood ash to remove cobalt and lead from Zemilli paint factory waste water sample at a pH of 6.8.

Initial Conc. Of* Co (II) *(mg/l)	***Initial conc. Of* Pb(II) *(mg/l)***	***Dose of wood ash (mg/ml))***	***Final conc. Of* Co (II)**	***Final conc. Of* Pb(II)**	***% removal of* Co (II)**	***%removal of* Pb(II)**
3.7	5.4	5	1.03	1.29	67	62
3.7	5.4	10	0.66	0.81	76.5	72.5
3.7	5.4	15	0.4	0.49	80	83
3.7	5.4	20	0.29	0.16	85.5	90
3.7	5.4	25	0.29	0.16	85.5	90

The experimental result made for this particular paint waste water provides information about the amount of adsorbent (wood ash) that must be added in paint waste water to remove heavy metals. As can be seen from table 4.6 and figure 4.6, 20gm/l of wood ash is required to remove 85.5% of cobalt and 90% of lead that is available in Zemilli Paint Factory paint waste water at a pH of 6.8 and at a contact time of 90 minute for lead and 90 minute for copper. Therefore, the dosage of wood ash was taken as 20mg/l for both heavy metals of concern.

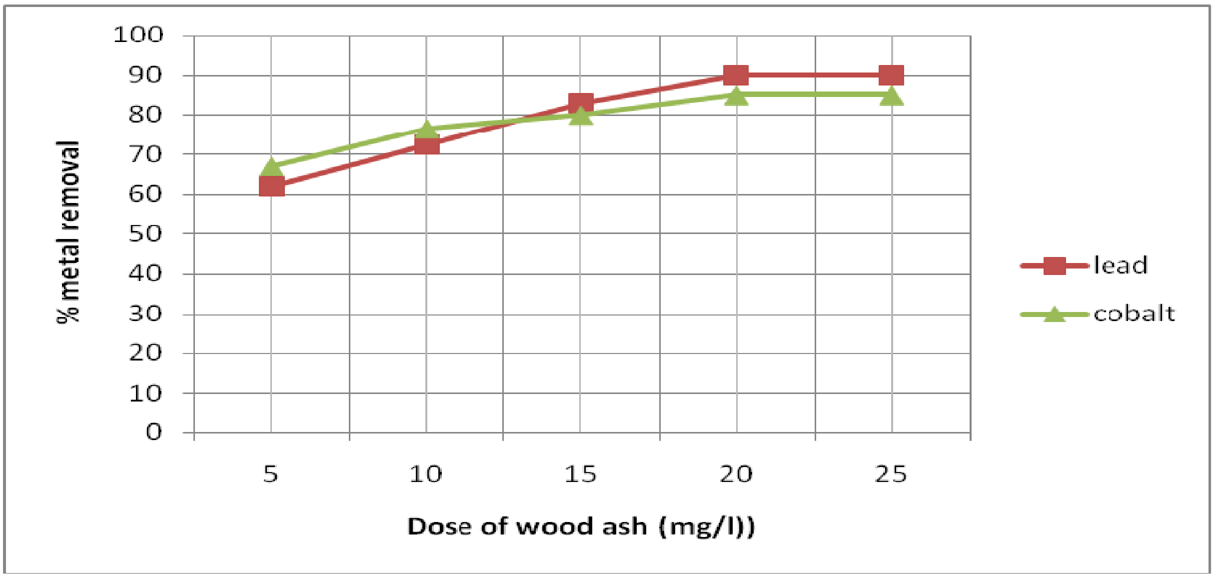


Figure 4.6: Dose of wood ash needed to remove cobalt (II) and lead (II) from paint factory waste water.

4.2.2.2 Equilibrium Study and Adsorption Isotherms

The equilibrium study has been conducted based on the commonly used monolayer and multi layer adsorption isotherm models of Langmuir and Freundlich. To examine the relationship between sorbed (qe) and aqueous concentrations (Ce) at equilibrium, sorption isotherm models are widely employed for fitting the data. Langmuir and Freundlich models have been tested to fit the equilibrium data.

According to the plots of 1/*q*e versus 1/Ce for Langmuir isotherms and ln K_f versus ln C_e for Fleundlich, the experimental data was found to fit better to Langmuir model plot. The results of their study revealed that the removal of Pb (II) from aqueous solutions by using wood ash as an adsorbent seems to follow the Langmuir as well as the Fleundlich isotherm. The sorption affinity (n) of cobalt was found to be 2.27 and that for lead was found to be 2.71. It has been shown by using mathematical calculations that the sorption affinity (n) values between 1 and 10 indicate effective adsorption.

Like the findings of other workers, the maximum adsorption capacity and sorption affinity for lead is greater than that for cobalt. And this is linked to the greater affinity of the active sites for lead.

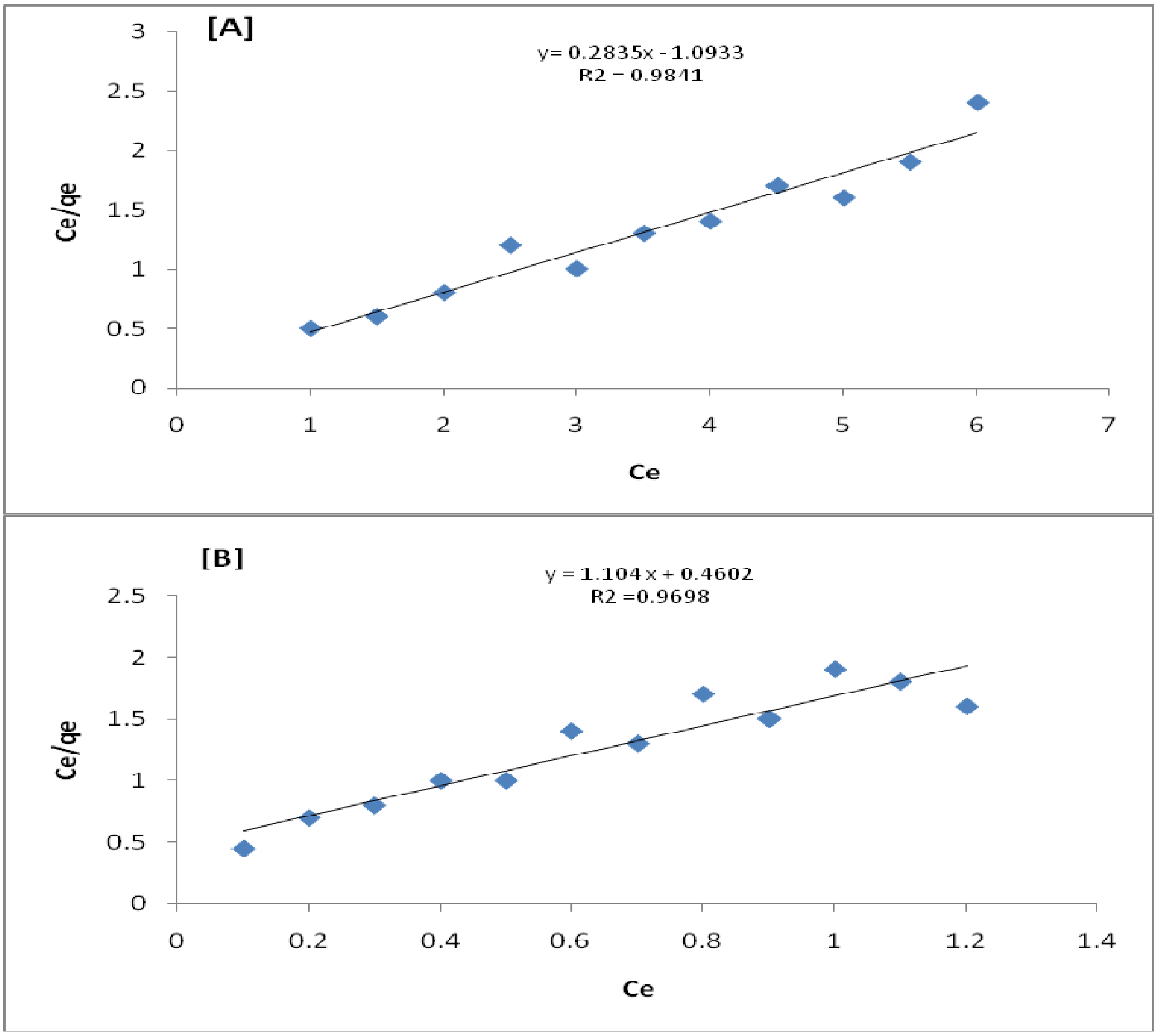


Figure 4.7: Langmuir isotherm for heavy metal removal by wood ash, for pH = 6.8, T = 30 °C (A: lead; B: Cobalt).

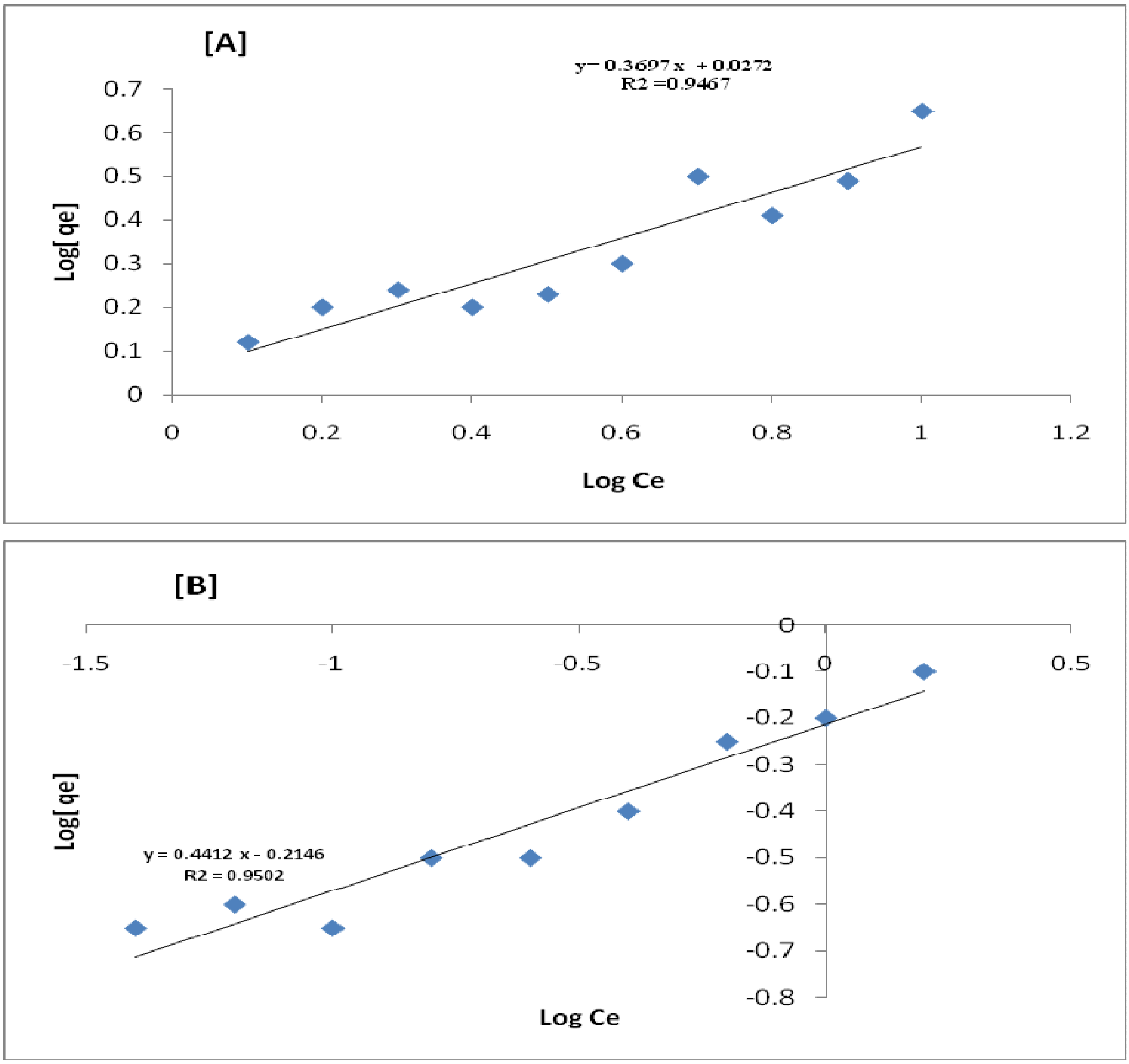


Figure 4.8: Freundlich isotherm for heavy metal removal by wood ash, for pH = 6.8, T = 30 °C (A: lead; B: cobalt).

Table 4.7: Parameters for Langmuir and Freundlich adsorption models

metals	parameters of the Langmuir model			parameters of the freundlich model		
	Q_{max} (mg/g)	b (1/mg)	R^2	K_f	1/n	R^2
cobalt	0.91	2.4	0.96	0.61	0.44	0.95
lead	3.53	0.25	0.98	1.064	0.369	0.94

4.2.2.3 Kinetic Study

The effect of wood ash dose on the sorption kinetics of lead (II) and cobalt (II) ion was studied at a pH of 6.8 for lead and cobalt and 5.4 mg/l and 3.7 mg/l initial metal concentration. The sorbent dose was varied between 5 and 20 gm/l. For all the sorbent doses, the amount of Lead (II) and cobalt (II) ion sorbed at each concentration increased rapidly in the beginning and slowly at the end. While at higher biomass concentrations (20 gm/l) the equilibrium reached within 60-90 min, at lower biomass concentrations (5 and 10 gm/l) equilibrium was not observed even until 90 min. probably at high sorbent dosage the available ions are inadequate to cover all the available sites on the sorbent. Thus, the time of contact required to reach saturation varied with the biomass dose. It is shows that within a short time a large fraction of the total amount of lead (II) and cobalt (II) ion was removed but the uptake capacity of lead (II) and cobalt (II) ion per unit amount of sorbent (mg/g) decreased with increase in adsorbent concentration. Pseudo-second order mechanism, described by

$$dq_t/dt = k\,(q_e - q_t)^2 \ldots\ldots 4.2$$

At different sorbed dosages the rate constant, k, the equilibrium sorption, qe and the initial sorption rate, h, were calculated by pseudo- second order equation. Where, k_2 is the rate constant of pseudo-second order sorption (g/mgmin). Integrating and applying boundary conditions t = 0 and q_t = 0 to t = t and qt = q_e, Equation (4.3) becomes

$$t/q_e = 1/h + 1/q_e * t \ldots\ldots 4.3$$

If second order kinetics is applicable, the plot of t/qt against t, should give a linear relationship from which the constants q_e, h and k_2 can be determined.

The values of *k*, *qe* and *h* for different sorbent doses are given in Table 4.8. There is a decrease in *qe* with increase in sorbent dosage the ion uptake capacity at equilibrium (qe) decreased from 3.38 mg/g to 1.506 mg/g as the sorbent dose increased From 10 gm/l to 20 gm/l for lead (II) and from 2.78 mg/g to 1.41 mg/g for cobalt (II). Whereas the values for rate constant (k) and initial sorption rate (h) seem not to show any trend. This may be attributed to the nature of the data obtained after measurement in atomic absorption spectrophotometer.

Table 4.8: Parameters for Pseudo-second order kinetic model for varying adsorbent dose

Metal type	Wood ash dose (gm/l)	Ion uptake capacity at equilibrium (mg/g)	Initial sorption rate (mg/g*min)	Rate constant [k] (g/mg*min)	Correlation coefficient [r^2]
Lead	5	4.801	390.951	3.215	0.999
	10	3.38	250.331	10.412	0.999
	15	2.02	196.124	8.067	0.999
	20	1.506	150.072	0.494	0.999
Cobalt	5	2.78	215.19	52.943	0.999
	10	2.15	174.154	3.591	0.999
	15	1.49	152.25	1.894	0.999
	20	1.41	140.0	1.146	0.999

4.3 Recovery of heavy metals after separation from its chelating agents

It is well known that solution pH affects solubility of metal ions and concentration of counter ions existing on the functional groups of biomass cell wall. Therefore, pH is an important parameter for the removal of metal ions from aqueous solutions [29].The role of pH on absorption processes can be explained as the following:

a) concentration of H^+ ions in the solution can affect the solubility of metal ions
b) H^+ ions can be replaced with positively charged ions, which are present in the active binding site of biomass, and
c) H^+ ions can affect the ionizing degree of sorbet during the reaction.

Chelating agents, such as EDTA, can form stable and soluble complexes with heavy metals and thus substantially increase heavy metal removal from contaminated water. In view of high stability constants of EDTA with heavy metals, EDTA-washing has been extensively studied for remediation of contaminated soils [36].

4.3.1 Determination of desorption potential of Na2EDTA for cobalt (II) and lead (II)

In order to determine the desorption ability of Na_2EDTA which shows higher efficiencies to desorbs the sorbed Co^{2+} ions from the biomass surface in other experiments,[1] desorption experiment was carried out following the sorption process. sorption capacity of the wood ash was found to be 96% for Cu^{2+} and 95.4% for Pb^{2+}under the studied experimental conditions [1], and these values were taken into consideration as a constant values to determine the desorption efficiency of Na_2EDTA contacting with the wood ash in the desorption study. The result of desorption efficiency Na_2EDTA of is shown in Table 4.9.

Table 4.9: Desorption efficiency of Na_2EDTA used for the recovery study

No	*adsorbed Cobalt (II) in mg/l*	*Copper (II) after adding Na_2EDTA in adsorbed metal solid (mg/l)*	*Desorption efficiency (%) of Co*	*adsorbed lead (II) in (mg/l)*	*Lead (II) after adding Na_2EDTA in adsorbed metal solid (mg/l)*	*Desorption efficiency (%) of Pb*
1	3.5	3.11	89	5.2	3.79	73
2	3.5	3.15	90	5.2	3.9	75
3	3.5	3.08	88	5.2	4.05	78
4	3.5	2.97	85	5.2	3.95	76

The experiment is carried out at $25^{O}C$, mixed at 200rpm with mixing time of 2hr, Solid to liquid ratio for desorption process was 5 and the Desorption solution (Na_2EDTA) has a concentration of 0.25M. The results of desorption experiment as given in table 4.9 shows that, higher desorption efficiencies of up to 90% for Co^{2+} and up to 78% for Pb^{2+} by using the solution of Na2EDTA. Based on the result of the study conducted with a bacterium biomass [31], reported that, solutions of HCl and HNO3 could recover more than 75% of sorbed Ni^{2+} and Co^{2+} ions on the biomass. The result of another study (Al-Qodah, 2006) showed that, HCl solution used for the desorption of Co^{2+} and Cd^{2+} give a desorption efficiency ranging between 70% and 85% for both of the metal ions, depending on the type of the biomass used in the study. reported that, by using HNO_3 solution of 0.1 mol/l and EDTA solution, he got a desorption efficiency of 85% and 82%, respectively, and he found out 0.1 mol/l $CaCl_2$ solution could recover almost 30% of sorbed Pb^{2+} ions, he also concluded that, while using of distilled water as desorption solution had no remarkable effect. In addition to findings of the desorption study, which was examined by Deng et al. (2007), several other studies are reached the same conclusion similar to this study. The study made by (Papandreou et al., 2007) pointed out that, desorption of Co^{2+} and Cd^{2+} ions could not be achieved in the case of using of distilled water as desorption solution . The extraction process of lead and copper with EDTA from the absorbed material should be followed by the recovery process in which the complex solution is treated further under appropriate conditions, including contact time, pH, and precipitant concentration. The recovered,relatively bio-stable chelator can then be reused in the next extraction-recovery cycle [32].

The study revealed that Na_2EDTA solution showed a good performance during the reuse study without a possible destruction on metal binding sites of the biomass when compared with the performance of HNO_3 and HCl solutions. The reason can be explained as Na_2EDTA can successfully bind many metal species to a coordinate bond to form a strong chelating compound. Although there are several types of EDTA chemicals (i.e., Cu–EDTA, H_4EDTA, Na_2EDTA) representing a variation depending on the main usage aim, the common feature for all of them is to have amino acid molecules existing in the chemical structure. This amino acid is widely used to sequester divalent and trivalent metal ions such as Mn(II), Cd(II), Ni(II), Cu(II), Pb(II), Co(III), and Fe(III). Binding of the metal ion to the coordinate bond of EDTA agent also occurs via four carboxylate and two amine groups [32].

4.3.2 Separation of Pb (II) and Co (II) from their chelating agent

Strong chelating agents such as EDTA extract heavy metals from contaminated matters more completely. However, an increasing challenge remains to recover both the extracted metals and the chelating agents for reuse. Reuse of the chelator at least three to four times is necessary for the process to be economical. Thus, chelation remediation with focus on recovery and reuse must be demonstrated. EDTA extracted heavy metals was amenable to recovery with the use of cationic and anionic precipitants such as calcium sulfide ions. It is capable of being reused several times with some loss of extraction activity. EDTA is relatively bio-stable and is only degraded partially under specialized condition, that is, via acclimated culture. The reuse potential of EDTA for metal extraction is high and this makes its use economically favorable as a strong, reusable and yet relatively bio-stable chelating agent. Many Experiments are conducted to demonstrate the effectiveness of recovering heavy metals and chelator from their complex solution by many authors in different methods [37]. These methods includes: degradation of heavy metal-EDTA complex and precipitation of heavy metal by calcium sulfide, Electrolytic recovery of binary metals, recovery of heavy metals by using electrochemical membrane cell and Photooxidation of Pb-EDTA by a H_2O_2/UV. In my case, Recovery of metals increases with increasing of the total metal concentration and to obtain an economically acceptable metal recovery, the complexed metal concentration should be sufficiently high. Finally, Pb-EDTA degradation by a H_2O_2/UV process was made by. According to the study, Pb EDTA degradation by a H_2O_2/UV process was shown to be accompanied by simultaneous lead precipitation. Photooxidation of Pb-EDTA was significantly degraded when H_2O_2 is combined with UV irradiation. This work shows that H_2O_2/UV process is an efficient process not only for degradation of the Pb-EDTA complex but also for the simultaneous removal of lead by precipitation. The precipitation of lead has been observed during irradiation in the presence of H_2O_2. Pb seems to be precipitated as lead hydroxide. The nature of metal was shown to have an important effect on metal–EDTA degradation and metal removal by the H_2O_2/UV process. In this study, Pb-EDTA was degraded more rapidly at pH 3 than at pH 6 and 8. A progressive metal removal was found when the pH of the solution was higher than 6.0. This confirms the important role of pH in metal precipitation. Therefore, except for the method of treating metal-EDTA complex with calcium sulfide; which produce metal sulfide (a more stable element); the other methods give free metal at the end the process. This makes the other processes more preferable than the sulfide process in terms of obtaining free metals at the end of the process, which can be used in other application directly. However, these processes are more costly, are not easily available and operable. As a result, calcium sulfide can be employed to recover Co (II) and Pb (II) from Metal-EDTA complex as metal sulfide which is more stable than the elemental lead and copper and for effectively reuse the recovered EDTA [38].

5. DESIGN AND SIZING OF THE ADSORPTION COLUMN

Disposal of waste water is common to many countries worldwide. Despite an increasing emphasis on alternative options; waste to energy conversion, recycling and reusing, retains an important role in most of developed countries as in developing countries where, the more sophisticated strategies have little applicability and basic drainage is more common. Paint waste water is the liquor that is collected at waste water tank. The amount of paint waste water generated in Zemilli paint factory is dependent on the production program of the paint, water generated rate, operational practice, and; precipitation, percolation and evaporation rate of waste water.

Increases in the extent of regulation of discharges of waste water effluent into the environment, will impose more restrictive limits on factory's operations that will be constructed on-site paint waste water treatment facilities and discharge their effluent into surface watercourses. Design of such treatment systems must continually advance to meet such discharge limits reliably and cost effectively. Although knowledge about paint waste water composition and variations in strength have increased greatly during recent years, many paint waste water treatment plants continue to be constructed that prove incapable of operating adequately, or of meeting required discharge standards reliably, consistently, and cost-effectively. Zemilli paint factory has chosen the new site at dukem-gelan, 20km South-east of Addis Ababa. The total area of the new site is 14,000 m^2. The design is being undertaking and it is believed that, the site will incorporate paint waste water treatment plant. Therefore, it is believed that this paper will contribute its part and can be used as a guideline during design of paint waste water treatment plant.

5.1 Determination of paint waste water generation rate

The key factors that affect paint waste water generation rate at Zemilli paint factory are:

I. **Production plan/demand:** the production program of the factory is one of the factor for the quantity of the waste water, if there is color different for each consecutive batches, there must have used much quantity of solvent for cleaning each tanker and machines. When the production program of the factory shifts more on solvent based paint there will be high concentration of heavy metal generated because of heavy metals intentionally used for solvent based paints for drying purpose. the production program in recent years composed of 30% solvent based paints (synthetic paint) and 70% water based paint (plastic paints) out of the total amount of production program [2].

II. **Operational practices:** the factory and operational practices are of critical importance in determining the amount of waste water produced and ultimately collected. Good surface water control during operation of the factory, which includes minimizing the area of the working face, diversion of clean water away from the working face, and timely and appropriate use of daily and intermediate sludge, are critical management methods needed to minimize the quantity of waste water produced at the factory.

III. **The factory layout:** waste water generation rate can vary depending on the production program, the availability of tankers, batch to batch color difference and other characteristics of the production. Zemilli paint factory, the paint waste water generation rate per batch (each 1000 lit) per day is 15liter/batch/day. The annual paint production in 2009/10 was 7,065,234 liters, and it generates around 353.5 liter/day [2].

5.2 Design of heavy metal adsorption tank

Heavy metal adsorption tank is designed for one day accumulation of the paint waste water from the Zemilli paint factory. Raw paint waste water is charged in the heavy metal adsorption tank and then discharged to biological treatment plant after the heavy metals are removed using wood ash by gravity.

First, raw paint wastewater and wood ash will be charged into the rapid mixing tank where the raw paint wastewater and the coagulant mix and it has a volume predetermined in material balance calculation, for the coagulation process at the optimum speed and such time can be used as time of mixing. Then the mixture passed into the slow mixing tank, for the flocculation process at optimum speed and time. A settling time allowed in the slow mixing tank.[47]

5.2.1 Principle of Adsorption System Design

The design of adsorbent units requires a number of information which is obtained from series of batch laboratory studies with regard to the amount of adsorbent and waste water usage. The purpose of conducting laboratory analysis also used to predict what will happen in a full-scale column with various operating parameters. These parameters include flow rate, feed and product concentration, column and bed height, particle size, service and contact time, treated volume of water, amount of adsorbent, pH, temperature and viscosity of the wastewater [42].

5.2.2 General design criteria

- Number of adsorption column(unit) = 1
- Shape of the tank = Cylindrical tank
- The adsorption column is designed for daily flow rate basis.

Parameters of paint waste water and wood ash used for design function.

- Viscosity of paint waste water = 0.00089kg/m.s or 50 ku
- Maximum paint waste water flow rate (Max.Q_{design}) = 500 lit/day or 0.5 m^3/day
- Maximum initial(influent) concentration of heavy metal(Max.Co_{design}) = 5.4 mg/l
- Maximum adsorption efficiency(%E_{design}) = 95%
- Density of paint waste water = 1.015318g/cm3 = 1015.318kg/m3
- Density of wood ash =0.986 g/cm3 = 986.00kg/m^3
- Selected Particle size of the wood ash = 50-80 µm
- pH of the raw waste water (used for design) = 6.8
- Average temperature of the paint waste water = 25 ^oc

5.2.3 Designing batch adsorption from equilibrium data

Generally adsorption process proceeds through varied mechanisms such as external mass transfer of solute onto adsorbent followed by intra-particle diffusion. Unless extensive experimental data are available concerning the specific adsorption application, determining the rate-controlling step is impossible. Therefore, empirical design procedures based on batch adsorption equilibrium conditions are the most common method to predict adsorber performance. Adsorption equilibrium is a dynamic concept achieved when the rate at which solute adsorb onto a surface is equal to the rate at which they desorbs [47].

Knowledge of adsorption models is very important; in addition to informing us of the adsorption capacity of a system, it enables us to evaluate to what extent an adsorption system can be improved, as well as helping us to predict the type of condition in which we have to work in order to broaden our study and estimate the necessary operation condition for the system to be as effective as possible. There are a number of batch adsorption models which have been used to explain the adsorption of solute on to the adsorbent. Some of them are Langmuir, Freundlich, the sips, the Redkich- Peterson, BET (Brunauel, Emmet and Teller) and the Toth isotherms. Among these the most commonly used equilibrium models to understand the adsorption systems are Freundlich and Langmuir isotherm equation [43]. These models are simple and have an ability to describe experimental results in wide ranges of concentration. Both models can be easily transformed in to linear forms to obtain adjustable parameters just by graphical means or linear regression analysis. In my case The Langmuir isotherm is select used for design purpose because of it is also best fit to the result.

Batch adsorption models are simple and useful to design batch treatment units. A commonly used fixed-bed mathematical model for flow and reaction in porous materials is the one dimensional advection dispersion equation that assumes linear sorption isotherm of the solute onto the solid surface.

$$\partial C/\partial t = D_e\, \partial_2 C/\partial x_2 - v_x \partial C/\partial X - \rho_s * 1-\varepsilon/\varepsilon * K_d\, \partial C/\partial t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5.1$$

Where,

C = the concentration of the solute;
De = effective diffusion coefficient;
ρ_s = the density of the solid phase;
ε = the porosity of the bed;
q = mass of solute sorbed per unit of sorbent;
v_x = average linear velocity of pore fluid in the x direction; and
K_d = the linear distribution coefficient.

The main objective of the above model is to predict the equilibrium point in more accurate manner. But in order to apply this models we need to have physical and kinetic parameter which can be obtained either from batch adsorption studies or form estimated literature values. In addition to that, the models require the solution of a number of non-linear partial differential equations which include physical as well as kinetic parameters. These equations can be solved only by numerical methods that are time consuming and tedious [44]. Therefore, I need to seek other simplified models to design batch adsorption column.

The operation of batch adsorption column is commonly expressed in terms of mass balance.

5.2.3.1 Material balance

In order to design adsorption column the amount of material that flow in to and out from the system should be known. The process of paint waste water pretreatment can be seen in the following figure. During adsorption process of heavy metal by wood ash, raw paint waste water and the wood ash charged in to the adsorber and the treated paint waste water leave the reactor as depicted in the figure below.

Adsorption isotherms can be used to predict the design of single-stage batch adsorption systems [56]. Based on the best fit isotherms, a single stage adsorber as shown in Fig. 5.1was designed for different solution volumes.

Consider an effluent containing V m^3 of solution and the heavy metal concentration reduced from C_0 to C_1 g heavy metal per m^3 solution. The amount of adsorbent is M kg and the solute loading changes from q_0 to q_1 mg heavy metal per kg adsorbent. When fresh adsorbent is used, $q_0 = 0$ and the mass balance equates the heavy metal removed from the waste water to that picked up by the wood ash. The mass balance equation for the sorption system in Fig. 5.1 can be written as

$$\mathbf{V\ (C_0 - C_1) = M\ (q_0 - q_1)} \text{ ………………………………………….5.2}$$

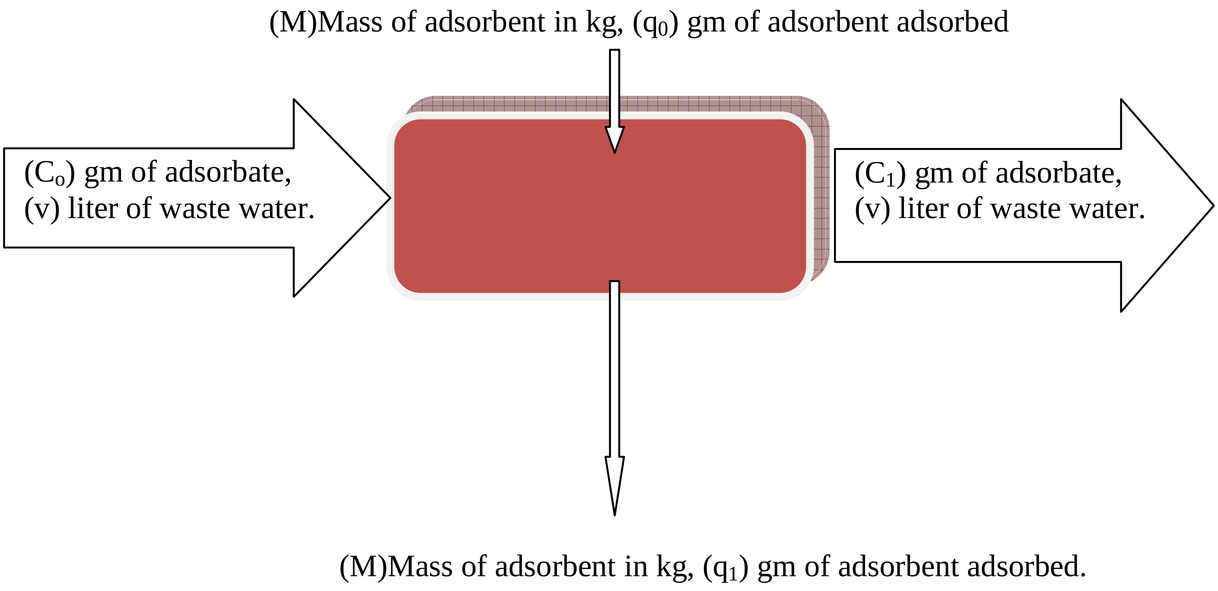


Figure. 5.1: Single stage contacting of a batch of fluid with a batch of adsorbent.

If the system is allowed to come to equilibrium, then, $C_1 >> Ce$ and $q_1 >> qe$ .In the case of the adsorption of heavy metal on wood ash the Langmuir isotherm gives the best fit to experimental data. Consequently, the Langmuir equation can be best substituted for q_1 in the rearranged form of Eq. 5.3 giving adsorbent/ adsorbate for a given change in dye concentration, $C_0 – C_e$, at this particular system

$$\mathbf{M/V = C_o – C_e/q_1 = C_o – C_e/q_e = C_o – C_e/\, K_LC_e/1+a_LC_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5.3}$$

Fig. 5.2 shows a series of plots derived from Eq. 5.2 for the adsorption of heavy metal on wood ash. An initial heavy metal concentration of 5.4mg/l is assumed and Fig. 5.2 shows the required amount of wood ash to reduce the heavy metal content by 80%-95% at various volumes of effluents. In the case of a single-stage batch adsorption system, the design procedure is now outlined. For example, 500 lit/day or 0.5 m^3 /day of 95 % of paint waste water with 5.4 mg/l are to be treated with wood ash, then the amount of wood ash needed can be determined by rearranging equation 5.3:

M = V* [(Co-Ce)/qe]

= 500 lit [5.4 mg/l – 0.27 mg/l)/75 mg/kg(from the result data at 95%removal)]

= **34.2 kg**

By using the same methods ,to calculate the amount of adsorbent used for each flow rate (influent volume) for different removal efficiency; The required masses of wood ash are 23.9, 26.0, 28.7 and 34.0 kg for 80%, 85%, 90% and 95% heavy metal removal respectively.

After that, to calculate the amount of treated amount of water, by using material balance for each heavy metal removal capacity. For 500 liter, maximum concentration of effluent waste water and 95 % removal, by using equation 5.2:

$$\mathbf{V\,(C_0 – C_e) = M\,(q_0 \cancel{-} q_e)}$$

500 liter (5.4 mg/l) – V (0.27 mg/l) = – 34 kg (75 mg/kg)

V= 456 liter

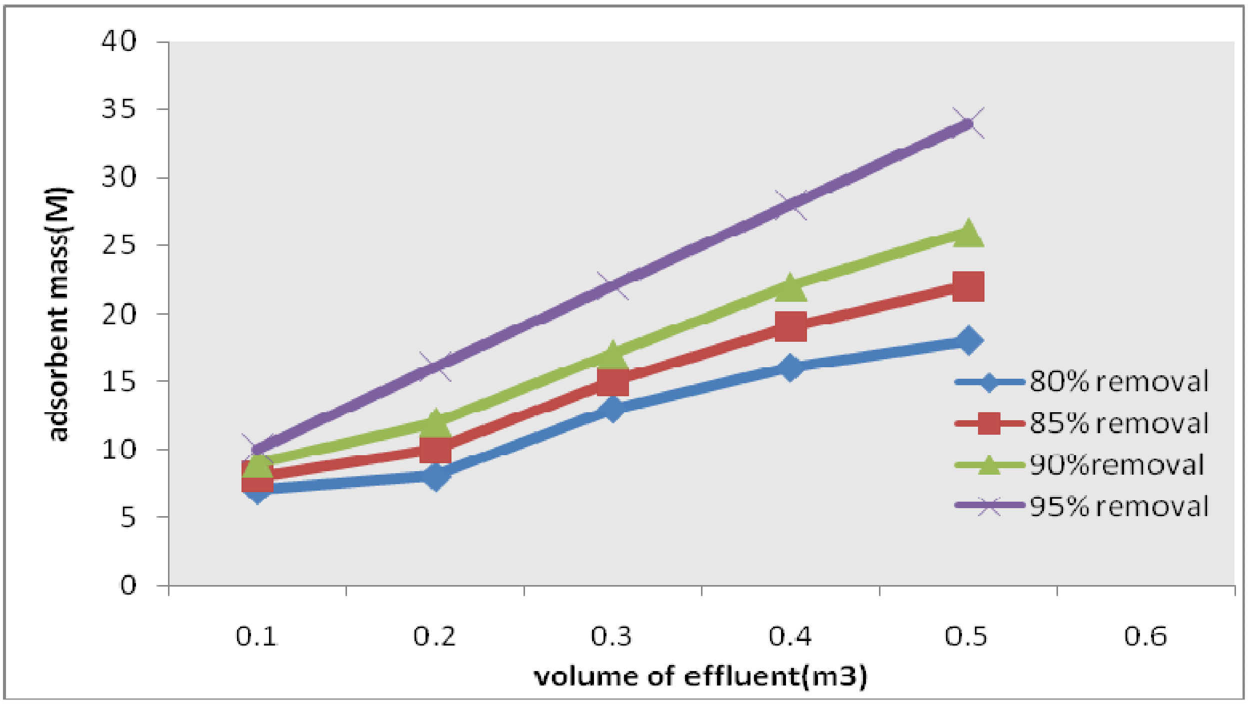


Figure. 5.2: Adsorbent mass (M) against volume of effluent (V) for various percentage of heavy metal removal at 5.4mg/l initial waste water concentration.

The process is batch wise and daily collection and treatment of paint waste water is assumed.

- The volume of adsorption tank (the volume occupied by the paint waste water and the adsorbent) can be determined by:

$V = (Q_{design} + Va) * T$ ……………………………………………………………..5.4

Where, V - volume of adsorption column

Q_{design} – maximum generation rate of paint waste water for the design period, (0.5 m3/day)

T- Detention time, determined by the experimental result of the equilibrium contact time, (90 min.)

Va - volume of wood ash added per cycle= (mass of wood ash /density of wood ash)

Va = 34 kg/986.0kg/m3

= 0.345 m^3

By substituting values in the above formula, the volume of the adsorption tank will be:

Taking 25% of the tank as free board, the total volume of the adsorption tank becomes:

$$V = [(0.5 + 0.345)*1.5\ \text{hr}] *1.25$$
$$= 0.544\text{m}^3$$

Standard size of reactor available in the market is 0.500m^3 or 0.550m^3 therefore; use a volume of 0.550m^3.Mild steel or stainless steel construction tank should be select.

$$\mathbf{V= \Pi D^2/4 *H \ldots\ldots 5.5}$$

$$0.55\ \text{m}^3= [\Pi D^2/4]*H$$

Where, D is diameter of the tank

H is height of the tank

- ✓ Take height to diameter ratio of H: D = 2

$0.55\ \text{m}^3 = \Pi D^3/2$

$D = 0.683\text{m}$

Total area of the column $(A) = \Pi D^2/4$

$= 0.366\ \text{m}^2$

$H = 2\times D =$ **1.36m**

For determining the service time of the column, the balance on the adsorber can be expressed according to the following equation:

$$\mathbf{Qv\ Co = QvCt + V_p\ dC/dt + m*dq/dt \ldots\ldots 5.6}$$

Where, Q_v is the volumetric flow of the solution in the column (liter/min),

C_0 and C_t , respectively, the influent and effluent solute concentrations (mg/l),

Q_vC_0 is the influent flow of solute in the column (mg/min),

Q_vC_t is the effluent flow of solute leaving the column (mg/min),

Batch type sorption is usually limited to the treatment of small volumes of effluent, whereas fixed bed systems have an advantage over this limitation. In fixed bed the adsorbate is continuously in contact with a given quantity of fresh adsorbent thus providing the required concentration gradient between adsorbent and adsorbate for adsorption.

From mass balance of a fixed-bed reactor, the determining factors of the balance for a given bed depth of the column are the linear flow rate (v), the initial waste water concentration, the adsorption potential and the pore volume even if the later parameter may be neglected. Therefore, in order to optimize the adsorption process in a packed-bed column it is necessary to examine these parameters and to estimate their influence [45].

By varying the above process parameters, the optimum conditions for the column operation can be predicted through different design methods. There are a number of simple design models available which are based upon general assumption.

The applicability of simplified models is extensively studied for the removal of organic solutes by activated carbon. And their applicability to model heavy metal adsorption is now emerging.

Ghorai [46] indicated that bed depth service time (BDST) model was applied successfully for heavy metal adsorption on to wood ash.

5.2.3.2 Bed Depth Service Time (BDST) Design Model

In a fixed-bed system, the main design criterion is to predict how long the adsorbent material will be able to sustain removing a specified amount of heavy metal from paint waste water before regeneration is needed. This period of time is called the service time of the bed [44]. The BDST model describes a relation between the service time of the column and the depth of column.

$$\ln[C_o/C_b - 1] = \ln(e (KN_o/v)D - 1) - KC_oT \ldots\ldots 5.7$$

In this relation $e^{(KNo/v)D} >> 1$ thus $\ln(e^{(KNo/v)D}) - 1 = KC_oT_b$ that is the reason why Hutchins [49] proposed the following linear relation between the column bed depth (D) and the service time (T_b):

$$T_e = N_o/ C_o V * D - 1/ KC_o \ln(Co /C_e - 1) \ldots\ldots 5.8$$

Where Te = the service time at equilibrium (h),

No = the bed capacity (mg/cm^3),

D = the fixed-bed depth (cm),

V = the linear flow rate through the column (cm/hr), Co and Ce are, respectively, the influent and the equilibrium heavy metal concentration (mg/l) and

K = the adsorption rate constant (liter/mg/hr).

The equation of a straight line on BDST curve is expressed as **y = ax + b**; where y = service time, x = bed depth, a = slope, and b = ordinate intercept. The numerical value of the slope (a) = N_0/C_0V and the intercept (b) = -{1/KC0 [ln (C_0/C_e–1)]}, the adsorptive capacity of the system, N0, and the rate constant, K, can be evaluated from the slope and intercept of a straight line plotted as the service time against the bed depth from experimental data, respectively. The minimum bed depth (D_{min}) which represents the theoretical depth of adsorbent able to prevent the adsorbent concentration from exceeding Ce, is obtained when Te = 0, according to the following equation:

$$D_{min} = v/KNo \ln (Co/Ce - 1) \quad \text{………………………………………… ...….5.9}$$

The slope of the line presented by **y = ax + b** can be used to predict the performance of the bed, if there is change in the initial solute concentration Co_1 to a new Co_2. Hutchins [48] proposed that the new slope $\mathbf{a_2}$ and new intercept $\mathbf{b_2}$ can be estimated by Eq. 5.8 and Eq. 5.9, respectively:

$$a_2 = a_1 * Co_1/Co \quad \text{……………………………………………………….....5.10}$$

$$B2 = b1 * \frac{Co1 \ln [(Co2/Cb) -1]}{Co2 \ln[(Co1/Cb) - 1]} \quad \text{……………………………………………...5.11}$$

McKay *et al.* [50] stated that if design data are required for a change in volumetric flow rate of solute to the same adsorption system, the new slope with the intercept remaining unchanged can be written as:

$$a_2 = a_1 * Q_1/Q_2 = a_1 * v_1/v_2 \quad \text{………………………………………………5.1}$$

- ✓ **Bed Depth Service Time Model results**

Figure 5.3 shows the BDST plots (Te versus D), which is constructed from the data in Table 5.1 for the influent heavy metal concentration of 5.4 mg/l and flow rates of 0.3, 0.4 and 0.5 m^3/day at equilibrium time for 28, 42, 56 and 70 cm bed heights. The coefficients No and K for the three flow rates are calculated based on Eq. 5.6. The slopes and intercepts for the BDST plots for the three flow rate are shown in Table 5.1.

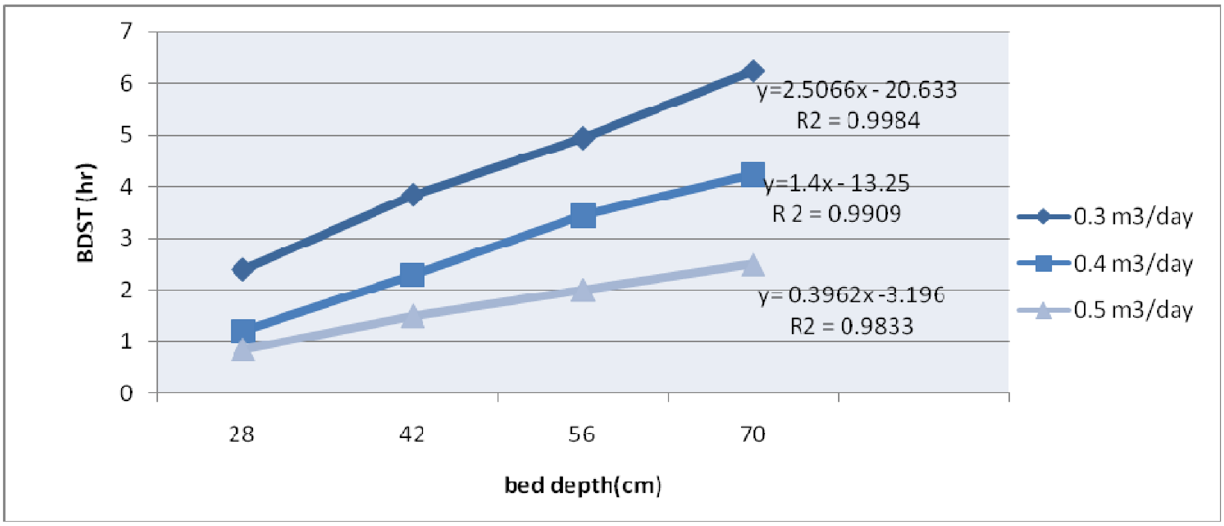


Figure. 5.3: BDST plot at equilibrium in a fixed-bed column at different flow rates: 0.3; 0.4; 0.5 m^3/day (Co = 5.4 mg/l).

Table 5.1: Constants of BDST curve

flow rate(m3/day),Q	slope	intercept	D_{min}(cm)	N_o(mg/cm^{-3})	K(liter/mg*hr)*10^{-3})	X(mg/g)
0.3	2.5	-20.53	25.19	8.69	6.12	24.07
0.4	1.4	-13.25	26.46	9.31	9.48	25.79
0.5	0.39	-3.196	24.58	4.58	39.3	12.7

Table 5.2: Data of variable bed depth at a fixed flow rate in a fixed-bed column for the removal of 5.4mg/l of lead by wood ash.

flow rate, Q (m^3/day)	bed depth, D (cm)	column volume, V (m^3)	mass of adsorbent, M(kg)	expected out put volume, Ve(m^3)	column service time, Te(hr)
0.3	28	0.509	13	0.234	2.40
	42	0.525	15	0.254	3.85
	56	0.541	17	0.268	4.95
	70	0.550	22	0.290	6.25
0.4	28	0.509	16	0.323	1.20
	42	0.525	19	0.349	2.30
	56	0.541	22	0.352	3.45
	70	0.550	28	0.378	4.25
0.5	28	0.509	18	0.407	0.85
	42	0.525	22	0.425	1.50
	56	0.541	26	0.436	2.00
	70	0.550	34	0.456	2.50

The data in Table 5.1 show that Ve and Te increased with decreasing flow rate or increasing bed depth. The equations of linear relationship were obtained with R_2 = 0.9984, 0.9909 and 0.9833 for 0.3, 0.4 and 0.5 m^3/day flow rates, respectively. The adsorption capacity (No) of the adsorbent was calculated to be 24.07, 25.79 and 12.7 mg/gm for 0.3, 0.4and 0.5 m^3/day flow rate, respectively. This shows that as the flow rate increases the adsorption capacity decreases. This may be due to decrease in contact time.

The BDST model can be applied to predict a model slope at other flow rates once the slope at a given flow rate is determined. The y-intercept value change is insignificant with respect to changing flow rate [51], the main assumption in the BDST mode is that the adsorbate is adsorbed on the adsorbent surface immediately such that there is no diffusion problem.. The calculated and experimental values of slopes are in good agreement. It is the advantage of the BDST model that any experimental test can be reliably scaled up for other flow rates without further experimental data and analyses. The schematic diagram of designed adsorption column with optimum design parameters is shown in the figure 5.4.

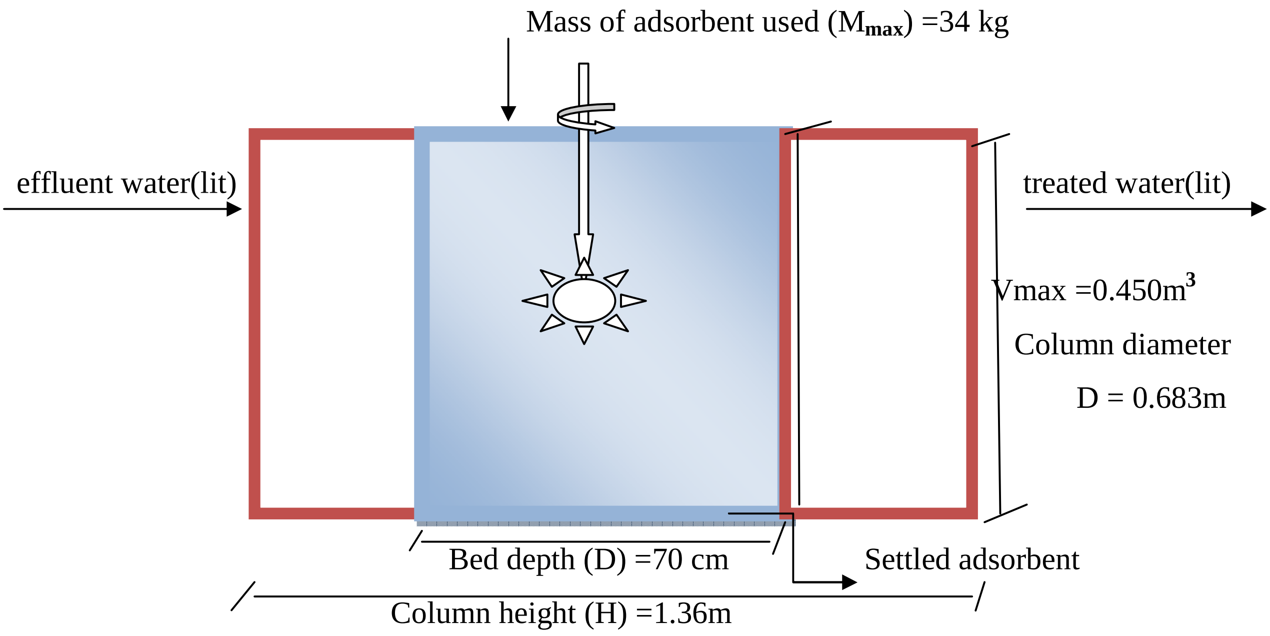


Figure. 5.4: The schematic diagram of designed adsorption column

5.2.4 Effects of design parameters

The model used, as described above, determines the outlet adsorbate concentration at different times based on different operating conditions. The models are studied by varying the different important parameters such as bed depth, flow rate and influent concentration. [52].

5.2.4.1 Effect of Bed Depth

The adsorption of heavy metals on to wood ash is presented in the form of equilibrium points where the concentration ratio C_e / C_o is plotted versus time. Figures 5.4 show the breakthrough curves of heavy metal adsorption on to wood ash at different bed depths (28, 42, 56, and 70 cm) and at a constant flow rate of 0.5 m3/day. Results indicate that the breakthrough volume Ve and breakthrough or equilibrium time Te increases with increasing bed depth. The breakthrough time Te is directly related with D according to Eq. 5.4, thus as the bed depth increases the breakthrough time also increase and which is in turn leads to an increase in treated water volume (Ve). When the bed depth increases, the adsorption performance increases due to the increase in adsorbent mass which provides greater adsorption sites.

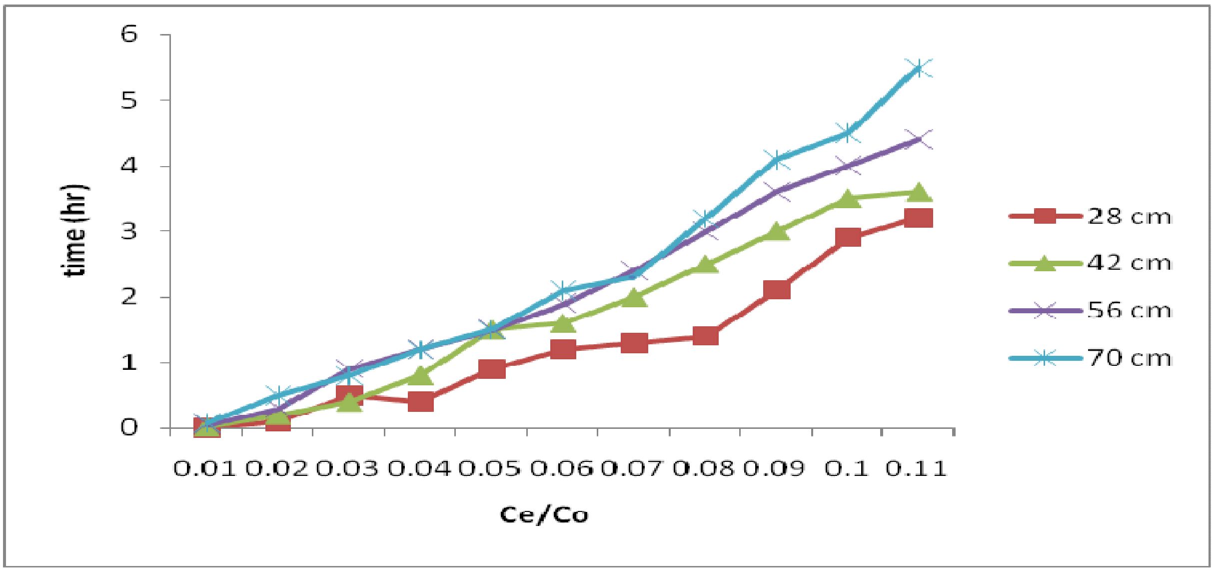


Figure. 5.5: Effect of bed depth on equilibrium time at a constant flow rate of 0.5 m^3 /day (C_o = 5.4mg/l).

5.2.4.2 Effect of flow rate

Figure 5.5, shows that the influence of flow rate on the time of breakthrough or equilibrium at fixed-bed depth of 70 cm. An increase in flow rate from 0.3 to 0.5 m^3 /day reduces the volume of treated at the breakthrough and therefore decreases the service time of the bed. As can be seen from Table 5.2, 96.5% of water was treated at a flow rate of 0.3 m^3 /day while 94.5% was treated at a flow rate of 0.4 m3/day and the break through time also reduced from 4.25 to 2.5 h for 0.4 and 0.5 m^3/day flow rates, respectively. This is due to the decrease in contact time between the heavy metal and the adsorbent at higher flow rate. As the adsorption rate is controlled by intraparticle diffusion, an early breakthrough occurs and leading to a low bed adsorption capacity [46]. When the flow rate decreases the contact time in the column is longer, intra-particulate diffusion then becomes effective. Thus the adsorbate will have more time to diffuse in to the particles of the adsorbent and a better adsorption capacity is obtained. The slope of the BDST plot will be higher for smaller flow rates.

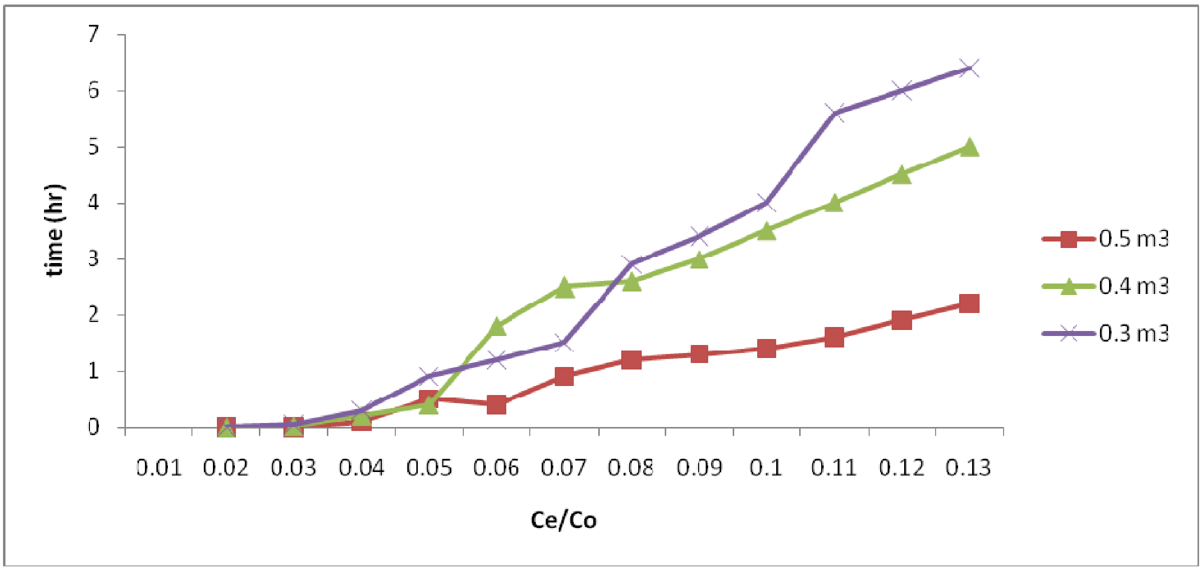


Figure. 5.6: Effect of flow rate on breakthrough time in a 70 cm fixed-bed column: 0.3; 0.4; 0.5 m^3/day (C_0 = 5.4 mg/l).

5.2.4.3 Effect of influent concentration

The effect of influent concentration at 3.7 and 5.4 mg/l heavy metal with fixed flow rate of 0.5 m3/day is shown in Figure 5.6. It can be seen that rising in the influent concentration reduces the breakthrough time and also the volume of treated water. A high influent concentration may saturate the media more quickly, and thereby decreasing the breakthrough time. The service time Te (2.5 hr) which is calculated using Eq. 5.8 and 5.9 for 5.4 mg/l solution with 70 cm bed depth was somewhat greater than to the experimental value which is 1.5 hr.

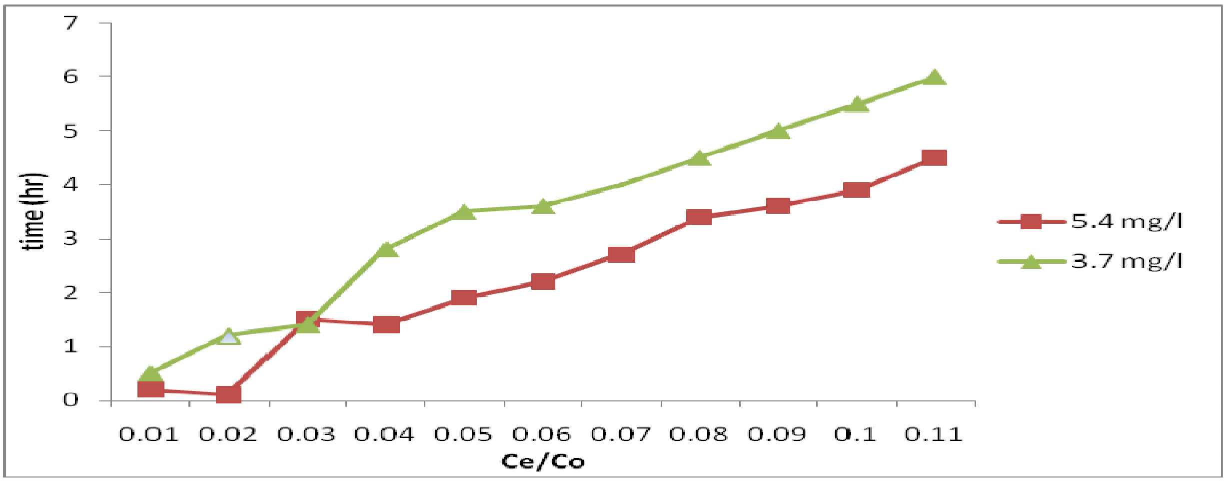


Figure. 5.7: Effect of initial heavy metal concentration on bed service time (Q_v = 0.5 m^3/day, D = 70 cm.

6. CONCLUSIONS AND RECOMMENDATION

6.1 Conclusion

As a result of the performed analyses on paint waste water treatment; which is generated from Zemilli paint factory ; to remove heavy metals with locally available material wood ash , the following conclusions and remarks are given: The study examined removal and recovery of Co^{2+} and Pb^{2+} ions from paint waste water by using indigenously prepared adsorbent, wood ash under differential experimental conditions such as contact time, pH and adsorbent dose; to investigate optimum values of the mentioned parameters. It is shown that the changes in those parameters affect the adsorption process and changes the obtained values of the amounts of ions adsorbed. The differential parameters of the process such as, pH, dose of ash and equilibrium time were optimized at 8, 20 gm/l and 90 min, for cobalt and 10, 20gm/l and 90min for lead respectively. The adsorption of metal ions is heavily dependent on these parameters of the paint wastewater. Equilibrium and kinetic studies were conducted for the adsorption of lead and cobalt from paint waste water on to wood ash. The equilibrium data have been analyzed during Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of lead and cobalt on to wood ash. The kinetics of adsorption of lead and cobalt on to wood ash was studied by using pseudo-second order equation, for the examined system; the pseudo second-order kinetic model provided the best correlation of the experimental data. The pseudo second order equation based on the adsorption capacity on the solid phase and is in agreement with chemisorptions mechanism being the rate controlling step. The adsorption of lead and cobalt on wood ash can also is successfully interpreted by the pseudo –second order equation. The adsorption equilibrium was reached within 1.5hr at room temperature. In this study, cobalt removal efficiency of wood ash was 94.5% and lead removal of 97.0% was achieved at optimum studied condition. Significant data were obtained through this study for the removal of lead and cobalt by wood ash adsorption. Wood ash appears to be a promising adsorbent for the removal of cobalt and lead. Based on the results noted for cobalt and lead, wood ash may also be suitable for other heavy metals too. At these adsorption levels, a process using wood ash for the removal and recovery of heavy metals is potentially more economical than current process technology. Additionally, Metals stripping by Na_2EDTA solution, it showed good desorptive performance to regenerate the biomass. During the study higher desorption efficiencies of up to 90% for Co^{2+} and up to 78% for Pb^{2+} by using the solution of Na_2EDTA Adsorption column design was also studied in this work. The adsorption column is designed based on different design parameters and its dimensions are sized by optimized conditions. Through this study, essential data was obtained for engineering design.

6.2 Recommendations

- It is recommended that wood ash can be used, as a low cost and abundant source, for the removal of heavy metals and it may be an alternative to more costly materials. For wood ash as adsorbent of heavy metal the treatment method is expected to be economical and environmental.
- Based on the results presented, and that wood ash is suggested that significant potential as absorbent for application in the remediation of metal contaminated wastewater including paint waste water.
- There are high oscillations of the paint waste water quantity and quality during time. Paint waste water contains many constituents and its quality is multidimensional. Due to that, when designing paint waste water treatment plant, special attention should be paid to the paint waste water design parameters in terms of its quantity and quality.

REFERENCES AND BIBLIOGRAPHY

1. Yegenetfere Argaw, leachate treatment to remove heavy metals by using moringa stenopetala (the case of Addis Ababa MSW dumping site) MSc thesis Addis Ababa university, Ethiopia, June, 2010

2. Zemilli Paint Factory, Company's production complied documents, 1999 – 2010

3. M. Malakootian, A. Almasi, 1H. Hossaini, Pb and Co removal from paint industries effluent using wood ash, 2008

4. Paul Nylen and Edward Sunderland, Modern surface coatings: - a text book of the chemistry and technology of paints, varnishes and lacquers, 1965

5. H. Asilian, Sh. Moradian fard, A. Rezaei, S. B. Mortazavi and A. Khavanin The removal of color and COD from wastewater containing water based paint by coagulation process,1998.

6. Wikipedia the free encyclopedia retrieves on September 25, 2010.

7. Charles U. Pittman Jr.and Dinesh Mohana, Arsenic removal from water/wastewater using adsorbents—A critical review, 2006

8. Wossen Tafere, Optimization of physicochemical parameters for the removal of chromium from waste water by Moringa Stenopetala seed extract, Masters Thesis. Addis Ababa University, Ethiopia, 2008.

9. EPA, Environmental Policy of Ethiopia. Environmental Protection Authority of Ethiopian in Collaboration with Ministry of Economic Development and Cooperation, Addis Ababa – Ethiopia, April 2, 1997.

10. The Federal Government of the Democratic Republic of Ethiopia water resources management policy, 1998.

11. Tesfaye Zewdie, Groundwater and Public Health risk analysis in the vicinity of Addis Ababa city solid waste dumping site, Reppi, MSc thesis, Addis Ababa University, Ethiopia, 15-24, 2007.

12. American Public Health Allocation (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF), Standard Method for the Examination of Water and Wastewater, 20th edition, APHA Publication office, Washington D.C.,1998.

13. Girma Hailu , Environmental law of Ethiopia.78-95,2000.

14. Mark A. Shannon, Science and Technology for Clean Drinking Water and Sanitation Director Water CAMPWS James W. Bayne Professor of Mechanical Science and Engineering. University of Illinois Urbana-Champaign, 2002.

15. Anteneh Mesfin, Biosorption of selected heavy metals by brewery derived yeast biomass, MSc thesis, Addis Ababa University, Ethiopia, may 2009.

16. Pataule Didier Kalibantonga adsorption of heavy metals from solution by South African industrial clay. MSc thesis, Department of Chemical and Metallurgical engineering, Tshwane University of Technology, 29-45, 62-72, 2005.

17. D.M.Ruthven, Principles of Adsorption and Adsorption Processes, Wiley, New York, 1984.

18. M.C. Ncibi, Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis, J. Hazard. Mater. 153, 207–212, 2008.

19. Babel, S., Kurniawan, T.A., Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J. Hazardous Mater. B97, 219–243, 2003.

20. Pushpa Kumari, Parul Sharma, Shalini Srivastava and M.M. Srivastava, Biosorption studies on shelled *Moringa oleifera* Lamarck seed powder: Removal and recovery of arsenic from aqueous system, Department of Chemistry, Faculty of Science, Dayalbagh Educational Institute, Dayalbagh, India International Journal of Mineral ProcessingVolume 78,Pp 131-139. (2005).

21. Liping Deng, Xiaobin Zhu , Xinting Wang, Yingying Su and Hua Su, Biosorption of copper(II) from aqueous solutions by green alga *Cladophora fascicularis* , Volume 18, , 393-402, Earth and Environmental Science, 2006.

22. K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems: Review, Chemical Engineering Journal 156, 2–10, 2010.

23. Abdus-salam and adekola, the influence of pH and adsorbent concentration on adsorption of lead and zinc on a natural goethite department of chemistry, university of Ilorin.

24. Emrah bulut , mahmut zacar , ayhan stencil adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design, department of environmental engineering, engineering faculty, sakarya university, , Turkey ,February 2008.

25. Baranowska, k. Srogi, Włochowicz, Szczepanik determination of heavy metal contents in samples of medicinal herbs department of analytical and general chemistry, Silesian technical university, Poland April, 2002.

26. P. senthil kumar, k. kirthika, equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder department of chemical engineering, college of engineering, India.

27. Tait chirenje1, lena q and liping , Retention of Cd, Cu, Pb and Zn by wood ash, lime and fume dust soil and water science department university of Florida Gainesville.

28. Laura Bulgariu1, Mioara Ratoi1, Dumitru bulgariu, equilibrium study of Pb(II) and Hg(II) sorption from aqueous solutions by moss peat ”gheorghe. asachi” technical university of IASI, faculty of chemical engineering and environmental protection, department of environmental engineering and management.

29. Shuguang Lu, Stuart W. Gibb, Copper removal from waste water using spentgrain as biosorbent, College of Resources and Environmental Engineering, East China University of Science and Technology, No. 130, Meilong, Shanghai, PR China, 2008.

30. M. Abdullahi, Characteristics of Wood Ash/OPC Concrete, Civil Engineering Department, federal University of Technology, P.M.B. 65, Minna, State of Nigeria, June 2006.

31. Man-Seung Leea,, Jong-Gwan Ahnb, Jae-Woo Ahnc, Recovery of copper, tin and lead from the spent nitric etching solutions of printed circuit board and regeneration of the etching solution, 2003.

32. Mehmet Kılıç, Hüseyin Yazıcı, Murat Solak, A comprehensive study on removal and recovery of copper (II) from aqueous solutions by NaOH-pretreated Marrubiu globosum ssp. Globosum leaves powder: Potential for utilizing the copper (II) condensed desorption solutions in agricultural applications. Bioresource Technolog100 2130–2137, 2009.

33. Ruey-Shin Juang, M, and Shiow-Wen Wang, Metal recovery and EDTA recycling from simulated washing effluents of metal-contaminated soils, Department of Chemical Engineering, Yuan Ze University, Taiwan, 2000.

34. Ruey-Shin Juang M and Shiow-Wen Wang, Electrolytic recovery of binary metals and EDTA from strong complexed solutions, Department of Chemical Engineering, Yuan Ze University, Taiwan, 1999.

35. D. Jiraroja, F. Unoba, A. Hage`geb, Degradation of Pb–EDTA complex by a H_2O_2/UV process .Faculty of Science, Department of Chemistry, Chulalongkorn University, Bangkok, Thailand, 2005.

36. Weihua Zhang a,1, Daniel C.W. Tsang b, Irene M.C. Loc, Removal of Pb by EDTA-washing in the presence of hydrophobic organic contaminants or anionic surfactant .School of

Environmental Science & Engineering, Sun Yat-Sen University, China Kowloon, Hong Kong.65, 2007.

37. P. K. Andrew Hong a; Chelsea Li a; Shankha K. Banerji b; Tulsi Regmi, Extraction, Recovery, and Biostability of EDTA for Remediation of Heavy Metal- Contaminated Soil. Department of Civil and Environmental Engineering, University of Utah, Salt Lake City.China Kowloon, Hong Kong, 1999.

38. Ruey-Shin Juang, Shiow-Wen Wang, Li-Chun Lin, Simultaneous recovery of EDTA and lead(II) from their chelated solutions using a cation exchange membrane. Journal of Membrane Science 160, 1999.

39. S. Petrov, V. Nenov, Removal and recovery of copper from wastewater by a complexation-ultrafiltration process, pp 201-209, 2003.

40. Csuros, Maria, Environmental sampling and analysis for metals, 2002.

41. Vasanth, K. K.; Subanandam, K.; Ramamurthi, V.; Sivanesan, S. Solid Liquid Adsorption for Wastewater Treatment: Principle Design and Operation, Anna University, in Chennai-India, February 2004.

42. Ko Chun, K. D. Mass transfer modeling for fixed-bed sorption of metal ions on bone char. PhD. Thesis, the Hong Kong University Science and Technology, Hong Kong, Feb.2002.

43. Orhan, A.; Onder Ozbelge, H.; Timur, D. Use of general purpose adsorption isotherms for heavy metal-clay mineral interactions. J. colloid and Interface Sci, 198: 130-140, 1998.

44. Liljana, M.; Vera, M.; Vladimir, N. Adsorption of basic dyes in a fixed-bed column. Korean J. Chem. Eng, 18 (2): 190-195, 2001.

45. Christian, T. V.; Henri, F.; Catherine, P.; Yuh-Shan, H. Removal of lead (II) ions from synthetic and ream effluents using immobilized Pinus Sylvestris sawdust: Adsorption on a fixed bed column. J. Hazardous Material B, 123: 135-144, 2005.

46. Ghorai, S.; Pant, K. K. Equilibrium, kinetics and breakthrough studies for adsorption of Fluoride on activated alumina. Sep. Puri. Technol, 42(3): 265-271, 2005.

47. Coulson and Richardson’s, Chemical engineering design, vol.6 department of Chemical engineering, university college of Swansea,589-594, 1996.

48. Kent s. Knaebel A “how to” guide for adsorber design adsorption research, inc. Dublin, ohio, 2006.

49. Hutchins, R. A. New methods simplify design of activated carbon systems, Am. J. Chem. Eng, 80: 133-138, 1973.

50. McKay, G.; Blair, H. S.; Gardner, J. R., The adsorption of dyes on to chitin in fixed-bed columns and batch adsorbers. J. Appl. Polym. Sci, 29:1400-1409, 1984.

51. Danny C. K, Ko. ; Vinci, K. L.; John, F. P., Gordon, M. Improve design and optimization models for the fixed-bed adsorption of acid dye and zinc ion from effluents. J. Chem. Technology and Biotechnology, 77: 1289-1295, 2002.

52. Eyobel Mulugeta Damte, Removal of fluoride from water using granular aluminum hydroxide: adsorption in a fixed-bed column, MSc thesis Addis Ababa University, Ethiopia 2006.

ANNEXES

Annex 1: List of apparatus

I. Atomic Absorption spectrophotometer and associated equipments:

- Burner head, conventional, single 7.6cm (3in) long slot.

II. Analytical Instruments

Separator funnels: 250ml, with Teflon stopcocks, Sample bottles, pipettes, measuring cylinder, pH meter, spoons, Screen, sieve analyzer, vacuum filter, reagent bottle, oven, Attrition Mill, Bucher funnel, Crucibles, Hettich universal II centrifuge, Digital balance, Excella E 24 incubator shaker, moisture analyzer, Conical flask, Digital pH meter, Desiccators, Muffle furnace, Pycnometer, Griffin shaker, Membrane filter.

Annex 2: List of chemicals and materials

I. Acetylene, standard commercial grade

II. De-ionized distilled water

III. Indicators

IV. Nitric acid conc.

V. Sodium hydroxide

VI. Na_2EDTA

VII. Hydrochloric acid conc.

VIII. Wood ash

X. Advantec, filter paper

Annex 3: Laboratory procedures

3.1 wood ash collection and preparation

I. Dry wood ash was collected from different selective home kitchen by checking their source is wood.

II. The ash was stored at room temperature.

III. The ash is sieved and separated from any other dirt.

IV. The sieved ash is then measured its ash content using dry and wet methods.

V. measure the other test parameters such as dry density, porosity and moisture content of the ash.

3.2 paint waste water collection

Nine different sampling points were prepared from the immediate outlet up to the equalization thank. The samples then collected following the standard procedures of sample collection.

3.3 Sample preparation and preservation

Paint waste water samples were filtered through a 0.45-μm filter paper prior to preservation. Filter papers are acid washed and dried before use. After the sample is filtered, the filtrate were taken as a sample for dissolved metals and acidified for preservation purpose. (According to Environmental sampling analysis)

3.4 Determination of heavy metal content

Heavy metal concentration was determined using atomic absorption spectroscopy (Shimadzu AA-680G V-5) with an air-acetylene flame as described by APHA (1990) [31].

3.4.1 Preparation of AAS Standard Solutions

Standards for the establishment of calibration curves for AAS were prepared as follows:

Make up 20, 40, 60, 80 and 100 mg/L standard solution of Pb (II), Co (II), Cr (VI), Zn (II), Hg (II), Cd (II) and Cu (II) by diluting 4, 8, 12, 16 and 20 ml of the 500 mg/L standard solution to 100 ml (using a 100 ml volumetric flask). Those are precautions to be taken when preparing a standard solution:

1. To ensure accuracy in preparation, great care must be taken at all stages, with careful, accurate weighing, careful transfer of solid and clean glassware.
2. Solids that are to be used to make standard solutions must fulfill some criteria, i.e. they must be pure, dissolve in water easily, should not decompose and have a relatively high molar mass.

3.4.2 Procedure for analysis by an Atomic Absorption Spectrometer

The procedure for analysis is as follows:

1. Choose the proper (the relevant) hollow cathode lamp.
2. Align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width (set prescribed monochromator slit width), and adjust the hollow cathode current (set prescribed lamp current) according to the manufacturer’s recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant.
3. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer (optimize the lamp orientation for maximum).

4. Aspirate distilled water (when not running a standard or sample). The absorbance should be zero; this number (0 ppm, 0 abs) is a data point for the subsequent calibration curve.
5. Run a series of standards of the element under analysis and construct a calibration curve by plotting the concentrations of the standards against the absorbance.
6. Aspirate the samples and determine the concentrations from the calibration curve.
7. Read the metal concentration value in mg/l from the calibration curve.

The analysis on the AAS of each sample was carried out in duplicate and the mean was computed for each set of values.

3.4.3 Parameters and operating conditions for the AAS

3.4.3.1 AAS Parameters

1. Lamp: hollow cathode lamp
2. Fuel: Acetylene
3. Oxidant: Air

3.4.3.2 Operating Conditions for the AAS

The operating conditions of the AAS for each metal ion are shown in the table below:

metal ion	lamp current (mA)	wavelength (nm)	slit width (nm)
pb(ll)	15	283.3	0.7
Co(ll)	15	341.5	0.7

3.5 Heavy metal removal

50ml of paint waste water which contain heavy metal were prepared and a predetermined amount extract of wood ash will be added at a predetermined condition. The mixture shaken for specified time at 200rpm, centrifuged for 15 minutes at 300rpm and then the supernatant taken to be analyzed for the given metal concentration on an atomic absorption spectrophotometer.

Percentage metal uptakes (%E) were calculated by use of equation.

$$\%E = \frac{\underline{(Co, — C_f)}}{Co} \text{ x } 1OO$$

Where, C_0 and C_f are the initial and final concentrations respectively of metal ions in solution. Plots of % metal bound for a given metal and wood ash were made in order to study the pH dependence of the metal sorption reaction by the ash.

ANNEX 5. MULTIFACTOR COMBINATION TABLE

The factors: pH, contact time and dose of wood ash; and the response variables: Percentage removal of cobalt (II) and percentage removal of lead (II) with a factor level of four, for each factor and the replicate.

Contact time(min.)	***PH***	***Dose of wood ash (g/l)***	***Ci for Co (mg/l)***	***Cf for Co (mg/l)***	***R of Co (%)***	***Ci for Pb (mg/l)***	***Cf for Pb (mg/l)***	***R of Pb (%)***
30	4	5	3.7	2.1	43.3	5.4	2.5	53.7
30	4	10	3.7	1.7	54.1	5.4	2.4	55.6
30	4	15	3.7	1.6	56.8	5.4	2.1	61.2
30	4	20	3.7	1.3	64.9	5.4	1.8	66.7
30	6	5	3.7	1.8	51.4	5.4	2.35	56.2
30	6	10	3.7	1.65	55.4	5.4	2.2	59.0
30	6	15	3.7	1.5	59.5	5.4	2.0	63.0
30	6	20	3.7	1.1	70.3	5.4	1.8	66.7
30	8	5	3.7	1.2	67.6	5.4	1.7	68.6
30	8	10	3.7	0.9	75.7	5.4	1.5	72.3
30	8	15	3.7	0.8	78.4	5.4	1.4	74.1
30	8	20	3.7	0.6	83.8	5.4	1.25	76.5
30	10	5	3.7	1.3	64.9	5.4	1.4	74.1
30	10	10	3.7	1.3	64.9	5.4	1.2	77.5
30	10	15	3.7	1.1	70.3	5.4	1.1	79.2
30	10	20	3.7	0.7	81.1	5.4	1.0	81.2
60	4	5	3.7	1.6	56.8	5.4	1.2	77.5
60	4	10	3.7	1.5	59.5	5.4	1.1	79.2
60	4	15	3.7	1.3	64.9	5.4	0.9	83.4
60	4	20	3.7	1.1	70.3	5.4	0.9	83.4
60	6	5	3.7	1.5	59.5	5.4	1.2	77.5
60	6	10	3.7	1.3	64.9	5.4	1.1	79.2
60	6	15	3.7	1.3	64.9	5.4	1.1	79.2

60	6	20	3.7	1.0	73.0	5.4	1.0	81.5
60	8	5	3.7	1.5	59.5	5.4	1.0	81.5
60	8	10	3.7	1.2	67.6	5.4	1.1	79.2
60	8	15	3.7	1.2	67.6	5.4	1.0	81.2
60	8	20	3.7	1.1	70.3	5.4	0.8	85.2
60	10	5	3.7	1.4	62.2	5.4	0.92	83.5
60	10	10	3.7	1.3	64.9	5.4	0.85	85.0
60	10	15	3.7	1.3	64.9	5.4	0.8	85.2
60	10	20	3.7	1.0	73.0	5.4	0.6	89.0
90	4	5	3.7	1.1	70.3	5.4	1.0	81.2
90	4	10	3.7	1.0	73.0	5.4	1.0	81.2
90	4	15	3.7	0.8	78.4	5.4	0.8	85.2
90	4	20	3.7	0.9	75.7	5.4	0.58	89.0
90	6	5	3.7	1.0	73.0	5.4	1.02	81.0
90	6	10	3.7	1.0	73.0	5.4	0.84	85.0
90	6	15	3.7	0.8	78.4	5.4	0.7	87.1
90	6	20	3.7	0.7	81.1	5.4	0.6	88.9
90	8	5	3.7	0.7	81.1	5.4	0.9	83.5
90	8	10	3.7	0.4	89.2	5.4	0.7	87.1
90	8	15	3.7	0.3	91.9	5.4	0.5	90.8
90	8	20	3.7	0.2	94.6	5.4	0.5	90.8
90	10	5	3.7	0.7	82	5.4	0.9	83.5
90	10	10	3.7	0.6	83.8	5.4	0.68	87.0
90	10	15	3.7	0.32	92	5.4	0.5	90.8
90	10	20	3.7	0.4	89.2	5.4	0.3	94.5
120	4	5	3.7	0.9	75.7	5.4	0.7	87.0
120	4	10	3.7	1.0	73.0	5.4	0.55	90.0
120	4	15	3.7	1.08	75	5.4	0.35	93.6
120	4	20	3.7	0.4	90	5.4	0.3	94.5
120	6	5	3.7	0.75	78.8	5.4	0.6	88.9
120	6	10	3.7	0.7	80	5.4	0.65	87.5

120	6	15	3.7	0.5	86.5	5.4	0.6	89.0
120	6	20	3.7	0.35	91	5.4	0.5	90.8
120	8	5	3.7	0.52	87	5.4	0.4	92.6
120	8	10	3.7	0.35	91	5.4	0.3	94.5
120	8	15	3.7	0.4	89.5	5.4	0.25	95
120	8	20	3.7	0.25	93.5	5.4	0.2	96.5
120	10	5	3.7	0.52	87	5.4	0.35	93.6
120	10	10	3.7	0.42	90	5.4	0.25	95.0
120	10	15	3.7	0.3	92	5.4	0.2	96.5
120	10	20	3.7	0.2	94.5	5.4	0.15	97.0
Replicates								
30	4	5	3.7	2.0	43.0	5.4	2.5	53.7
30	4	10	3.7	1.7	54.1	5.4	2.4	55.6
30	4	15	3.7	1.65	55.4	5.4	2.1	61.2
30	4	20	3.7	1.3	64.9	5.4	1.8	66.7
30	6	5	3.7	1.8	51.4	5.4	2.3	57.2
30	6	10	3.7	1.65	55.4	5.4	2.2	59.0
30	6	15	3.7	1.45	59.5	5.4	2.0	63.0
30	6	20	3.7	1.0	72.3	5.4	1.8	66.7
30	8	5	3.7	1.2	67.6	5.4	1.7	68.6
30	8	10	3.7	0.9	75.7	5.4	1.52	72.0
30	8	15	3.7	0.89	78.4	5.4	1.4	74.1
30	8	20	3.7	0.6	83.8	5.4	1.25	76.5
30	10	5	3.7	1.2	64.9	5.4	1.45	73.0
30	10	10	3.7	1.35	62.5	5.4	1.2	77.5
30	10	15	3.7	1.1	70.3	5.4	1.12	78.2
30	10	20	3.7	0.7	81.1	5.4	1.0	81.2
60	4	5	3.7	1.7	53.8	5.4	1.2	77.5
60	4	10	3.7	1.5	59.5	5.4	1.1	79.2
60	4	15	3.7	1.3	64.9	5.4	0.9	83.4
60	4	20	3.7	1.0	73.3	5.4	0.9	83.4

60	6	5	3.7	1.5	59.5	5.4	1.2	77.5
60	6	10	3.7	1.25	64.0	5.4	1.1	79.2
60	6	15	3.7	1.3	64.9	5.4	1.1	79.2
60	6	20	3.7	1.1	70.0	5.4	1.0	81.5
60	8	5	3.7	1.5	59.5	5.4	1.0	81.5
60	8	10	3.7	1.2	67.6	5.4	1.1	79.2
60	8	15	3.7	1.15	67.6	5.4	1.0	81.2
60	8	20	3.7	1.0	71.3	5.4	0.8	85.2
60	10	5	3.7	1.4	62.2	5.4	0.92	83.5
60	10	10	3.7	1.3	64.9	5.4	0.7	86.0
60	10	15	3.7	1.2	62	5.4	0.8	85.2
60	10	20	3.7	1.0	73.0	5.4	0.6	89.0
90	4	5	3.7	1.1	70.3	5.4	1.0	81.2
90	4	10	3.7	1.25	71.0	5.4	1.1	79.2
90	4	15	3.7	0.8	78.4	5.4	0.8	85.2
90	4	20	3.7	0.9	75.7	5.4	0.58	89.0
90	6	5	3.7	1.0	73.0	5.4	1.02	81.0
90	6	10	3.7	1.0	73.0	5.4	0.85	86.0
90	6	15	3.7	0.8	78.4	5.4	0.7	87.1
90	6	20	3.7	0.7	81.1	5.4	0.5	90.9
90	8	5	3.7	0.7	81.1	5.4	0.8	83.5
90	8	10	3.7	0.4	89.2	5.4	0.8	87.1
90	8	15	3.7	0.3	91.9	5.4	0.55	91.8
90	8	20	3.7	0.2	94.6	5.4	0.5	90.8
90	10	5	3.7	0.7	82	5.4	0.7	87.5
90	10	10	3.7	0.6	83.8	5.4	0.68	87.0
90	10	15	3.7	0.32	92	5.4	0.5	90.8
90	10	20	3.7	0.45	89.2	5.4	0.3	94.5
120	4	5	3.7	0.9	75.7	5.4	0.7	87.0
120	4	10	3.7	1.0	73.0	5.4	0.55	90.0
120	4	15	3.7	1.08	75	5.4	0.35	93.6

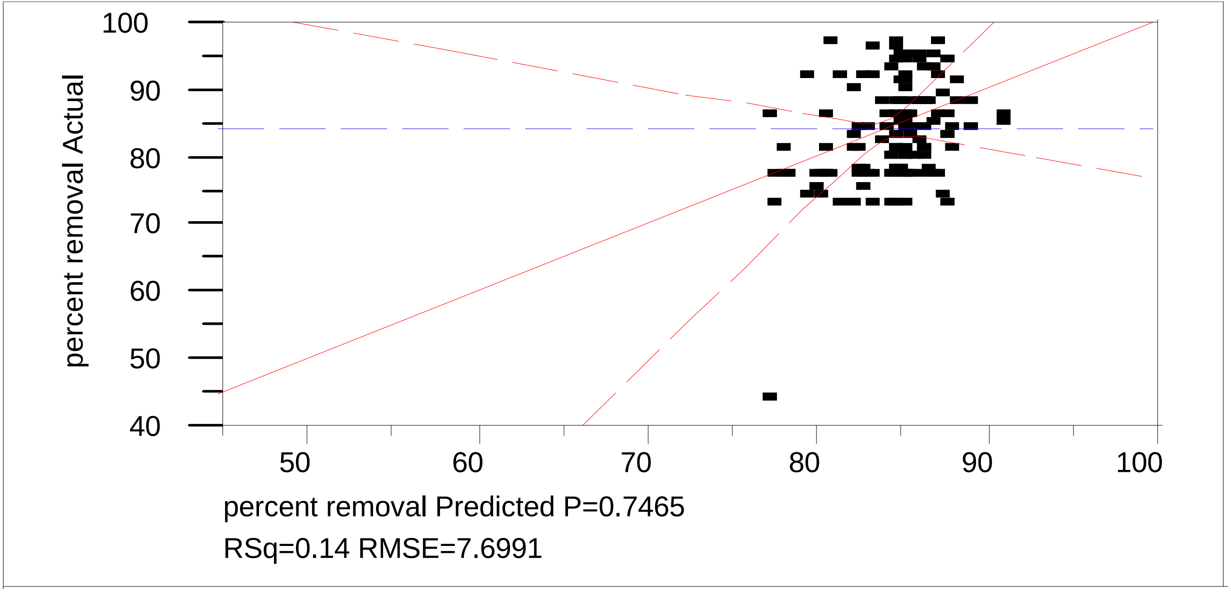
120	4	20	3.7	0.4	90	5.4	0.3	94.5
120	6	5	3.7	0.7	78.8	5.4	0.6	88.9
120	6	10	3.7	0.7	80	5.4	0.65	87.5
120	6	15	3.7	0.5	86.5	5.4	0.6	89.0
120	6	20	3.7	0.25	93	5.4	0.5	90.8
120	8	5	3.7	0.52	87	5.4	0.4	92.6
120	8	10	3.7	0.35	91	5.4	0.3	94.5
120	8	15	3.7	0.4	89.5	5.4	0.25	95
120	8	20	3.7	0.25	93.5	5.4	0.2	96.5
120	10	5	3.7	0.52	87	5.4	0.35	93.6
120	10	10	3.7	0.40	91	5.4	0.25	95.0
120	10	15	3.7	0.3	92	5.4	0.2	96.5
120	10	20	3.7	0.22	94.0	5.4	0.15	97.0
30	4	5	3.7	2.1	43.3	5.4	2.5	53.7
30	4	10	3.7	1.52	54.5	5.4	2.23	55.0
30	4	15	3.7	1.5	56.0	5.4	2.1	61.2
30	4	20	3.7	1.3	64.9	5.4	1.7	67.0
30	6	5	3.7	1.8	51.4	5.4	2.35	56.2
30	6	10	3.7	1.65	55.4	5.4	2.0	58.5
30	6	15	3.7	1.4	59.0	5.4	2.0	63.0

ANNEX 6. STATISTICAL ANALYSIS

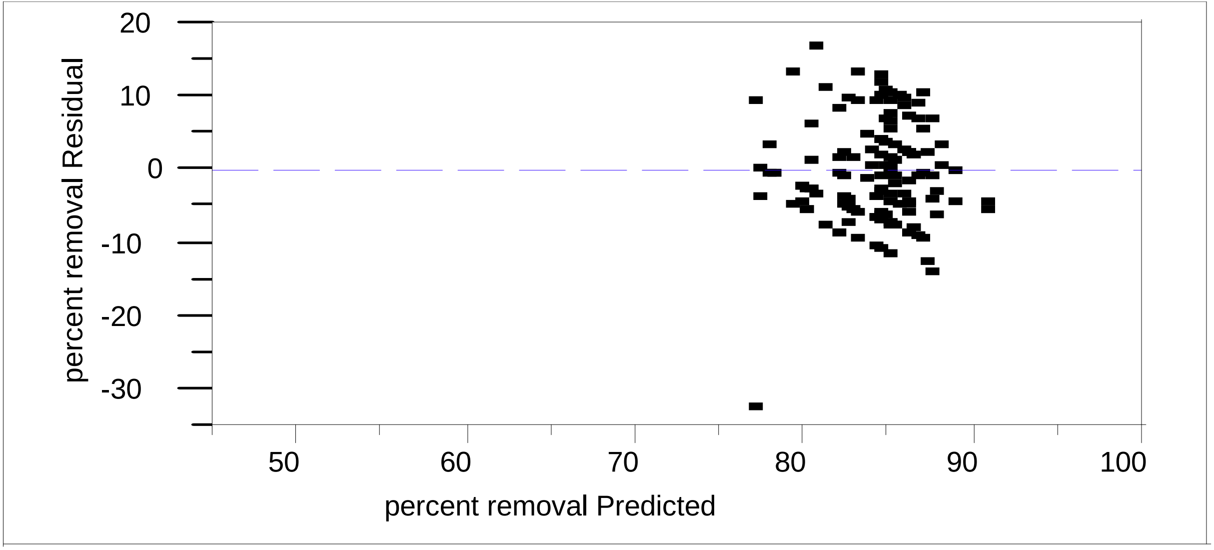
6.1 Linear regression and analysis of variance

Response percent removal

Actual by Predicted Plot



Residual by Predicted Plot



Descriptive statistics of cobalt

	Mean	Std. Deviation	N
pH	7.0000	2.30374	64
Dose	20.00	9.30349	64
contact time	90.00	23.503	64

Tests of Between-Subjects Effects

Dependent Variable: Removal of Co

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	1798867.169	1	195867.169	77.911	.003
	Error	7278.804	2.907	2536.984(a)		
DOSE	Hypothesis	36674.333	3	12191.444	114.216	. 000
	Error	937.345	8.646	106.741(b)		
CONTACT TIME	Hypothesis	937.345	3	.373	.096	.958
	Error	12.293	3.158	3.282(c)		
pH	Hypothesis	7327.074	3	2442.358	22.141	.000
	Error	1131.088	8.256	200.310(d)		
DOSE * CONTACT TIME	Hypothesis	19.588	9	2.176	.540	.832
	Error	118.820	25	4.030(e)		
DOSE * pH	Hypothesis	977.351	9.05	108.595	26.944	.000
	Error	118.820	25.2	4.030(e)		
CONTACT TIME * pH	Hypothesis	51.716	9.05	5.746	26.944	.226
	Error	118.820	25.2	4.030(e)		
DOSE * CONTACT TIME * pH	Hypothesis	108.820	25.2	4.030		
	Error	.000	0	.(f)		

a. MS(T CONTACT TIME) + MS(pH) - MS(CONTACT TIME * PH)

b. MS(DOSE * CONTACT TIME) + MS(DOSE * pH) - MS(DOSE * CONTACT TIME * pH)

c. MS(DOSE * CONTACT TIME) + MS(CONTACT TIME * pH) - MS(DOSE * CONTACT TIME * PH)

d. MS(DOSE * pH) + MS(T CONTACT TIME * pH) - MS(DOSE * CONTACT TIME * pH)

e. MS(DOSE * CONTACT TIME * pH)

Model summary

R	R square	adjusted R square	Std. Error of the Estimate
.854	.682	.758	12.349

The independent variable is Dose of wood ash..

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	51234.135	1	36434.135	232.323	.000
Residual	9825.866	62	124.482		
Total	45260.001	63			

The independent variable is Dose of wood ash.

Coefficients

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
	B	Std. Error	beta			Lower Bound	Upper Bound
(Constant)	-12.31	4.241		-2.698	.009	-20.396	-3.031
contact time	-0.282	.381	-.523	8.099	.001	1.71	5.155
pH	4.150	.407	.384	11.173	000	3.684	5.372
Dose	4.951	.173	.884	21.793	000	4.113	4.795

Dependent Variable: Removal of Cobalt

Regression equation for % removal of cobalt:

[% Removal of cobalt = 4.951Dose (gm/l) + 4.150pH – 0.282contact time (min.) – 12.31]

Tests of Between-Subjects Effects

Dependent Variable: Removal of Pb

Source		Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	Hypothesis	142799.316	1	131789.316	8.500	.054
	Error	54785.687	3.001	14925.819(a)		
DOSE	Hypothesis	11761.707	3	3587.236	9.213	.044
	Error	34651.313	8.999	397.987(b)		
CONTACT TIME	Hypothesis	4.277	3	1.9826	85.186	.171
	Error	.017	.780	.022(c)		
pH	Hypothesis	43773.340	3	14454.447	397.498	.001
	Error	3251.841	8.999	398.007(d)		
DOSE * CONTACT TIME	Hypothesis	.408	9	.034	.567	.849
	Error	1.784	27	.066(e)		
DOSE * PH	Hypothesis	3462.174	9	399.019	4523.097	.000
	Error	1.784	27	.066(e)		
CONTACT TIME * pH	Hypothesis	.484	9	.054	.414	528
	Error	1.745	27	.012(e)		
DOSE * CONTACT TIME * pH	Hypothesis	1.884	27	.066		
	Error	.000	0	.(f)		

a. MS(T CONTACT TIME) + MS(pH) - MS(CONTACT TIME * pH)

b. MS(DOSE * CONTACT TIME) + MS(DOSE * pH) - MS(DOSE * CONTACT TIME * pH)

c. MS(DOSE * CONTACT TIME) + MS(CONTACT TIME * pH) - MS(DOSE * CONTACT TIME * pH)

d. MS(DOSE * pH) + MS(T CONTACT TIME * pH) - MS(DOSE * CONTACT TIME * pH)

e. MS(DOSE * CONTACT TIME * pH)

Model summary

R	R square	adjusted R square	Std. Error of the Estimate
.889	.751	.673	11.985

The independent variable is Dose of wood ash.

ANOVA

	Sum of Squares	df	Mean Square	F	Sig.
Regression	449857.404	4.5	16326.468	71.952	.000a
Residual	13974.670	64	263.08		
Total	49164.074	69			

The independent variable is Dose of wood ash.

Coefficients

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.	95.0% Confidence Interval for B	
	B	Std. Error				Lower Bound	Upper Bound
(Constant)	-10.036	8.952		-1.798	-.077	-43.916	1.804
contact time	-0.280	.167	218	.127	.899	-.313	.356
pH	3.543	.837	.361	4.184	.000	1.800	5.217
Dose	4.849	.356	.799	13.265	000	4.217	5.560

Dependent Variable: Removal of lead

Regression equation for % removal of cobalt:

[% Removal of lead = 4.849Dose (gm/l) + 3.543pH – 0.280contact time (min.) – 10.03]

Declaration

I, the undersigned, hereby declare that the work contained in this thesis entitled " *Heavy Metal Removal from Paint Industries Wastewater Using Wood Ash as an Adsorbent: A Case of Zemilli Paint Factory*" is my own Original work and it has not previously in its entirety or in part submitted it at any other University for degree. And that all source of materials used for the thesis have been duly acknowledged.

Biruk Tsegaye	____________________	__________________
Name	**Signature**	**Date**

This is to certify that the above declaration made by the candidate is correct to the best of my knowledge.

Belay Woldeyes (Dr.Ing.)	____________________	_____________
Advisor	**Signature**	**Date**