HAWASSA UNIVERSITY
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COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE

DEPARTMENT OF CHEMISTRY

REMOVAL OFHEAVY METALS FROM RIVER WATER USING ACTIVATED CARBON OF EUCALYPTUS GLABULUS BARK (BAHIRZAF)

BY

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oct,2024
Hawassa,Ethiopia

REMOVALOF HEAVYMETALSFROMRIVER WATER USING ACTIVATEDCARBONOFEUCALYPTUSGLABULUSBARK (BAHIRZAF)

By:Yidagnu Ferede

A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY OF HAWASSA UNIVERSITY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

Advisor:Professor Sisay Tadesse

OCT,2024
Hawassa,Ethiopia

Declaration

I hereby declare that this M.Sc thesis is my original work and has not been presented for a degree in any other university and that all sources of materials used for this thesis have been duly acknowledged.

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Date of Submission: ________________2024
Hawassa University,
Signature: ____________

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This is to certify that the thesis entitled "**Removal of Heavy Metals from River Water using Activated Carbon of *E.glabulus* bark (bahirzaf)"** submitted in partial fulfillment of the requirements for the degree Master of Science in Chemistry of the graduate program of the Department of Chemistry, Hawassa University, and has been carried by **Yidagnu Ferede, I.D NO _______** under my/our supervision. Therefore, I recommend that the student has fulfilled the requirements and hence hereby can submit the thesis to the department.

Prof. Sisay Tadesse	___________________	___________________
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We, the undersigned, members of the Board of Examiners of the final open defense by **Yidagnu Ferede**, we have read and evaluated his thesis entitled "**Removal of Heavy Metals from River Water using Activated Carbon of *E.glabulus* bark (bahirzaf)"** and examined the candidate.This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirements for the degree of Master of Science in chemistry.

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ACKNOWLEDGEMENT

Above all, I would like to praise my Almighty God, who enabled me to succeed in my work. I would like to express my deepest gratitude and respect to my advisor, **Prof. Sisay Tadesse** for his inspiration guidance, assistance, critical comments, supervision, and overly enthusiasm throughout my thesis work I am also thankful for his encouragement and for his patience throughout my research. So, his selflessly and tirelessly providing consistent support will be in my memory for ever. I also thank my family, friends and lab analysts of Ermias Haile and Tilaun Tumiso.

I am very grateful to the Hawassa University Chemistry Department for their cooperation during my thesis works and allowing me to use the facilities.

I would like to say thanks to laboratory technicians of environmental chemistry and hydraulic engineering of Hawassa University for their unreserved help in analyzing the physical and chemical parameters of water and waste water. Here also, the generous support and contribution of all my family, my best friends and relatives are deeply acknowledged and will be emphasized and are focal points in all cases of my future life

Finally, the Ministry of Education acknowledged for the financial support.

Abstract

Heavy metal pollution has become one of the most serious environmental problems nowadays. The removal of heavy metals from the environment is of special concern due to their persistence. Batch experiments were conducted to test the ability of activated carbon for the removal of lead, nickel, copper and zinc from water Heavy metal pollution in the marine system has become a seriousthreattodayandofgreatenvironmentalconcernastheyarenon-biodegradableandthuspersistent. Eucalyptus glabulus bark locally named as 'Bahirzaf' collected aleta wendo town from area around were used for activated carbon preparation. Dumps and polluted water Activated carbon wasprepared synthesized from bio-waste materials of the plant Eucalyptus barks.

This work deals with the preparation of activated carbon from Eucalyptus leave store move heavy metal ions: such as Cu(II),Pb(II),Zn(II),and Ni(II)from aqueous solution. Chemical activation of the carbon was done by H_3PO_4, H_2SO_4, *KOH and Characterization includes pH. The optimum temperature used to prepare activated carbon of Eucalyptus leaves was 500* ^oC *while the optimum pH value and contact time for activated carbon of Eucalyptus leaves was determined as6and60minrespectively.Theoptimumenvironmentsforadsorbentsdosewasdetermined0.041 g in 25 ml solution. Thermodynamic analysis asserted endothermic and spontaneous nature of the system with involvement of chemical adsorption process. Equilibrium data were represented better by the Freundlich model than the Langmuir model which describes a multilayer adsorption.*

Keywords: *Activated carbon, Eucalyptus glabulus bark, heavy metals, Isotherm, heavy metal removal, and Thermodynamics.*

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1. INTRODUCTION

1.1 Background

Heavy metals are any element in the d-block of the periodic table, or transition metals; they also have been named with toxic metals. Several methods are used for the treatment of wastewater effluents. Among these includes precipitation with coagulation and flocculation, ion exchange. But, some of these methods such as precipitation and ion exchange have significant drawbacks which are associated with their high costs, less efficiency, requiring large amounts of reagent and solvent and generation of toxic sludge. Therefore, there is a great demand for developing cheaper, environment-friendly and efficient heavy metal treatment procedures to minimize the amount of toxic heavy metals from industrial effluents.

Heavy metals are natural elements characterized by their rather high atomic mass and their high density. Although typically occurring in rather low concentration, they can be found all through the crust of our planet. Commonly, a density of at least 5 g cm^{-3} is used to define a heavy metal and to differentiate it from other, “light” metals. Other, broader definitions for “heavy metals” require an atomic mass higher than 23 or an atomic number exceeding 20; these definitions are highly error prone and confusing. Both alternative definitions cause the inclusion even of nonmetals; resorting to the atomic mass criterion, the maximum number of elements classified as “heavy metals” rockets high to 99 out of the in total 118 building blocks of our universe. Looking at the periodic table of elements, we learn that heavy metals *sensu stricto* (according to the density criterion) occupy the lion’s share, namely, columns 3–16, of the periods 4 to 6, encompassing the transition metals, post-transition metals, and lanthanides.

Adsorption using activated carbon is the most widely used technique for the removal of toxic heavy metals. The primary significant characteristic of this magnificent adsorbent is its high porosity nature which results in larger surface areas to bind the toxic heavy metals. Thus, adsorption is the most prevalent and effective physical working method for the treatment of toxic heavy metal from contaminated waters. But, the effectiveness and economic feasibility of the treatment process lies largely on the cost of bio-sorbent. Moreover, the use of activated carbon is not chosen because of its high-cost values. Therefore, there is a need in the designing and preparing of low-cost adsorbents using locally available bio-sorbent materials.

Eucalyptus camaldulensis (E. camaldulensis), which is readily available and used as a major energy source by the local communities, can be used in the removal of toxic heavy metals from industrial wastewaters. Therefore, the objective of this study was to investigate the bio-sorbent prepared from E. camaldulensis as an alternative choice of commercial activated carbon in the removal of Pb, Cd and Cr from aqueous solution and industrial wastewater in batch mode studies; study the influence of various parameters such as pH, initial concentration of metal ion, contact time and adsorbent dose on the removal efficiency of the bio-sorbent and determine the best-fit isotherm equation, the experimental equilibrium adsorption data using Langmuir and Freundlich isotherm models.

These elements are a cause of environmental pollution from a number of sources, including lead in petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain. Moreover, they arise from the purification of metals, for instance smelting of ores, preparation of nuclear fuels, and electroplating. They precipitate into soil, underground water, and surface water. Unlike organic contaminants, heavy metals do not normally undergo biological decay and are thus considered a challenge for remediation. Although a few heavy metals, such as zinc, are required by humans, excessive levels can be detrimental. On the other hand, heavy metals, such as lead, copper, and cadmium, are toxic metals that have no known vital or beneficial effect on human beings, and their accumulation over time in the bodies of humans can cause severe illness such as damage to the kidney, liver, and reproductive system, and causes cancer (Lentech., 1998). Heavy metals could reach human bodies through ingestion, inhalation, and dermal absorption. Consequently, the minimization of human heavy metals exposure is becoming more and more important.

Many governments have started to commit laws to hinder discharging heavy metals into water bodies and using toxic substances such as lead, and change the water supply lines by using other materials like UPV. However, heavy metals still find their way to water supplies.

Accordingly, many studies have been done for removal of heavy metals. Ion exchange, reverse osmosis, and chemical precipitation have been investigated for the removal process, but they are too expensive or incapable of meeting treatment objectives. Adsorption has been proved to be a potentially feasible alternative. Adsorption by using activated carbon is the most common method, but this too may be expensive, particularly if proper raw materials are not available and therefore the carbon has to be imported.

The metals increase in concentration at every level of food chain and are distributed onto the next higher level–a phenomenon called bio-magnification . Heavy metals even at low concentrations can reason toxicity to humans and other forms of life. The poisonousness of metal ion is owing to their ability to bind with protein molecules and prevent replication of DNA and thus subsequent cell division.

Thus, locally generated agricultural wastes such as cotton stalk, rice straw, sugar cane bagasse, and others have been tested in the production of activated carbon in developing countries (Logan, 2002). The use of these raw materials in carbon production shows from the past studies that they are available at low cost, contain high carbon content, and may be effective in the removal of heavy metals.

Not only should microbial biomass be used directly, but biosorbents derived from it in a simple process should be most low-priced for economical metal-removal process applications. If, for any reason, by-products of fermentation processes would not be available, biosorbents could be. Considering the number of candidate biomass types and the number of metals of interest, all multiplied by the number of experimental or process parameters, the task of prospecting for new and potentially feasible metal biosorbents has a very wide scope.

1.2 Statements of the Problem

The effects of insufficient water resource and sanitation cannot be unnoticed. Water can be polluted by different contaminants; including human activities like house hold leftover, dirt, hospital liquid waste and wet coffee industrial waste effluent. The inadequacy of water can be encountered for consumption, industrial supplies and plant growing. This study was answering the following research question.

- What is the adsorption capacity of the powder *Eucalyptus bark used* as adsorbents?
- How operative is this bio sorbent in removing the impurities from water?
- What are the effect of parameters (time pH, dosage, and heavy metals like Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}concentration) on the adsorption efficiency and adsorption capacity?

1.3 Significances of the Study

This study is advantageous to diminish wastages of water and it afford the approach to decontaminate waste water for re-using purpose in industry and everyday use.

1.4 Objective of the Study

1.4.1 General objective

The general objectives of the study was to remove Lead, Zink, Cupper, and Nickel (Pb^{2+},Zn^{2+},Cu^{2+} and Ni^{2+})from aqueous solution using *Eucalyptus bark* based activated carbon.

1.4.2 Specific Objective

- To prepare activated carbon from *Eucalyptus bark*.
- To Evaluate the effects of solution PH, adsorbent , dose, contact time and Pb^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+} ions initial concentration on the removal of pollutants by activated absorbent.
- To investigate Pb^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+} ions adsorption mechanisms of activated carbon absorbent through adsorption isotherms, kinetics and thermodynamic studies.
- To apply the activated carbon adsorbent to treat water contaminated with (Pb^{2+}, Zn^{2+}, Cu^{2+} and Ni^{2+}).

2. LITERATUREREVIEW

2.1 Heavy metals pollution and health Effects

Water is a basic need for all living forms on the planet. Clean water is essential for living a healthy life since polluted water can pose citizen's health at risk through direct or indirect contact with dangerous chemicals (Sajid et al., 2018). Environmental contamination has been exacerbated by industrial revolution and anthropological activities. Significant pollutant discharges into the ocean have resulted in huge hazards to the coastal environ ments. Because of their chronic toxicity, non-biodegradability, and environmental bioaccumulation, heavy metals (HMs) are incredibly harmful environmental pollutants (Valdés et al., 2014). Heavy metals can be transferred and biomagnified via food chains and seriously threaten human health (Liu et al., 2018; Mansour and Sidky, 2002). Effective monitoring and surveillance of heavy metal concentrations in the marine environment is also highly sought (Ahmed et al., 2015). At the local, regional, and national levels, problems are now being raised because of the HMs concentration and their effects, distribution, and environmental origin (Kumar et al., 2019). The bioaccumulation patterns of HMs, such as mer cury (Hg), arsenic (As), Nickel (Ni), cobalt (Co), copper (CU), cad mium (Cd), and chromium (Cr), have a significant influence on the lives of most organism (Rahman and Singh, 2019). Heavy met als from different distribution sources have a negative influence on marine biota (Kahlon et al., 2018).

These HMs have an impact on beneficial organisms such as fishes and other invertebrates (Morkunas et al., 2018). Heavy met als from the surrounding water and foodstuffs accumulate in mar ine species (Hao et al., 2019). In certain cases, excessive levels of heavy metals in marine ecosystems are directly related to environ mental contamination. According to several research studies, the concentration of heavy metal bioaccumulation differed substan tially amongst marine species. Variations in heavy metal accumulation of aquatic organisms are possibly related to their different living environments, feeding patterns, and trophic levels (Liu et al., 2018; Rajeshkumar et al., 2018).

The purpose of this review is to give insight into the overall geo graphical pattern of heavy metal outlets in the aquatic ecosystem as well as human sources. It also discusses heavy metal pollution in marine food components. Furthermore, the effects of such com ponents on the environment and human life are thoroughly dis cussed in order to explain the physiological/molecular processes involved in the use of metallic toxins in aquatic foods. Finally, the review examines remedil techniques (e.g., ecosystem remedia tion and the application of genetic engineering). These manage ment strategies are intimately linked to human population safety by eliminating or mitigating the transfer of HMs pollutants from the aquatic environment to the food chain.

Heavy metals are toxic chemicals that have specific gravity greater than 5 g.cm-3 and consistence 5 and five times greater than specific gravity of water at 4 ^{o}C (Abas *et al.,* 2013). Even though the chemical forms of heavy metals can be changed, they are not subject to chemical or biological destruction. Therefore, after release into the environment they are persistent contaminants. Natural processes such as bedrock and soil weathering, wind and water erosion, volcanic activity, sea salt spray, and forest fires release heavy metals into the environment. While the origins of anthropogenic releases of heavy metals are lost in antiquity, they probably began as our prehistoric ancestors learned to recover metals such as gold, silver, copper, and tin from their ores and to produce bronze.

The modern age of heavy metal pollution has its beginning with the industrial revolution. Anthropogenic utilization has also increased heavy metal distribution by removing the substances from localized ore deposits and transporting them to other parts of the environment. In a global context, the major problem of surface water pollution is heavy metal discharge from industrial activities (Narain *et al.,* 2011; Alfarra *et al.,* 2014; Pawar *et al.,* 2014). The development of industrial sector in the African continents is the primary cause of heavy metals being released into water, air and soil in all countries, including Ethiopia.

Most industries are the point source of heavy metals (Pehlivan *et al.,* 2008); these industries include electroplating, chemical and petrochemical, metal and mining, leather, textile, ceramic, cement, fertilizer, tanneries, batteries, paper, pesticides and others. These industries release their wastewater containing various harmful heavy metals without treatment into the environment (Fasinu and Orisakwe, 2013). These harmful toxic chemicals include elements such as uranium (Ur), selenium (Se), zinc (Zn), silver (Ag), gold (Au), nickel (Ni), cadmium (Cd), mercury (Hg), copper (Cu), chromium (Cr), arsenic (As), lead (Pb) and others (Ahalya et al., 2003). The presence of these harmful heavy metal elements, even at low concentrations, affects the health of humans and other living organisms (Srivastava et al., 1995; Duruibe et al., 2007). The fact that these elements are highly soluble in water and not easily degradable by soil, makes their presence in water bodies more alarming (Kurniawan et al., 2006). According to the study conducted by Biney and Ameyibor, (1992) untreated industrial wastewater containing heavy metals (Cd, Cu, Zn, Pb, Hg and Fe) released into fresh water bodies can also be stored in the bodies of aquatic organisms, for example in Pink Shrimp. Therefore, the need to treat wastewater is of great importance in order to safeguard the environment and reduce associated health problems. According to the World Health Organization (WHO) reports and other studies (WHO, 1984; El-Gendy *et al.,* 2011; Sahniet, 2011; Shahmohammadi *et al.*, 2011; Isah and Lawal, 2012; Sonde and Odoemelam ,2012; Muiruri *et al.,* 2013), the heavy metals which are of greatest concern with regard to human health are Pb, Cd, Hg, Cr, Cu, Zn and Fe. Most products such as pharmaceutical products and dental products, some drugs, and Unani drugs, cosmetic products like shampoos, lipsticks, hair colors and others contain heavy metals (Sahni *et al.,* 2011; Bocca *et al.*, 2014).

Heavy metals are elements of high density, and they are toxic at even low concentrations. They can also be defined as the elements in the d-block in the periodic table such as cadmium (Cd), Lead (Pb), copper (Cu), and mercury (Hg). Heavy metals are natural components of the Earth's crust. Some heavy metals are vital to maintain the metabolism in our bodies at certain concentrations such as zinc. However, the excess of these heavy metals can lead to poisoning via drinking water contamination, high ambient air concentrations, or eating contaminated food. It's well known also that the specific gravity of heavy metal elements is more than five times the specific gravity of water where the specific gravity of water is 1 at temperature 4oC. For instance, the specific gravity of some toxic heavy metals is: lead, 11.34; cadmium, 8.65; copper, 8.93; and mercury, 13.546 (Lef, 1998).

Heavy metals are very dangerous and carcinogenic due to the fact that they can bioaccumulate in our bodies resulting in increasing the concentration of chemicals in the biological organism compared to the chemical's concentration in the environment.

There are 35 metal elements that may be considered harmful because of their residential exposure. Twenty five elements of those metals are considered as heavy metals such as arsenic, cadmium, copper, gold, iron, lead, and zinc. The excess amount of these elements results in reducing the mental and nervous functions, damaging the blood composition, lungs, kidneys, liver, and other essential organs. Furthermore, long term exposure to heavy metals may induce Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. It is also known that heavy metals cause cancer. The recognition of these diseases is due to the fact that the symptoms are usually severe, rapid in onset, and associated with cramping, nausea, vomiting, pain, sweating, headaches, and difficulty breathing. There are some other symptoms resulting from the exposure to excess amount of heavy metals such as emotional instability, and insomnia (Lef, 1998).

Heavy metals can reach surface water either through industrial and consumer wastewater discharged into water bodies or from acidic rain leached to the soils and releasing heavy metals into groundwater and surface water. According to the Egyptian Environmental Affairs Agency (EEAA, 2007) last annual report, there were 91 plants in Egypt discharging their industrial wastes into the Nile River with total draining amount of 4.952 $x10^9$ m^3/year resulting in 99.64% of the total industrial effluents resulting in releasing huge amounts of heavy metals contaminant (Abdelshafi 2007).

2.1.2 Cadmium Health Effects

Cadmium could be produced as a byproduct during the refining of some heavy metals, namely zinc and lead; however, besides the detrimental impacts of cadmium, it has a significant use if it is recycled. Cadmium is commonly used in nickel/cadmium batteries for its high tolerance to physical and electrical stress. Furthermore, it can be used in coating for its high corrosion resistance, pigments, and electronic compounds such as batteries. Cadmium could reach our bodies through food if it has been added to agricultural soil or fertilizers in various ways, such as atmospheric deposition and discharging industrial wastewater into surface water. Long term exposure can lead to severe lung diseases and lung cancer.

2.1.3 Copper Health Effects

Copper can reach our bodies through drinking water in copper pipes. Although copper is a vital element that our body needs, high doses of copper can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Moreover, people that have Wilson's disease are at risk for health effects from overexposure to copper (Lenntech, 1998).

2.1.4 Lead Health Effects

Lead has a significant role in many industries because it is ductile and easily shaped. It has been used in many sectors and products: batteries, petrol additives, chemical compounds, pigments, and cables (NMA, 2009). Accordingly, lead can find a pathway to human beings through drinking water, food, air, soil and dust. Overdoses of lead and long term exposure can tend to severe impacts especially on infants. High concentrations of lead may cause problems in the synthesis of hemoglobin, effects on the kidney, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system.

According to the Environmental Protection Agency (EPA 2006) the long-term exposure of lead can be severe and tends to decreased growth, hyperactivity, impaired hearing, and brain damage. Recent studies have stated that lead may have an impact on mental and psychological developments in children; for instance children may lose up to 2 Intelligence Quotient (IQ) points if the blood lead level rises from 10 to 20 µg/dl. Lead mainly can be found in foods from the deposition of dust and rain containing lead on crops and soil. It can also accumulate in the human body from point source emissions. For example, lead can exist in drinking water from old lead piping and from illegal discharging of industrial waste water of high concentrations into surface fresh water (Lenntech, 1998).

2.2 Technologies for heavy metal removal

Heavy metals are the cause of various disorders and diseases due to that fact they can be easily stored in the body of living organisms without breaking down. Therefore, it is important to remove heavy metals from polluted water using conventional techniques. There are many conventional methods for the removal of toxic chemicals/heavy metals, including the following; ion exchange processes; membrane filtration; adsorption; electrochemical treatment; photochemical oxidation; and ozonation and biological processes (Crostat,2012). These technologies have been widely applied for some time and can be classified into three clusters: physical, chemical and biological treatment techniques (Abas *et al.,* 2013). However, these heavy metal removal technologies have their own disadvantages such as their expensive due to initial and operational costs; are less efficient, carry high costs for disposal; consist of complex processes and require large land areas.

2.2.1 Chemical precipitation

Chemical precipitation is the most widely used for heavy metal removal from inorganic effluent. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Equation [2.1]

$$M^{2+} + 2(OH)^{-} = M\,(OH)^{-}$$

Those equations indicated that 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 (Ahalya *et al.,* 2003). Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, in expensive equipment requirement, and convenient and safe operations. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Baraket, 2011). In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Bose *et al.,* 2002).

2.2.2 Ion exchange

Ion exchange is a reversible chemical reaction where in an ion (an atom or Molecule that has lost or gained an electron and thus acquired an electrical charge) from Solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. An organic ion exchange resin is composed of High-molecular weight polyelectrolyte's that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin. Most of the resins Used are synthetic because their characteristics can be tailored to specific applications. Synthetic resin made by polymerization of organic compounds in a porous three dimensional Structure. Ion exchange resins are classified as cat ion exchangers, whom it has positively charged mobile ions available for exchange, and anion exchangers (Yang *et al.,* 2001).

2.2. 3 Electro dialysis

Electro dialysis is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cat-ions toward the cathode, crossing the anion exchange and cat-ion exchange membranes (Chen, 2004).

Problems associated with the electro-dialysis process for wastewater renovation include chemical precipitation of Salts with low solubility on the membrane surface. To reduce the membrane fouling, Activated carbon pre-treatment, possibly preceded by chemical precipitation and some form of multimedia filtration may be necessary(Malkoc and Nuhoglu, 2007) .

2.2.4. Membrane filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultra-filtration, nano filtration and reverse osmosis can be employed for heavy metal removal from wastewater. Unique specialties enable UF to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane (Vigneswaran *et al.*, 2004). The main disadvantage of this process is the generation of sludge (Wingen felder *et al.*, 2005).

2.2.5 Reverse osmosis process

The reverse osmosis process depends upon a semi-permeable membrane through which pressurized water is forced. Reverse osmosis, simply stated, is the opposite of the Natural osmosis process of water. Osmosis is the name for the tendency of water to migrate from a weaker saline solution to a stronger saline solution, gradually equalizing the saline composition of each solution when a semi-permeable membrane separates the two solutions. In reverse osmosis, water is forced to move from a stronger saline Solution to a weaker solution, again through a semi-permeable membrane. Because molecules of salt are physically larger than water molecules, the membrane blocks the Passage of salt particles (Barakat , 2011) . The end result is desalinated water on one side of the membrane and a highly concentrated, saline solution of water on the other side. The disadvantage of this method is that it is expensive (Ahalya *et al.*, 2003).

2.2.6 Ultrafiltration

Ultra-filtration technologies can be used in a variety of ways in wastewater treatment and water reuse systems. Ultra-filtration can reduce the amount of treatment chemicals, has smaller space requirements, and reduce labor requirements. On the contrary in this method uses more electricity, may need pre-treatment, and requires replacement of membranes (Eckenfelder, 2000).

2.2.7 Coagulation–flocculation

Coagulation–flocculation can be employed to treat wastewater laden with heavy metals. Principally, the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation (Shammas, 2004).To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky floccules (Ayoub *et al.,* 2003). The general approach for this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles (Licskó, 1997). In spite of its advantages, coagulation–flocculation has limitations such as high operational cost due to chemical consumption. The increased volume of sludge generated from coagulation–flocculation may hinder its adoption as a global strategy for wastewater treatment. This can be attributed to the fact that the toxic sludge must be converted into a stabilized product to prevent heavy metals from leaking into the environment. To overcome such problems, electrocoagulation may be a better alternative than the conventional coagulation, as it can remove the smallest colloidal particles and produce just a small amount of sludge. However, this technique also creates a flock of metallic hydroxides, which requires further purification, making the recovery of valuable heavy metals impossible (Persin, and Rumeau, 1989)

2.2.8. Flotation

Flotation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment (Wang 2004). The attached particles are separated from the suspension of heavy metal by the bubble rise. Flotation can be classified as:

I. dispersed-air flotation,
II. (dissolved air flotation (DAF),
III. Vacuum air flotation,
IV. Electro flotation and
V. Biological flotation.

Generally, in developed countries toxic heavy elements discharged from different industrial areas along with polluted liquid waste, have been successfully removed by high resolution and costly treatment methods (Abas *et al.*, 2013). However, in developing countries the application of such advanced technologies for wastewater treatment is technically complex and expensive (Yadanaparthi *et al.*, 2009).

2.3 Factors Affecting Adsorption

2.3.1 Nature of the Adsorbent

The adsorption process is mainly a surface phenomenon in which adsorption depends on the portion of the total surface area available to the adsorption process. The adsorption capacity is directly proportional to the specific surface area (Weber, 1972 and Vernon *et al.*, 1967) found that the physicochemical nature of the surface of carbon is an important factor in the adsorption process, and should be considered in selection or preparation of carbons for specific applications.

2.3.2 Nature of the Adsorbate

The adsorption process is mainly affected by the nature of the adsorbate in the sense of its solubility in the solute. The adsorption capacity is inversely proportional to the solubility of an adsorbate in the solute, and this is the Lundelius rule, one of two rules used to predict the effect of a solute's chemical character on its uptake (Weber, 1972).

The greater the solubility, the stronger the solute-solvent bond is and therefore the smaller the extent of adsorption. The molecular size of the adsorbate is of significance too. The molecular size relates to the rate of uptake of solutes from aqueous solution by porous adsorbents so that the smaller the molecular size, the faster the reaction is. However, it must be kept in mind that the adsorption process dependence on molecular size can be generalized only within a particular chemical class.

Stafiej *et al.* (2007) studied the adsorption of heavy metal ions with carbon nanotubes. She investigated the effect of both pH value and ionization of the metal on the adsorption process. She found that the pH value plays a vital role on the adsorption process in particular. When the solution pH value is higher then the pH of the zero point of charge (pHpzc), the negative charge on the surface provides electrostatic interactions that are favorable for adsorbing cationic species. The decrease of pH tends to neutralize the surface charge; thus, the adsorption of cations should decrease. Also, it was found that the low adsorption that happened in the acidic region can be attributed in part to competition between H+ and the metal ion M+2.

2.4 General Properties of heavy metals

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0.Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel (Amuda *et al.*, 2007). The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the world health organization (WHO). Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Chronic heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers (Bekiari and Sotiropoulou, 2008).

Non-biodegradable contaminants pose a serious health and environmental hazard and removal of these wastes cannot be achieved using secondary methods. Hence, tertiary/advanced wastewater treatment methods such as ion exchange, precipitation, membrane separation, electrolysis and adsorption_ can be used to remove these recalcitrant wastes. So far, a number of efficient methods have been developed for heavy metal removal. Fenglian *et al.* (2011) and Rao *et al.* (2011) reviewed various methods for the removal of heavy metals such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation, floatation, etc. Generally, these processes are efficient in removing the bulk of metals from solution at high or moderate concentrations. However, chemical processes produce a large amount of metallic sludge, making metal recovery difficult. The sludge also needs further disposal. In addition, effluent after such treatment usually has unacceptably high total dissolved solids. When applied to dilute metal waste or lower concentrations of metal ions, these processes are either ineffective or not cost effective and require high level of expertise; hence they are not applied by many end-users However, most of these methods are costly and require high level of expertise; hence they are not applied by many end-users. For these reasons, adsorption technology has gained a wider application due to its inherent low cost, simplicity, versatility and robustness. Low cost adsorbents derived from agricultural by-products and industrial solid wastes could be used to remove recalcitrant wastes from synthetic wastewater. Conversion of these materials into adsorbents for wastewater treatment would help to reduce the cost of waste disposal. The adsorption of toxic waste from industrial wastewater using agricultural waste and industrial by-products has been massively investigated (Basu *et al.,* 2006; Srivastava *et al.,* 2006). The technical feasibility of various low-cost adsorbents for heavy metal removal from contaminated water has been reviewed (Babel *et al.,*2003).Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as chitosan, zeolites, and other adsorbents, which have high adsorption capacity and are locally available. There are many sources of activated carbon from organic waste.

2.5 Activated Carbon

Activated carbon is known to be a very effective adsorbent for some dissolved substances (adsorbates) because it has a highly porous and reactive surface (Droste, 1997). The pore volume is commonly distributed over a narrow range between 4 to 30 angstroms (Å) (Cooper, 2002). The diameter of activated carbon pores has been classified into micropores (diameter < 2 nm), mesopores (2-50 nm), and macropores (diameter > 50 nm) (Amphol, 2008). Although there are many adsorbents that can be used to treat contaminants in water, such as Magnesia, recycled iron, and activated alumina, activated carbon is considered among the best due to its large surface area (600-1400 m2/g). Activated carbon has shown acceptable removal efficiency for organic contaminants such as halo acetic acids (HAAs), but it also may have high removal efficiency for inorganic contaminants such as mercury, lead, cadmium, and other toxic metals (Weber, 1972)

2.6. The plant of Eucalyptus

The wood of Eucalyptus camaldulensis is very useful in manufacturing furniture and other household products, leaving huge amounts of sawdust waste, which consequently results in surface pollution. Recycling of eucalyptus sawdust to produce activated carbon may help reduce surface pollution on one hand, and water decontamination on the other. Therefore, we hypothesized that recycling of eucalyptus sawdust and synthesizing activated carbon using H3PO4 would serve as an efficient adsorbent for the removal of Pb2+ and Cu2+ from wastewater streams. To the best of our knowledge, no study has been published on the preparation of activated carbon from Eucalyptus sawdust waste with chemical activation using H3PO4 as activating agent. Hence, Eucalyptus sawdust was used as a precursor for the production of chemically activated carbon using H3PO4 as activating agent in this study. The efficacy of the produced adsorbent to adsorb Pb2+ and Cu2+ from aqueous solutions was investigated. Batch equilibrium and kinetics sorption experiments were conducted to study the effects of contact time, pH, adsorbent dose and initial metal ions concentrations on adsorption of Pb2+ and Cu2+ onto eucalyptus sawdust biomass-derived activated carbon. Various equilibrium and kinetic sorption models were employed to identify the operating sorption mechanism

3. MATERIALS AND METHODS

3.1. Chemical and Reagents

Analytical-grade chemical reagents were all used in the present study. All the necessary solutions are prepared with distilled water and analytical reagents. Pb $(NO_3)_2$ (alpha), Ni $(NO_3)_2$ (Nice.), 37% HCl (Aldrich, A.C.S. Reagent, Germany),Cr $(NO_3)_3$ (LOBA. CHEMIE), Cd $(NO_3)_2$ (NICE.), Co $(NO_3)_2$ (FINKEM.), Cu $(NO_3)_2$ (FINKEM), KOH (Central Drug House of (P) Ltd. INDIA.),98% H_2SO_4 (LOBACHEMIE.),85% H_3PO_4 (MUMBI30), were used. Distilled water was used for rinsing apparatus prior to analysis, dilution and preparation of all solutions throughout the experiment.

3.2 General Information about the Tree

Eucalyptus Glabulus locally called Bahirzafin Amharic and in Sidammo affo Shrubor tree which has15-25m high. Habitat: This evergreen tree is wide spread in Africa from guine a to Ethiopia and as far as Angola and Mozambique. Ethanolic extract of seeds of eucalyptus leave contain acyclohexane diepoxidede rivative called crotepoxide,which has a significant tumor-inhibitory activity (Kupchan etal., 1968).

3.3. Instrument and Apparatus

Using a digital analytical balance, the biomaterial of the Eucalyptus leaf sample was measure (ADAM, Model AFP-110L, England) with120 g loading capacity and±0.0001 precision. Flame Atomic absorption spectroscopy (Buck Scientific, Model 210VGP AAS, USA) equipped with deuterium background corrector and air-acetylene flame atomizer will be used for determination of the selected metals (Ni, Cu, Zn, and Pb) in water samples. Drying oven (Digit heat, J. P. Selecta, Spain) will be used for drying the samples placed on porcelain crucibles. Portable pH meter (Model HI9024, HANNA Instrument), Fourier Transform Infrared spectrometry (Perkin Elmer Spectrum 65 FTIR spectrometer) and furnace was used for carbonization of biomaterial.

Scanning Electron Microscope (SEM), (Jeol-JSM-IT300LA). Measuring cylinders (Duran, Germany), pipettes and micro pipettes (Pyrex, USA), were used for measuring different volumes of sample solution, acid reagents and metal standard solutions. Volumetric flask (50 and 1000 ml) was also used during Dilution of sample and preparation of metal standard.

Scanning Electron Microscope (SEM), (Jeol-JSM-IT300LA). Measuring cylinders (Duran, Germany), pipettes and micro pipettes (Pyrex, USA), were used for measuring different volumes of sample solution, acid reagents and metal standard solutions. Volumetric flask (50 and 1000 ml) was also used during Dilution of sample and preparation of metal standard.

3.4. Methods

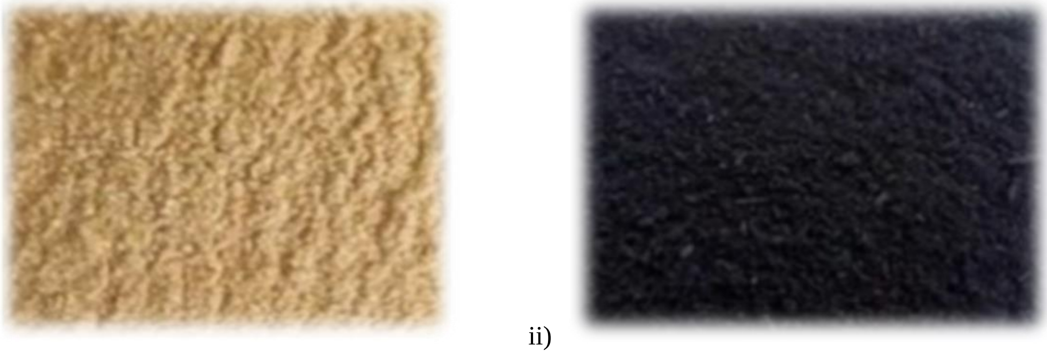
3.4.1 Preparation of metal solutions

All chemicals used were of analytical grade. Stock standard solutions, having concentrations of 1000 mg/l. of Ni (II), Zn (II), Cu (II**)** and Pb (II) were prepared by dissolving 3.18 g of Nickel nitrate (Ni $(NO_3)_2$; (Nice laboratory chemicals, India), 1.5980 g of lead nitrate (Pb (NO_3); (Fin-kem research chemicals, India), 3.801 g of hydrated copper (II) nitrate,(Cu $(NO_3)_2*3H_2O$), and 2.896 g of hydrated Zinc (II) nitrate Zn $(NO_3)_2*4H_2O$) respectively. Then, the solutions were diluted to a final volume of 1000 ml. these solutions were used to prepare working solutions of various concentrations by appropriate dilution.

3.4.2. Experimental Design for Preparation of Activated Carbon

The research utilized *Eucalyptus Glabulus* bark, known locally as 'Bahirzaf,' gathered from the vicinity of Aleta Wendo town for the preparation of activated carbon. The material was cleansed by washing with distilled water to eliminate impurities, then dried in an oven at 100 degrees Celsius for 24 hours. The dried bark was crushed and grinded. Then, the powder was soaked with different chemicals such as (H_2SO_4, H_3PO_4, and KOH) solution overnight followed by decantation through212µmsieve and repeated was hing the modified biomaterial using distilled water to remove the free activating agents until the pH of super natantremained neutral. Then, the filtrate was dried over night at 100^oCin a tabular oven. Then the activated *EB* powder was subjected to carbonization at different temperaturerangingfrom400°C to 700 ^{o}C in a tubular furnace for 2 hour.

After completing the carbonization process it was cooled in desiccators; crushing and sieving to desired mesh size 250 µm to eliminate the effect of sieve size in the study and stored in a glass bottle.



i) ii)

Figure 1: (i) powdered dried sample of *Eucalyptus Glabulus bark,* (ii) Activated carbon of *Eucalyptus bark*

3.4.3. Effect of Soaking Chemicals

The effect of soaking of different chemical agents such as phosphoric acid, sulfuric acid, and potassium hydroxide on the porous characteristics was studied. Which means1gof the biomaterial was soaked in3ml of H_3PO_4, H_2SO_4, and KOH. Then, the activated biomaterial was washed well to neutralize excess chemicals and dried in oven at100C^{o}. The dried activated biomaterial is carbonized at 400 ^{o}C, 500 ^{o}C, 600 ^{o}C and 700 ^{o}C to prepare there spective activated carbon.

3.4.4. Effect of Carbonization Temperature

Carbonization temperature is one of the most manipulating factors for the growth of porosity during Activation process (Sivakumar*etal.,* 2001).Effect of carbonization temperature on porous characteristics of developed activated carbon was investigated in the range of 400–700^{0}C.

3.5. Surface Characterization study

3.5.2. Scanning Electron Microscope (SEM)

Scanning electron microscope is a type of microscope which is used for visualization of porous structure of a material. The activated carbon sample was analyzed in a SEM to visualize the porous structure. The magnification was adjusted for getting a clear picture.

3.5.3. FTIR (Fourier Transform Infrared spectrometry)

The FTIR study was conducted on activated adsorbent sample to determine various organic and inorganic groups on the surface before and after adsorption was conducted. So that the organic and inorganic group which participates in the adsorption process was determined by viewing the change in frequency occurred due to adsorption of heavy metal on adsorbent

3.6. Batch Adsorption Study Using Activated Carbon Prepared At Optimum Point

3.6.2. Effect of Adsorbent Dose

The adsorption of heavy metal by adsorbents of *Eucalyptus* bark activated carbon was investigated using the following adsorbent doses: 0.001, 0.02, 0.04, 0.06, 0.08, 0.10 and 0.12 g was added to different conical flask containing 25 ml of 30 ppm heavy metal solution, the flask was closed and placed in a laboratory shaker, used by keeping other variable constant (at optimal contact time and temperature). After adsorption time was completed the adsorbents were centrifuged and removed from the solution and the concentration of residual heavy metal in each solution was determined using AAS.

3.6.3. Effect of Contact Time

The effect of contact time on removal of heavy metal was studied for a period of 15 to105 min and 0.04g of the adsorbents (activated carbon) was added to different conical flask containing 25 ml of 30 ppm heavy metal solution, the flask was closed and placed in a laboratory shaker, for each of the different contact times chosen (15, 30, 45, 60, 75, 90 and 105 minute). The content of each flask was filtered and the concentration of residual heavy metal in each solution was determined using FAAS.

3.6.4. Effect of pH

The effect of pH on the heavy metal adsorptions onto activated carbon was studied at pH range of 3.0 to 9.0. For this 25 ml of heavy metal solutions with initial concentration of 30 ppm, was taken in 50 ml Erlenmeyer flasks and pH was adjusted to pH of 3.0- 9.0 using required quantity of 1N HCl or 1N NaOH before mixing the adsorbent .Then 0.04 g of activated carbon respectively was added to the solutions and shaken in a laboratory shaker in room temperature and at optimum time.

3.6.5. Isotherm Study/Equilibrium Study

Equilibrium isotherms was studied by taking 25 ml of mixture of salts of Zn, Pb, Cu, and Ni solution of(5,10, 20, 30, 40, 50 and 60 ppm) in 25 ml Erlenmeyer flask. 0.05g activated carbon was added to the solution and shaken in shaker. FAAS was employed to determine the remaining concentrations of metal ions in the sample after adsorption at the desired time intervals. To establish the adsorptions capacity of adsorbents experimental data was fitted against Langmuir and ferundlich isotherm equations.

3.6.5. Thermodynamic Study

Thermodynamics study were conducted by taking 25 ml a mixture of Zn (II), Pb (II), Ni (II), and Cu (II) solutions with initial concentrations of 30 ppm in 50 ml Erlenmeyer flasks .Solutions was shaken at different temperature (20, 30, 40, 50, and 60℃) and the filtrate was analyzed for the remaining Zn (II), Pb (II), Ni (II), and Cu (II) concentrations. Flame Atomic Absorption spectrophotometer was employed to determine the remaining concentrations of metal ions in each sample after adsorption at the desired time intervals.

3.6. Data Analysis

Excel spread sheet and statistical soft ware's (Origin pro 9) was used for the statistical analyses. The results of data analyses were presented using Tables and Figures are necessary.

3.7. Ethical consideration

The laboratory analysis followed proper scientific procedures and the results will be recorded honestly in data collection formats. The researcher had taken specific steps to ensure the consent of the participant and their information was kept confidential based on the objective of the research. In addition, authors of books and Journals used will be cited properly. Scholars, individuals and organizations who contributed for the successful completion of this study will be properly acknowledged.

4. RESULTS AND DISCUSSION

4.1. Optimization of impregnation chemicals

The following is the result of using chemicals for impregnation in the process of creating microporous activated carbon.

4.1.2. Effect of impregnation chemicals

Figure 2 illustrates how impregnated chemicals affect the process of making microporous activated carbons. The highest adsorption capacity is always provided by the prepared activated carbon of eucalyptus bark made by impregnation with H_3PO_4.

Table 1: Effect of impregnation chemicals on the preparation of activated carbon for Pb

Impregnation chemicals	Percent of Removal (%) for *Eucalyptus Glabulus*bark
H_2SO_4	95.8
H_3PO_4	98.7
KOH	91.1

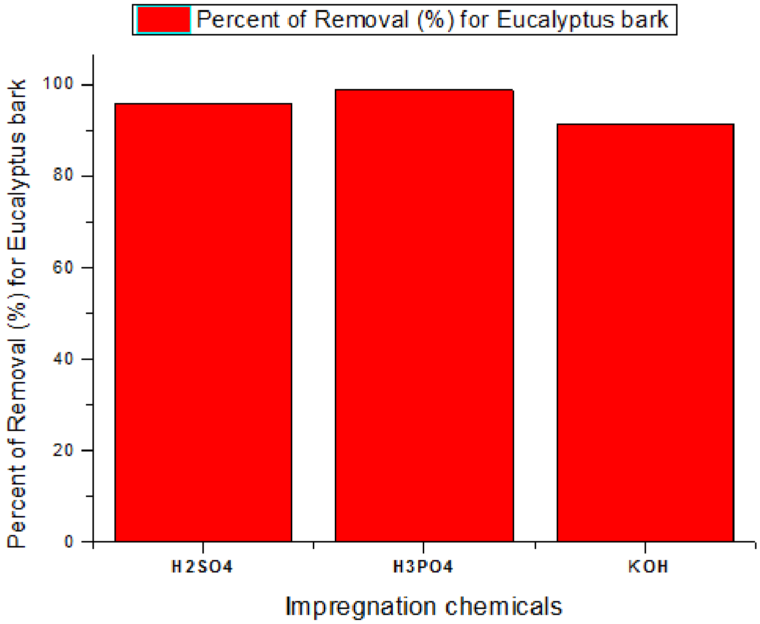


Figure 2: Effect of impregnation chemicals on preparation of activated carbon

4.2. Characterization of the prepared activated carbon

4.2.1. FT-IR (Fourier Transform Infrared spectrometry)

It is believed that a molecule's vibration spectrum is one of its special physical characteristics. Thus, by comparing the spectrum from a unknown with a previously recorded reference spectrum, the infrared spectrum can be utilised as a fingerprint for identification.

The FTIR spectrum analysis of phosphoric acid treated activated carbons of *Eucalyptus* bark displays a number of functional groups on their surface indicating the complex nature of the adsorbent. The adsorption capacity of activated carbons depends upon porosity as well as chemical reactivity of functional groups at the adsorbent surface. The IR spectrum of unloaded adsorbent (*Eucalyptus* bark) and heavy metal loaded adsorbent (*Eucalyptus* bark) powder is presented below: it shows the presence of different functional groups present in *Eucalyptus* bark. The broad and strong absorption peaks around 3537 cm^{-1} is an indicative of hydroxyl groups. The bands at 3023 cm^{-1} in IR spectra of the adsorbent may be due to the C-H stretching vibrations. The shift in the peak of OH stretching from 3537 cm^{-1} to 3300 cm^{-1} and the peaks of C-O stretching becomes very weak after an adsorbent is loaded with lead, copper, nickel and zinc. This may be because of the result of the formation of a complex between an adsorbent and adsorbate or electrostatic attraction between the metal ions and various surface oxygen containing functional groups carried by the activated carbons.

Table 2: Other functional groups present in *Eucalyptus* bark are listed in the table below

Functional groups	**Range of wave number**	Unloaded	Loaded
OH stretching	3200-3600 cm^{-1}	3537 cm^{-1}	3300 cm^{-1}
C=C stretching	1566-1650 cm^{-1}	1614 cm^{-1}	1588 cm^{-1}
C-OH stretching	1200-1300 cm^{-1}	1243 cm^{-1}	1224 cm^{-1}
C-O stretching	1030-1124 cm^{-1}	1117 cm^{-1}	1098 cm^{-1}

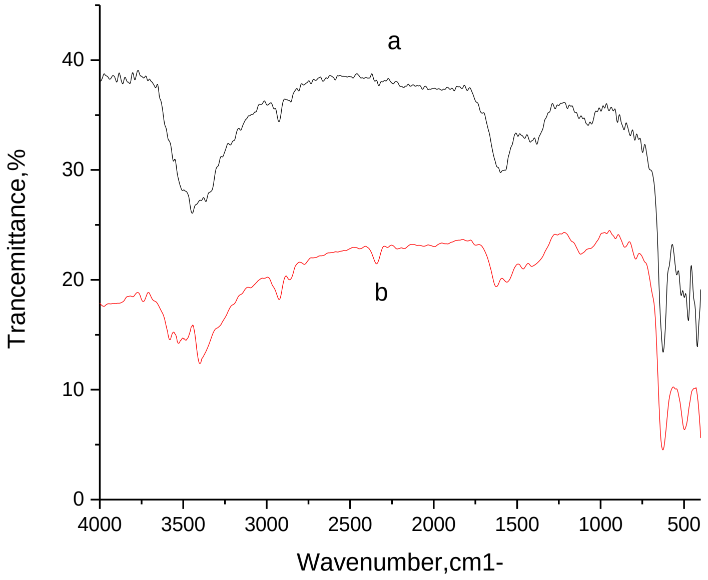
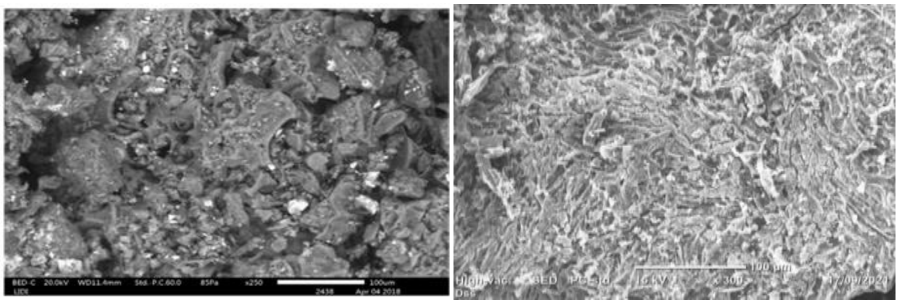


Figure 3: FT-IR Spectra of activated carbon prepared of *Eucalyptus Glabulus* bark before (a) and after (b) adsorption

4.2.2. SEM (Scanning Electron Microscope)

Scanning electron microscope is a type of microscope which is used for visualization of porous structure of a material. The activated carbon sample was analyzed in a SEM to visualize the porous structure. The magnification was adjusted for getting a clear picture. The prepared activated carbons were examined by Scanning Electron Microscope (SEM) to analyze the surface of the adsorbents. SEM of the chemically activated carbons by H_3PO_4 before and after adsorption was presented in Figure 5. In activated carbon of a *Eucalyptus* bark before adsorption was well –developed porous surface was observed at higher magnification. The pores observed from SEM images are having diameter in micrometer range. From the Figure 5, it can be observed activated carbon of *Eucalyptus* bark adsorbents before adsorption have rough texture with heterogeneous surface and a variety of randomly distributed pore size. However in the same manner the surface area of activated carbons of *Eucalyptus* bark after adsorption was became smooth and the porous surface of activated carbons was filled.



a) b)

Figure 4: SEM for activated carbon (a) before adsorption and (b) after adsorption for *Eucalyptus Glabulus* bark

4.3. The effect of operating parameters

4.3.1. Effect of quantity of Adsorbents

In this experiment, the effect of change in adsorbents dose on adsorption of heavy metals was studied by keeping the other variables constant and change in adsorption. The percentage removals of heavy metals is seen to increase with adsorbent dose and it is observed that there is a sharp increase in percentage removal with increase adsorbent dose for the studied metal ions gets ride to dynamic equilibrium. After equilibrium that the binding site of the adsorbent was more saturated and the graph shown constantly increase. The maximum removal of *Eucalyptus bark* 99 % at 0.04 g . Due to the greater availability of the exchangeable site or surface area. Where a further increase in the quantity of dose had no significant effect to the adsorption effect.

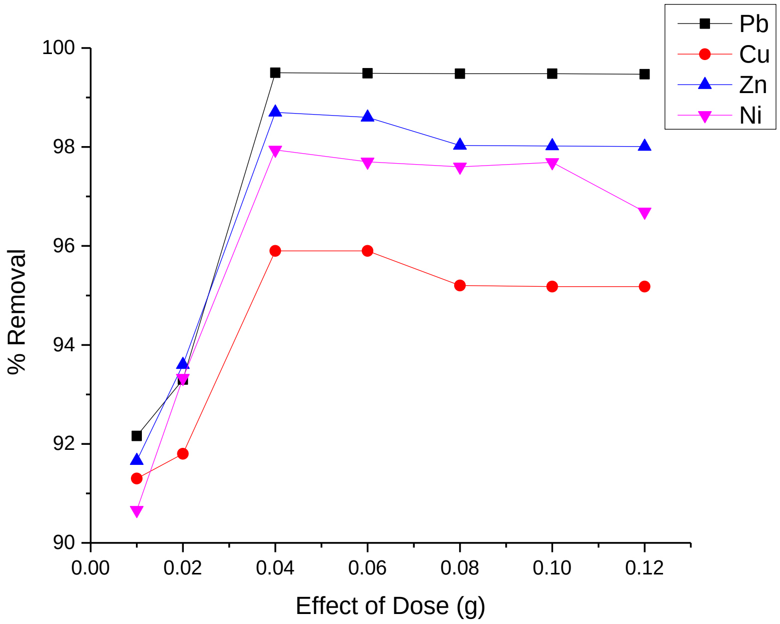


Figure 5: Effect of adsorbent dosage on adsorption of Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} on *Eucalyptus Glabulus bark*

4.3.2. Effect of initial concentration of metals

Removal of the metal ions (i.e. Lead, Copper, Nickel and Zinc) was studied for concentrations ranging from 10 to 50 mg/l. the percentage removal of Zn (II), Ni (II), Cu (II) and Pb (II) at different concentrations from 1000 ml solution of different initial concentrations is shown in Figure 7. As can be observed from the figure, the removal of the metal ion was found to generally increase with increase in initial concentration. The increase in percent removal was fast for smaller concentrations of Pb (II), Ni (II), Cu (II) and Zn (II). For higher concentrations, a slight increase in removal efficiency of the metal ion was observed with increase in concentration.

At low concentration, the ratio of available surface of the adsorbents to the initial Ni (II), Cu (II), Pb (II) and Zn (II) concentration is larger, so the removal is higher. However, in case of higher concentrations this ratio is low, hence the percentage removal is also less. Increasing metal ion concentration increased adsorption capacity for each adsorbent, which could be attributed to increased rate of mass transfer due to increased diffusivity of driving force.

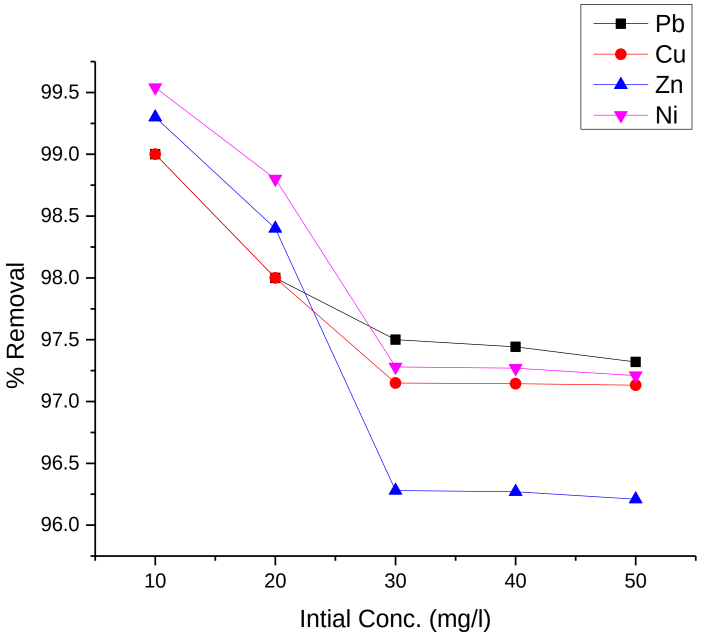


Figure 6 : Effect of initial metal ion concentration on adsorption of Zn (II), Ni (II), Cu (II) Pb (II), adsorbents dose is 0.04 g.

4.3.3. Effect of contact Time

Contact times are one of the important parameter for successful adsorption application.

Figure 8: shows the adsorption efficiency of Pb (II), Ni (II), Zn (II) and Cu (II) ions as a function of contact time. It is evident from figures that the removal of the metal ions increases as the contact time increase. It can be seen from figures 8: that the rate of uptake of Pb (II) was fast until equilibrium was attained. Equilibrium was attained in 60 minutes for the adsorbents *Eucalyptus bark*. At these optimum contact times the maximum percentage adsorption of Pb (II) was 98.63 % by the adsorbents *Eucalyptus bark*. On further increase in contact time to 3 hours, the percentage removal either remains almost constant or decreases very slowly.

The optimum contact time for Zn (II) was 45 minutes for the *Eucalyptus bark*. At these optimum contact times the maximum Adsorption efficiencies of the adsorbents of *Eucalyptus bark* for (Zn (II) were 96.33 %. Similarly, Cu (II), 97.66 % and 96.45 % Ni (II) adsorption onto *Eucalyptus bark*. A constantly increase in the Adsorption of *Eucalyptus bark* With the rise in time may be due to either the damage of active binding sites in the *Eucalyptus bark* increasing tendency to saturation of metal ions from the interface to the solution.

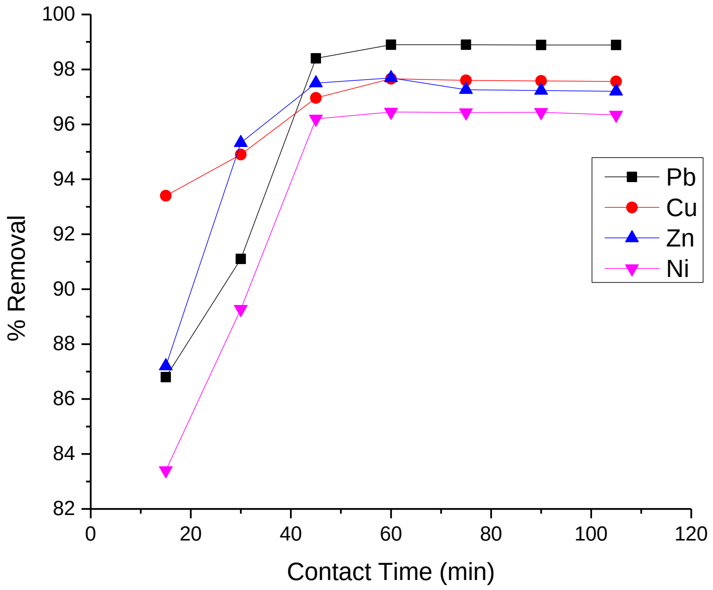


Figure 7: Effect of contact time Ni (II), Cu (II), Zn (II), Pb (II) on to *Eucalyptus Glabulus bark*, (contact time =60 min and adsorbent dose =0.04 g)

4.3.4 The Effect of pH

It is clear that pH is one of the prominent factors in any adsorption experiments because of its effect on the adsorption efficiency .There also there was significant increase of removal efficiency for the lower pHs' than the higher ones .This might be explained as follows; at higher pH the process tends to reach equilibrium quickly, since the competition between H+ and heavy metal ions is highly reduced and most of adsorbents active sites are occupied by the adsorbate which leads to the electrostatic repulsion of previously adsorbed metal ions and free ions in the solution the initial pH value of the solution has more influence than the final pH, which influences among the adsorbents surface metal binding sites and the metal chemistry in water. The pH of each solution was examined at different initial pH levels covering a range of 3-9 for various metals.

Regarding lead, Figure 9 illustrates that the best adsorption efficiencies were noted for *Eucalyptus Glabulus bark*, and at pH 6, Eucalyptus bark removed 99.7% of Pb (II). Pb (II) ions are in competition with hydrogen ions for the adsorbents' surface at pH 3, which prevents Pb (II) ions from accessing the adsorbents' binding sites due to repulsive forces and causes a partial release of the metal ion. At pH > 6.0, the Pb (II) gets precipitated due to hydroxide anions forming a lead hydroxide precipitate. Hence, the optimum pH value was obtained to be 6.0-7.0. The predominant adsorbing forms of lead are Pb2+ and PbOH+ which occurred in the pH range of 5- 6 (A.S. Bhatt, et al.,(2012)). At pH higher than 6-7 precipitation of lead occurred and removal due to adsorptions started to decrease slowly. As we have seen Figure.9: as maximum removal of Cu (II) obtained 99.5 % , as maximum removal of Ni (II) 99.2 %, Maximum adsorption of the all metal ions was observed at acidic pH of 5.0-6.0 when 95.46 % Zn (II) was removed by *Eucalyptus bark*.

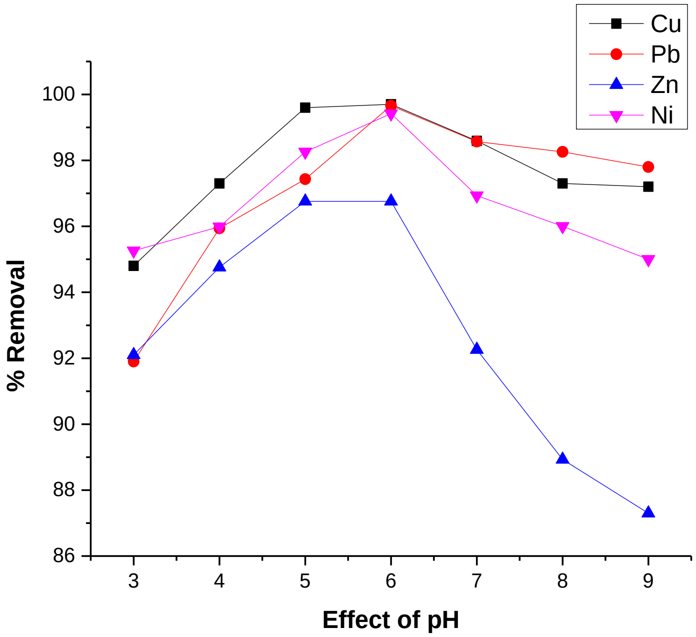


Figure 8: Effect of pH for A) Pb (II), B) Cu (II), C) Ni (II), D) Ni (II) on to *Eucalyptus bark Glabulus* adsorbents dose = 0.04 g,

4.3.5. Effect of temperature

Temperature increases between 0°C and 60°C had an impact on the adsorption of Zn (II), Cu (II), Pb (II), and Ni (II) utilising *Eucalyptus bark* powder, indicating an endothermic reaction. The maximum adsorption capacity yields were noted on Figure 10. The results indicate that 98.2, 98.5, 98.23, of 96.75% and 98.6 percent removed by *Eucalyptus bark* powder. While , after equilibrium a constantly decrease in adsorption capacity of Zn (II),Cu(II),Ni (II)and Pb

(II) high temperature (above 50°C) shown weak interaction between the active sites adsorption where the reaction is exothermic and adsorption reaction favored by low temperature. Adsorption involves particular relationships between the temperature of the solute and the characteristics of activated carbon. Thus, not all carbon and solutes experience the same quantitative impacts of temperature. Because adsorption reactions are exothermic, the extent of adsorptions should rise as temperature decreases. However, the higher temperatures also accelerated the solute's rate of diffusion through the liquid to the adsorption sites, which ultimately resulted in more adsorptions. The effect of temperature plays a significant impact in the adsorptions of solutes against gases. A rise in temperature reduces adsorptions because it makes a gas more likely to exit the contact. On the other hand, the temperature-solvent affinities interface is more prominent in liquid-based adsorptions (M.P. Elizalde- Gonzalez, et al., 2008).

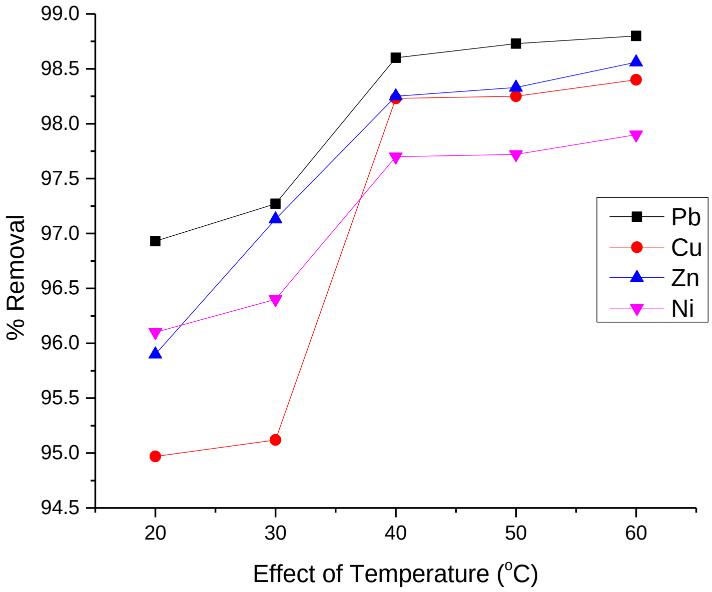


Figure 9 : Effect of Temp. for A) Pb (II), B) Cu (II), C) Zn (II), D) Ni (II) on to *Eucalyptus bark Glabulus* adsorbents dose = 0.04 g.

4.5. Adsorption Equilibrium Study

The variation in the amount of adsorbate adsorbed by the adsorbent with concentration at constant temperature can be expressed by means of a curve termed as adsorption isotherm or the process of adsorption is usually studied through graphs is known as adsorption isotherm.

Adsorption isotherms or known as equilibrium data are the fundamental requirements for the design of adsorption systems. The equilibrium is achieved when the capacity of the adsorbent materials is reached, and the rate of adsorption equals the rate of desorption. The theoretical adsorption capacity of an adsorbent can calculated with an adsorption isotherm. The successful representation of the dynamic adsorptive separations of solute from solution by an adsorbent depends up on good descriptions of the equilibrium between the two phases. The equilibrium adsorption isotherms were depicted by plotting solid phase concentration (q_e) against liquid phase concentration (Ce) of solute. Adsorption isotherms are useful for finding out the adsorption capacity of the adsorbent, the solute-solution interaction and the degree of accumulation of adsorbate on the surface of the adsorbent. In the present study, the adsorption of metals onto activated carbons was studied by two adsorption isotherm models: Langmuir and Freundlich isotherms.

4.5.1. Langmuir Isotherm

The Langmuir isotherm is applicable to homogeneous adsorption where the adsorption of each adsorbate molecule on to the surface has equal adsorption activity energy and is represented as follows (A.S. Bhatt, et al.,2012)

$$q_e = \frac{V(Co-Ce)}{m} \qquad (1)$$

Where V is the volume, Co and Ce is the initial and equilibrium concentration of the metal ion and m is the mass of the adsorbent.

The Langmuir parameters were obtained by fitting the experimental data to linear equations derived from

$$q_e = \frac{QmaxbCe}{1+bCe} \ (2)$$

Where q_e (mg/g) is the amount of adsorbate adsorbent per unit weight of adsorbent at equilibrium concentration, C_e (mg/l) concentration of adsorbate at equilibrium in solution after adsorption, the Q_o (mg/l) and b (L/mg) are the Langmuir constants related to the maximum monolayer capacity and energy of adsorption, respectively.

The linear form of Langmuir equation is given as

$$\frac{Ce}{qe} = \frac{1}{Qmaxb} + \frac{Ce}{Qmax} \qquad (3)$$

The adsorption data were analyzed according to the linear form of equation. The plots of C_e/q_e versus C_e are linear which indicate that the adsorption data fitted reasonably to the Langmuir isotherm. The constants Q_{max} and b were evaluated from the slope $1/Q_o$ and intercept $1/Q_{max}b$ (Figure 11 and Table 3).

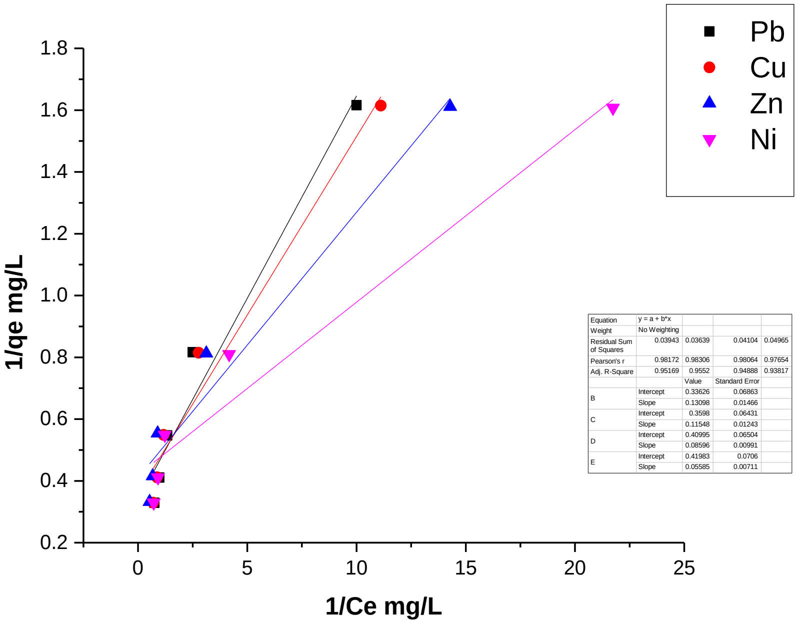
$$1/qe = \frac{1}{Qmax} + \frac{1}{CeQmaxb} (4)$$

A plot of 1/qe versus 1/Ce at constant temperatures gives straight lines and values of b and Qmax are calculated from the slope and intercept of the plots respectively.

Moreover, in order to ensure that the adsorption process is favorable, irreversible or unfavorable for Langmuir kind adsorption process. Langmuir isotherm is then categorized using a dimensionless constant separation factor (R_L), which can be defined as:

$$R_L = \frac{1}{1+Cob} \ (5)$$

Where b is the Langmuir constants and C_o the initial heavy metals concentration (mg/L), R_L values indicates the types of isotherms. The parameter R_L values indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if R = 1, favorable if $0 < R < 1$ and irreversible if R= 0. From the data calculated in Table 3, R_L values between 0 and 1 indicating that Langmuir isotherm is favorable. R^2 (correlation coefficient) values approaching to one, clearly suggest that Langmuir isotherm holds good to explain adsorption of metals on activated carbons.



Equation	y = a + b*x			
Weight	No Weighting			
Residual Sum of Squares	0.03943	0.03639	0.04104	0.04965
Pearson's r	0.98172	0.98306	0.98064	0.97654
Adj. R-Square	0.95169	0.9552	0.94888	0.93817
		Value	Standard Error	
B	Intercept	0.33626	0.06863	
	Slope	0.13098	0.01466	
C	Intercept	0.3598	0.06431	
	Slope	0.11548	0.01243	
D	Intercept	0.40995	0.06504	
	Slope	0.08596	0.00991	
E	Intercept	0.41983	0.0706	
	Slope	0.05585	0.00711	

Figure 10: Langmuir equilibrium isotherm model for the adsorption of the four metal ions on to the adsorbent dose 0.04g

4.5.2. Freundlich Isotherms

Freundlich adsorption isotherm in 1909, gave an empirical relationship between the quantity of adsorbate adsorbed by unit mass of solid adsorbent and concentration at a particular temperature. The most important multisite or multilayer adsorption isotherm for heterogeneous surfaces is the Freundlich isotherm which is characterized by the heterogeneity factor 1/n, and is represented by the equation:

$$q_e = K_F C_e^{1/n} \qquad (6)$$

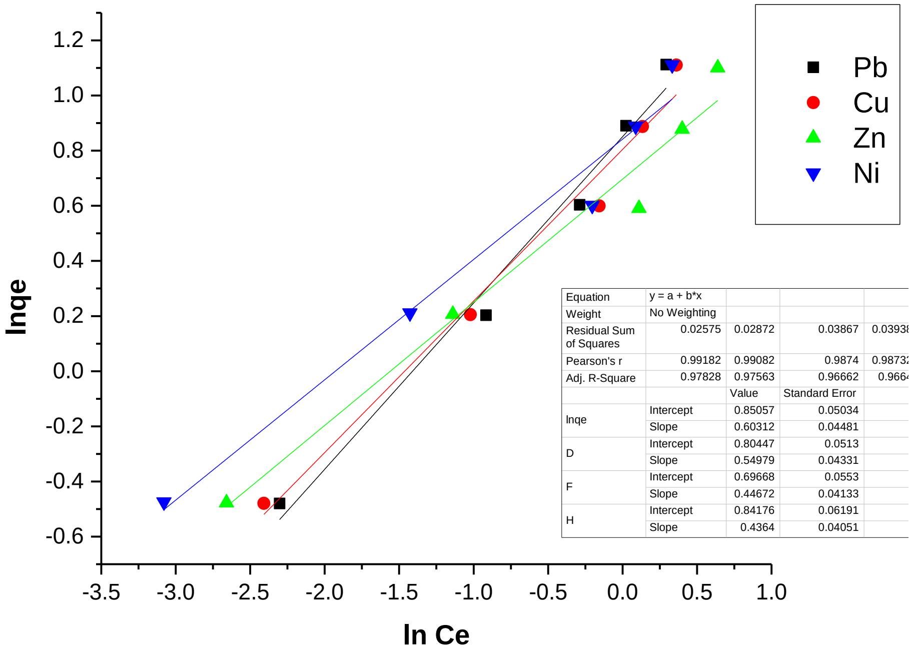
Where, the K_F and 1/n are Freundlich constants related to adsorption capacity and intensity of adsorption respectively. The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. The linear form of Freundlich equation is:

$$\mathrm{Ln}\, q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (7)$$

Values of K_F and n were calculated from the intercept and slope of plotes $\ln q_e$ vs $\ln C_e$ and a straight line indicates the confirmation of the Freundlich isotherm for adsorption (Figure11).

The values of n should be greater than one confirming good adsorption of heavy metals onto the adsorbent (Table 3) otherwise desorption becomes predominant. If a value of n = 1, the adsorption is liner, for n< 1, the adsorption is chemisorptions, and for n> 1 the adsorption is afavorable physical adsorption (H. Yuh-shan, 2004).

Based on the correlation coefficients (R^2), it is clear that the adsorption of metal ions on to activated carbon is best fitted to the Freundlich adsorption isotherm for the entire range of concentrations. The fact that the Freundlich isotherm fits the experimental data very well may be due to heterogeneous distribution of active sites on the carbon surface, since the Freundlich equation assumes that the surface is heterogeneous. The values of n for Freundlich isotherm were found to be greater than 1, indicating that metal ions are favorably adsorbed by activated carbons.



Equation	y = a + b*x			
Weight	No Weighting			
Residual Sum of Squares	0.02575	0.02872	0.03867	0.0393
Pearson's r	0.99182	0.99082	0.9874	0.9873
Adj. R-Square	0.97828	0.97563	0.96662	0.966
		Value	Standard Error	
lnqe	Intercept	0.85057	0.05034	
	Slope	0.60312	0.04481	
D	Intercept	0.80447	0.0513	
	Slope	0.54979	0.04331	
F	Intercept	0.69668	0.0553	
	Slope	0.44672	0.04133	
H	Intercept	0.84176	0.06191	
	Slope	0.4364	0.04051	

Figure 11: Freundlich equilibrium isotherm model for the adsorption of the four metal ions onto the adsorbents dose of 0.04g

Table 3: Freundlich and Langmuir models regression constants for Pb (II), Zn (II), Cu (II) and Ni (II)

Adsorption isotherms		Freundlich isotherms			Langmuir isotherms			
Adsorbents	Metals	K_f	n	R^2	q_{max}	b	R^2	R_L
	Units	mg/g	l/mg		mg/g	l/mg		
Eucalyptus bark	Ni (II)	0.84176	2.291475	0.9664	0.4099	0.05585	0.9382	0.37376
	Zn (II)	0.69668	2.238538	0.9666	0.4109	0.08596	0.9489	0.27942
	Cu (II)	0.80447	1.818876	0.9756	0.3598	0.11548	0.9552	0.22399
	Pb (II)	0.85057	1.658044	0.9783	0.3363	0.13098	0.9517	0.20286

The value of *n* between1and 10 represents beneficial adsorption process. The Freundlich isotherm model gives best fit with the equilibrium adsorption data, which have highest correlation coefficient values of (0.964 -0.978). As the experiment al results for four metals gave good fitto Freundlichmodel,it can be interpreted that the adsorption process takes place to finite number of heterogeneous adsorption sites and it is based on multilayer coverage on the adsorbents.

The alues of separation factor, RL, indicate then ature of the adsorption process. In the present study, the alues of RL were observed to be fractions i.e., in the range of zero toone (0.202-0.37), which indicate that the adsorption process was favorable for all the adsorbents investigated in the present study.

4.6. Thermodynamic study

4.6.1. Thermodynamic study for heavy metal

The thermodynamic parameters that help us to understand the nature of the adsorption of heavy metal on adsorbents are the standard change in Gibbs free energy ($\Delta G°$), the standard change in entropy ($\Delta S°$),and the standard change in enthalpy ($\Delta H°$). The relation between $\Delta G°$, $\Delta H°$ and $\Delta S°$ is as follows (H. Yuh-shan, et al, 2004) :

$$\Delta G° = \Delta H° - T\Delta S° \quad (8)$$

The nature of the adsorption of heavy metal on the prepared ACs was predicted by estimating the thermodynamic parameters. The change in thermodynamic parameters such as Gibb's free energy $(\Delta G°)$, enthalpy $(\Delta H°)$ and entropy $(\Delta S°)$ were evaluated from the following equations (J. Fito, et al, 2019) :

$$\Delta G° = -RT\ln Kc\_ \qquad (9)$$

Where, kc is the equilibrium constant and calculated as:

$$Kc = \frac{CAe}{Ce} \qquad (10)$$

C_{Ae} (mg/g) and Ce (mg/l) are the equilibrium concentrations for solute on the adsorbent and in the solution, respectively. The kc values were used to determine the $\Delta G°$, $\Delta H°$ and$\Delta S°$. The kc expressed in terms of the $\Delta H°$(KJ/mol) and $\Delta S°$(KJ/mol) as a function of temperature:

$$\ln Kc = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad (11)$$

$\Delta H°$and $\Delta S°$ were obtained from the slopes and intercepts of the plots of ln kc against 1/T Shown in Figure 13. The free energy change $(\Delta G°)$ indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption. The increase in negative value of $(\Delta G°$ with increase of temperature showed that the adsorption of heavy metal on prepared AC samples increased with the rise in temperature. The positive values of $\Delta H°$ shown in table 4.Confirmed the endothermic nature of the adsorbents for heavy metal adsorption in the studied range 0 – 60°C. The positive values of $\Delta S°$ confirmed the randomness of the adsorption process and the adsorption was endothermic.

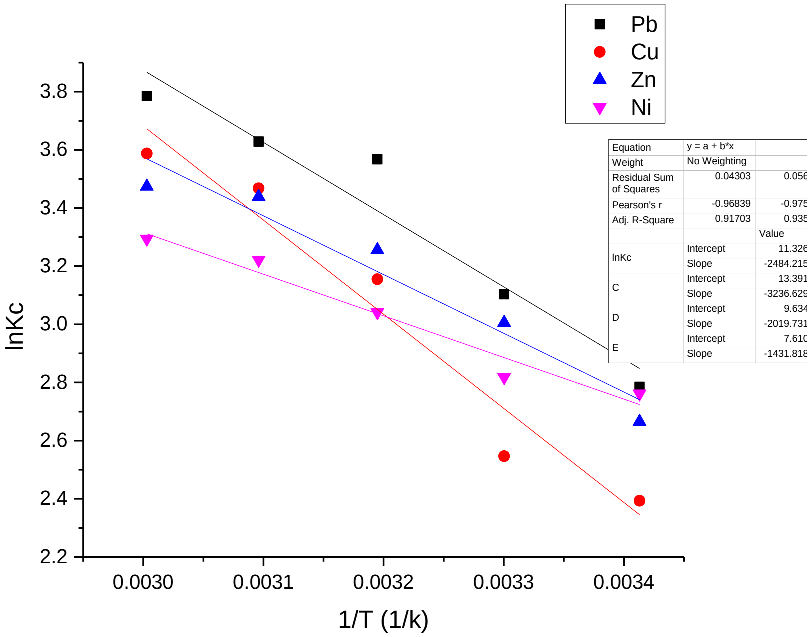


Figure 12: Van't Hoff plot for thermodynamics study for activated carbon of *Eucalyptus Glabulus bark*

Table 4: Thermodynamic parameters for the adsorption of heavy metal on activated carbon of *Eucalyptus bark*

AC Type	Metals	ΔG (J/mol)					ΔH (J/mol)	ΔS (J/mol)
		20 °C	30 °C	40 °C	50 °C	60 °C		
Eucalyptus bark	Pb	-7270.37	-7817.36	-9283.99	-9742.91	-10477.9	11.3266	-2484.2
	Cu	-5829.97	-6163.62	-9233.54	-9580.61	-9931.92	13.3918	-3236.6
	Zn	-6493.140	-7572.78	-8571.73	-9235.06	-9618.343	9.6341	-2019.7
	Ni	-6726.835	-7097.85	-7913.61	-8650.46	-9119.445	7.61092	-7097.8

Table 5: Comparison heavy metal up take capacity using different bioadsorbents at the same pH=6

Heavy Metal	**Adsorbents**	**Removal Efficiency**	**Reference**
Pb(II)	*Oriza sativa*	98 %	

	husk		(A.Saeed,et al,2005)
	Passiflora Edulis	95.07 %	
	This study	98.58%	
Cu(II)	Banana peel	91.5 %	(G. K and P.S koblewsk, et al, 2010**)**
	Passflora edulis	93.11 %	
	This study	99.1%	
Ni(II)	Coconut husk	85 %	(C. RajI, et al, 1997)
	This study	98.4%	
Zn(II)	Coir	90.87 %	(A.C. Ahmed,et al,2006)
	This study	97.64%	

4.7. Treatment of contaminated water

Real contaminated wastewater sample was used to assess the removal efficiency of Zn (II), Cu(II), Pb(II) and Ni(II) using activated carbon of *Eucalyptus bark*. The adsorption efficiencies of the adsorbents were tested at optimum operating parameters. The concentrations of selected heavy metal ions in wastewater samples were determined using FAAS. Quality control measures were taken to assess contamination and reliability of data. As indicated in the Table , it has been found that almost 89.72±0.012, 82.78 ±0.02, 87.92 ± 0.022 and 85.59 ± 0.074 all metal ion were removed.

Table 6: Results of Real Wastewater sample Analysis for Pb(II) , Cu(II), Zn(II) and Ni(II).

Heavy metal	*Concentration in real water sample(mg/L)	Adsorbent	*Concentration at equilibrium(mg/L)	%Removal
Zn(II)	9.3 ±0.089	AC	1.0 ±0.020	89.72±0.012
Cu(II)	5 ±0.016	AC	0.9 ±0.05	82.78 ±0.02
Pb(II)	1.49 ±0.2699	AC	0.18±0.065	87.92 ± 0.022
Ni(II)	4.06 ± 0.209	AC	0.37 ±0.034	90.75 ± 0.074

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the present study, it is clearly shown that the activated carbon of *Eucalyptus bark* under proper modification by chemical activation with phosphoric acid (H_3PO_4) is an effective adsorbent for the removal of Cu (II), Pb (II), Ni (II) and Zn (II) ions from aqueous solution. The batch adsorption process dependent on the adsorbent dosage, contact time, solution pH, initial concentration of metal ions and temperature, the Fourier transformation of infrared Spectroscopy techniques indicates the activated carbons have alcoholic surface functional groups and Scanning electron microscope indicates as the activated carbon have porous structure on the surface. Thermodynamic analysis asserted endothermic and spontaneous nature with involvement of chemical adsorption process. Equilibrium isotherms were measured experimentally at all temperature and results were analyzed by the Langmuir and Fireundlich equations using linearized correlation coefficient.

5.2 Recommendation

I recommended the following for further studies.

- Preparation of activated carbon by *Eucalyptus bark* was not done yet for various activities, thus it needs further studies.
- Extensive investigation should be carried out to produce ACs with even better surface characteristics through different routes.
- Utilization of ACs to treat various other pollutants present in water contaminated with heavy metals should be undertaken.

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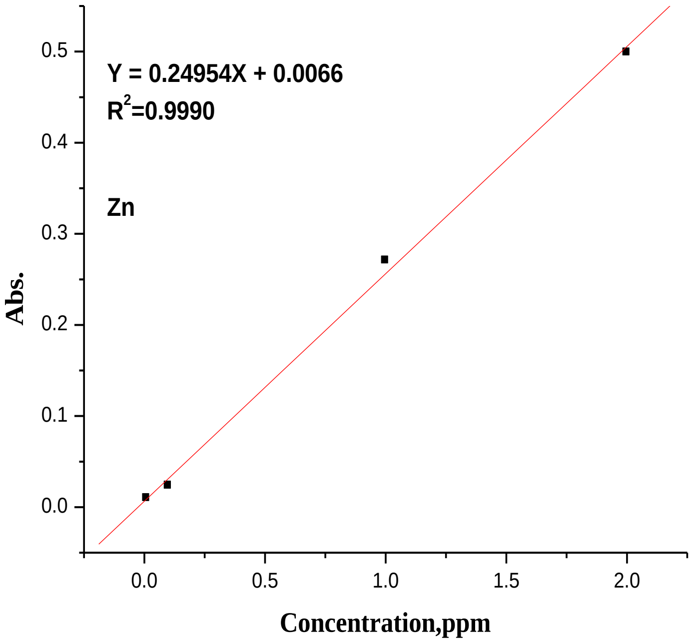
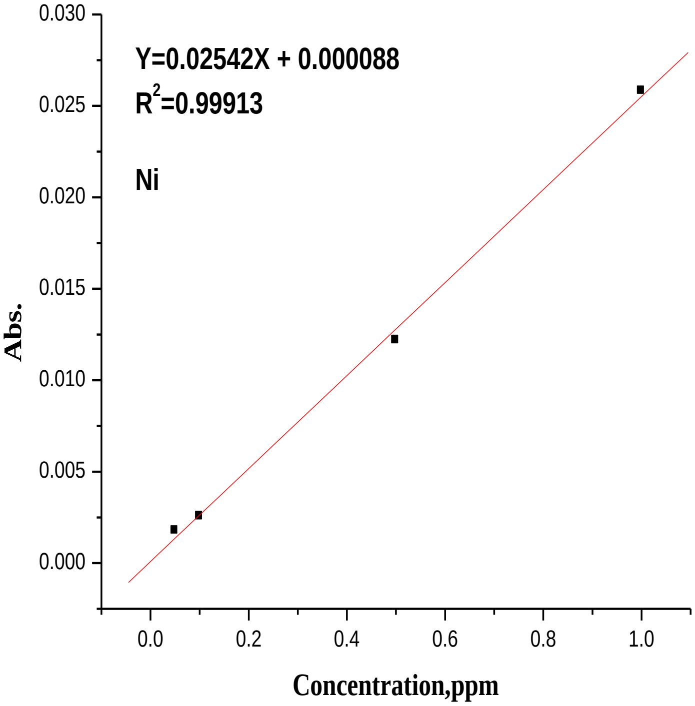
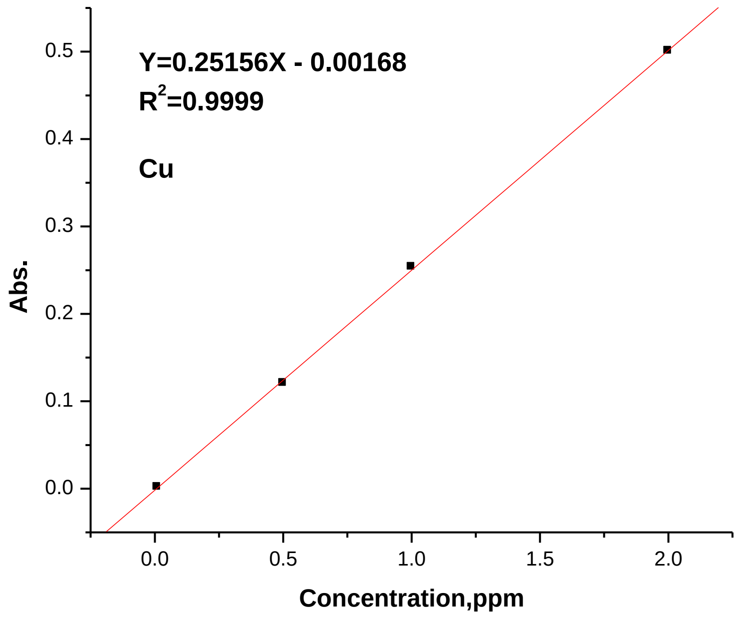
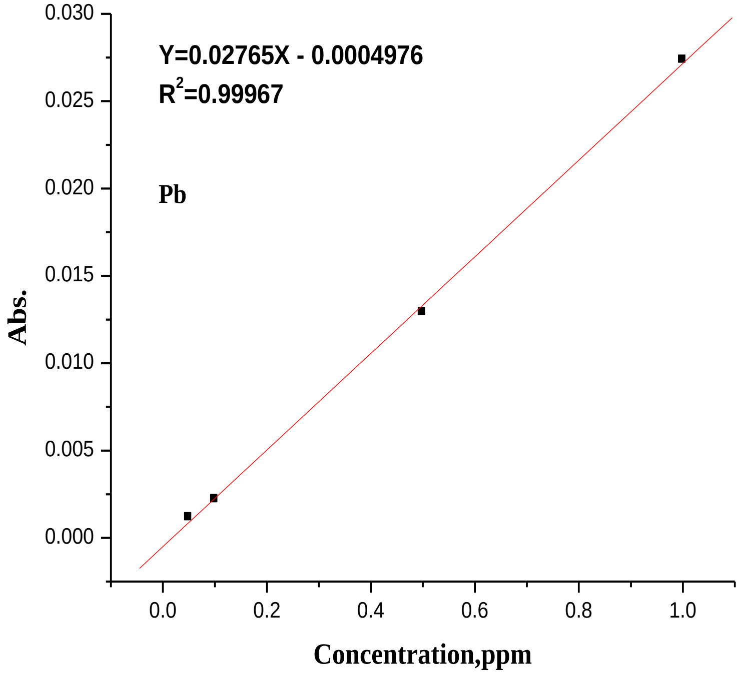
Appendix A: Calibration curve of heavy metals







Y=0.25156X - 0.00168
R^2=0.9999
Cu
Abs.
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.5
1.0
1.5
2.0
Concentration,ppm



Y=0.02765X - 0.0004976
R^2=0.99967
Pb
Abs.
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0.0
0.2
0.4
0.6
0.8
1.0
Concentration,ppm