ADDIS ABABA UNIVERSITY

Addis Ababa Institute of Technology

School of Chemical and Bio Engineering

Removal of Some Selected Heavy Metal Using Modified Bagasse and Eucalyptus Bark from Gold Mining Waste Water: Case Study of Ezana (Meli) Gold Mining Development Plc Industries

By: Mebrahtom Hagos

A Thesis

Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering (Environmental Engineering Stream)

Advisor: Dr. Eng. Abubeker Yimam

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BY: Mebrahtom Hagos

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DECLARATION

I, the undersigned, declare that this thesis entitled **"**Removal of Some Selected Heavy Metal Using Modified Bagasse and Eucalyptus Bark from Gold Mining Waste Water: Case Study of Ezana (Meli) Gold Mining Development Plc Industries*"* is my original work, and has not been presented by any other person for an award of a degree in this or any other University, and that all resources of materials used for this thesis have been duly acknowledged.

Name: Mebrahtom Hagos

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_____

Date of submission June, 2018

This thesis has been submitted to the University with my approval as the University Advisor.

Name Dr. Eng. Abubeker Yimam
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ABSTRACT

This study investigated the potential use of modified bagasse (MSB) and eucalyptus Bark (EB) treated from sample wastewater in batch mode experiments. The discharge of untreated gold mining wastewater contaminates with heavy metals such as Cu (II) and Pb (II), which is threatening ecosystems, carcinogenic to the human & hinder development of plants. Since the removal by adsorption is cost effective, not time consuming and environmentally friendly, it has been widely studied by many scholars for remediation of heavy metals. Characterization of bagasse and eucalyptus bark were analyzed using proximate analysis like MC (%), Ash value (%), ϱ_b *(g/cm*^{3}*), VM (%), fixed carbon (%) and % (C,* N_2*). FTIR analysis revealed the presence of multiple functional groups in the adsorbent, some of which were involved in the sorption process and x-ray diffraction (XRD)* used to measure the crystalline content of adsorbent materials. *The result indicated that the effluents discharged from Ezana Gold extraction were mainly contains the following: TSS (ppm), turbidity (NTU), EC (µs/cm), TDS (ppm), COD (ppm), temperature(°C), pH, cyanide WAD with <11°C (ppm) and heavy metals such as Fe > Cu >Pb >Mn > Cr (VI) >Zn > Co > Ni > Cd (ppm). They were determined by atomic absorption spectroscopy. The major pollutants selected from the process effluent were* Cu^{2+} *and* Pb^{2+} *due to exceeded standard discharge limits. The objective of the study was removal of* Cu^{2+} *and* Pb^{2+}*from rich Ezana wastewater using modified sugarcane bagasse and eucalyptus bark powder as an adsorbent. The selected parameters were pH, adsorbent dose and time. A maximum removal of (*Cu^{2+}*,* Pb^{2+}*) by modified bagasse (88.45%, 94%) and eucalyptus bark (92%, 99%) respectively was achieved. The adsorption data were well fitted to the Langmuir isotherm model and pseudo-second order kinetic model for both modified bagasse (Cu, Pb) and eucalyptus bark (Cu, Pb). This indicated that Eucalyptus bark powder was more effective than modified bagasse (MSB) and it can be used as an alternative low cost adsorbent for the removal of copper and lead from Ezana mining wastewater.*

Key words: Adsorption, Cu^{2+} *and* Pb^{2+}*, Modified bagasse and eucalyptus bark, Isotherm and kinetics*

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LIST OF ACRONYMS

BBD	Box Behnken design
EB	Eucalyptus bark
CERCLA	Comprehensive environmental response, compensation and lability act
EFFORT	Endowment fund for rehabilitation of Tigray
FAAS	Flame atomic adsorption spectroscopy
IFC	International finance corporation
MIE	Mesfin industrial engineering
MSB	Modified sugarcane bagasse
PFA	Perflouro alkoxy alkanes
ppm	Parts per million
rpm	Revolution per minute
RSM	Response surface methodology
SB	Sugar bagasse
TOC	Total organic carbon
VMS	Sodium Meta bisulfite
WAD	Weak acid dissociable

1. INTRODUCTION

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. The present study focused on adsorption of selected heavy metals (Cu, Pb) using Modified sugarcane bagasse and Eucalyptus bark. These heavy metals were selected due to their maximum concentration ; Cu (8360 to 59280 ppm) and Pb (6.4 to 1652 ppm) of Ezana (Meli) (Abraham et al., 2015).

A large number of biological researches focused on the use of microorganisms such as bacteria, agricultural wastes plant biomaterials for removal of heavy metals and metalloids have adverse impacts on human health. Many conventional techniques such as chemical precipitation, membrane filtration, ion exchange, carbon adsorption with co-precipitation have been used to treat waste water effluents. However, they are not suitable for high concentration of metals and incur high cost. There are a lot of merits of adsorption including low cost, locally abundant, require, less maintenance, simple alkali and acid treatment etc. The purpose of treating the adsorbent with acid was to remove lignin part of the material prior to adsorption there by increasing their percent removal (Tripathi e al., 2015).

Various kinds of treating agents like H_2SO_4, NaOH are used for sugarcane bagasse. Sulfuric acid was used to treat eucalyptus bark for removal of lignin which packs the cellulose and it increases the carboxyl active groups on used for increase the adsorption efficiency (Gurgel at al., 2008). The bio adsorbents have affinity for heavy metal ions to form metal complexes or chelates through their functional groups like carboxyl, hydroxyl, phosphate, sulfate, thio ether, phenol, carbonyl amide. For decontamination of heavy metals from wastewater, the treated adsorbent sugarcane bagasse is comparatively better than untreated one, because untreated adsorbent can further generate the problems such as low adsorption capacity, high COD & TOC due to release of soluble organic compounds in plant (Shrikant Bhosale, 2015). The effect of physical parameters such as pH, adsorbent dosage and contact time was investigated to examine the efficiency of modified sugar cane bagasse and eucalyptus bark.

Batch study was conducted using heavy metal containing real wastewater sample laboratory from four selected sites of tailing storage dam. The heavy metal were analyzed by digesting with acid to prevent precipitation due to high acidity of the sample then diluted with deionized water. Analysis of the result showed Cd (0.02), Cr (VI) (0.43), Cu (71), Ni (0.1), Pb (16), Fe (313.11),

Zn (0.34), Mn (0.94) in ppm. The other physiochemical characterization were pH 8-8.5, EC (µs/cm) 2980, turbidity in (NTU) 7800, T^{o} (10-33°C), TDS (1213ppm), TSS (750ppm), COD (120ppm). The initial concentration (Cu, Pb) in ppm from the sites (6 hour difference) are in the out let discharge of the slurry east direction (71, 16), south (30, 3.8), west (51, 10.2) and north (40, 6) respectively.

1.2. Problem statement

Tailings are one of the mining wastes produced during mineral processing operation and the dam should be sealed with a liner with a mixture of water and finely ground rock that is left over after the valuable metals are completely or incompletely extracted from its host ores. The content of the tailings themselves depend on what mineral being mined, technology used to process the ore to ensure safety of tailings disposal and mining plants must have a tailings management facility as a final storage area. However, the gold mining operations in Ezana (Meli) do not have such kind of storage facility because their tailings were discharged as slurry through pipelines into only one tailings pond, which is covered by geotextile membrane on the bottom and plastic geo membrane on the above. The wastewater are recycled using the overflow return water pump from tailing pond to prevent seepage but these is not sustainable due to creation of a small perforation plastic geo membrane wastewater are leaching in to the ground water; the dam due to smaller in size frequently overflows during summer and is discharged to the nearby river. The presence of different heavy metals in wastewater due to toxicity and non- biodegradability, tends to accumulate in down streams. In Ethiopia the application of advanced technology is technically complex, expensive, and non-feasible. Having the above mentioned problems in mind, the factory need to develop on-site facilities to treat their own effluents using low-cost technologies based on locally available, cheap, environmental friendly sorption materials like bagasse and eucalyptus bark in order to minimize the contaminant concentration.

1.3. Objective of the research

1.3.1. General objective

The aim is to investigate the efficiency and the practical applicability of low-cost adsorbents modified sugarcane bagasse and eucalyptus bark for removal of some selected heavy metals from wastewater of gold industries.

1.3.2. Specific objectives

The specific objectives of the research are:

- To characterize the effect of modified bagasse and eucalyptus bark
- To characterize the gold mining waste water
- To investigate effect of modified sugarcane bagasse and eucalyptus bark as adsorbent
- To optimize the process parameters like pH, contact time and adsorbent dosage
- To investigate the batch kinetics of adsorption and sorption isotherm with different models

1.4. Significance of the study

After accomplishment of the study, it will contribute to the application of adsorption by giving sufficient information on a low cost adsorbent residue. To prevent contamination, it takes more resources to dispose of this residue. Removal of Cu and Pb using modified sugar cane bagasse and eucalyptus bark has a lot of merits such as low cost, environmentally friendly, and locally abundant, less operating and maintenance cost etc. Furthermore, removal of heavy metals from industrial waste streams is becoming increasingly important to neutralize the hazard from the industrial waste and not harmful to plant and animal life (Mohd et al., 2010) & (Prapurna et al., 2006).

1.5. Scope of study

The scope is to test wastewater for the removal of only specific heavy metals Cu and Pb using modified sugarcane bagasse and eucalyptus bark as an adsorbent. It is the most pertinent way of evaluation of water quality with respect to gold mining. Wastewater quality analysis of the heavy metals were done using atomic adsorption spectrophotometer. Batch study was conducted using Cu and Pb from wastewater sample. The influence of pH, adsorbent dosage and contact time were investigated to optimize the conditions for maximum copper and lead removal at constant concentration, particle sizes, mixing speed.

2. LITERATURE REVIEW

2.1. Gold extraction and digestion of metallurgical samples using acids

The potential for environmental contamination by mine waste are overburden, waste rock, tailings, slags, mine water, water treatment sludge, gaseous wastes etc (UNEP, 2000). The gold-bearing ore is crushed these will be erected in the open air and ground to approximately 100 microns and transported to a leaching plant where lime, cyanide and oxygen are added to the ground and slurred ore. The lime raises the pH, while the oxygen, cyanide oxidize and complex the gold see equation 2.1:

$$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4\,Na\,[Au\,(CN)_2] + 4NaOH \ldots\ldots (2.1)$$

The method of gold extraction is by leaching with NaCN (cyanidation) is currently the most widely used methods. In a typical heap leach operation, vast quantities of rock are crushed and piled onto clay and plastic liners in huge decks (Enquiry, 2010).

The NaCN is required for solubilizing the adsorbed gold cyanide complex and the caustic (NaOH) is added to maintain a high pH to minimize the evolution of HCN gas. Upon the completion of this stage the gold cyanide complex is still adsorbed to the carbon (i.e, no gold is removed into solution during this stage) but the attraction between the complex and the carbon is 'weakened', allowing it to be easily desorbed in the elution stages. The cyanide solution thus dissolves the gold from the crushed ore. Next, the gold bearing solution is collected. Finally, the gold is precipitate out of the solution (Acheampong et al., 2010). Carbon in Leach is the leached/dissolved gold adsorbed on activated carbon while at the same time and in the same tank the leaching reaction still takes place (Name, 2017).

Leach Process: The milled ore (slurry) agitated in the leach tanks by mechanical means, to increase the contact of cyanide with oxygen and gold to enhance the efficiency of the leach process. The cyanide then dissolves gold from the ore and forms a stable gold-cyanide complex according equation 2.1.

Grinding: The slurry from the milling process will be transferee to the leach tanks by pumping or by means of gravity. The sequence of treatment after milling is going to be: leaching of gold, separation of gold bearing solution from solid, precipitation of gold from solution.

CIP process: In the CIP technique, the gold cyanide complex is adsorbing onto activated carbon (adsorption process) on figure 2.1 until it comes to equilibrium with the gold in solution. Because

the carbon particles are much larger than the ore particles, the coarse carbon can be separate from the slurry by screening using a wire mesh. The gold loaded carbon is then removed and washed before undergoing "elution" or desorption of gold cyanide at high temperature and pH. The rich eluate solution that emerges from the elution process was passing through electro wining cells where gold and other metals are precipitate onto the cathodes. Smelting of the cathodes material further refines the gold and produces gold ingots suitable for transport to a refinery (Ripley et al., 1996). Mercury amalgamation and gravity concentration are the other processes for obtaining gold concentrate from gold ore.

In the carbon-in-pulp adsorption process are takes place as a gold cyanide complex, in a series of six agitated CIP tanks. This will be followed by gold recovery process (elution/stripping, electro-winning and smelting) and use reagent circuits such as cyanide storage tank agitator, fresh water tank, fresh water pump, reagent pump, and carbon storage tank.

Gold recovery: Elution/ stripping circuit is the process of extracting gold from loaded carbon these separated from pulp by 10% HCl then stripped of its gold charged by elution (Ababa, 2016)**.** Zadra process are a process by which a hot solution of caustic soda (1%) and NaCN (1%) is circulating through a column of loaded carbon to an electro-winning cell and then back to the column.

The ore geochemistry samples base metals from the mineralized core in Ezana (Meli) show significantly higher values for Cu (8360-59280), Zn (1700-5280), Pb (6.4-1652) ppm (Abraham et al., 2015). A NaCN solution is spray onto the mound (baseball), passes through the rock layers, and in doing so extracts the gold out of the ore.

The technique of open leaching is not used in Europe however, and should not be recommended, because of the potential impacts on human health and the environment (Enquiry, 2010). Due to the existing different weather conditions, major parts of the plant Ezana (Meli) was installed without cover. These uncovered parts are crushing, milling (grinding), thickening, CIL plant and detox plant (Name, 2017). Gold is extracted from ores or concentrates by the alkaline cyanidation process as shown in the figure 2.1(Acheampong et al., 2010) however, the recommended one from the Meli gossans is figure 2.2 (Ababa, 2016).

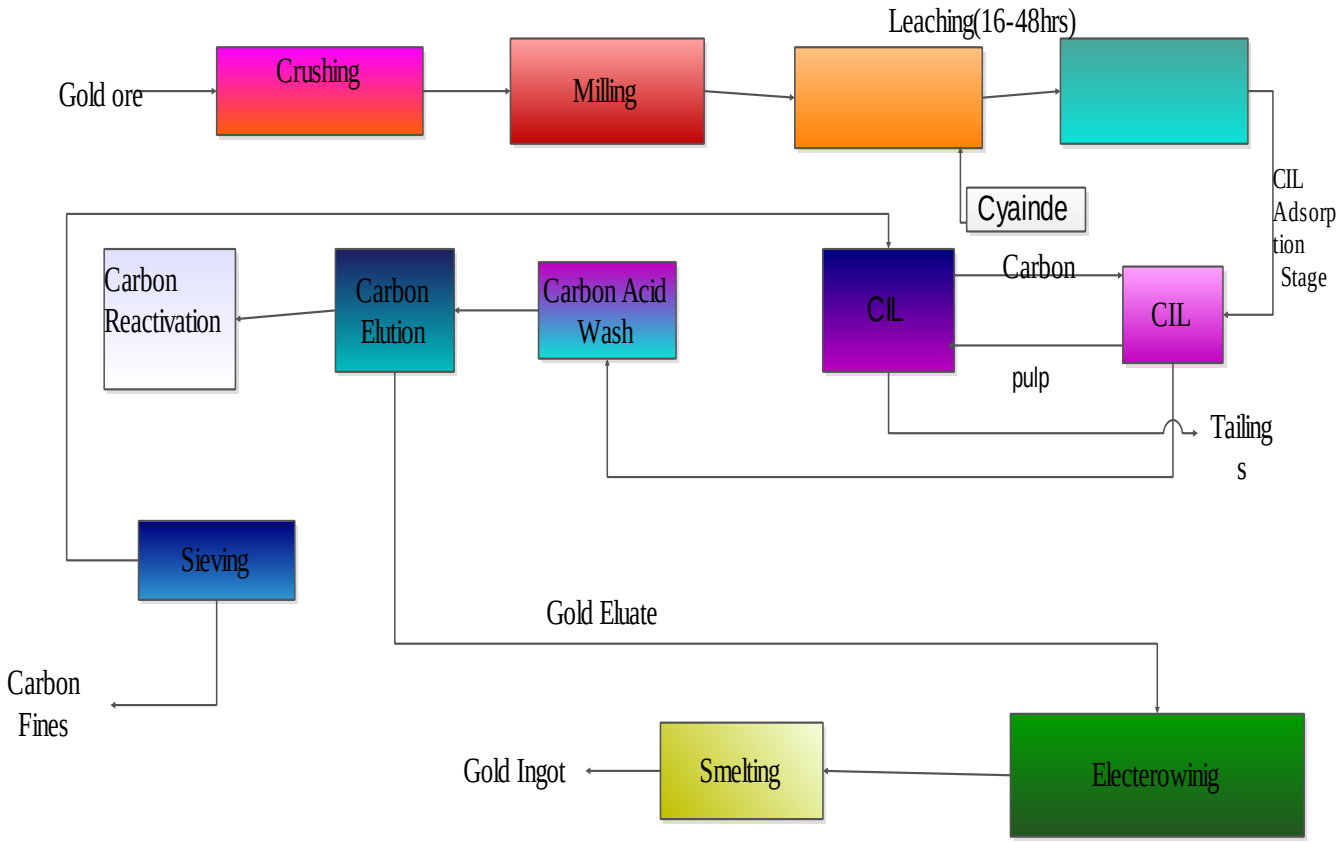

Figure 2.1: Gold is generally extracting from ores (concentrates) by the alkaline cyanidation

Up to 97% of the gold is thus extracted, enabling the most microscopic bits of gold could be extracted from low-grade ore.

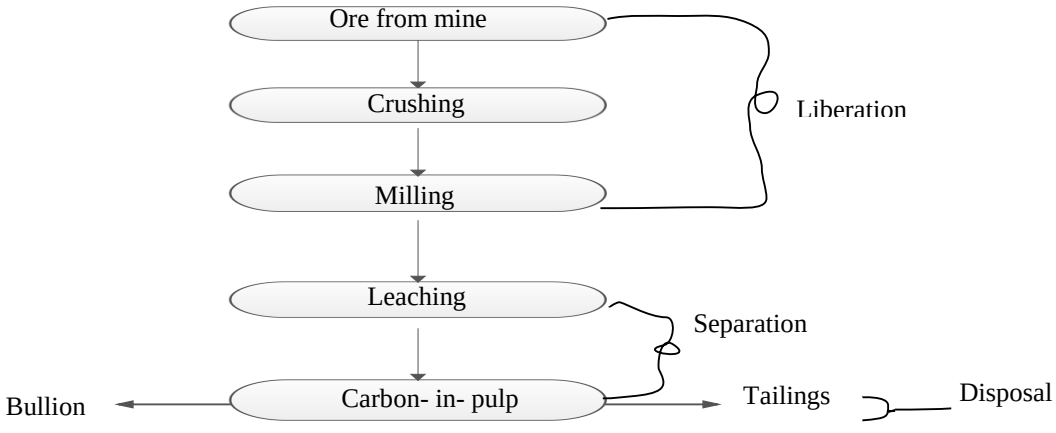

Figure 2.2: Recommended block diagram to recover gold

Microwave digestion is a particularly effective means of accelerating dissolution of metallic samples. Samples should ideally be in powder form, however, metals may be fine wires, filings, shavings or turnings. If the dissolution is carried out in a closed vessel, sparking can present a serious safety hazard as the hydrogen gas produced can be ignited. When attempting to digest a sample for the first time, the acid and the sample should be allowed to react thoroughly, before placing the open vessel in the microwave oven. If a closed vessel is required, all oxygen must be purged from the container. The sample can be reacted in an open beaker for 2 min and for a further 1 min in the microwave oven, followed by a second addition of acid and return of the sample to the microwave oven for an additional minute. This procedure is repeating to achieve dissolution. As teflon containers cannot be used for hot H_2SO_4 acid mixtures, tall glass beakers are preferred (Fisher et al., 2008). The choice of acid or mixture of acids is governed by the oxidizing and reducing agents efficiency in dissolving the matrixes. To be efficient, the acid must form a soluble salt with the metal ion being determined. Hydrochloric, per chloric and nitric acids are commonly used to digest samples for analysis and combinations of acids are also used (Fisher et al., 2008).

Hydrochloric acid: As a concentrated excellent for some metal oxides and metals that are oxidized more easily than hydrogen, at high pressure and temperature attacks many silicates and numerous refractory oxides, sulphates and fluorides, to produce generally soluble chloride salts. As concentrated it is not used to digest organic materials, although it is an effective acid for basic compounds such as a mines and alkaloids in aqueous solutions and some organometallic compounds (Fisher et al., 2008).

Nitric acid: It is a strong oxidizing agent, which can be obtained in high purity suitable for trace level analyses. It can be used for liberating trace elements from botanical and biological matrices to form highly soluble nitrate salts. These acid relatively low boiling points of 120^{o}C, decompositions are time consuming when carried out in open vessels. In order to break down a complex organic matrix, it is usually necessary to have a temperature above 120^{o}C, or the addition of another oxidizing agent such as per chloric acid or H_2O_2. Under the excitation of microwave energy, nitric acid can reach a temperature of 176^{o}C with 5 atmospheres which is more than 50^{o}C above its boiling point. Substantial increases in oxidation potential are achieved at this temperature and pressure, resulting in faster reactions (Fisher et al., 2008).

Per chloric acid: Hot concentrated per $HClO_4$ is a strong oxidizing agent, which completely decomposes organic materials and attacks metals unresponsive to other acids. The hot acid is used to take elements to their highest oxidation state, potentially explosive when in contact with organic materials and easily oxidized inorganics. Cold concentrated and hot dilute per chloric are less hazardous.

Sulphuric acid: Concentrated H_2SO_4 is used for the decomposition of alloys, hydroxides, inorganic oxides, metals, ores and organic tissues. These is one of the few acids that can melt teflon PFA before it boils consequently, careful monitoring of the temperature is required. The temperature range can concentrated these acid destroys almost all organic compounds. When the temperature is raised a few degrees above its normal boiling point of 339ºC for a solution containing 98.3%, w/w of H_2SO_4, digestion times are reduced (Fisher et al., 2008).

Hydrofluoric acid: Used for dissolving silica-based materials i.e converted to SiF_4, which can be evaporated leaving other elements of interest. These can be combined with other acids to prevent silica from liberating up trace elements in biological and botanical matrices. If the fluoride ion concentration is high, stable metal fluoride complexes are formed and can be kept in solution. Rare earth fluorides are sparingly soluble and may be lost from solution under these conditions (Fisher et al., 2008).

2.1.1. Carbon in leach plant, detoxification and thickening

SMBS and $CuSO_4$ addition: The aim of the lime has to be added to keep the pH-value (8-10)-probes are installed in detox tank one and detox tank two (Name, 2017). Both pulp and solution detox investigations were conducted with sodium metabisulfite (SMBS) used as the reactant with the pH maintained at 9 by controlled NaOH addition. The critical WAD CN^- line shown in both figures 2.3 and 2.4 if the WAD cyanide concentration above which free cyanide is present thus the detox process stops because the SMBS addition rate is insufficient. If $CuSO_4$ was not added to restart the detox process and the SMBS addition rate increased. Thickening the slurry particles start to settle and the sediment is forming a high slurry to improve settling flocculent is added (Petruk, 2000). Overflow water is recirculated back to the process water tank (070-200-SVE) using the overflow return water pump (400-515-TWP) (Name, 2017).

2.1.2. Gold room with safety and security

The safety and security of the gold room is labelled “high-security area” as all operations conducted there entailing handling of high-grade products. The doors for vehicle access to the gold room are electrically powered roller shutter type with battery backup. An area for oxy-acetylene gas bottles and welding machine is provided outside the gold room in no-man’s land, hoses and cables are piped through the wall (Name, 2017). The treatment of the gold sludge produced from the electro-winning cells are include filter cake handling, drying and calcination, smelting (bullion, slag) silica (sand) (SiO_2), soda ash, borax (B_2O_3), oxidizing agent (MnO_2, KNO_3)**.** The gold room operators are exposed to a number of potential hazards are toxic and corrosive eluent solutions flowing under pressure and at high temperatures, in the electro-winning section and possible evolution of toxic gasses such as NH_3, SO_2, CO etc. The danger of explosion from the production of H_2 and O_2 gasses in the EW cells, emissions of high temperature gasses, dust from the oven and furnace, emissions of arsenic fumes from the calcine ovens and molten slag , gold bullion and High ambient temperatures in the gold room.

2.2. Tailing disposal site and its management

In the factory the management of cyanide in the tailing dam have properly constructed as shown in figure 2.3. However, still lining is required a special emphasis has to be given to the protection any form of leakage from the dam. To protect overflow, aside from proper design of spillway, diversion ditch was constructed. According to Ababa (2016) based on report in the impact assessment observation the construction should include the basin of which should be first lined with low-permeability soil and then with a suitable low permeability liner comprised of high density polyethylene geo-membrane liner or bitumen impregnated geo-textile liner to prevent seepage but now these is not apply.

To control cyanide used for gold leaching occur due to human error, mechanical failure, and nature include by reducing the use of cyanide, by applying (Enquiry, 2010);operational strategies to minimize cyanide addition, automatic cyanide control, if applicable, peroxide pretreatment, destroying the remaining free cyanide prior to discharge in the pond. The impacts of cyanide for plants, some soil bacteria, and several species of invertebrate organisms produce natural cyanide and related compounds. Nevertheless, cyanide compounds are seldom present in uncontaminated

waters in measurable concentrations. However, cyanide compounds degrade rapidly when diluted and do not persist in the environment (Enquiry, 2010).

Figure 2.3: Properly designed tailing dam axis and stored water

2.3. Wastewater analysis

According to Ababa (2016) water quality analysis reported which was the only water points in the project area are the borehole, which is being used by Meli mining and the surrounding villages and the Lahote River. Both in situ and laboratory test results indicate that the quality of the water was good for drinking. However, the water appears to be hard. Most of the water samples are skewed towards the $NaHCO_3$ type, Ca^{2+}, Mg^{2+} & Mn (high value) are also important cations. There is substantial sulfate, which might have been derived from sulfide minerals associated with the mineralization. From the physical - chemical point of view, the water is below the permissible limit for drinking (for the measured parameters). The wastewater analysis order to characterize the wastewater the parameters were measured for the two sampling points. These are temperature, pH, EC, turbidity, TSS, TDS, DO, SO_4^{2-}, NH_4^+, NO_3^-, PO_4^{3-}, COD, BOD, heavy metal ions such as As , Fe, Cu, Pb, Zn and free cyanide (CN^-) and Hg, Cd and Ni are not present in the effluent produced at the Obuai mine (AGA Obuasi 2010). COD and BOD_5 were determined in the laboratory according to procedures described by the standard methods for the examination of water and wastewater (APHA, 1995). The Fe, Cu, Pb, Mn, Co, Cd, Cr, Ni, Zn concentration in samples of Meli was determined by using FAAS after sample wastewater digestion. For heavy metal analysis of the samples, the direct air-acetylene flame method using an AAS was used. The cyanide

concentration was measured in the laboratory using microquent cyanide test kits. The main sources from mining operation are mine water, mining and extraction. Here again, the quantity and characteristics of the wastewater are widely variable (H B Dharmappa et al., 1995). However, According to research Sivskumar et al. (1994b) considering the nature of waste waters source general characteristics can be derived: high suspended solid (100-2000g/l), near neutral PH (7-9), moderate dissolved solid (100-500mg/l as $CaCO_3$) and the result of laboratory analysis are almost within the result. The laboratory result of these studies are within these range TSS (750ppm), PH (8-8.5), TDS (380ppm).

2.4. Sources of heavy metals

These are enter to the environment through natural and anthropogenic activates like weathering of rocks naturally produce heavy metals (Hossain, 2013). Among these the major particularly in the industrialize world (Birungi et al., 2015): acid mine drainage associated with mining operations the types of all other degradation and pollution of the environment. Three kinds of heavy metal are concern the toxic metals (such as Hg, Cr, pb, Zn, Cu, Ni, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides (such as U, TH, Ra, Am, etc) (Hossain, 2013).

Table 2.1: Chemical compositions of the gossan ore (Ezana) (Ababa, 2016)

Elements	Au (g/t)	Ag (g/t)	SiO_2 (%)	Fe (%)	Al_2O_3 (%)	Cu (ppm)	Pb (ppm)	Zn (ppm)	CaO (%)	MgO (%)	As (ppm)
Concentration	8.54	6.5	41.55	15.3	2.91	0.13	0.25	0.006	1.2	0.12	0.21

The geological exploration of work conducted in the auriferous Meli gossans ore confirmed the presences 352thusands of ton of ore with an average grade of 6.15g/t and 6.5g/t of gold and silver respectively. The ore characteristics / feed material specification as per metallurgy test work are Au (4.37g/t), Ag (6.4), SiO_2 (52.8%), Fe_2O_3 (%) 27.4, Al_2O_3 (%) 4.81, Cu (%) 0.17, Pb (%) (0.13), CaO (%) 0.23, MgO (%) 0.12, bulk density (kg/m3), SG ore (kg/m3), feed moisture (3%) (Name, 2017).

Table 2.2: Anthropogenic sources of heavy metal contamination (Ahamed, 2012)

Elements	Source	Effects and Significance
As	Mining by-product, pesticides, chemical waste	Toxic, possibly carcinogenic
Cd	Industrial discharge, mining waste, metal plating, water pipes	Replaces zinc biochemically, causes high blood pressure and kidney damage, destroys testicular tissue and red blood cells, toxic to aquatic biota
Cr	Metal plating, cooling-tower water additive (chromate), normally found as Cr(VI) in polluted water	Essential trace element, (glucose tolerance factor), possibly carcinogenic as Cr(VI)
Fe	Corroded metal, industrial wastes, acid mine drainage, low pE water in contact with iron minerals	Essential nutrient (component of hemoglobin), not very toxic, damages material (bathroom fixtures and clothing)
Mn	Mining, industrial waste, acid mine drainage, microbial action on manganese minerals at low PE	Relatively nontoxic to animals, toxic to plants at higher levels, stains material (bathroom fixtures and clothing)
Hg	Industrial waste, mining, pesticides, coal	Acute and chronic toxicity
Mo	Industrial waste, natural sources, cooling-tower water additive	Possible toxic to animals, essential for plants
Zn	Industrial wastes, metal plating, plumbing	Essential element in any metallo enzymes, aids wound healing, toxic to plants at higher levels; major component of sewage sludge, limits land disposal of sludge

2.5. Importance of copper and lead

Copper: It is widely used engineering purposes for making of alloys, ceramic, pesticides, manufacture of wires etc (Landner et al., 1999). The complex nature of discarded products containing a variety of materials in addition to Cu makes it very difficult if not impossible to recycle for its copper content (Prapurna et al., 2006). The permissible limit for Cu is 1.3 (USEPA) mg/L ("Joginder Singh," 2013). Even if in human health are required for normal metabolic processes in the body cannot synthesize Cu. The U.S. EPA has determined that Cu level in drinking water should not exceed 1300 ug/L. Bempah et al. 2013, found a concentration of 92.17 mg/kg in gold mine tailings in Ghana. In environment, most Cu compounds will settle to soil then bound to water either sediment. In surface water Cu can travel great distances, suspended either on sludge particles or as free ions. Cu does not break down in the environment, thus it accumulates in plants and animals when it was found in soils. Prescribed limit for copper in drinking water is 0.05mg/L as per WHO norms and also 0.05 mg/L as per prescribed limits,1993 (Shrivastava, 2009).

Lead: Although slowly soluble in acidic conditions it is used to provide a corrosion resistant cover for electrical cables and is used extensively in chemicals production plants (Prapurna et al., 2006). Children are exposed to leads right from their birth for children (Report, 2002). organic lead is more bioavailable and toxic than inorganic lead, but the primary source of organic lead has been leaded petrol, now phased out from the market in the EU (Report, 2002). In the environmental effect is binds strongly to particles, such as soil because of the low solubility of most of its salts, lead tends to precipitate out of complex solutions. In the environment is mainly particulate bound with relatively low mobility and bioavailability. The permissible limit of lead is 0.01/0.05 mg/L (WHO/USEPA) and for copper is 1.3 (USEPA) mg/L, ("Joginder Singh," 2013). the concentration ranging between 80 mg/kg (Abdul-W. et al ,2012).and 510 mg/kg (Ogola et al,2002) have been reported in gold mine tailings.

2.6. Wastewater treatment methods

Most commonly used chemical methods of treating effluent are by the process of coagulation and flocculation of the pollutant from the effluent. However, in most cases it is difficult to say only one of these methods is involved in the treatment process because these methods are inter-related to one another (Panizza et al., 2004; UNIDO, 2011.).

2.6.1. Chemical precipitation

This method has been widely used for process involves alteration of the wastewater's pH in order to precipitate the metals from the solution. The metals precipitate from the solution in the form of metal hydroxides (De Philippis et al., 2009). Dissolved metal ions are changed to the insoluble form due to the chemical reaction which takes place between the precipitant agent and the ions (Santoleri *et al.*, 2000). For this process precipitant agents such as lime and calcium hydroxide are commonly used in many countries because of their availability (Kurniawan *et al.*, 2006). These are cost effective, simple, requires low maintenance and disadvantage are resulting in generation of large volume of sludge, affected by low pH and presence of other salts. These agents help to bring the solution into basic condition and the ions to form a metal hydroxide. The disadvantage of this processes according to (USEPA, 2000) are requirement of working with corrosive chemicals which increase operator safety concerns and an addition of treatment chemicals, especially lime, may increase the volume of waste sludge by up to 50 %.

2.6.2. Electro-chemical process

It involves the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. This method involves different phenomena such as electro-deposition, electro-coagulation, electro-flotation and electro-oxidation (Shim *et al.*, 2014). Electro-chemical methods are very important for the removal of a broad spectrum of heavy metals such as Zn^{2+} , Cu^{2+} , Ni^{2+} , Ag^{+} and Cr mean that pure metal can be recovered for recycle, no reagents involved and rapid process are effective for certain metal ion. The drawbacks of these methods are involvement of relatively large capital investment and the expensive electricity supply (Fu and Wang, 2011).

2.6.3. Ion exchange

It is one of the most frequently used methods of treatment heavy metal leaden wastewaters. This process uses an interaction or interchanging of ions between the wastewater and solids. For this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin, where an insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin. These are effective, pure effluent metal recovery is possible. The disadvantage

of this process includes high cost, selectivity of ions , formation by products and expensive resins, highly sensitive to pH of solutions (Rao and Prabhakar, 2011).

2.6.4. Coagulation

According to Akbal and Camcı (2010), coagulation is a phenomenon in which the charged particles in colloidal suspension are neutralized by mutual collision with counter ions and are agglomerated, followed by sedimentation. In this process there are two kinds of coagulation; chemical and Electrical. In the case of chemical coagulation, process coagulants can be either natural or synthetic. Electro-coagulation of Fe and Al plates are used as anode and cathode. The study also showed that in chemical coagulation, Cu, Cr, and Ni removal of 99.9% was achieved with $Al_2(SO_4)_3$ and $FeCl_3$ dosages of 500, 1000, and 2000ppm, respectively and it was found that electro-coagulation with iron electrodes enables a fast and effective reduction of metals (99.9% of Cu, 99.9% of Cr, and 98% of Ni). For heavy metal removal, it is economically feasible. However, both have their drawbacks, in the case of chemical coagulation the need for chemicals and in the case of electro-coagulation the need for electrical energy. The other draw back coagulation/flocculation is high sludge production and formation of large particle.

2.6.5. Biological remediation of heavy metals

Bioremediation is medial process, which uses different living organisms, primarily microorganisms, to utilize and degrade environmental contaminants into less toxic forms. It uses naturally occurring bacteria and fungi or plants to degrade, accumulate and detoxify substances hazardous to human health and/or the environment (Vidali, 2001). There are three principal advantages of biological processes can be carried out in situ at the contaminated site, bioprocess technologies are usually environmental benign (no secondary pollution), it is cost effective (Volesky et al., 1995; Chandra et al., 1998; Vijayaraghavan et al., 2008). The other is feasible in removing some metal and drawback technology yet to be established and commercialize.

2.7. Adsorption process

Adsorption techniques for wastewater treatment have become popular in recent years due to their efficiency in the removal of pollutants that are too stable to be removed by biological methods. It occurs when a gas or liquid solute adheres to a surface (adsorbent), forming a molecular or atomic film (adsorbate). This process differs from absorption, in which a substance diffuses into a liquid or solid to form a solution (Ong Pick Sheena, 2011). Adsorption occurs naturally, but industrialists

have perfected adsorption methods to clean up hazardous waste in wastewater or purify drinking water. These are superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Uddin *et al*., 2009), but it requires regeneration. Hence, they can attract adsorbates. Adsorption can be classified into physisorption and chemisorption, both differs in the nature of bonding. The difference between physisorption and chemisorption's is listed in Table 2.3 (Ong Pick Sheena, 2011).

Table 2.3: Difference between physio sorption and chemisorption

Physisorption	Chemisorption
Involves van der Waals force between adsorbate and adsorbent, occurs in any solid/fluid or solid/gas system, reversible process	Involves formation of chemical bonds between adsorbate and adsorbent, a highly specific process, irreversible process
Perturbation of the electronic states of adsorbent and adsorbate is minimal	Changes in the electronic states may be detectable by suitable physical means
Low enthalpy of adsorption, may formed multi-molecular layer, no activation energy is involved, equilibrium can be achieved quickly	High enthalpy of adsorption, monolayer is formed, often involves activation energy, may take a longer time to achieve equilibrium

Source: (Butt *et al*., (2003); Myers, (1999))

2.7.1. Mechanism of adsorption

Adsorption is a mass transfer process, which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent (Grassi, et al. 2012). In the case of wastewater treatment, the interface is between the adsorbent solid surface and the liquid phase of the wastewater. If the bonding between the molecules of the adsorbed substance and the adsorbent solid surface is physical, the adsorption is physisorption, which is controlled by the vanderwaals forces. However, if the bonding is due to chemical

attraction, this is called conception and it creates very strong forces of attraction between the adsorbent and the adsorbate. Both forms of adsorption can take place either simultaneously or successively if certain conditions were attained (Grassi, et al. 2012). Because determining whether the adsorption is due to chemical or physical forces is a difficult task, the term Sorption is sometimes used to describe the process (Metcalf et al., 2003).

2.8. Adsorption isotherms

An adsorption isotherm models are used to describe the phenomenon governing the retention (or release) or agility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH (Foo et al., 2010). Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed (Allen et al., 2003). The equilibrium adsorption isotherms were depicted by plotting solid phase concentration (q_e) against liquid phase concentration (Ce) of solute. Adsorption isotherm explains the interaction between adsorbate and adsorbent with critical for design of adsorption process. The Langmuir and Freundlich isotherms are the most frequently used models to describe the experimental data of adsorption. In the present work, these two isotherms were applied to investigate the adsorption process of Cu (II) and Pb (II) on MSB and EB at different conditions of process parameters. The adsorption equilibrium study was carried out for metal concentrations varying from 10 to 120mgL^{-1}.

2.8.1. Langmuir adsorption isotherm

Langmuir isotherm is valid for single-layer adsorption based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane (A.O, 2012). It is based on the assumption that all the adsorption sites have equal affinity for molecules of the adsorbate and there is no transmigration of adsorbate in the plane of the surface (Birungi et al., 2015). Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick.

The Langmuir adsorption is the best model between the entire isotherm model and it is successfully applied in many adsorption processes. The Langmuir equation is given by:

$$q_e = \frac{q_m bCe}{1 + bCe} \quad \text{.....(2.2)}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), Ce the equilibrium concentrations of the solute in the bulk solutions (mg L^{-1}), q_m the maximum adsorptions capacity (mg g^{-1}), and b is the constant related to the free energy of adsorptions (L mg^{-1}).

The above equation 2.2 can be linearized to different and one of these linier forms is

$$\frac{Ce}{qe} = \frac{1}{kaq_m} + \frac{Ce}{q_m} \quad \text{.....(2.3)}$$

A plot of Ce/qe Vs Ce should yield a straight line if the Langmuir equation is obeyed by the adsorptions equilibrium. The slope and the intercept of this line then give the values of R_L and b. A further analysis of the Langmuir equations can be made on the basis of a dimensionless Equilibrium parameter, R_L, also known as the separations factor, given by;

$$R_L = \frac{1}{1 + bCo} \quad \text{.....(2.4)}$$

If the average of the R_L values for each of the different initial concentrations used is between 0 and 1, it indicates favorable adsorptions. The adsorption of Cu and Pb by EB isotherm followed Langmuir better than Freundlich isotherms (D. Bark, Kongsuwan et al., 2006).

2.8.2. Freundlich adsorption isotherm

Freundlich isotherm model is one of the most widely used mathematical models which fit the experimental data over a wide range of concentration. The experimental results of Cu and Pb by SB fit well with linearized Freundlich adsorption isotherm model (Prapurna et al., 2006). This isotherm model is based on heterogeneous surface, distribution of active sites, their energies & enthalpy changes logarithmically.

The Freundlich equation is given by (Singh et al., 2011):

$$q_e = K_F Ce^{1/n} \quad \text{.....(2.5)}$$

The logarithmic form of equation:

$$\log qe = \log k_F + \frac{1}{n} \log Ce \quad \text{.....(2.6)}$$

Where q_e is the amount of metal ion adsorbed after adsorption per specific amount of adsorbent (mg/g), *Ce* is equilibrium concentration (mg/L), K_F and *n* are Freundlich equilibrium constants. The adsorption isotherm data of Cu on bagasse with best modeled by both Langmuir and Freundlich isotherm (Parameters, View, & Babu, 2018).

2.9. Adsorption kinetics

In order to determine the rate-limiting step during the adsorption process different kinetic models have been used to analyze the experimental data. These models include first-order, pseudo-second-order and intra-particle diffusion.

2.9.1. Pseudo first order model

The pseudo first-order kinetic model has been widely used to predict the metal adsorption kinetics. The metal adsorption kinetics following the pseudo first-order model is given by (Ho and McKay, 1999a.):

$$\frac{dq}{dt} = K_1\left(q_1 - q_t\right) \text{.....(2.7)}$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption, q_t (mg/g) denotes the amount of adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium. After definite integration by application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (2.7) becomes.

By plotting log ($q_e - q_t$) versus t, the adsorption rate can be calculated.

$$log\ \left(q_e - q_t\right) = log\ q_e - \left(\frac{k_1}{2.303}\right)t \text{.....(2.8)}$$

2.9.2. Pseudo-second order model

The adsorption kinetic data can be further analyzed using Ho's pseudo second-order kinetics (McKay and Ho, 1999 b,c). This is represented by:

$$\frac{dq}{dt} = K_2\left(q_e - q_t\right)^2 \text{.....(2.9)}$$

Integration of Eq. (2.8) and application of the conditions $q_t = 0$ *at* $t = 0$ and $q_t = q_t$ at $t = t$, Gives:

$$\frac{t}{q_t} = \frac{1}{\left(k_2 q^2{}_e\right)} + \frac{t}{q_e} \text{.....(2.10)}$$

Where k_2 (g/(mg min)) is the rate constant, k_2 and q_e can be obtained from the intercept and slope. The results on Cu and Pb removal by EB the kinetics data was appropriately fitted with pseudo second-order kinetic model where adsorption rate constant and equilibrium adsorption capacities increased with initial heavy metal concentration (D. Bark et al., 2006).

2.10. Factors influencing adsorption process

PH adsorption: The effect is depends on the charge on the adsorbent surface and affect through the dissociation of functional groups on the active sites on the surface of the adsorbent. If the surface charge of the adsorbent is positively charged, the H^+ ions may compete effectively with the cations of the solution causing a decrease in the amount of metal ion adsorbed (Islam, 2011; Safety, 2013). The low pH (< 3) values result in soluble species, there was excessive protonation of the active sites at carbon surface and this often refuses the formation of links between metal ion and the active site. At moderate pH values (3-6), linked H^+ is released from the active sites and adsorbed amount of metal ions is generally found to increase. At higher pH values (>6), the precipitation is dominant or both ion exchange and aqueous metal OH formation (not necessarily precipitation) may become significant mechanisms in the metal removal process. The pH ranges suitable for the survival and nourishment of most biological life is quite narrow and critical i.e., 6.5 to 8.5. A pH of below 6.5 may be corrosive to plumbing fixtures, reticulation and the general guideline value is within 6.5 and 8.5 to all mine water discharges directly determine by pH meter from different sites (Tripathi et al., 2015). Some authors reported that at higher pH, metal complex forms and results in precipitation therefore the separation may not be due to adsorption. it was apparent that the metal adsorption capacity (q) of the Cu (II) and Pb (II) was very low at strong acidic medium and the adsorption capacity increases with increasing pH value and reached its maximum at pH 6.5 (Abudaia et al., 2013).

The dose of adsorbent: The removal of metal ions increases with an increase in the adsorbent dosage due to increasing more active sites on dosage will be available to which more amount of metal pollutants can be attached (Safety, 2013). However, further increase in the amount of adsorbent will have a negative effect on the adsorption process. This means either the metal adsorption decreases or it becomes steady because the active site for adsorption is blocked by screening effect (Hammaini *et al.*, 2007). The adsorption process is mainly affected by the nature of the adsorbate in the sense of its solubility in the solute; The capacity is inversely relation 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 significance too and 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 (Smith, 2009). However, it must be kept in mind that the adsorption process dependence on molecular size can be generalized only within a particular chemical class.

Contacting time: The removal efficiency increased with an increase in contact time before equilibrium is reached (Safety, 2013). The time of contact between the adsorbate and adsorbent is the determinant factor of the kinetics and equilibrium of the adsorption process. Every waste treatment options should be effective economically (Tangjuank *et al.*, 2009). Therefore, studying the effect of contact time on adsorption experiment is very important for its practical applications.

2.11. Sugarcane bagasse and eucalyptus bark as adsorbent

Bio sorption of heavy metals batch studies using bagasse have investigated the adsorption capacity of charred xanthates sugarcane bagasse for the removal of specific heavy metals. The optimum pH for Cd (II), Pb (II), Ni (II), Zn (II), and Cu (II) bio sorption using CXSB was 5, 4, 4, 6 and 5, respectively with the order of adsorption capacity are $Pb^{2+} > Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+}$ at pH 4 (Homagai et al., 2010). Mercerization facilitated the removal of lignin and polyoses which normally pack the cellulose fibers; therefore, their removal allowed easier reaction between the hydroxyl group of the cellulose and the succinic anhydride; hence, facilitated the conversion of cellulose I to cellulose II. Sorption of heavy metal ions is enhanced with the increase of carboxylic acid group (Gurgel et al., 2008).

Sugarcane bagasse by using succinic anhydride modification of the adsorption properties by allowing the carboxylic group to react was conducted on the treatment. The results showed that the bagasse treated by tri ethylene tetramine had the highest adsorption capacity of Pb and Cd, where it reached twice the capacity compared to the unmodified bagasse (Ngah et al., 2008). The efficiency of removing Cu ions and Zn ions from $CuCl_2$, $ZnCl_2$, using naturally based adsorbents like MSB. Cu (II) solution were kept in contact for various times (10 to 60min) % removal was obtained 85-90% and time (1-4) hrs % removal is 60-70% (Kishor et al., 2012). The other report that studied was the batch adsorption of Cu(II) SB reached equilibrium by 60 min of contact and

achieved 60% removal of Cu (II); a highest up to 30.9 mg/g for Cu (II) at pH 5.5 (Johnson et al., 2008).

The adsorption of selective removal of Pb (II) and Cu (II) ions from aqueous mixture was investigated using sugarcane bagasse adsorbent had higher selectivity to Cu (II) ions. Batch studies conducted at room temperature at constant initial concentrations of each metal ion to be present in the test sample 50ppm and the PH (7.05 to 8.09) at equilibrium, during all the batch studies (Prapurna et al., 2006). Thomas Anish Johnson, Niveta Jain, H C Joshi and Shiv Prasad studied that use of agricultural and agro-processing industry waste (bagasse) as metal adsorbents from wastewater. Batch adsorption reached equilibrium by 60 min, achieved 60% removal of Cu (II); a highest up to 30.9 mg/g for Cu (II) at pH 5.5 (Johnson et al., 2008). Kamal Rana, Mitali Shah investigated by activation of adsorbent is carried out by treating it with concentrated H_2SO_4 (0.1N) and is kept in an oven maintained at 150ºC for 24hr. The pH (2-5) as increases % removal increases in Cu by SB maximum removal is obtained at pH 5 after that it will decrease slightly, hence removal is 96.4% with a dosage (0.25 – 1.0g/100ml) (Rana et al., 2014).

Parameters et al.(2018) from aqueous solutions the effect of pH removal of Cu on the batch adsorption studies are 100 mg/l Cu by sugarcane bagasse at 32ºC and adsorbent dosage 0.2 g/100 ml. It is obvious that the increasing pH from 2-10 percentage removal is decreased from 65% to 59% and maximum % removal of Cu was at pH 5. Almost above 65% of Cu removal was observed at this pH at 100 mg/l Cu concentration. As dosage increases % removal increases in Cu by sugarcane removal, hence removal is 94.6% the contact time (30 –120 min) (Rana et al., 2014). The % removal Cu increases from 85% to 93% by increasing the adsorbent dosage from 2 – 10 g/l and for a constant initial Cu concentration of 200 mg/L in the solution (Parameters et al., 2018). However, the adsorption capacity is decreases from 4 to 0.995 mg/g by increasing the adsorbent amount from 2 to 10 g /l. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium (Parameters et al., 2018).

In the adsorbent of EB literature reported are Bark et al., (2006) has been studied in the removal of metal ion from synthetic waste water by activated carbon from EB. The Cu (II) and Pb (II) adsorption by activated carbon from EB are the optimum pH 5 and reached equilibrium within 45 minutes for whole range of concentration (D. Bark et al., 2006). According to Patnukao et al., (2008) investigated on adsorption demonstrates that the adsorption capacities of Cu and Pb increased with pH. At higher, pH values (> 6) generally decrease the electrostatic repulsion

between cations and the positively charged surface, which promotes higher adsorption capacity. Therefore, maximum adsorption often occurs at high pH level. However, at this pH range, the formation of insoluble hydrolyzed species $(CuOH)^+$, $(PbOH)^+$, $Cu(OH)_2$, and $Pb(OH)_2$ might also take place, and this condition is often not desirable as the metal precipitation could lead to a misunderstanding for the adsorption capacity (Patnukao et al., 2008).

2.12. Agricultural wastes as adsorbent

Copper removal using chistoan was increased to maximum and then decreased with pH variation from 4 to 9 at temperature 25^0C, 100 rpm and the maximum % removal was about 89% at pH 5, contacting time 360 min and the maximum % removal of was 88.17% at the dosage of 200 mg. The dominant species was free Cu (II) and Pb (II) was mainly involved in the adsorption process when the pH < 5. When the pH > 5, copper ions started to precipitate as $Cu(OH)_2$, this had been confirmed by Ramya et al., (2005). Increases in metal removal with increased pH can be explained on the basis of the decrease in competition between proton and metal cations for same functional groups and decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH (>pH 5) is due to formation of soluble hydroxyl complexes (R. Ramya et al., 2003).

Spent grain obtained from brewery can be used to treat Pb (II) and Cd (II) ions as demonstrated by Low et al., 2000. Sawdust, obtained from wood industry is an abundant byproduct which is easily available in the countryside at negligible price and used for the removal of Cu^{2+} and Zn^{2+} ions was conducted by S˘c´iban et al. (2006a). Wheat bran, a by-product of wheat milling industries proved to be a good adsorbent for removal of many types of heavy metal ions such as Pb (II), Cu (II) and Cd (II). The study on effectiveness of lead adsorption by NaOH treated lalang by (Hanafiah et al. (2006a)). (Abia et al. (2003)) carried out an experiment of determining the optimal concentration of thioglycollic acid ($HSCH_2COOH$) for the removal of Cd (II), Cu (II) and Zn (II) ions by cassava waste.

3. MATERIALES AND METHODES

3.1. Description of the study area

The study area Ezana (Meli) is located in NW Tigray 371km from Mekelle, 61km SW of Shire indasillasie town, accessible via an asphalted road to Endabagunan and by a gravel road to Meli, 1067km from Addis Ababa. The size of the exploration-mining site and its immediate environs is around 51,200m^2, gold deposit at altitude 1200 m, atmospheric pressure 840 mbar , temperature (5-45)°C, average rainfall 900 mm, relative humidity - average 46 % , wind speed - maximum 25 m/s (Name, 2017).

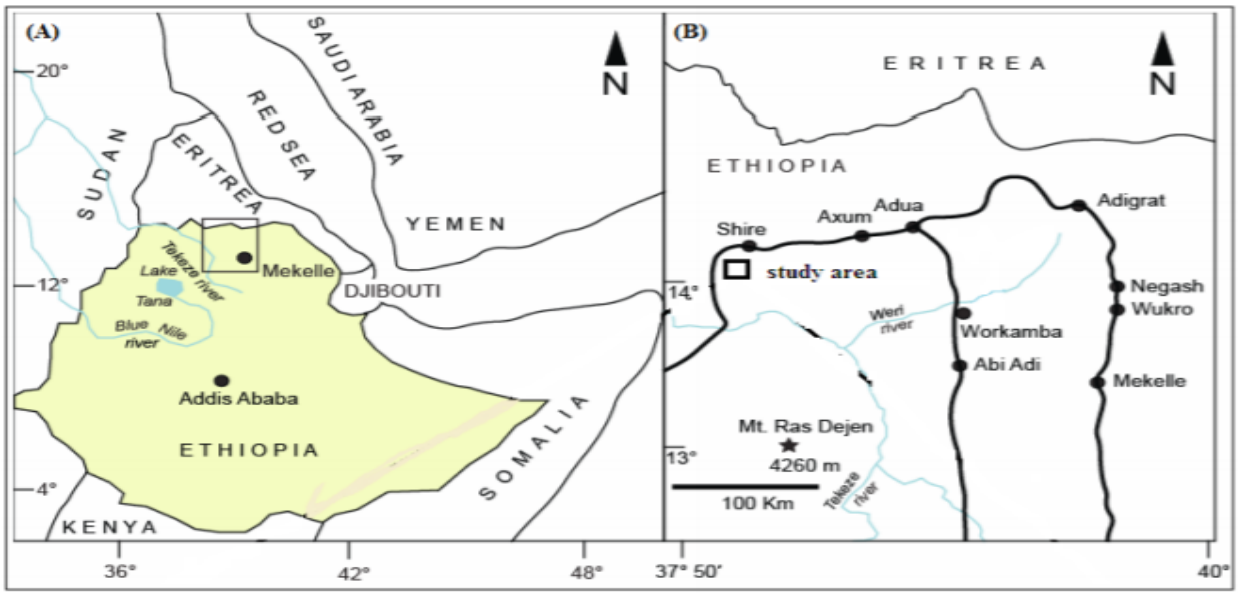

Figure 3.1: Location and accessibility of the factory (A) Ethiopia (B) the study area

3.2. Materials

3.2.1. Chemical

Most of the chemicals were analytical grade and collected from Ezana gold mining development Plc laboratory (Mekelle, Meli) and chemical shops in Addis Ababa. NaOH, H_2SO_4 were used as modifying agent of bagasse, to adjust the solution pH and pretreatment of eucalyptus bark by H_2SO_4. The distilled water was used throughout the experimental studies. NaOH, HCl, H_2SO_4 and HNO_3 were used for desorption experiment, titration and solutions pH adjustment. Mercury sulfate, $FeCl_3$, $K_2Cr_2O_7$ were used for COD and KI, $AgNO_3$ for determination of cyanide using

titrimetric in the outlet waste water, The HNO_3, $HClO_4$, HF were also used for digestion of the wastewater sample.

3.2.2. Equipment

The major equipment's like batch reactor was used for removal of heavy metal using adsorbent, shaker, FAAS (AA-6300 (SHIMADZU)) gases: acetylene + air obtained from Ezana (Mekelle, Meli) model NovAA400P, Germany for estimation of metal ion concentration, some of the equipment also obtained from AAU college of natural science chemistry department (FTIR, XRD). The equipment like airtight container, oven/dried, heating bath, micropipette, mechanical stirrers, common laboratory glassware (flasks, beaker), analytical instrument used for the preparation sorbent. Analytical instruments like digital balance for weight measurement, pH-meter for reading pH, electrical conductivity & turbidity tube. The titrimetric by using standard solution to titrate cyanide, turbidity meter used to determine turbidity of the sample, digester for COD.

3.3. Method

3.3.1. Physico-chemical characterization of the adsorbents

The samples are characterized by proximate analysis, Fourier transform infrared spectroscopy (FTIR) & X-ray diffraction (XRD) analysis.

3.3.1.1. Proximate analysis

It consists of determination of moisture, ash, fixed carbon, volatile matter contents & bulk density were carried out on different components of bagasse and eucalyptus bark ground to fine powder of -72 mesh size as per Indian standard method (Submitted et al., 2014). Following are the details of this analysis:

Moisture content: The moisture content was determined using ASTM D2867-91 method. These is determined by loss on drying method. Then subsequent incubations weight was achieved at the interval of 30 min until constant. A crucible amount weighed, for each adsorbent 1g of SB and EB was taken in figure 3.4, and then the crucible was placed in an electric hot air oven maintained at 105^0C for 3 hours. After 3 hrs, cool in dissector then measure the amount of the adsorbent, the evaporating dish amount are measure and returned to the oven at the same temperature as in the previous step. Finally, the moisture content is calculated using the equation 3.1.

According to Nwabanne and Mordi (2009) the crucible was taken out, cooled in portable desiccators and weighed again. Heating and weighing was continued until obtaining value and the

loss in weight of the powder gave a % of the MC in the sample of powdered EB used for adsorption. Then a % of MC was determined using equation (3.1):

$$Moisture\ content(\%) = \frac{(W_1 + W_2) - W_3}{W_2} * 100 \quad \text{.....(3.1)}$$

Where, W_1= weight of the dish, W_2 = weight of the sample, W_3 =weight of residue after drying

Then the crucibles had taken out of the oven and the samples was weighed. The loss in weight expressed as the moisture content (MC) in the sample.

Ash content: Ash is defined as the quantity of mineral matter which, after application of the described working methods, remains as incombustible of testing substance (Cauvain and Young, 2009). Ash content determination was done according to the ASTM D2866-94 method by 1g of the powdered stem bark were accurately weighed and transferred into a crucible. The crucible and its contents were gently heated over bunsen burner flame until it became free from moisture and completely charred. The heat was increased gradually until most of the carbon was vaporized and then heated strongly such that the inorganic ash could be seen (residue free from carbon) as almost white. Then after cooling the ash in desiccators, weighed and the weight was recorded. Then the heating continued until the weight became constant. Then the ash value was calculated using equation 3.2:

A 1g residual MSB and EB from the above step was placed in a crucible and transferred into a preheated muffle furnace at a temperature of 550^{o}C for 3 hours. The crucible was cooled in a desiccator and weighed again. The heating, cooling and weighing cycle was repeated until constant weight was obtained, then the weight lost was recorded as the ash content of the activated carbon sample.

The % ash content (dry basis) was calculated as:

$$Ash\ content = \frac{(W_3 - W_1) * 100}{W_2} \quad \text{.....(3.2)}$$

Where, W_1 = weight of the dish, W_2 = weight of the sample, W_3 = weight of residue after igniting

Volatile Matter content: 1g of air-dried, powdered in to 850 and 500µm sample was taken in crucible. The crucible was covered with silica lid for both SB and EB. Then crucible was kept in a furnace for 7 min at the temperature of 800°C. The crucible is take out of the furnace and allowed to cool in a dissector.

The % volatile matter content in the sample was calculated by using the formula given below:

$$\%\ volatile\ matter(VM) = \%\ loss\ in\ weight - \%\ moisture \quad \text{.....(3.3)}$$

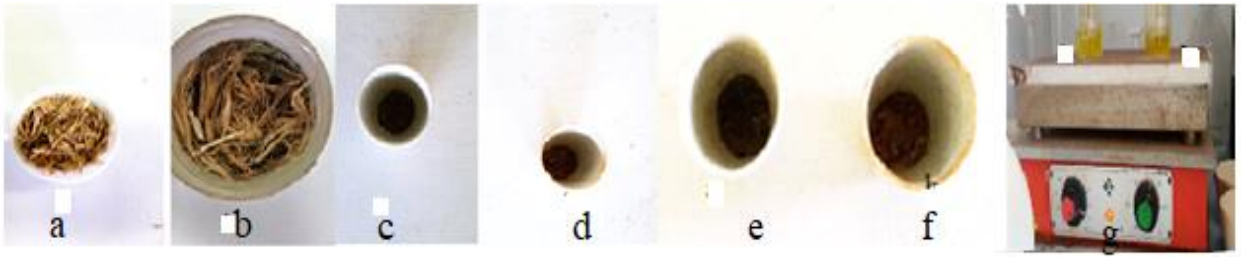

Figure 3.4: Sample used for (a, b) MC, AC (c, d), VM (e, f), Carbon value (g) both adsorbents

Bulk density: The bulk density was determined according to ASTM D2854-96 method that 25cm^3 density bottle was weighed the SB & EB. The sample was packing by repeatedly tapping the bottle using the bulk density apparatus in order to fill up to the marked level of the bulk density apparatus. The bottle was there weighed and the difference in the volume gave the weight of powder taken in the bottle. The bulk density of the powder was calculated by taking the ratio of weight of powder taken in the bottle with the tapped volume of the density bottle.

The SB and EB powder is calculated by placing a known amount of raw in a 100 ml cylinder to a specified volume and tapping the cylinder for at least 1-2 min and measuring the volume of powder. Then the result was calculated using the equation 3.4.

$$Bulk\ density\left(g/cm^3\right) = \frac{Weight\ of\ dry\ sample(g)}{Volume\ packed\ sample\left(cm^3\right)} * 100 \quad \text{.....(3.4)}$$

Carbon and nitrogen value: Elemental analysis of both adsorbent was estimated using standard methods. The total Nitrogen was determined using Kjeldahl method and total carbon was determined by loss on ignition method. The total carbon yield was determined after sample processing in terms of raw material mass by wet oxidation methods and loss ignition. 2g of sample was put on crucible and ignited for 2 h at 950^{0}C, according to (Juan *et al.*, 2004).

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$$Yield\ CH = \frac{W_{ch} * 100}{W_{ox}} \quad \text{.....(3.5)}$$

W_{ch} = weight of carbon retrieved from the furnace, W_{ox} = dried weight of carbon sample

Fixed Carbon*:* The fixed carbon content in the simple was determined by using the formula given below:

$$\%\ Fixed\ Carbon = 100 - (\%\ Moisture + \%\ Volatile\ Matter + \%\ Ash) \quad \ldots\ldots\ldots\ldots\ldots(3.6)$$

3.3.2. Preparation and characterizations of sample wastewater

The wastewater sample was collected from Ezana gold mining factory discharged in to the dam by selecting from four sites (south, west, north, east inlet into the dam). For transporting and taking sample, plastic bottles were used and the bottle were cleaned using HNO_3 acid and distilled water (Victoria, 2000). The concentration of waste water from 4 sites and maximum value obtained for Cu (71ppm) and 16ppm (Pb) at east outlet slurry in to the dam. The analysis was undergone using FAAS.

3.3.2.1. Determination of heavy Metals (Cu, Fe, Mn, Pb, Cd, Cr, Ni, Co, Zn)

A blank sample was detailed so as to allow a blank correction to be made done by transferring 100ml of distilled water in to beaker (Islam, 2011). The water sample was digested with100cm^3 were transferred in to beaker and 5ml concentrated HNO_3 was added. The beaker with the content was placed on a hot plate and evaporated down to about 20min then beakers were cooled, another 5ml of concentrated HNO_3 was added (Islam, 2011). The beakers were covered with watch glass and returned to the hot plate. The heating was continued, and then small portion of HNO_3 was added until the solutions appear light colored and clear. The beaker wall, watch glass was washed with distilled water and the samples were filtered to remove some insoluble materials that could clog the atomizer. The elements that were accredited in the Ezana laboratory institution was Au, Ag, Cu, Zn, Ni, Pb & Co. However, the others non-accredited (Mn, Fe, Cr, Cd) is possible to read by changing the flame. To the whole laboratory runs of Cu(II) & Pb(II) sample wastewater 40ml were used in to conical flask 250ml and 10ml HNO_3 with time 6hr, temperature 90-100^oC in the digester then dilution with 100ml flask & filled in to test tube then read using AAS.

3.3.2.2. Determination of cyanide from tailing dam effluent

The procedure site selection in the tailing dam sample collection and 50ml wastewater volume into beaker 100ml from each. Then added 0.5g of KI as a reagent and the titration procedure of this method uses $AgNO_3$ with *p*-dimethyl amino benzalrhodanine indicators and used for measuring concentrations of cyanide not exceeding 0.1 mg/L (0.025 mg/250 ml of absorbing liquid). Then

$AgNO_3$ an amount with 0.074M fill to burette & titrated using small stirrer drop by drop until the first changed in color from yellow to brownish-pink and to mix KI with wastewater or to homogenize. The titration should be performed slowly with constant stirring, titrate a water blank using the same amount of NaOH and indicator used in the sample. The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples (Cyanide in Waters and Extracts, 2014). A 5ml burette should be conveniently used to obtain a precise titration. Drinking water plastic was the reference if the sample wastewater after added KI is not change indicated that no cyanide if change were occurred cyanide was present.

Figure 3.6: Diagrammatic procedure for laboratory test of cyanide

3.3.3. Preparation of the adsorbents

3.3.3.1. Sugarcane bagasse

Sugarcane bagasse was collected from Wonji sugar factory. The sample was first washed by tap water then dried in the sun light for one week. Then it was washed again with distilled water several times to remove the dust particles and then dried at 105^{o}C for 24 hrs. The powder material were sieved using the same sieve 850µm (Sanchez et al., 2011). Many methods were used for adsorbent modification to change surface of cellulose, such as acid and base to oxidize cellulose, using organic acid to change functional groups in biological polymers, from hydroxyls to esters, or acid (Ngah et al., 2008).

Bagasse were treated by 1M NaOH first put in to shaker for 1hour to homogenize and then by H_2SO_4, in stirring 30 – 120 min at a speed of 200rpm with alkali and sulphric acid; and boiling for 2 hours at 85°C. The treated SB was washed by distilled water to remove excess soluble substances until neutrality and then dried at 80°C within 24 hrs before used as adsorbent (Pham et al., 2015). SB is composed of cellulose (40–50%), polyoses (25–30%), and lignin (20–25%) (Gurgel et al., 2008).

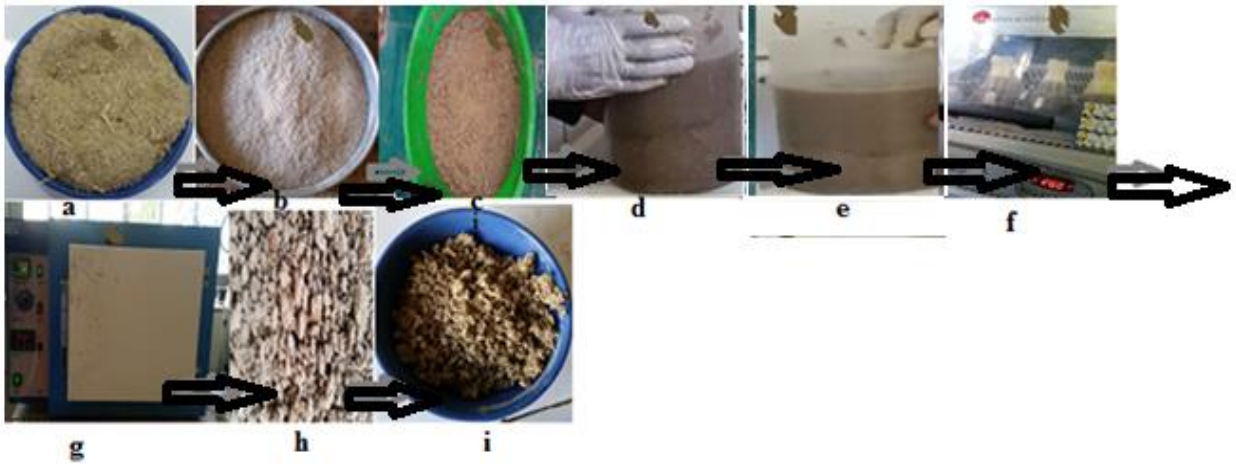


Figure 3.2: Diagrammatic procedure of preparation of modified sugarcane bagasse

(a) Raw SB washed with tap water and dry by sunlight (b) grinded SB with particle size (850 µm) (c) washed with distilled water and dried in oven (d) soaking with NaOH and dried in oven (e) soaking with H_2SO_4 (f) during shaking for both d and e (g) dried in oven (h) treated SB by H_2SO_4 dried in oven (i) SB treated by NaOH

Those three organic polymers that constitute SB are a huge source of hydroxyl and phenolic groups whose sorption properties can be enhanced by chemical modification (Ngah et al., 2008).

3.3.3.2. Eucalyptus bark

Bark of *E. camaldulensis* tree species which were collected from the local area Addis Ababa was washed, dried using oven and ground into small particles size (Presented et al., 2015), in these studies the sample was crushed manually in to a small pieces and dried in sun light for 3days. It was then washed by distilled water and oven drying at 105˚C for 24hrs (M. E. Bark, 2014). After that the sample was grounded in to 500 µm. The grounded EB was washed by using distilled water then dried in in oven for 24hrs. It was then soaked using 0.1M H_2SO_4 acid and heated for about 60 min in a hot water bath at 92^0C then kept aside for overnight and washed several times with distilled water to remove acid, any impurities present in it and dried in an air-oven at 105 ^{0}C for about 6 hr. The dried material was sieved into 500 µm (stored in an airtight container) and used as an adsorbent for overall studies. It was then taken in a clean beaker and made into slurry by using 500ml of deionized water of 0.1m H_2SO_4 acid. After that it was washed several times with distilled water to remove acid and any impurities, present in it until neutral pH.

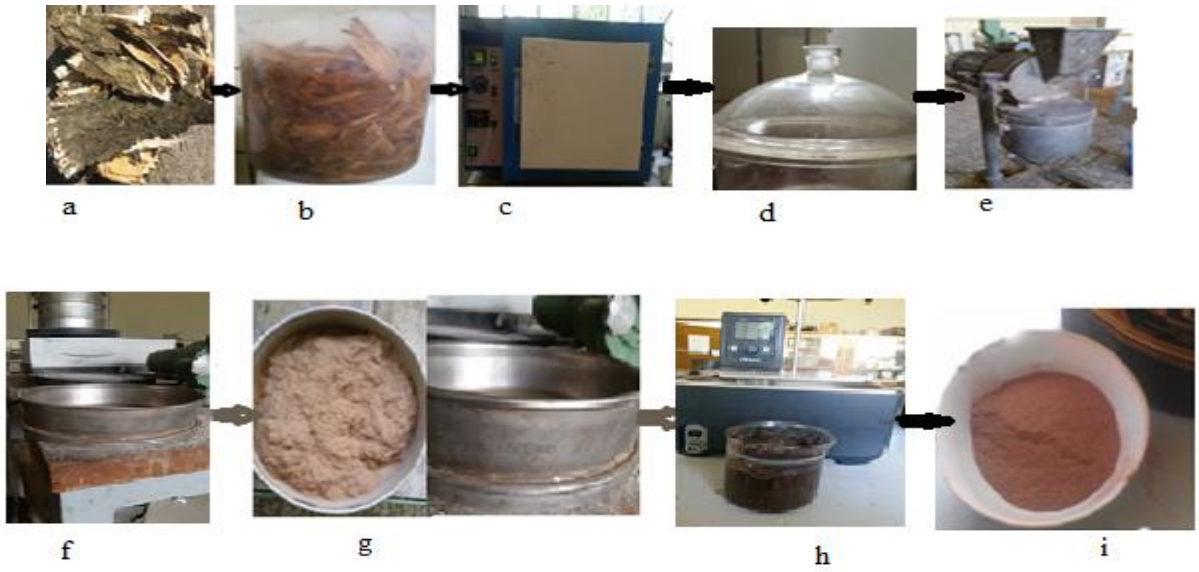


Figure 3.3: Diagrammatic procedure of preparation of eucalyptus bark

(a) Collected sample bark (b) bark washed by distilled water (c) dried in oven (d) dissector (e) centrifugal mill (f) Mesh 0.5-1mm (g) grinded bark and sieve 500µm (h) bark in hot water bath with H_2SO_4 (i) Powder treated bark

3.3.4. Treatment and optimizations

The real sample of wastewater that was obtained from Ezana gold mining factory was analyzed for the amount of Cu, Pb, Cd, Co, Ni, Cr, Mn, Fe and Zn use FAAS prior to the experiment for these studies select Cu and Pb. After obtaining, the result of the amount of Cu and Pb from analysis of the sample wastewater the maximum concentration of directly into these studies then adsorption efficiency of MSB and EB powder was evaluated under different pH, contacting time and adsorbent size. Adsorption efficiency in percent and milligram of Cu and Pb adsorbed per gram of adsorbent was calculated using the equations 3.7 and 3.8, respectively. Finally, average of the triplicate results was presented.

$$\%R = (\frac{Co - Cf}{Co})100 \quad \text{.....(3.7)}$$

Where % R is percent removal C_o is initial concentration and C_f concentration after adsorption

$$q = V(\frac{Co - Cf}{M})100 \quad \text{.....(3.8)}$$

Where q is metal removal in mg/g, Co is initial concentration, C_f is concentration after adsorption, m is adsorbent mass in gram and v is volume of wastewater used during the experiment.

3.3.4.1. Batch adsorption studies

All experiments was carried out in batch mode due to use for small scale operation, high conversions that can be obtained by leaving the reactant in the reactor for long periods of time. These were conducted at room temperature, constant initial concentration from real wastewater Cu (71mg/l), Pb (6mg/l). From the initial laboratory test result detoxification of the tank (not include in the scope), east outlet pipe the dam, S, W, N would be collected Cu^{2+} (75, 71, 30, 51, 40) ppm and Pb^{2+} (25, 16, 3. 8, 10.2, 6) ppm, respectively.

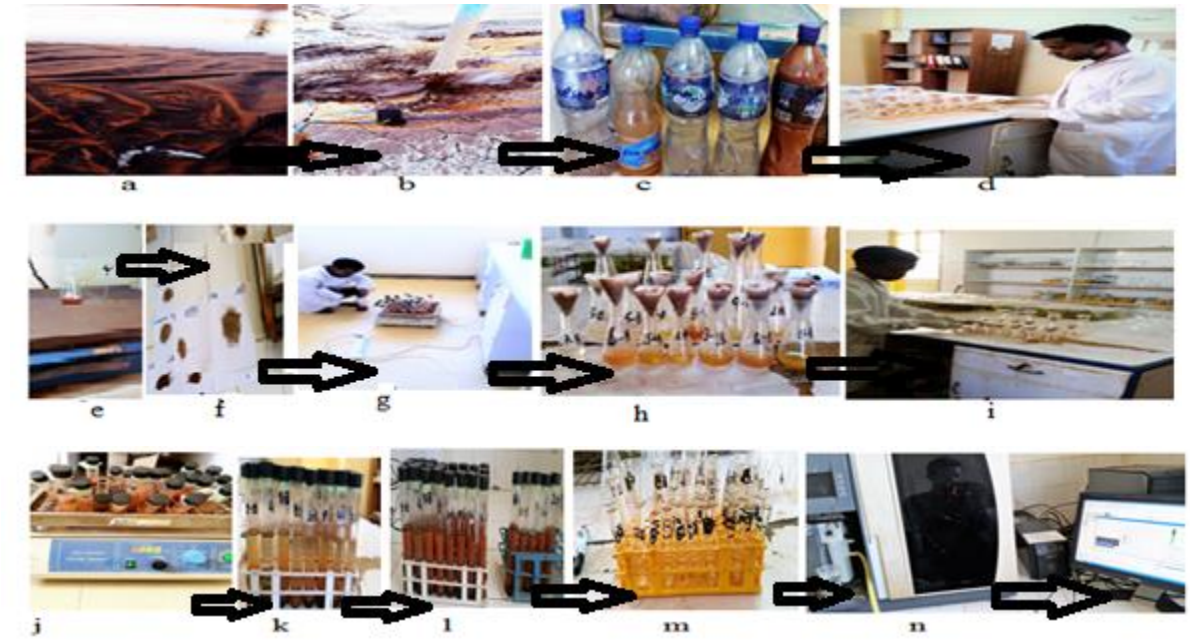


Figure 3.5: Diagrammatic procedure of adsorption in the laboratory test

(a) partial part of the dam (b) out let slurry by pipe to the dam (c) sample prepared from 5 sites (d) sample filtered from sludge (e) sample digester using acid (f) sample adsorbent weighed (g) and (j) sample during shaking with MSB and EB (k) and (l) samples after adsorption prepared to filtering MSB and EB (h) and (i) during filtration using filter paper from adsorbent (m) filtered sample prepared for AAS reading (n) samples during reading using FAAS.

Due to using of as detoxification reagents, SMBS and CuSO4 in the factory the concentration of Cu (II) and Pb (II) were higher than others except Fe explained in table 4.3. The agitating speed is

200 rpm for MSB and 175rpm for EB from different literature report the most efficient weighed quantities of the adsorbent in 40ml of wastewater (Cu, Pb) at the required pH, contacting time and adsorbent dose. These experiments are running in different Erlenmeyer glass flasks of 100 ml of capacity. First, determined amount of adsorbent added to each flask. After shaking the sample was taken, filter by the Whatman membrane filter paper of pore size 0.45 μm using a syringe as shown the figure 3.6 (d) below. Finally, the sample was analyzing by FAAS for the remaining Cu (II) and Pb (II). The experiments were conducted by using Cu is 71ppm and Pb 16ppm the maximum concentration that is discharge in to the dam from slurry pipe as shown in the figure 3.6 (b) presented. In these studies for kinetics were used from detoxification tank (75, 25) ppm and effect of concentration from selected sites Cu (30, 40, 51) and Pb (3.8, 6, 10.2) ppm. Equilibrium of this experiment was studied using isotherm models (Langmuir, Freundlich) and kinetics model (first order, second order).

3.3.4.2. PH

To examine the effect of pH on the adsorption process and to find the optimum pH, the experiments was carried out under three levels pH (2, 5 & 8). The pH of the solution adjusted by the addition of 0.1M NaOH and H_2SO_4 as needed. These experiments are work at different contact times while keeping the adsorbent dose constant and different adsorbent doses while keeping the contact time constant, the shaker at 200 rpm MSB and 175rpm EB at room temperature. The experiments were carried out in triplicate and the average results were used for calculations.

3.3.4.3. Contact time

The effect of contact time on the adsorption efficiency and the optimum contact time for the process was studied by conducting the experiment under 30, 90, 150min of contact of adsorbent. The wastewater sample for various pH by keeping the amount of adsorbent dosage constant and for various adsorbent dose while keeping constant PH. Nevertheless, agitation speed in rpm, room temperature, particle size and initial concentration constant throughout your experiment. These durations were selected because many studies in the literature show that too much contact time will not have a significant change on the adsorption.

3.3.4.4. Adsorbent dosage

The selected dose based on different reports are 0.6, 18 & 3g on the removal of Cu & Pb used to study the effect of adsorbent dosage on the removal efficiency of the SB and bark powder. The

experiments are conducting under different pH, while keeping contact time constant and under different contact time while keeping constant PH.

3.3.5. Response surface design

It is a statically method, the regression model equation and operating condition were determined in an experimental approach used (M.E.BARK, 2014). Box-Behnken designs a kind of RSM often used to study the influence of test factor, response value with accurate determination of relationship between influence factor and response value.

3.3.5.1. Design of Experiments using Box-Behnken designs

These is less expensive to run with the same number of factors, efficiently estimate the first and second-order coefficients however, they can't include runs from a factorial experiment, it is always have 3 levels per factor & unlike central composite designs which can have up to 5. In addition, unlike central composite designs, Box-Behnken designs never include runs where all factors are at their extreme setting, such as all of the low settings. A BBD central composite design is applied in this experiment with the Cu^{2+}, Pb^{2+} adsorption rate as response value removal efficiency of these elements. The experimental design involved 3 factors with 3 levels pH, contact time and sorbent dosage were chosen as independent variables and the sorption % were the output response. In the adsorption process due to most researchers concluded that the smaller particle size was higher efficiency so that by these cases select uniform mesh size MSB (850µm) & EB (500µm).

Design expert 6.0.8, was used for regression analysis of the data and to estimate the coefficient of the regression equation. The equations were validate by the statistical test called ANOVA with the significance of each term in the equation is to estimate the goodness of fit in each case. Countor plots and response surface had drawn to determine the individual, square and interactive effects of the test variable on percentage removal of both metals. Each independent variable had 3-levels (-1, 0, +1). A 2^4 factorial central composite design was designed with 8 star points, and 9 replicates at the center points which gives 17 runs for each adsorbent with total experiment is 34.

The BBD is suitable for the exploration of quadratic response surfaces and generates a second degree polynomial model, which in turn is used in optimizing a process using a small number of experimental runs. The levels of the independent variables as shown in table 3.1 are selected based on preliminary research done by many researchers. In the optimization process, the response can

be related to chosen variables by linear or quadratic models (Hassani et al., 2015) & (Elmoubarki, 2017). A quadratic model is given in equation below:

$$\%\ \text{Removal}\ \eta\ (\text{Cu, Pb}) = Y_i = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X^2_1 + b_{22}X^2_2 + b_{33}X^2_3 \quad (3.9)$$

Where Y is the response, b_0 is the constant, b_i is the linear coefficient, b_{ii} represents the quadratic coefficient, b_{ij} is the interaction coefficient, X_i is the coded variable level and i *or* j is the number of independent variables.

Table 3.1: BBD experiment factors and level for both MSB and EB

Factor	Level		
	-1	0	+1
Adsorbent dosage (g)	0.6	1.8	3
PH	2	5	8
Time (min)	30	90	150

4. RESULT AND DISCUSSION

4.1. Characterization of adsorbents

4.1.1. Proximate values of sugarcane bagasse and eucalyptus bark

This section of the work is present to address specific objective to which is intended to describe physio- chemical and surface characteristics of sugarcane bagasse and eucalyptus produced at previously predicted optimum production parameters using equation 3.1 to 3.6.

Table 4.1: Result of proximate analysis both adsorbents

parameters	Adsorbent value		Reference	
	Sugarcane bagasse	Eucalyptus bark	Sugarcane bagasse	Eucalyptus bark
MC (%)	6.2	2.273	7 (Olorunnisola, 2014)	5.1 (Sarin & Pant, 2006)
AC (%)	2.7	7.763	2-15 (Pham et al., 2015), 7.21 (Olorunnisola, 2014)	19.0 ± 0.5 (Sarin & Pant, 2006) , 4.88±0.09 (Patnukao et al., 2008)
ϱ_b (g/cm^3)	0.30375	0.8676	0.280 (Olorunnisola, 2014), 0.47(Asadi-Kesheh, Mohtashami,Kaghazchi, Asasian, & Soleimani, 2015)	0.251 (Patnukao et al., 2008), 1.55 (Presented et al., 2015)
VM (%)	78	64.5	70.94 (Olorunnisola, 2014)	65.7 ± 2.0 (Sarin & Pant, 2006)
C, N (%)	11,6.5	12, 3.7	13.5 ,7.8 (Sarin & Pant, 2006)	16 , 2.362 (Presented et al., 2015)
FC (%)	13.1	25.46	16 (Olorunnisola, 2014)	21(Presented et al., 2015)

Moisture content-MC, Ash content-AC, Bulk density-ϱ_b, Volatile matter-VM, C,N_2-carbon, nitrogen, Fixed carbon-FC

4.1.2. The specific surface area determination

Surface area of the adsorbent were determined by sears method. A sample containing 0.5g of the modified bagasse (MSB) and eucalyptus bark (EB) was acidified with 0.1M HCl to pH 3 – 3.5,

the volume was made up to 50cm^3 with de-ionized water after addition of 10g of NaCl. The titration were carried out with standard 0.1M NaOH in a thermostatic bath at 25^{o}C from pH 4.0 to pH 9.0. The volume required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed using the following equation (A.O, 2012):

$$S\ (m^2/g) = 32V-25 \quad \text{.....(4.1)}$$

The result where V is the volume of 0.1M NaOH solution in ml required to achieve pH of 9 from pH 4 with 0.5g of sorbent and 10g of NaCl in 50ml of distilled water. The amount of NaOH used for titration from pH 4 to 9 was MSB (0.96ml), EB (1.8ml) which gives 0.282 m^2/g. These which would be not far as such Surface area SB (m^2/g) 0.59 ± 0.05 (Sarin & Pant, 2006), 1.239 (m^2/g), (Patnukao et al., 2008) and EB result obtained was 55.1 m^2/g similar to 66 m^2/g (Asadi-Kesheh et al., 2015), 1.53 m^2/g 6.53 (PH_o =5.05) (Joseph et al., 2009).

4.1.3. Fourier transform infrared spectroscopy analysis

As you shown in figure 4.1 & 4.2 some important changes in some bands of modified bagasse (MSB) and eucalyptus bark (EB). FTIR spectera of MSB the adsorption band at 3411cm^{-1} is attributed to sterching vibration of hydroxyl groups on SB in spectrum a clearly, this band intensty became weak after the reaction.

Table 4.2: FTIR absorption frequencies (cm^{-1}) of both adsorbents

Adsorbent	Metal ion adsorption	O-H	C-H	C=O & N-H	C=C	C-O-C
MSB	Before treated	3422	2924	1618	1369	1045
MSB	After (loaded) treated	3437	2940	1618	1385.5	1074.5
EB	Before treated	3425	2927	1611	1392	1033
EB	After(loaded) treated	3425	2917	1621	1312,1412	1043

New absorption bands appeard at 1566cm^{-1} (asymmertic-COO- sterching) and 1674cm^{-1} which is a shift of C=O sterching vibration caused by superpostion of C=O in the amide I and C-O in COO in spectrumb. The adsorption at 1035cm^{-1} is due to the beta - one, 4-glycosadic bond and the band at 1633cm^{-1} is due to the C=O and –NH_2. Lignin is a polymer with high content of C and H_2 as a

result could be explained by the extraction of lignin from the SB (Karnitz et al., 2010). In the figure 4.1 the range between 1200 cm^{-1} and 1100 cm^{-1} is region of hemicellulose and cellulose in result, which attained a maximum value around 1035 cm^{-1} due to C-O stretching (Castañón-Rodríguez et al., 2015).

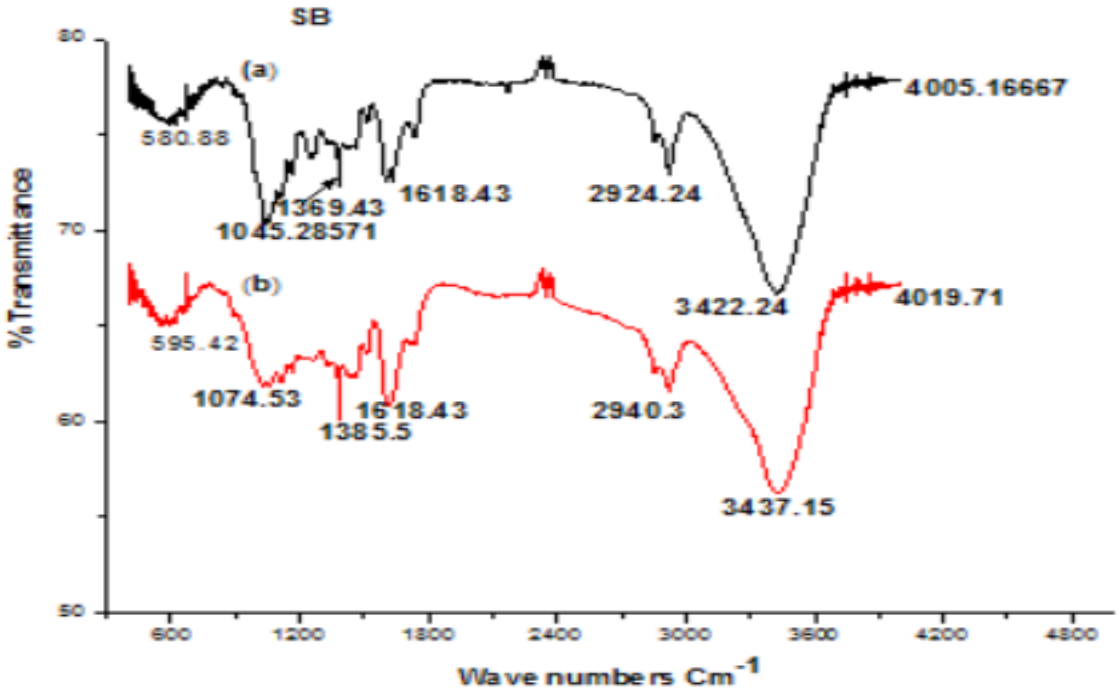


Figure 4.1: FTIR analysis of modified bagasse (a) before and (b) after metal ion adsorption

The peak observed at 2918cm^{-1} was associated with the stretching vibrations of CH bond of methyl, methylene and methoxy groups. The peaks around 1600- 1627cm^{-1} corresponded to the C=C stretching which might be attributed to the presence of aromatic/olefinic or N-H bending bands. Hence there has been considerable interest for introduction of N-containing functional group on the surface of the adsorbent to enhance the adsorption capacity. The trend of the FTIR spectrum for all the lignocellulose precursors contains some main peaks which are almost similar. Some major peaks around 2800-2900cm^{-1}, 1500-1650 cm^{-1} and 1000-1200 cm^{-1} are related to C-H stretching of alkane, C=C stretching of aromatics, C-O-C stretching vibration of esters, ether and phenol groups. The O-H stretching vibrations at bandwidth of 3400-3800 cm^{-1} are present in the raw precursors (Chowdhury, 2013).

According to Lun et al., (2017) the region between 3800 cm^{-1}-3000 cm^{-1} indicates the crystalline structure of cellulose. This range covers the sum of the vibration of valence bands of the H_2 bond of the O-H group with the bands of infra-molecular and intermolecular hydrogen bonds.

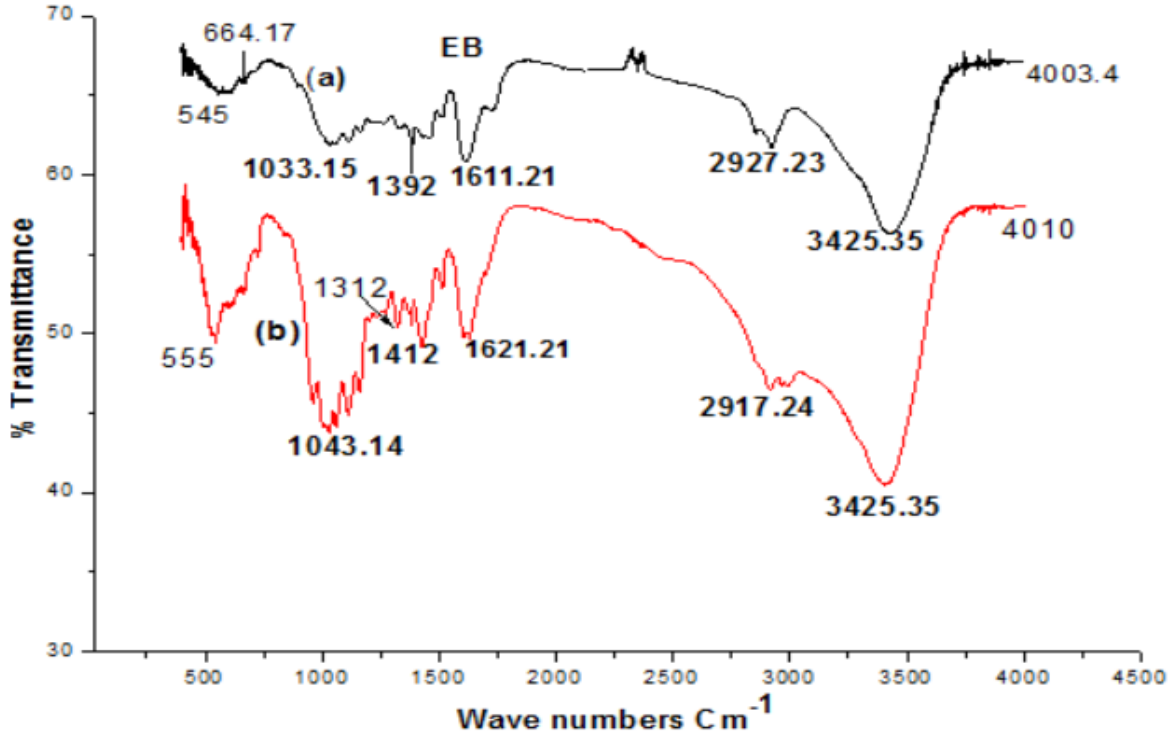


Figure 4.2: FTIR analysis of eucalyptus bark (a) before and (b) after metal ion adsorption

The shift in band position supports that –OH and C=O groups interacts with heavy metal (Pb, Cu) during bio sorption process. The possible bio sorption may be due to physical bio sorption, complexation with functional group, Ionic exchange, chemical reaction with bio sorbent sites (Joginder Singh, 2013). The IR spectrum of unloaded and loaded with (Cu, Pb) bark powder is presented in figure 4.2 it shows the presence of different functional groups. The broad and strong absorption peak around 3425 cm^{-1} is an indicative of hydroxyl groups. The bands at 2924 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 3424 to 3436, the peak of C-O stretching become very weak after an adsorbent is loaded with Cu and Pb (Presented et al., 2015).

FTIR spectrum of the given raw bagasse and bark loaded with different metals shows that the peaks are five in table 4.2 (before adsorption) had shifted slightly after binding with metals. This

was due to the participation of these functional groups in the binding of metal ions. The shifting of wave number depends on the concentration of metal present in the given sample agreed by the literature survey (Abuzer et al., 2011; Hao Chen et al., 2010). Finally, the absorbance peak of acids at 1597 cm^{-1} and 1377 cm^{-1} are described to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic groups (Abudaia et al., 2013).

4.1.4. X-ray diffraction analysis

X-ray diffraction analysis (XRD) is used to measure the crystalline/ non-crystalline phase content of adsorbent materials. The crystalline phases were identified by comparing the intensities and positions of the Bragg peaks with those listed in the JCPDS-ICDD cards (Faria et al., 2012). The diffraction intensities were measured between Bragg angles (2θ) of 5–69º (Ramli et al., 2015). The crystallinity index (CI) was calculated by Segal's formula using intensity measurement at 22.5º and 18.5º (amorphous background) 2θ:

$$CI = \frac{(I_2 - Iam)}{I_2} * 100 \quad \text{.....(4.2)}$$

Where, I_2 denotes the maximum intensity of the 2 peak at about 2θ reading and Iam is the lowest intensity of the amorphous corresponding to 2θ value near to the peak 1.

The phases present were analyses using powder XRD in the 2θ region of 10-90^0 at 25^0C. Major peaks obtained during XRD were identified using EVA software are indicates the presence of a significant amount of amorphous material due to lignin and tannin in the samples and structure of eucalyptus bark remained unaltered even after treatment with base or acid (Faculty, 2016).

In the case of modified bagasse because the amorphous region observed in XRD refers to the total amorphous fraction of the sample and does not distinguish the source of the amorphous material (amorphous cellulose, hemicellulose/lignin). The crystalline index obtained by XRD refers to the whole sample and not only to the cellulose fractions. Therefore, when hemicellulose or lignin is removed from the sample, the CI tends to increase, due to a proportional reduction in the amorphous halo of the XRD diffractogram as shown in the figure 4.3 and 4.4. The XRD patterns of the cellulose crystallographic planes from the raw and prehydrolyzed bagasse, observed at 2θ showed two major peaks, one in the region of 15º, which corresponds to the amorphous region and other at 23º, which corresponds to the crystalline region (Erenbo et al., 2017). Based on this reported the graph as you shown in figure 4.3 the treated bagasse are two peaks one in the region

of 15.17º which corresponds to the amorphous region and at 22.44°C which corresponds to crystalline region.

The prehydrolyzed bagasse showed a slightly bigger area for the amorphous region (15º) as well as a reduced area for the crystalline region (23º), which showed a less pronounced peak (Castañón-Rodríguez et al., 2015). The modified bagasse showed in figure 4.3 from origin pro.v 8.0 software a much low area for the amorphous region (11.54º) as well as a large area for the crystalline region (20.86º), which showed a more pronounced peak. The treatment of SB with 5MNaOH allowed the transformation of cellulose from cellulose I into cellulose II. Owing to the removal of the great amount of lignin and polyoses, which are amorphous compounds presents in sugarcane bagasse (Krässig, 1993).

Eucalyptus bark, raw bagasse showed two peaks are present in the figure 4.4, one in the region of 15.17º, which corresponds to the amorphous region and other at 22.44º, which corresponds to the crystalline region. From the result of origin software showed a slightly bigger area for the amorphous region (15.17º) as well as a reduced area for the crystalline region (22.44º), which showed a less pronounced peak, these are an indicative of highly organized crystalline cellulose which are responsible for adsorption (Faculty, 2016). The XRD before and after treated eucalyptus bark indicating that the chemical elements present on the surface of raw and treated eucalyptus bark are same. The peaks obtained also gave good indication of highly organized crystalline cellulose on the adsorbent biomass (Faculty, 2016).

The XRD pattern of modified bagasse (MSB) and eucalyptus bark (EB) the characteristic are main peaks obtained at 2θ values of (11.54º, 20.86º) and (15.17º, 22.44º) respectively. From the two adsorbent the highest crystallize value are bark. The crystallinity index was calculated as the ratio between the sum of the areas of all the crystalline peaks and the total area of the spectrum. The crystallinity at highest intensity or peak 2 (I_2), peak1 (Iam) for modified bagasse (1396, 815) and eucalyptus bark (2204, 1489) respectively obtained from the software origin pro. Therefor the result CI using the equation 4.2 is 41.62% MSB and EB is 32.44%. These might be according to Jayme and Knolle, (1993) & (Ramli et al., 2015) the absence of great part of lignin and polyoses made possible for the hydroxyl ions directly acted on cellulose fibers promoting hydrolysis of the cellulose chains and consequently an increase of the cellulose amorphous fraction. A crystallinity index increasing related to rigidity of the cellulose structure, which leads to higher tensile strength of the powder (Faculty, 2016).

As you observed in figure 4.3 & 4.4, both crystalline and semi crystalline region can show in noticeable peak on the shoulder at different of reading of angle 2Θ ranging from 11°-23° these can suggest according to Ramli, Junadi, Beg, & Yunus, (2015) this kind of behavior because the small portion of the Cellulose II still presence

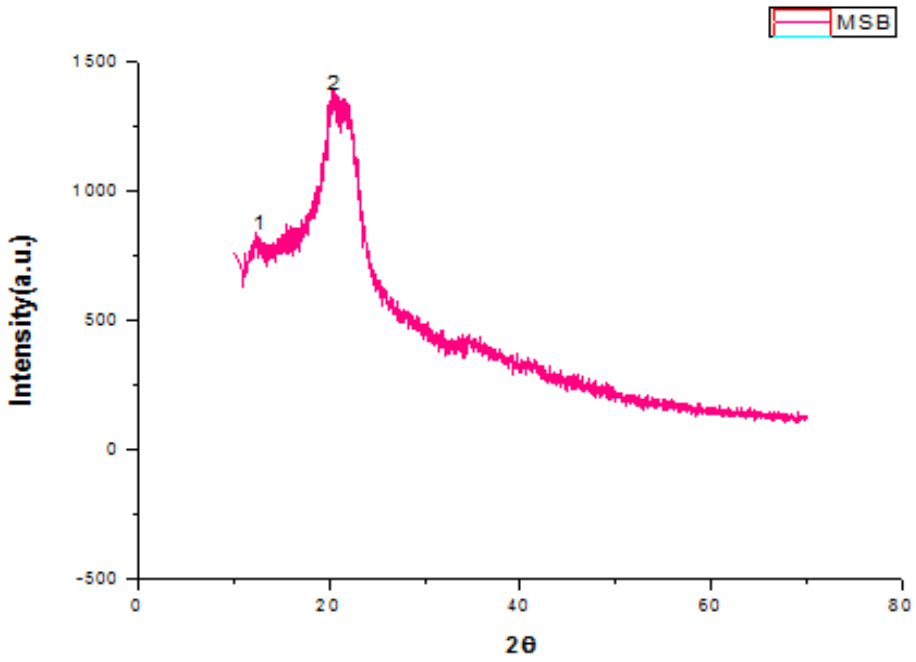


Figure 4.3: X-Ray diffractometer analysis for treated modified bagasse

In MSB with the assistance of alkali, treatment help extracting and increase number of hydroxyl group, however, in EB is only treated by H_2SO_4 the crystallinity higher than MSB. This might be due to the nature of the EB it can remove both amorphous and crystalline cellulose as a result reaction time, crystalline region might have degraded in small portion. Thus, as crystalline index increase the removal percentage would be increased and from these EB the highest adsorption efficiency. The larger accessibility cellulose the lower degree crystallinity (vice versa) as a result decrease crystallinity beneficial by esterification because the structure hydrogen bonding is destroyed and increase efficiency.

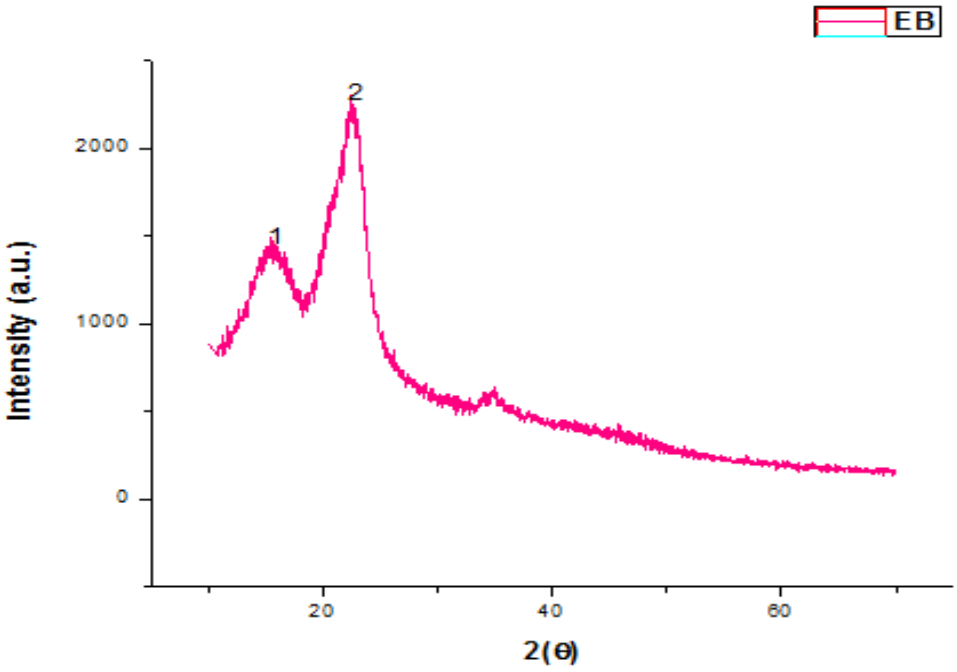


Figure 4.4: X-Ray diffractometer analysis for treated eucalyptus bark

4.1.5. Point of zero charge value

Point of zero charge (PZC) a fundamental important in physical chemistry which is the concept relating to physical phenomena. These is used to understand the mechanism of adsorption process under varying pH. Adsorption of cations is favored at pH > pHpzc while adsorption of anions is favored at pH < pHpzc. In the present study, the point of zero charge (pHpzc) was determined by solid addition method (Mall, Srivastava et al. 2006). This technique is based on estimating the concentrations of H^+ and OH^- ions, which determine the electric potential. A series of 0.1 M KNO_3 solutions (50 ml each) were prepared and their initial pH was set at 2–12 by addition of 0.1 M HCl or NaOH (Faculty, 2016). To each solution, 1g of adsorbent was added, the suspensions were shaken manually and solution was kept for a period of 24 h with shaking with 200rpm. The final pH of solution was recorded with a pH meter with initial and final pH (ΔpH) (Y-axis) was plotted against initial pH values (X-axis). The point of intersection of this curve yielded point of zero charge determination of modified bagasse (MSB) and eucalyptus bark (EB) is presented in figure 4.5. The results shown that pHpzc of treated biomass modified bagasse was around 4.5 and eucalyptus bark was found to be 4 in this study.

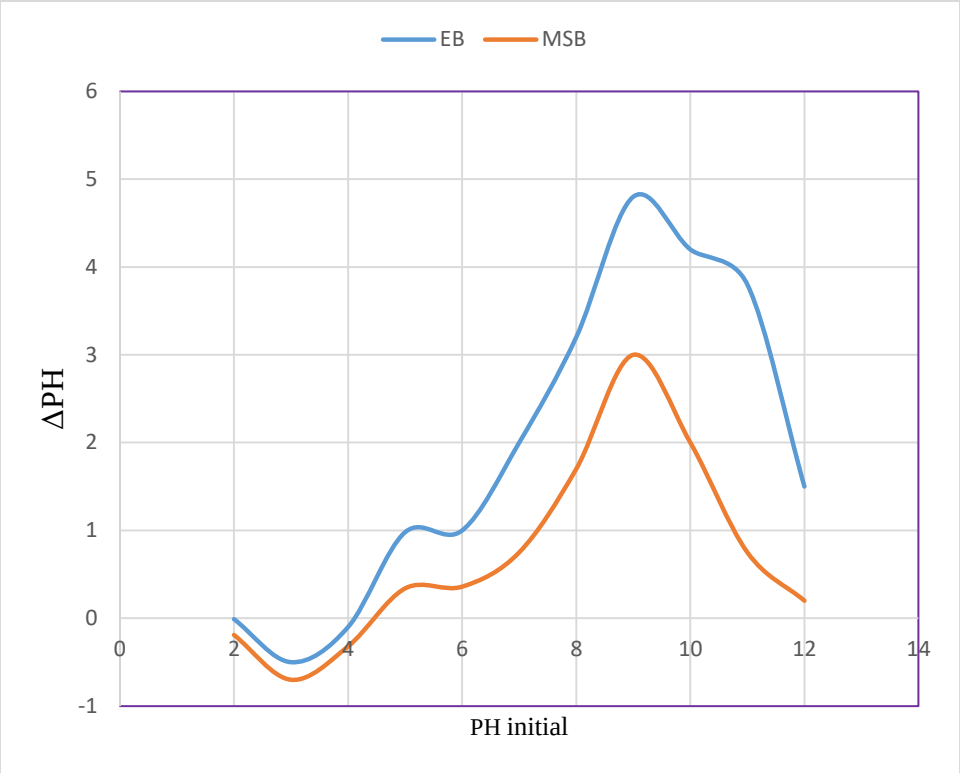


Figure 4.5: Point of zero charge of modified bagasse and eucalyptus bark

This indicates that pH values should be maintained greater than 4.5 to ensure a predominant negatively charged surface resulting in electrostatic attraction between adsorbate molecules and biomass of adsorbent. Below this PH, the surface charge of the adsorbent biomass acquires positively charged due to protonation of functional groups which making H^+ ions compete effectively with the Cu^{2+} and Pb^{2+} cations as a result these a decrease in the amount of adsorbate adsorbed is expected (Oliveira, Franca et al. 2008).

4.2. The laboratory result of wastewater from tailing dam effluent

Various regulatory bodies have set the maximum prescribed limit for discharging of toxic heavy metals into the aquatic ecosystem. The undesirable effects can avoid by treatment of the gold mining wastewater prior to discharge. The IFC effluent standard to discharge of some heavy metal and cyanide according to Ababa (2016) in the surface waste. The present study of laboratory analysis for Ezana wastewater sample were described on the table 4.3. The laboratory test result was taken from five sites with different hours of storage dam N, S, West, East out let effluent & finally in the detoxification tank (out of scope). The result carried out by digesting and without digesting with acid to prevent precipitations due to high acidity of the sample then diluted with

deionized water analyzed in ppm were Cd (0.02), Cr (VI) (0.43), Cu (71), Ni (0.1), Pb (16), Fe (313.11), Zn (0.34), Mn (0.94). The result of cyanide WAD obtained at room temperature (morning, evening) (0ppm) and cyanide WAD with temperature with <11^{o}C night (0.025ppm). These was determined using titrimetric method after pouring the sample waste water by plastic bottle with in 20min should be measured unless evaporation will be start especially on day time. The other physiochemical characterization was includes pH 8-8.5, EC (µs/cm) 2980, turbidity in (NTU) 7800, temperature (10-33^{0}C), total dissolved solid (1213ppm), total suspended solid (750ppm) and COD (120ppm). The maximum concentration (Cu, Pb) obtained from sites in ppm (morning, afternoon, evening), out let discharge of the slurry east direction (71, 16), south (30, 3.8), west (51, 10.2), north (40, 6) & finally in the detoxification tank (75, 25), respectively.

These test were only for Cu (II) and Pb (II), but other heavy metal are determined only from one site to analyze the concentration value due to cost (air + acetylene). The cyanide concentration in the process effluent measured during the night to check in low temperature below 11°C in the site of out let effluent (discharging from the pipe) one-hour difference 0.025mg/l and at other hours were zero. Most of the heavy metal were around the permissible limit except Cu and Pb due to using of copper sulfate, high content of Cu and Pb in the ore are higher than others. Except Fe (313.11), Cu (71) and Pb (16) ppm as significant parameters with high positive loading value & indicating the contribution from the ore. Chemical characteristics of process and tailings dam effluents of COD values were below the acceptable limit with ratio lower than 50 low level of organic matter in the waste water (Jouanneau et al., 2013).

There are high positive loading values for EC and TDS, which is an indication of mixed sources of pollution.

Table 4.3: The result of present study & effluent standard to discharge in the CERCLA list of priority chemicals (2005) for industrial wastewater Cont, 2017

Heavy metal	Standard USA	Permission level	Laboratory result	
			With digestion	Without digestion
Fe (mg/l)	-	2	313.11	6
Pb (mg/l)	0.015	0.15-0.2	16	3.12
Cd (mg/l)	0.005	0.06	0.02	0.01
Cr (VI) (mg/l)	0.01	0.05-0.1	0.43	below detection limit

Zn (mg/l)	5	0.5	0.34	below detection limit
Mn (mg/l)	0.05	1	0.94	0.02
Cu (mg/l)	1.3	0.3	71	18
Co (mg/l)	-	-	0.17	0.17
Ni (mg/l)	5	0.5	0.1	0.08
Temp. (°C)		40		10-33
Cyanide WAD @ T°<11°C(mg/l)		0.1		0.025
Cyanide WAD (mg/l)		0.5		0
PH		6-9		8-8.5
EC (µs/cm)		750		2980
Turbidity (NTU)		75		7800
TDS (mg/l)		50		1214
TSS (mg/l)		1000		750
COD (mg/l)		250		120

The quality of raw water varies widely from mine to mine depending on the local condition however from available data (rozkowski et al., 1994, Sivakumar et al., 1994b). As explained in literature review pH < 6.5 may be corrosive to plumbing fixtures, reticulation and the general guideline value is within 6.5 and 8.5 to all mine water.

Table 4.4: The following general characteristics can identified

Parameters	laboratory result of present study	(H B Dharmappa et al., 1995) and Rozkowskiand rozkowski,1994;Singh,1994Sivakumar et a.,1994b
High TDS (mg/l)	1213	500-2000
Low SS (mg/l)	750	10-100
Low COD (mg/l)	120	10-100
Near neutral PH	8-8.5	7-9.5
High conductivity (µs/cm)	2890	600-10,000

The tailings dam effluent pH gradually decreased over time due to neutralization of the alkaline environment by rainwater and possibly also as a result of CO_2 uptake (H B Dharmappa et al., 1995).

4.3. Optimization process

RSM was applied to model and optimize different process parameters effect of pH, adsorbent dose, contacting time in adsorption percentage of modified bagasse and eucalyptus bark. The operational parameters with optimum adsorption % were predicted using developed model. Accordingly, first model development and evaluation was discussed. Second, the effect of independent variables on response variables was examined. Then finally using the model optimum points of operational parameters were predicted.

4.3.1. Development and evolution of adsorption percentage model prediction

For each of thus experimental runs adsorption percentage was determined using the methodology described. Experimental results of adsorption percentage were fed to design expert 6.0.8 version, Minitab software, excel for graphical and multiple regression fitting sequential or extra sums of squares for the linear. A quadratic and cubic terms in the model there is a warning message concerning aliasing in the cubic model because the BBD does not contain enough runs to support a full cubic model. The small P value for quadratic term we decided to fit the second-order model to the removal efficiency of Cu and Pb response.

According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased (Montgomery, 2001). For adsorption capacity of both Pb (II) and Cu (II), quadratic model was suggested by the software. However, for Pb (II) in case of MSB both linear and quadratic models were suggested by the software. In this case, quadratic models were selected due to the higher order of polynomials. On the contrary, 2FI model was selected as suggested by the software for yield. The final empirical models in terms of coded factors after excluding the insignificant terms for both MSB and EB.

Design expert software was used to design the experiment and randomize the runs. Randomization ensures that the conditions in one run neither depend on the conditions of the previous runs nor predict the conditions in the subsequent runs. Randomization is essential for drawing conclusions

from the experiment, in correct, unambiguous and defensible manner. For adsorption capacity of Cu (II) by modified bagasse (MSB) & a quadratic model was suggested by the software. However, for Pb (II), the software suggested both linear and quadratic models.

Final equation in terms of coded factors MSB:

$$Percent\ Removal\ Cu = Y_{SB} = +87.27 + 4.64 * A + 8.13 * B + 3.03 * C - 14.44 * A^2 - 16.14 * B^2 - 0.56 * C^2 - 3.81 * A * B - 0.23 * A * C - 5.93 * B * C$$

……..(4.3)

Final equation in terms of coded factors:

$$Percent\ removal\ Pb = Y_{SB} = +89.70 + 8.35 * A + 3.04 * B - 1.59 * C - 8.61 * A^2 - 3.74 * B^2 - 1.19 * C^2 - 1.65 * A * B + 5.15 * A * C - 0.23 * B * C$$

.....(4.4)

Final equation in terms of coded factors EB:

$$Percent\ removal\ Cu = Y_{EB} = +88.60 + 5.77 * A + 6.91 * B + 4.96 * C - 26.60 * A^2 - 7.14 * B^2 - 3.03 * C^2 + 11.36 * A * B + 1.27 * A * C - 1.94 * B * C$$

.....(4.5)

Final equation in terms of coded factors:

$$Percent\ removal\ Pb = Y_{EB} = +97.17 + 2.86 * A + 3.66 * B + 3.69 * C - 11.34 * A^2 - 1.17 * B^2 - 1.98 * C^2 + 1.16 * A * B + 0.35 * A * C - 0.65 * B * C$$

.....(4.6)

Y_{SB} and Y_{EB} was the predicted response variable for adsorption percentage of SB (modified bagasse) & EB (eucalyptus bark) in terms of coded factors. The regressions coefficient and the determination coefficient (R^2) for the quadratic regressions model for Cu and Pb adsorption were presented in table 4.5. The coefficients with PH: A (x_1), adsorbent dose: B (x_2) and time: C (x_3) represent the effect of that particular factor for the both adsorbent. Coefficients with two factor (x_1x_2, x_2x_3 and x_3x_1) and others with second order terms (x_1^2, x_2^2 and x_3^2) show the interaction between the two variables and quadratic effect respectively. Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect (Das, 2017), (Montgomery, 2001) & (B. I. O. Engineering et al., 2015).

This model shows that the 3 factors (pH, dosage, time) on Cu by MSB, EB (Cu, Pb) has no negative linear coefficient on the amount adsorbed disposal from quadratic regression equation 4.3-4.6. The interaction effect explanation focus on the significant factors Cu by MSB (pH with adsorbent dose, adsorbent dose with contact time), Pb by MSB (pH with contact time), and Cu by EB (pH with adsorbent dose). This model showed that the contact time on Pb by MSB has a negative effect on the amount adsorbed disposal one hand, when the pH of the sample wastewater believes the percentage removal increases. On other hand, the % removal increases as increasing pH until optimum value reached beyond that started to decrease. The 3 factors on the removal of Cu and Pb have a positive effect except Pb^{2+} by MSB increasing the contact time were negative effect or not linearly increase. The positive effect on the removal of Pb^{2+} by MSB in terms of the interaction effects between pH with contact time can be explained by the contact time have much less effect than the pH is under high pH equation 4.4. The positive effect on the removal of Cu^{2+} and Pb^{2+} by EB in terms of the interaction effects between PH with the adsorbent dose can be explained by the pH have much less effect than adsorbent dose is under high adsorbent dose to both heavy metal equation 4.5 & 4.6.

The effect of negative interaction of order 1 equation 4.3 between the adsorbent dose and contacting time can have explained by the adsorbent dose with much more positive effect as a return, such that increasing the adsorbent dose increase linearly adsorption in Cu by MSB. Likewise, double interaction effect of pH, adsorbent dose and the dual interaction of the contacting time a negative effect on the percentage removal Cu by MSB such as a decrease in any of these parameters causes a decrease in the removal efficiency for all equation 4.3.

The effect of positive interaction of order 1 between the pH and contact time can have explained by the contact time with much more positive effect as a return, such that increasing the contact time increase linearly adsorption with pH in Pb by EB. Likewise, double interaction effect of pH, adsorbent dose and dual interaction of the contact time a negative effect on the percentage removal Pb by EB such as a decrease in any of these parameters from the optimum value causes a decrease in the removal efficiency for all.

The effect of positive interaction of order 1 between the pH, contact time and adsorbent dose described the contact time with much more negative effect as a return in the linear coefficient of equation 4.4, such that increasing the contact time did not increase linearly adsorption in Pb by MSB. Likewise, double interaction effect of contact time, PH and adsorbent dose are negative

effect on the percentage removal Pb by MSB such as a decrease in any of these parameters causes a decrease in the removal efficiency except decrease contact time from 150min to 90min increase removal of % Pb. Among these parameters removal Cu by MSB, the adsorbent dose is the most influence and PH for Pb by MSB. However, to obtain good removal of the Cu by MSB must increase its PH in to 5 and Pb by MSB adsorbent dose increase to 1.8g beyond these slightly decreases.

In this model certain factors such as the coefficient associated with the dual interaction of the main significant factor. The pH with adsorbent dosage for Cu by MSB (slightly significant in the table 4.7) and EB, pH with contact time for Pb by MSB, adsorbent dose with contact time which have very low values due to these assumed the terms is not influential. Therefore, interaction effects as significant model terms can be used for modeling the experimental system, but on the equation also included the non-significant factors. The quality of the model developed can be understood by the correlation coefficient R^2 indicates the ratio between sum of squares with total sum of squares and this depicts how well the models approximate the experimental data points. The small values of standard deviations and co-efficient of variation, CV reflect reproducibility of the model. The ratio obtained for all the responses reflects that the models can be used to navigate the design space. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable (Montgomery, 2001).

Table 4.4 and 4.5 shows the statistical summary for each model that was output by Design Expert V 8.0.6. A quadratic model was suggested, even though it has lower R^2 and adjusted-R^2 (Adj-R^2) values than a cubic model. This due to the cubic model was aliased, which means that the effects of each variable that cause different signals become indistinguishable. For a linear relationship, the R^2 and Adj-R^2 values are 0.6362 and 0.5370, respectively. It is clear that the linear relationship is not adequate for the experimental data (Qiu et al., 2014). The quadratic model was therefore selected to fit the experimental data. To assess the adequacy of a model, the coefficient of determination (R^2), the lack of fit test were commonly used and changes described by the model to the overall changes. Therefore, whatever R^2 is closer to 1, the power of fitted model is greater to describe the response changes as a function of the independent variables (Elmoubarki, 2017).

A negative predected R-Squared for Pb by EB implies that the overall mean is a better predictor of your response than the current model, ratio of 10.092 indicates an adequate signal and this model can be used to navigate the design space. The statistical significance of the model was investigated

by ANOVA. It is a collection of statistical models and their associated procedures (such as variation between groups) used to analyze the differences.

Table 4.5: Model summary statistics Cu, Pb by MSB and EB respectively

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	13.50	0.2465	0.0726	-0.2464	3918.19	
2FI	14.73	0.3097	-0.1045	1.1709	6824.44	
Quadratic	3.03	0.9795	0.9532	0.7966	953.62	Suggested
Cubic	1.15	0.9983	0.9933		+	Aliased
Linear	6.83	0.5178	0.4065	0.1521	1067.25	Suggested
2FI	7.00	0.6108	0.3773	-0.3281	1671.62	
Quadratic	3.55	0.9298	0.8395	-0.0339	1301.31	Suggested
Cubic	1.40	0.9938	0.9752		+	Aliased
Linear	17.80	0.1702	-0.0213	-0.4401	7150.98	
2FI	18.93	0.2785	-0.1544	-1.4726	12277.61	
Quadratic	5.25	0.9611	0.9110	0.4700	2631.95	Suggested
Cubic	2.82	0.9936	0.9743		+	Aliased
Linear	6.99	0.3070	0.1470	-0.1932	1094.31	
2FI	7.92	0.3152	-0.0956	-1.4477	2244.85	
Quadratic	2.48	0.9531	0.8927	0.4464	507.69	Suggested
Cubic	1.77	0.9863	0.9454		+	Aliased

The significance of the model, model terms are determined by applying the F-test and p-test. The larger the magnitude of F-test and smaller the p value, the more significant is the corresponding model and model terms.

The S-1 to S-17 for each were prepared for random set of variables to resolve experimental errors and reproducibility of the data. The associated p value purpose was to estimate whether F is large enough to indicate statistical significance. The values of p > F, less than 0.05 indicates that the model is considered to be statistically significant whereas values greater than 0.10 indicate the model terms are not significant mean that the experimental systems have modelled effectively with less error. If there are many insignificant model terms (not counting those required to support

Hierarchy), model reduction may improve the predicted model. Regarding this, the model is statistically significant at level of p-value <0.0001.

In the Cu and Pb by modifed bagsse (MSB) the model F-value of 37.23, 10.3 from table 4.6 and table 4.7 was 19.2, 15.8 by eucalyptus bark (EB) respectively implies that model was significant. There was only a Cu (0.01%), Pb (0.28%) by MSB and Cu (0.04%), Pb (0.07%) by EB chance that a "model F-Value" this large could occur due to noise. In this case using both adsorbent except BC (x_2x_3) significant in MSB (Cu), for Cu paramters A(x_1), B(x_2), C(x_3), A^2(x_1), B^2(x_2), AB(x_1x_2), Pb is A, B, A^2, AC by MSB illustrated on table 4.6 and Pb is A, B, C, A^2 by EB on table 4.7 were a significant model terms. Model correlation were find out with experimental values and predicted values from the optimal conditions.

The error was found to be (1.31, 1.92) by MSB on table 4.6 and 4.7 were (7.97, 3.13) by EB for (Cu, Pb) respectively which might be due to experimental errors, handling errors, composition of the wastewater etc.

Table 4.6: ANOVA analysis for removal percentage by using MSB (Cu, Pb)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	3079.28	9	342.14	37.23	< 0.0001 significant
A	172.61	1	172.61	18.78	0.0034
B	528.94	1	528.94	57.55	0.0001
C	73.27	1	73.27	7.97	0.0256
A^2	878.26	1	878.26	95.56	< 0.0001
B^2	1096.84	1	1096.84	119.34	< 0.0001
C^2	1.30	1	1.30	0.14	0.7183
AB	58.14	1	58.1	6.33	0.0401
AC	0.21	1	0.21	0.023	0.8849
BC	140.42	1	140.42	15.28	0.0058
Residuals	64.34	7	9.19		
Lack of Fit	59.09	3	19.70	15.01	0.121 not significant
Pure Error	5.25	4	1.31		
Cor Total	3143.62	16			

Model	1170.30	9	130.03	10.30	0.0028	significant
A	557.78	1	557.78	44.18	0.0003	
B	73.81	1	73.81	5.85	0.0462	
C	20.10	1	20.10	1.59	0.2475	
A^2	312.41	1	312.41	24.75	0.0016	
B^2	58.86	1	58.86	4.66	0.0677	
C^2	5.95	1	5.95	0.47	0.5145	
AB	10.92	1	10.92	0.87	0.3832	
AC	105.99	1	105.9	8.40	0.0231	
BC	0.21	1	0.21	0.016	0.9017	
Residual	88.37	1	12.6			
Lack of Fit	80.57	3	26.86	13.77	0.142	not significant
Pure Error	7.80	4	1.9			
Cor Total	1258.6	16				

Std. Dev.= 3.03, R-Squared= 0.9795, Mean= 72.62, Adj R-Squared= 0.9532 C.V.= 4.17, Pred R-Squared = 0.6966, PRESS = 953.62, Adeq Precision = 17.008 for Cu

Std. Dev.= 3.55, R-Squared= 0.9298, Mean= 83.33, Adj R-Squared= 0.8395, C.V.= 4.26 Pred R-Squared= -0.0339, PRESS = 1301.31, Adeq Precision= 10.092 for Pb

As could be seen from analysis of variance table 4.6, 4.7 this ratio was Cu (17.008), Pb (10.092) by MSB and Cu (11.476), Pb (12.133) by EB > 4 for adsorption % model indicating an adequacy of signal are desirable for both adsorbents. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The lack of fit F-value of Cu (15.01), Pb (13.77) implies not significant. The small values of standard deviations MSB (Cu, Pb), EB (Cu, Pb) were (3.03, 3.55), (5.25, 2.48) and co-efficient of variation (4.17, 4.26), (7.37, 2.74) from table 4.6 and 4.7. Hence, CV reflect reproducibility of the model for both adsorbents and metals removal.

Model diagnostic plots are graphical summaries for case statistics. The plots of residuals showed that how well the model satisfies the residual assumptions of the analysis of variance. Different model diagnostic plots were ploted are the normal probability plot compares the distribution of the residuals to a normal distribution (the straight line). Expect some scatter even with normal data. Look only for definite patterns like an s-shaped curve, which indicates that a transformation of the response may provide a better analysis. The residuals vs. predicted this plot checks for constant variance across the range of predictions. Non-constant variance is indicating by a pattern in the

plot (upward or downward curves, etc.). If the plot appears randomly scattered between the red lines, then the assumption of constant variance is confirmed. The predicted vs. actual a graph of the predicted response values versus the actual response values. It primarily used to detect a value, or group of values, that are not predicted well by the model. These values for the model are close indicating a correspondence between the mathematical model and the experimental data (actual value).

The correlations between the theoretical and experimental responses, calculated by the model, are satisfactory (Elmoubarki, 2017). Normal probability plot of the studentized residuals are used to check for normality of residuals. Figure 4.5 and 4.6(a) shows the relationship which is the straight line means that no response transformation was required and that there was no apparent problem with normality. Studentized residuals versus predicted values plots are used to check for constant error.

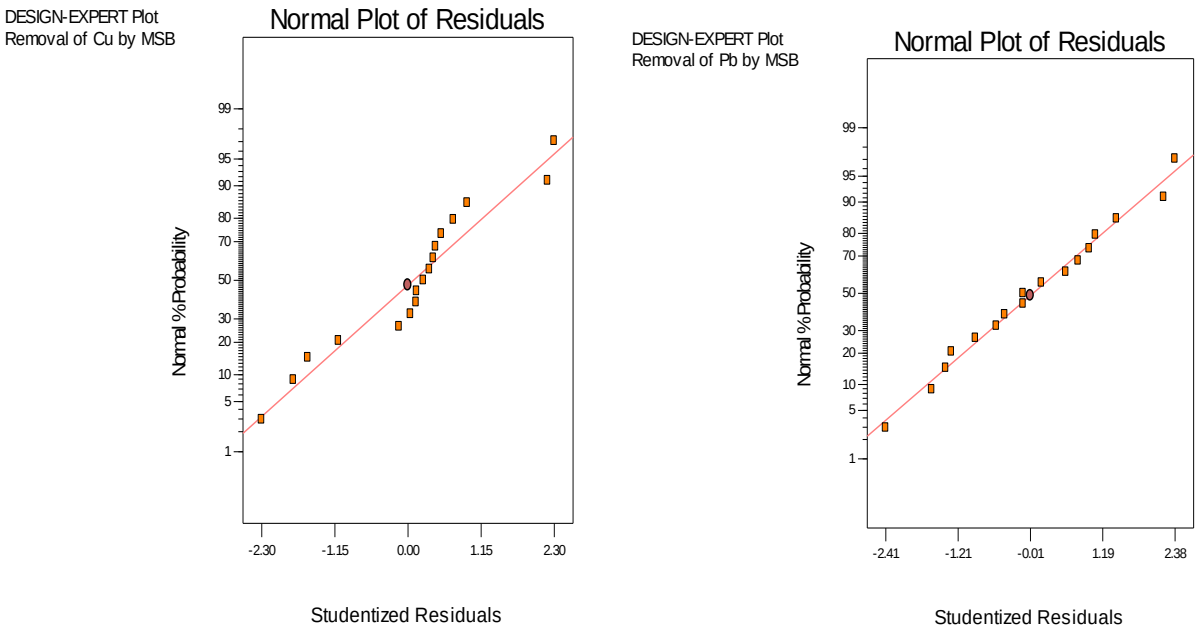
Table 4.7: ANOVA analysis for removal percentage by using EB (Cu, Pb)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	4772.25	9	530.25	19.20	0.0004	significant
A	266.23	1	266.23	9.64	0.0172	
B	382.26	1	382.26	13.84	0.0074	
C	196.52	1	196.52	7.12	0.0321	
A^2	2979.65	1	2979.65	107.92	<0.0001	
B^2	214.62	1	214.62	7.77	0.0270	
C^2	38.58	1	38.58	1.40	0.2758	
AB	516.43	1	516.43	18.70	0.0035	
AC	6.50	1	6.50	0.24	0.6423	
BC	15.02	1	15.02	0.54	0.4848	
Residual	193.27	7	27.61			
Lack of Fit	161.38	3	53.79	6.75	0.481	not significant
Pure Error	31.89	4	7.97			
Cor Total	4965.52	16				
Model	874.07	9	97.12	15.80	0.0007	significant
A	65.5	1	65.49	10.65	0.0138	
B	107.2	1	107.24	17.44	0.0042	
C	108.8	1	108.78	17.69	0.0040	

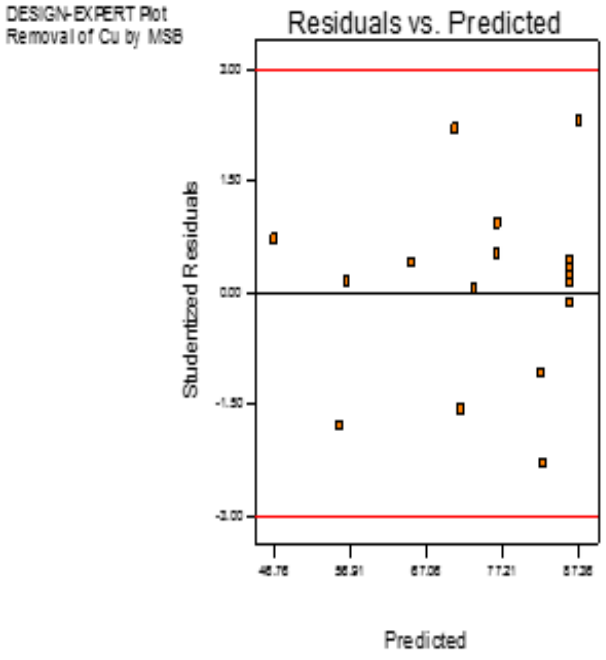
A^2	541.6	1	541.57	88.09	< 0.0001	
B^2	5.73	1	5.73	0.93	0.3666	
C^2	16.49	1	16.49	2.68	0.1455	
AB	5.41	1	5.4	10.88	0.3796	
AC	0.49	1	0.49	0.080	0.7859	
BC	1.69	1	1.69	0.27	0.6163	
Residuals	43.04	7	6.15			
Lack of Fit	30.5	10.2	3.25		0.1425	not significant
Pure Error	12.53	4	3.13			
Cor Total	917.11	16				

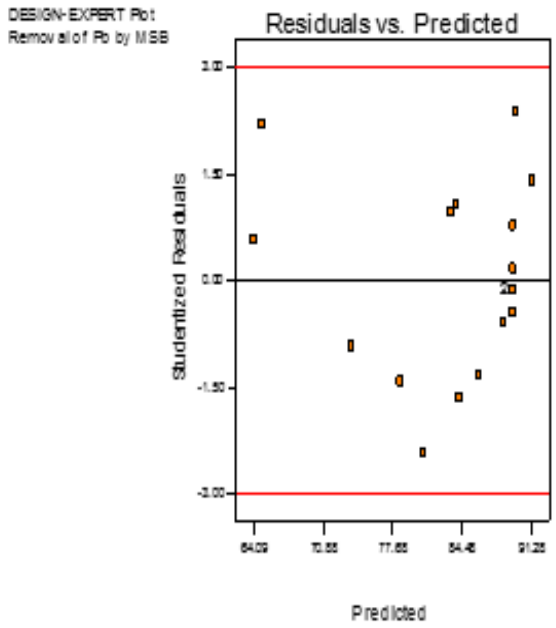
Std. Dev.= 5.25, R-Squared = 0.9611, Mean= 71.30,Adj R-Squared= 0.9110, C.V.=7.37, Pred R-Squared= 0.4700, PRESS=2631.95,AdeqPrecision=11.476 for Cu

Std. Dev.= 2.48, R-Squared = 0.9531, Mean= 90.35, Adj R-Squared= 0.8927, C.V.= 2.74, Pred R-Squared=0.4464,PRESS=507.69,AdeqPrecision=12.133 for Pb



(a)





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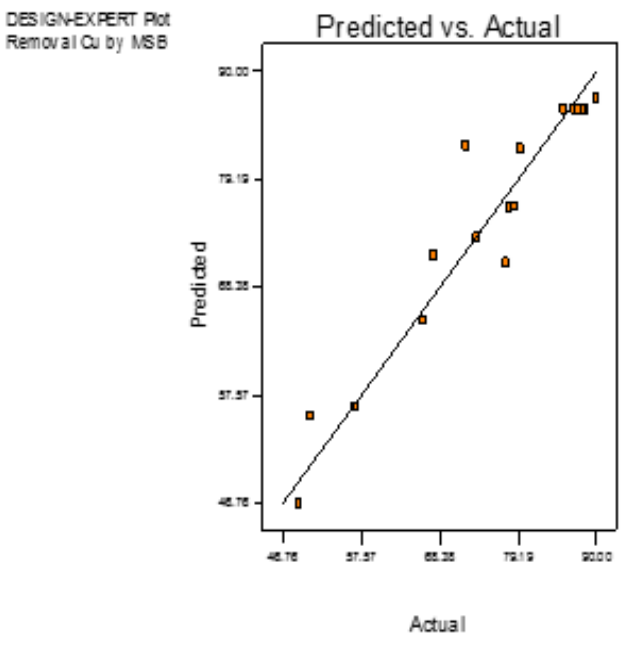
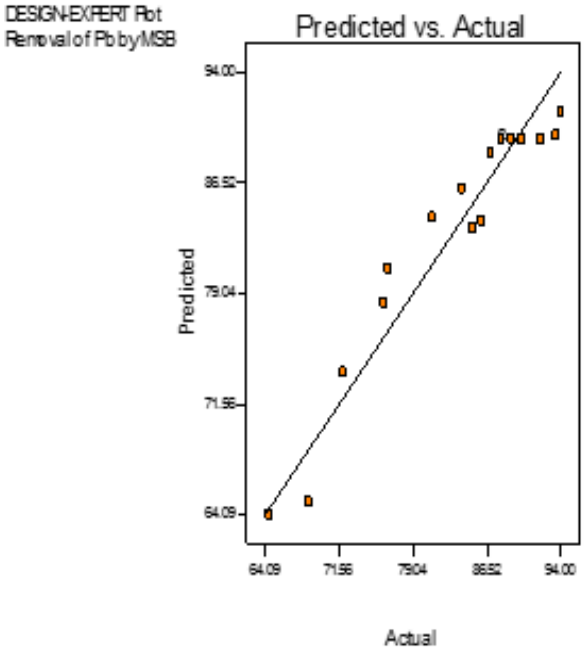
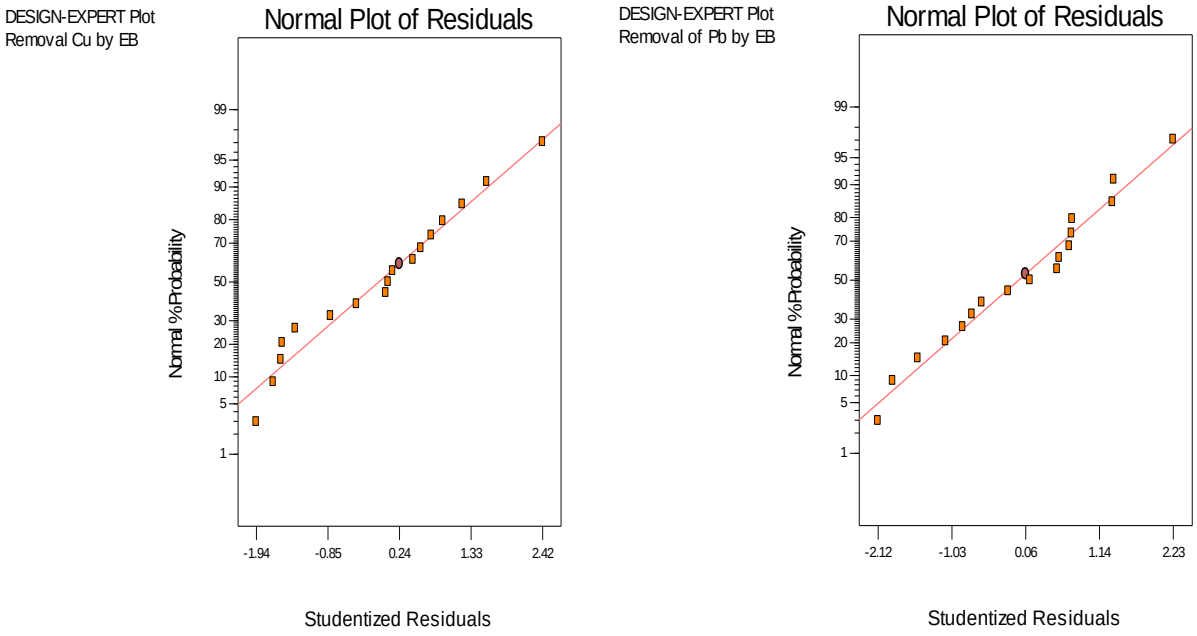


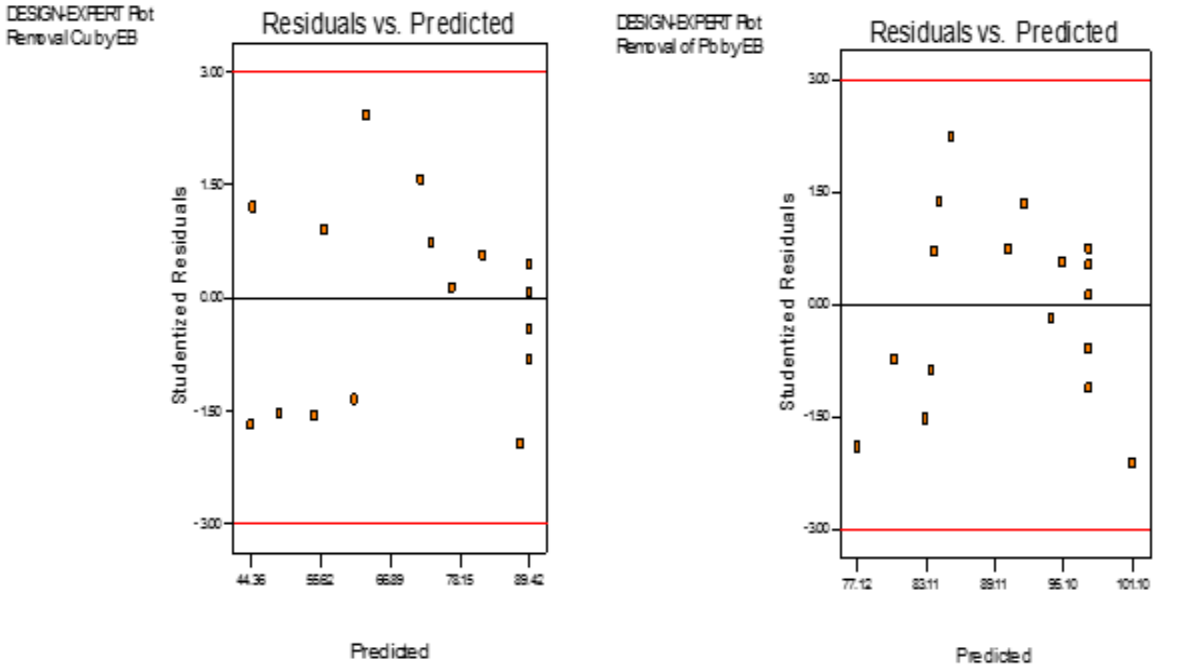


(c)

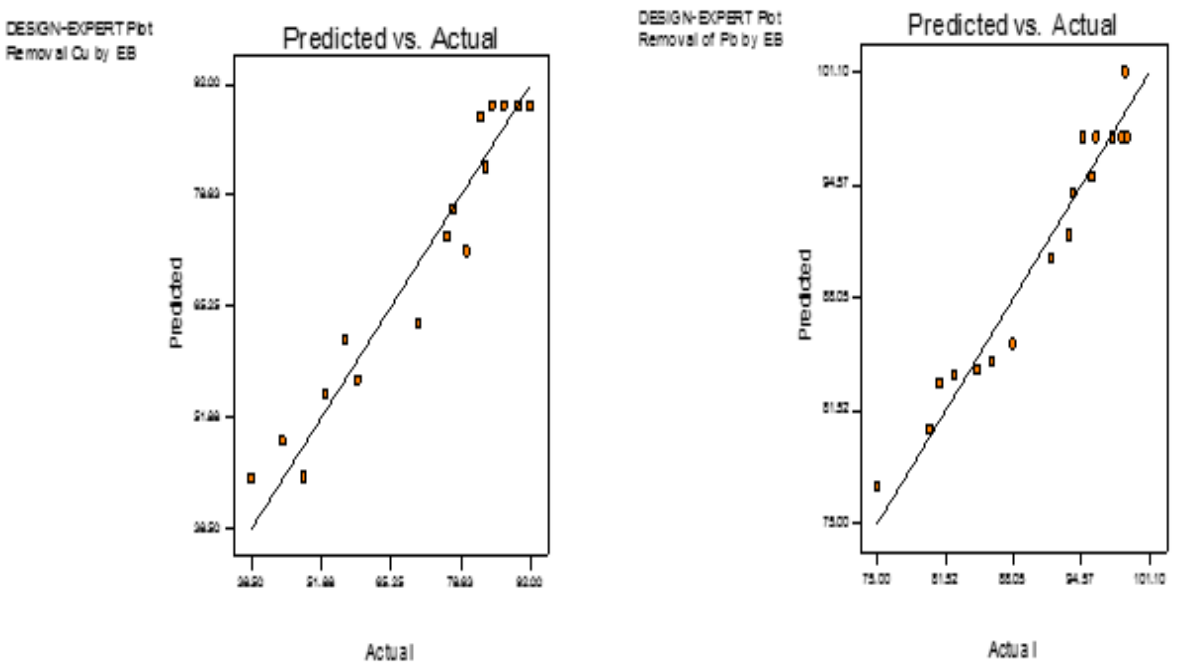
Figure 4.5: Model diagnostic plots of Cu and Pb by MSB


DESIGN-EXPERT Plot
Removal Cu by EB
Normal Plot of Residuals
Normal %Probability
99
95
90
80
70
50
30
20
10
5
1
-1.94
-0.85
0.24
1.33
2.42
Studentized Residuals
DESIGN-EXPERT Plot
Removal of Pb by EB
Normal Plot of Residuals
Normal %Probability
99
95
90
80
70
50
30
20
10
5
1
-2.12
-1.03
0.06
1.14
2.23
Studentized Residuals

(a)


DESIGN-EXPERT Plot
Removal Cu by EB
Residuals vs. Predicted
Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
44.36
55.62
66.89
78.15
89.42
Predicted
DESIGN-EXPERT Plot
Removal of Pb by EB
Residuals vs. Predicted
Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
77.12
83.11
89.11
95.10
101.10
Predicted

(b)

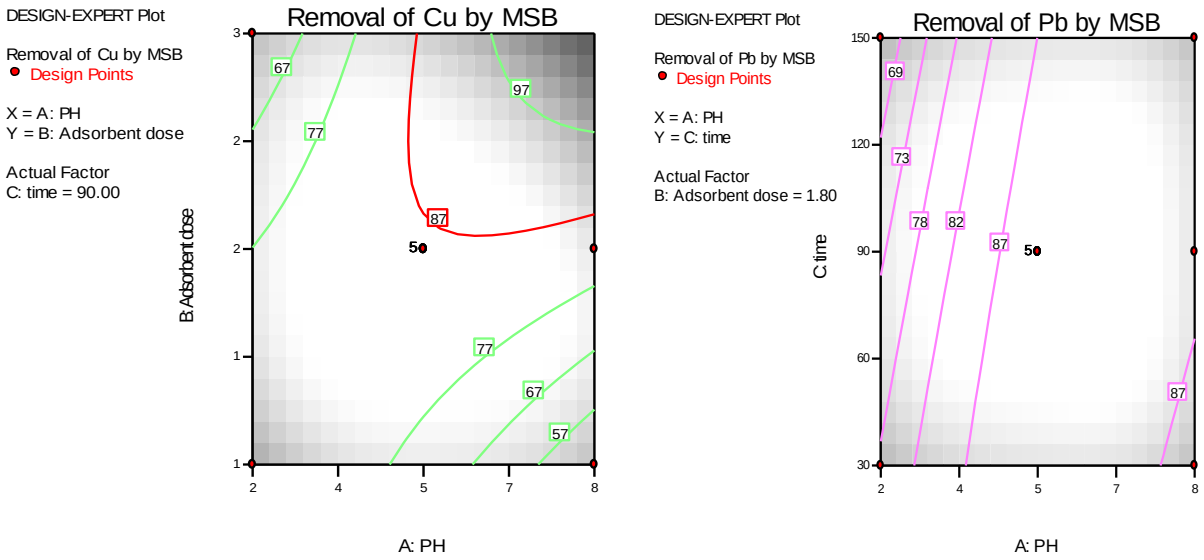


(c)

Figure 4.6: Model diagnostic plots of Cu and Pb by EB

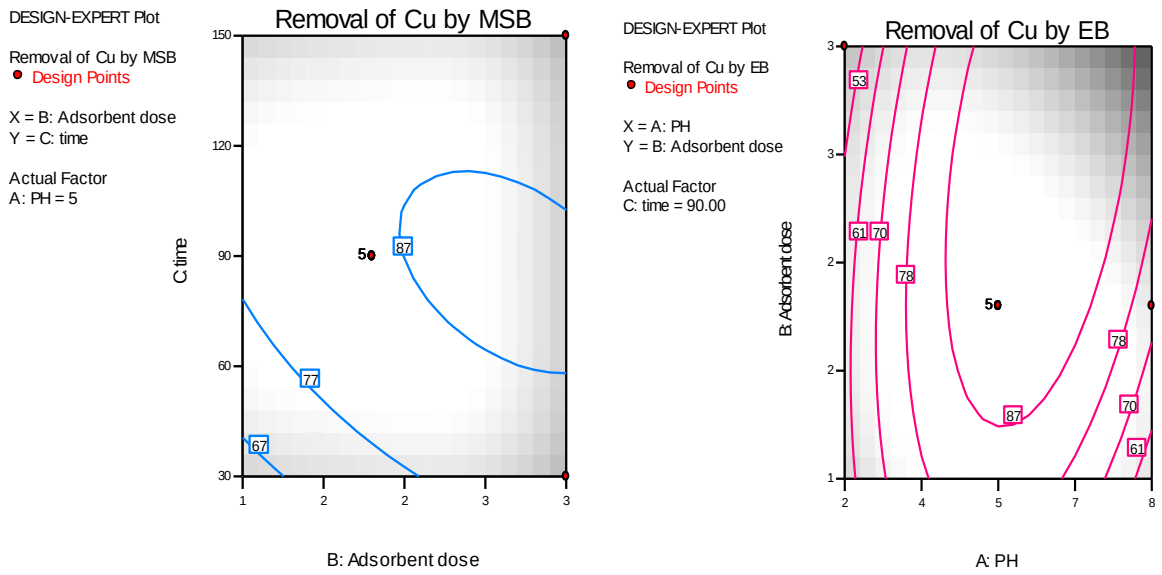
Externally studentized residuals were used to look for outliers, i.e., influential values not present in these graph rather it closer to the line. As shown figure all the model statistics and diagnostic plots are ok and so we can proceed to finish up with the model graphs icon. Figures 4.5 and 4.6 respectively show predicted vs. actual values for the responses for Cu and Pb % removal. As can be seen from these plots, the predicted values obtained were quite close to the actual values, indicating that the models developed were successful in capturing the correlation between the modified bagasse & eucalyptus bark preparation variables with the responses under investigation. However, some data points of Cu show relatively large residual values, due to the lower R^2 values compared to the other 3 models. The data points for studentized residuals vs. predicted plots figures 4.5 (b) and 4.6 (b) were scattered. The data points in these plots should be randomly scattered, demonstrating that the variance of the experimental observations were constant for all the values of response depicted by table 4.7 and 4.8. The data points obtained were between ±3.00 which implied that no response transformation was needed for the experimental design of this study (Myer et al., 1995).

The 2D surface contour curve represents an infinite number of combinations of selected two tested variables with the other two maintained at zero levels. Second-degree effects for modified bagasse (MSB) and eucalyptus bark (EB) in Cu both pH and adsorbent dose, Pb by MSB and EB the pH is significant as you shown in table 4.7 and 4.8.



(a)

The shape of the contour plots showed that natures and extents of the interactions between significant factor figure 4.7 (a) AB, (b) BC for Cu by MSB, (a) AC for Pb by MSB, AB for Cu by EB. In the second adsorbent of eucalyptus bark (EB) is not significant factors Pb due to might be concentration of the elements present was small with maximum surface area of adsorbent. An elliptical contour plot indicates a prominent (clear) interaction in the figure 4.7 (b) Cu by MSB. Whereas for circular 2D countor plot as you shown in the figure 4.7 (a) Cu slight significant, (b) Pb by MSB. The other combination of the parameters were not significant as you shown in table 4.6 and 4.7. These are a negligible effect appears as a circular contour plot (Qiu et al., 2014). Elliptical contour obtained for % adsorption of Cu by MSB the parameters pH with adsorbent dose are slight significant to be small interaction, in Pb by MSB there is an interaction between pH and contacting time as you have observe in the figure 4.7 (a). In the efficiency of Cu by EB the interaction of pH and adsorbent dose are main significant factor as you shown in the table 4.7 and figure 4.7 (b).



(b)

Figure 4.7: Contour plots for % removal of modified bagasse (Cu, Pb) & eucalyptus bark (Cu)

(a) PH vs. adsorbent dose Cu by MSB (b) pH vs. contacting time Pb by EB (c) adsorbent dose vs. contacting time Cu by MSB (d) pH vs. adsorbent dose Cu by EB

It was reported in the literature that too long or too short activation time and/or too high or too low PH, adsorbent dose could reduce the surface area and the adsorption capacity of MSB and EB (Chowdhury, 2013).

Generally, for study the 2D presented almost similar behavior as you seen the pH (2 to 5) increases then reduced to pH 8, time (C) (30 to 90min) then decreases to maximum value (150min) to both modified bagasse (MSB) (Cu, Pb) and eucalyptus bark (EB) (Cu, Pb). Due to pore walls and degradation of surface functional groups (Chowdhury, 2013).

However, Pb by MSB removal efficiency at 90min with pH 5 and 30min with pH 8 was the same. These might be due to not create precipitations rapidly adsorb to the adsorbent, but if it is increase beyond this time might have been change to other form. In the figure 4.7 (b) direct relationship

between pH and adsorbent dosage until some value, but beyond these starts to decrease the % adsorption Cu by EB.

According to Das, (2017) was evident from the interpretation of the % removal of Cu(II) ion decreased with increase of the initial Cu (II) ions concentration (150ppm), in these study the maximum concentration Cu was 71ppm from sample wastewater analyzed was taken as constant. This can be explained by the fact that all adsorbents have a limited number of active sites and at a certain concentration the active sites become saturated (Das, 2017). However, a sharp increase in the Cu ion removal occurred when the pH value of the solutions changed from 2.0 to 6.0. From pH 6 onwards, a steady decrease of adsorption of Cu ions was recorded. The % of Cu ion removal increased with increasing in adsorbent dose. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent. Furthermore, rate of adsorption increased with contact time (Das, 2017).

The interaction between pH and adsorbent dose in the graph between is 3g, the adsorbent dose has an influence since the amount adsorbed pass from 58 to 88.8%, when the time passes 90min are shown in figure 4.7(a) corresponding to 3D plots appendix B Cu by MSB. Thus, the contacting time equal to 90min, then decrease adsorbent dose causes an increase removal efficiency. The pH reduction cause an increase the removal % with contacting time positive synergetic effect when coupled with adsorbent dosage and pH. Proof of these in positive term in equation (pervious mathematical model) above coded equation. However, it can also be seen in the equation, the singular effect of the solution of sample wastewater pH on % removal was positive. This means an increase in the singular variable pH has a significant effect on the overall removal efficiency. In combination as a pair, however, the pH of the variables of the solution and adsorbent dose were statistically significant in terms of P value.

The interaction between adsorbent dosages with contacting time illustrated in the figure 4.7 (b) Cu by MSB. This one shows that if we keep the maximum level of adsorbent dose and the minimum level of the contacting time, the removal efficiency reached 88.8% of a hand. On the other hand, when the minimum guard adsorbent dose level and the maximum level of the contacting time the result is 73.5% at pH 5 in the 3D plots of appendix B. We can also see that the pH of sample wastewater had positive synergistic effects when coupled with adsorbent dosage and contacting time.

The interactions between the pH and contacting time Pb by modified bagasse (MSB) figure 4.7(a) with corresponding 3D plots illustrates in appendix B. This one shows that if we keep the maximum level of pH and the minimum level of the contacting time, the removal efficiency reached 81% with adsorbent dose 1.8g. We can see that the adsorbent dose had positive effects when coupled with the pH and the contacting time. However, the response is not convex that involve optimal variables were not well defined or interaction between factors is not good. This one shows that if we keep the maximum level of contacting time and the minimum level of the pH, the removal efficiency reached 68.5% with adsorbent dose 1.8g so that in these negative effect during coupling.

The interaction between the pH with adsorbent dosage was shown in figure 4.7 (b) of Cu by eucalyptus bark (EB) and corresponded with appendix B. This one shows that if we keep the maximum level of adsorbent dosage, the minimum level of pH removal efficiency was 48.5% with contact time 90min. We can see that the contacting time had negative effects when coupled with the adsorbent dosage and pH. If we keep the maximum level of pH and minimum level of the adsorbent dosage the removal efficiency 38.5% at contact time 90min. We can see that the contacting time also a negative effect when coupled with the adsorbent dosage and pH.

4.4. Batch adsorption of Copper and Lead

4.4.1. Effect of PH

The samples were adjusted to different pH levels from 2 to 8 with a unit interval. These are selected for the reason that further increase in pH of the solution leads to the precipitation rather than adsorption. As shown in figure 4.8, it was possible to observed the maximum removal of Cu (II) & Pb (II) by modified bagasse (MSB) at pH 5 (88.45%, 94%) >pH 8 (78%, 93.5%) > pH 2 (67.5%, 76.09%) respectively. It was almost in line with result of 85-90%, time (1-4) hrs. the % removal also (60-70)% (Kishor et al., 2012). The removal efficiency in both adsorbent (MSB, EB) were > Cu due to the concentration of Pb present in the sample wastewater was low. As explained in litrature review the solubility of metal increases resulting in a recontamination of the waste out let stream (Sarin et al., 2006).

The pH 8 was slightly decreased as a result of precipitation is dominant than adsorption. It might be become significant mechanism in the metal removal process. At low pH i.e. below pH 5/ pH 2 very less copper was removed due to excessive protonation of the active site at the carbon surface. It often refused the formation of link between metal ion and active site.

During this study Cu & Pb by modified bagasse (MSB), at pH 2 (30min, 1.8g), (150min, 1.8g) the % adsorption were (66.09, 76.09) & (67.5, 68.5) respectively. The removal efficiency at pH 8 described that 78% (30min, 1.8g), (150min, 1.8g) (93.5%) of adsorbed Cu and Pb by MSB respectively.

The maximum % adsorption of Cu and Pb by modified bagasse (MSB) was observed that pH 5 (90min, 1.8g) is 88.45% & 94% respectively reached in equilibrium. To both metals by modified bagasse sorbent removal increased varying pH from 8 (78%, 93.5%) to 5 (88.45%, 94%) and slowly started to decline to pH 2 as you seen in the figure 4.8. These result was similar with the reported of Cu by bagasse, hence removal was 94.6% (30 –120 min) by Rana et al., (2014), Johnson et al., (2008) & more favored than 60% at pH 5.5 (Johnson et al., 2008).

The other literature was Pb removal by bagasse we seen the minimum bio sorption using pH>6 (joginder singh, 2013). As the pH of sample wastewater increase from 2 to 5 removal efficiency would also increase from 76.09% to 94% and slightly decreased to 93.5% at pH 8. It was due to the metal (Pb^{2+}) hydrolysis and precipitation, so that the subsequent studies conducted at pH 5.

As a result of the overall charge on the surface of the adsorbent became negative and further increase the pH to 8 leads to the precipitation rather than adsorption (Islam, 2011; Safety, 2013). Even if the pH <5 the removal efficiency would be decreased to 67.5% due to excessive protonation of the active surface. Since the pH affected the adsorption, process through the dissociation of functional groups on the active sites on the surface of the adsorbent the removal efficiency.

However, the % adsorption was enhanced by digestion of sample wastewater to minimize precipitation using acid. The removal efficiency of Pb by MSB at pH 5 & pH 8 are almost similar. These may be due to digested the sample wastewater by acids before adding adsorbent, Pb changes from precipitation to metal free and contacting time was high at adsorbent dose 1.8g. Similar study were reported by Abudaia et al., (2013) (90% to 96.5%), Tripathi et al., (2015) (84% to 93%) and Homagai et al., (2010) (86% to 97%).

At low pH (< 3), there was excessive protonation of the active sites at carbon surface and this often refuses the formation of links between metal ion and the active site. The optimum pH for the adsorption of Cu and Pb to both adsorbents is 5 which was equal to the literature reported (Bark et al., 2006). At moderate pH values (3-6), linked H^+ is release from the active sites and adsorbed amount of metal ions is generally found to increase. The other laboratory result was Cu (II) by

eucalyptus bark at pH 2 (58.9%) (150min, 1.8g), pH 5 (92%) (90min with 1.8g) & pH 8 (79.75%) (90min, 3g). The second metal (Pb (II)) value would be (86%) at pH 2 (90min, 3g), (99%) using pH 5 (90min, 1.8g) and pH 8 (150min, 1.8g) (93.4%). At higher pH values (>6), the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation (not necessarily precipitation) may become significant mechanisms in the metal removal process (D. Bark et al., 2006).

The adsorption of Cu and Pb by eucalyptus bark (EB) as shown in the figure 4.8 the % removal order was occurred at pH 5 (90min, 1.8g) >pH 8 (90min, 3g)>pH 2 (150min, 1.8g). After pH 8 to pH 5 increase the % adsorption, at low pH i.e. below pH 5 very less Cu is removed. At PH 2 (58.9%) which is not far from the result of almost 65% of Cu removal was observed &100 mg/l Cu concentration (D. Bark et al., 2006). It might be due to handling error, experimental error like extraneous variables. The pH sample wastewater decrease from 8 to 5 the % removal rapidly changed from 79.75% to 92% and further decreased pH to 2 the removal efficiency also minimized by 33%. The reason due to explained above by modified bagasse similar to the value reported (D. Bark et al., 2006).

As you observed from the figure 4.8, the % adsorption efficiency of Pb by eucalyptus bark increased with an increase the pH (2 to 5) and further increase pH (5 to 8) started to decrease. This was in line with the result found by Sahmoune et al., (2010) was 82% to 99.8%. As the pH reduced from 8 to 5 the % removal would be changed from 93.4 to 99% and finally to pH 2 with 86% removal as you shown in the figure 4.8. Because pH affects the adsorbent active sites by retaining or releasing protons (Presented et al., 2015) & (Sahmoune et al., 2010). Therefore, when pH increases there would be more available active sites for lead ions than the competitive ions, especially H^+ since it would precipitated in the form of lead hydroxides with an increase in pH of the solution.

Generally, the effect of pH on the adsorption on figure 4.8 the highest % removal occurred at pH 5 for both modified bagasse (MSB) Cu & Pb. The result of (Cu by sugarcane bagasse) not far from the value obtained at pH 5.5 (Johnson et al., 2008) and the other reported at pH 5 with 100 mg/l (Parameters et al., 2018). The third report was at exactly pH 5 with concentration of 50mg/l removal efficiency Cu by algae from mining waste water 87% (Benchraka,2014).

The eucalyptus bark (Cu, Pb) value meets with the explanation to moderate pH values (3-6), linked H^+ is released from the active sites and adsorbed amount of metal ions is generally found to

increase (D. Bark et al., 2006). For the adsorption of these metals at pH 5, the efficient adsorbent was using eucalyptus bark (EB) as adsorbent for Cu the result would be 92% > 88.45% by modified bagasse (MSB).

It has also adsorbed that in the pH 8, the value obtained using EB for removal Cu (79.75%) > (78%) of MSB except at pH 2 was Cu by EB (58.9%) < by MSB (67.5%). Similarly, for Pb at pH 5 using EB (99%)> using MSB (94%) & at pH 2 using EB as adsorbent removal were 86%> 76.09% using MSB. As the pH increases, the metal uptake capacity also increases due to the presence of negatively charged functional groups on the adsorbent surface & resulting in increased binding sites (Janyasuthiwong et al., 2015). The % adsorption at pH 8 (93.4%) by EB almost no more difference with the value of Pb by MSB (94.5%). The pH of the aqueous medium not only affects the solubility of the metal ions but also the ionic form in which it was presented in the solution, the type and ionic state of the functional groups at the sorbent surface (Lodeiro *et al.*,2005).

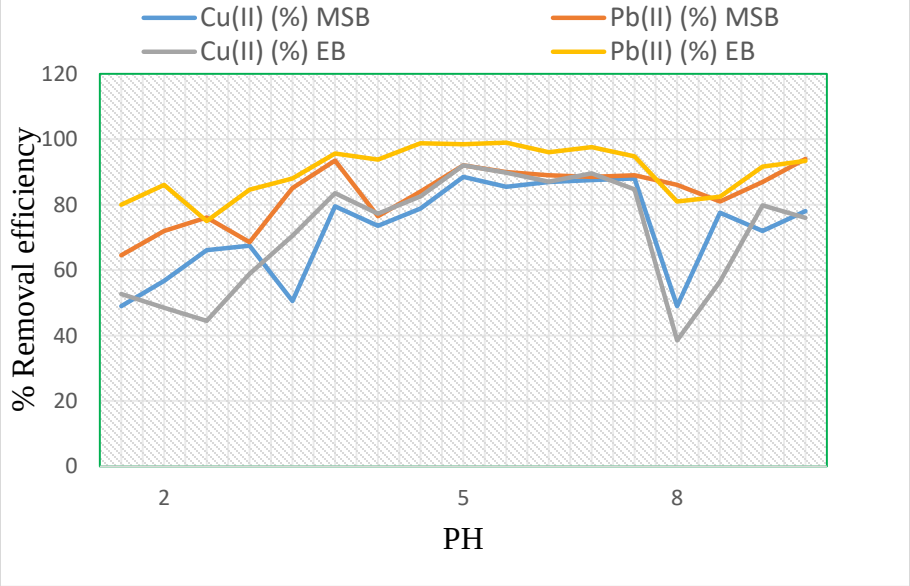


Figure 4.8: Effect of pH on percent removal of Cu (II), Pb (II) by MSB and EB

4.4.2. Effect of adsorbent dose

As it is shown in figure 4.9 the adsorbent dose have significant effect on the adsorption of the heavy metals under consideration. The effect manifest itself through an increase in % adsorption with an increasing in adsorbent dose. However, further increase in adsorbent dose lead to steady state and followed by decrease beyond adsorbent dose of 1.8g. The removal increased with

increasing the amount of adsorbent dosage for most of the result with small variation both heavy metals & adsorbents. The % removal of metal ions increases as dosage increases from 0.1 to 0.4 g these due to the number of active sites available for metal removal would be more as the amount of the adsorbent increases (Tripathi et al., 2015).

In this laboratory, the maximum values were attended mostly at 1.8g dosage with some exception in 3g and minimum adsorption was obtained at 0.6 g for both adsorbents. The % adsorption of Cu by bagasse increased with increasing of adsorbent dosage however, further increased the dosage leads to decrease (Kishor et al., 2012).

The removal of copper by modified bagasse the effect of adsorbent dosage at 0.6g (pH 5, 150min) was 73.5% increased to 1.8g (pH 5, 90min). As a result the removal efficiency would be increased to 88.45%, however beyond these declined to 3g (pH 5, 30min) to 79.5%. These result more approached with the reported value of 85% to 93% by increasing the adsorbent dosage from 2 – 10 g/l as you go up also started to decrease (Parameters et al., 2018).

The second metal i.e. Pb removal by modified bagasse (MSB) in the figure 4.9 have observed. In the adsorbent dose 0.6g (pH 8, 90min) was 86% then increased to 1.8g (pH 8, 90min) also increase linearly to 93.5%. The adsorbent increases to 3g (pH 5, 30min) almost it was no more variation with 94%. This is due to more surface area available for adsorption (Kishor et al., 2012). These might be also. The explanation almost similar effect in using MSB for Cu increasing adsorbent from 0.6g (86%) to 3g (94%). However, Pb by modified bagasse (MSB) the result of 1.8g & 3g approximately remains constant with small increment. These may be due to the availability of more active sites with short time (30min) in 3g at optimum pH. In case of the 1.8g (pH 8, 90min) the % removal also great by using digestion with acids i.e. adsorption was dominant (Safety, 2013). These results indicated that removal efficiency was directly related to the number of available adsorption sites. At initial stage, there are a large number of vacant surface sites which can readily absorb the cations (Chowdhury, 2013).

The removal efficiency of Cu (II) by eucalyptus bark (EB) at 0.6g (pH 5, 90min) was obtained 77.25%. Then the adsorbent dose is increased to 1.8g (90min, pH 5) directly relating to increasing of the removal to 92% however, further increase to 3g (30min, pH 5) leads to minimize the removal to 79.75%. The removal of Pb by eucalyptus bark (EB) using the adsorbent dosage 0.6g (90min, pH 8), 1.8g (30min, pH 5) & 3g (90min, pH 2) the result were 93.75%, 99 %, 86% respectively. As the adsorbent increase the percentage removal also increases may be due to the availability of

more active sites in adsorbent surface (Reddy *et al.*, 2014). Amount of adsorbent added to the solution determines the number of binding sites available for adsorption. Metals adsorption efficiency was increased with an increasing the adsorbent dose. This revealed that the adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose (Hammaini *et al.*, 2007).

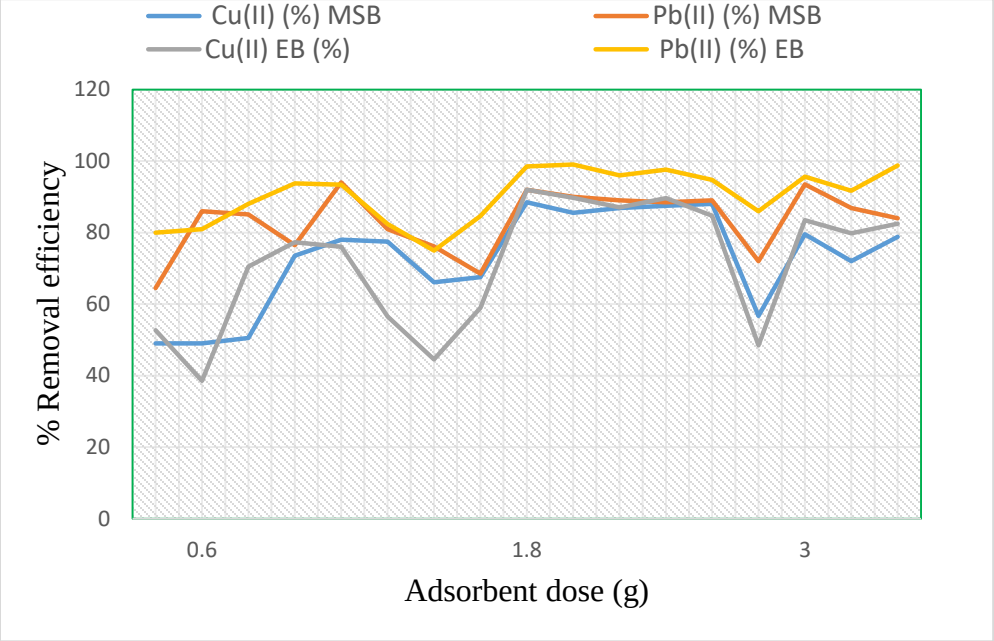


Figure 4.9: Effect of adsorbent dose on percent removal of Cu (II), Pb (II) by MSB and EB

4.4.3. Effect of contact time

The result were shown in figure 4.10, the maximum % adsorption of Cu and Pb by modified bagasse (MSB) was in contact with 30min (pH 5, 3g), 90min (pH 5, 1.8g) and 150min (pH 5, 3g) the results would be (79.5%, 93.5%), (88.45%, 92%) & (78.8%, 94%) respectively.

The extent of adsorptions increased rapidly in the initial stages but became slow in the later stages till the attainment of equilibrium except Pb by modified bagasse (MSB) slight increase beyond contact time 90min to 150min from 92% to 94%. A rapid up take of Cu (II) ions during the first 20 min of agitation, after which the rate of sorption became slower, attaining equilibrium in 60 min. Further increase in contact time had negligible effect on the amount of ions adsorbed (Tripathi et al., 2015). The effect of contact time in short (30min) and long time (150min) there was no exaggerated difference so 90min assumed to be suitable for subsequent bios sorption, these was

important in case cost, energy in waste water treatment plant due to remains constant the % removal in general conclusion increase with time.

The effect of Pb removal by modified bagasse (MSB) similar to Cu based on the result of the removal Pb^{2+} by bagasse maximum at 300min was assumed to be suitable for subsequent bio sorption experiment (Joginder Singh, 2013). Adsorbate solutions with higher initial concentrations might take relatively longer contact time to attain equilibrium due to the presence of a higher amount of adsorbate species (Hossain, 2013) & (Acheampong et al., 2013a).

As the contacting time increase removal percentage, also increase simultaneously reaches equilibrium, however further increase also leads to decrement similar report with (Sihabudeen, Ali, & Hussain, 2016). The second adsorbent (EB) result at which the time 30min (pH 5, 3g), 90min (pH 5, 1.8g) & 150min (pH 5, 3g) were obtained (83.5%, 95.6%), (92%, 99%) & (82.5%, 82.5%) removal of Cu and Pb by EB respectively. As a result of short contacting time (30min) greater removal efficiency than 150min, removal efficiency increase with time and reaches the maximum value at optimum time 90min and further increasing is not necessary due to consume high adsorbent dose at pH 5 gave low value. The other report of from literature would be Cu(II), Pb(II) similar with (D. Bark et al., 2006) & (Sarin et al., (2006).

The removal of metal ion from synthetic waste water by activated carbon from eucalyptus bark the adsorption reached equilibrium within 45 min (D. Bark et al., 2006). The % of adsorption is found to increase continually with time (30-2hrs) until the equilibrium is attained with saturation at 180min (Sihabudeen et al., 2016).

In general, the sorption performance of an adsorption system varies with the category, physio-chemical properties of the sorbent and sorbate used. After a lapse of time, the active surface sites had been exhausted. Thus, it becomes difficult to be occupied by the remaining cations. This happens due to repulsive forces between the solute (cations attached onto the solid surface) and the free ions (cations dispersed in the liquid phases) remaining in the solution in the divalent cation of Cu (II) and Pb (II). The curves are single smooth and continuous suggesting the formations of monolayer of adsorbate on the surface of the adsorbent.

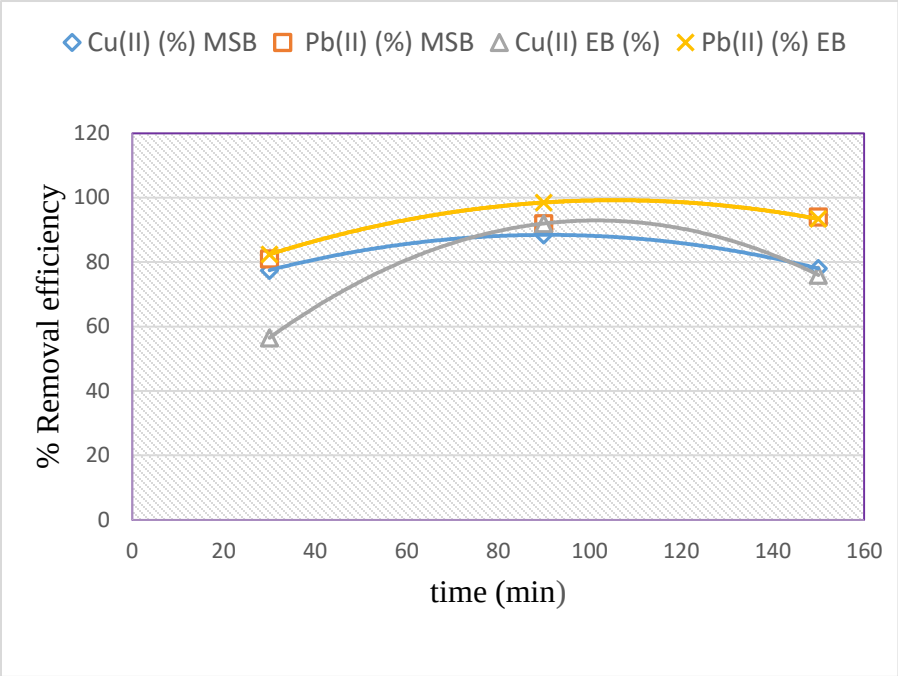


Figure 4.10: Effect of contacting time on percent removal of Cu (II), Pb (II) by MSB and EB

4.5. Adsorption isotherm

Equilibrium relationships between the adsorbate concentration in the liquid phase and on the adsorbent surface at a given condition, generally known as adsorption isotherms. These describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems (B. I. O. Engineering & Abdu, 2015). In this result the experimental data was analyzed against two parameter isotherm equations, namely Langmuir and Freundlich isotherm equations (A.O, 2012). The adsorption data for the removal of Cu and Pb was correlated with Langmuir and Freundlich models.

4.5.1. Langmuir model

The Langmuir adsorption is the best model between the entire isotherm model and it is successfully applied in many adsorption processes. These assumes uniform energies of adsorptions onto the surface and no transmigrations of adsorbate in the plane of the surface.

The Langmuir equation calculated using equation 2.2 integrated in to linear form 2.3 above is given. A further analysis of the Langmuir equations can be made on the basis of a dimensionless Equilibrium parameter, R_L, also known as the separations factor given by equation 2.4.

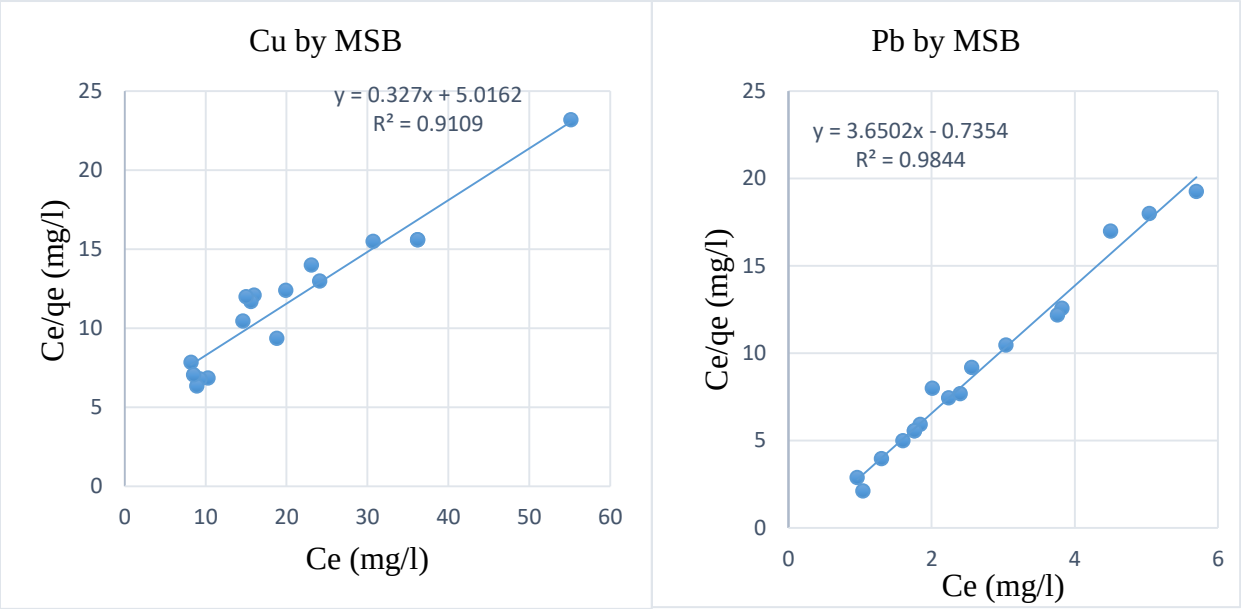


Figure 4.11: Equilibrium study of Cu (II) and Pb (II) by MSB using Langmuir model

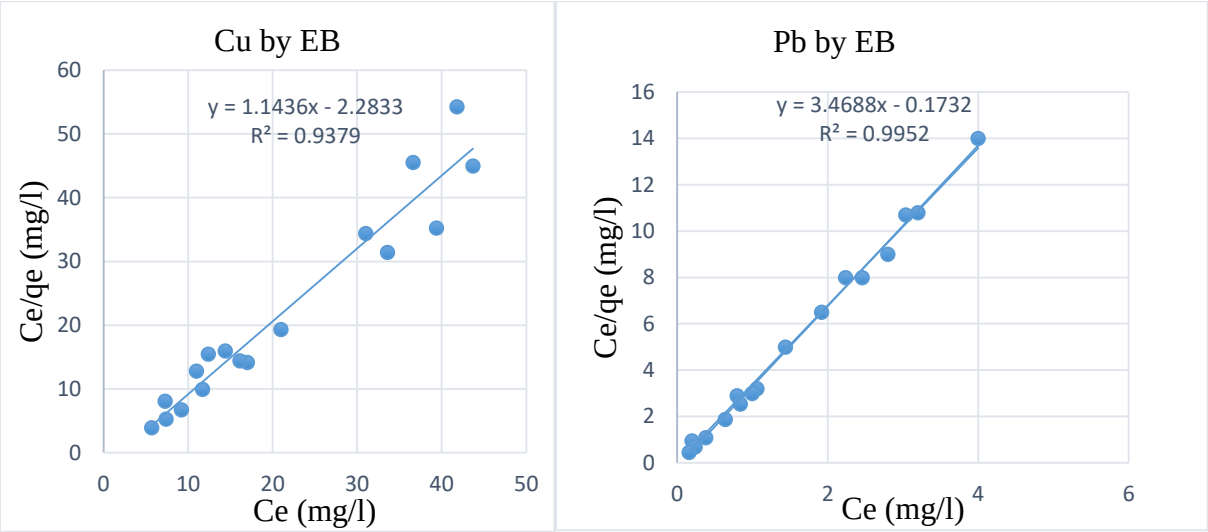


Figure 4.12: Equilibrium study of Cu (II) and Pb (II) by EB using Langmuir model

4.5.2. Freundlich models

The Freundlich equation is given by (Singh et al., 2011) in equation 2.5 change in to logarithmic form of equation 2.6 from literature review:

If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one, it indicates a normal adsorption.

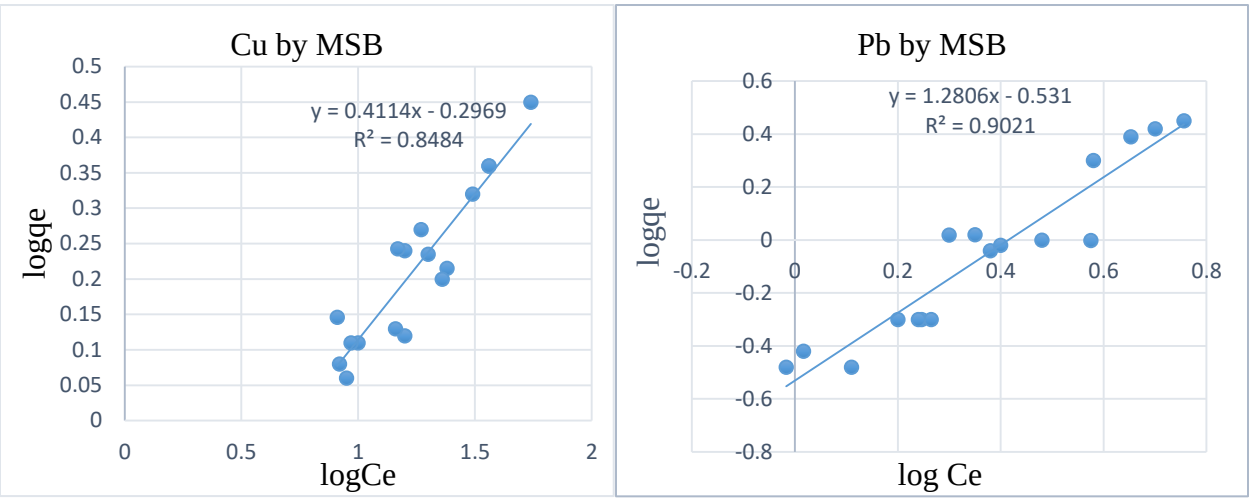


Figure 4.13: Equilibrium study using Freundlich models Cu (II) and Pb (II) by MSB

On the other hand, 1/n being above one indicates cooperative adsorption. K_f and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models. The value of 1/n for Cu by (MSB (0.4114), EB (0.2204)) and for Pb by EB (0.7744) while n= 1.2806 indicating that the sorption of Pb in to the MSB sorbent is favorable and the R^2 value is 0.9748.

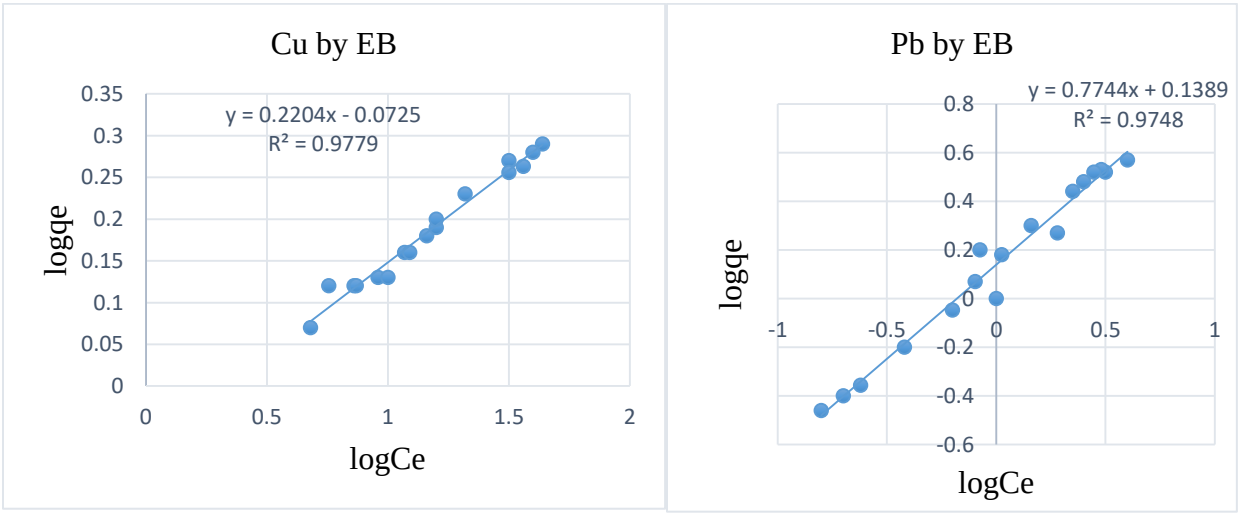


Figure 4.14: Equilibrium study using Freundlich models Cu (II) and Pb (II) by EB

Langmuir adsorption isotherm model which reflects adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Based on these results, it can be inferred that Cu and Pb is effectively adsorbed on modified bagasse (MSB),

eucalyptus bark (EB) and that the Langmuir model provides a satisfactory description of the adsorption equilibrium. Therefore, Langmuir model is selected to be the best model for describing the adsorption of Cu and Pb by both adsorbents.

Model parameters for Langmuir and Freundlich isotherm models were presented in table 4.8. The coefficient of determinations identified that Langmuir isotherm model better fit with the experimental data closely to R^2 >0.9999 for both adsorbent with the heavy metal (Cu, Pb). Isotherm models, value of respective parameters at different contacting time and correlations coefficient. The higher the b, the higher is the affinity of the adsorbent for metal ions. q_{max} can also be interpreted as the total number of binding sites that are available for adsorption and q as the number of binding sites that are in fact occupied by the metal ions at the concentration C_f (Volesky 1995). According to the result, the affinity order of both MSB and EB is Cu > Pb. The result on table 4.8 q_{max} (mg/g) is in line with the report of Cu & Pb by SB 4 to 0.995 mg/g (Parameters et al., 2018) & Cu (2.2mg/g) & Pb (0.3mg/g) by EB (Hanafiah et al. (2006a)) .

Table 4.8: Langmuir and Freundlich isotherm constants

Adsorbent	Langmuir Constant						Freundlich Constant					
	q_{max} (mg/g)		b(L/mg)		R^2		n		K_f (mg/g)		R^2	
	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
MSB	3.06	0.28	0.07	-2	0.9109	0.9844	2.43	0.78	0.51	0.3	0.8484	0.9021
EB	0.88	0.29	0.5	-3.2	0.9379	0.9952	4.54	1.3	0.85	1.4	0.9779	0.9748

4.6. Adsorption kinetics

Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution interface (E. Engineering, 2015). Several kinetic models are used to explain the mechanism of adsorption processes. Some of the works reported in the literature on adsorption kinetics of Pb and Cu using various adsorbents (Chowdhury, 2013). It was observed that most of the equilibrium data fitted well with the pseudo-first-order (Lagergren S., 1898) or pseudo-second-order kinetic models (Ho YS et al., 2000).

4.6.1. Pseudo-first order kinetics

To determine if the adsorption process fits with pseudo-first order model or not the experimental data which was conducted under the optimum experimental condition that was obtained from multi-factorial experiments (i.e. pH 5, adsorbent dose 20g/L, initial concentration 75 mg/L, 25ppm and room temperature).

These order introduced to equation 2.7 after definite integration by application of the conditions q_t =0 at t = 0 and $q_t = q_t$ at t = t, equation 2.8 above. By plotting log ($q_e - q_t$) versus t, the adsorption rate can be calculated. The kinetics model for pseudo first order adsorption is given for the MSB and EB. The different parameters of pseudo first order kinetics are given in table 4.9, from the table comparing the correlation coefficients of pseudo first and pseudo second order kinetics the best kinetics that fits the experimental data is preferably selected.

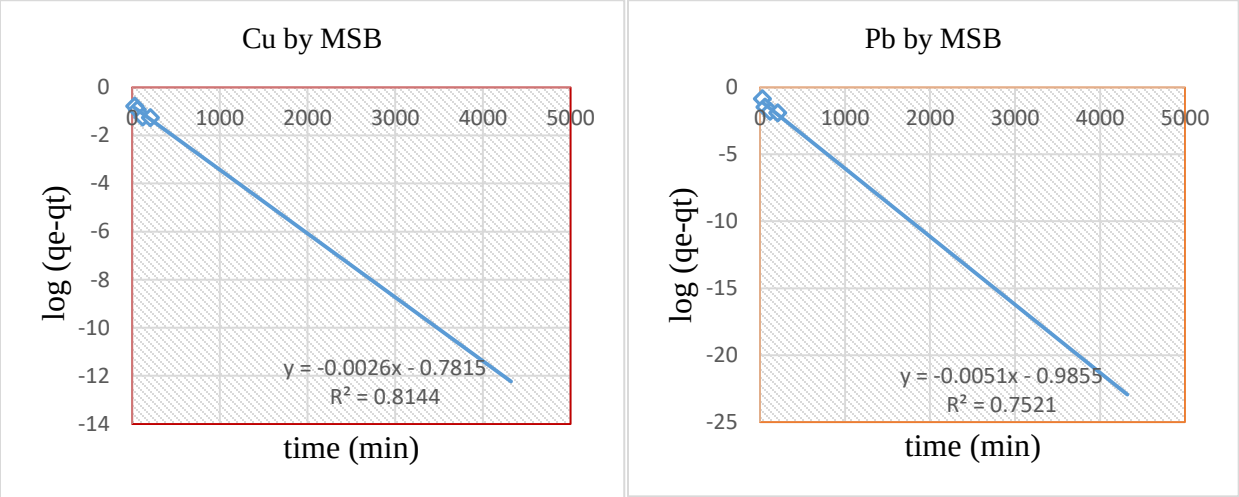


Figure 4.15: Pseudo-first order kinetic model fitting by MSB (Cu, Pb)

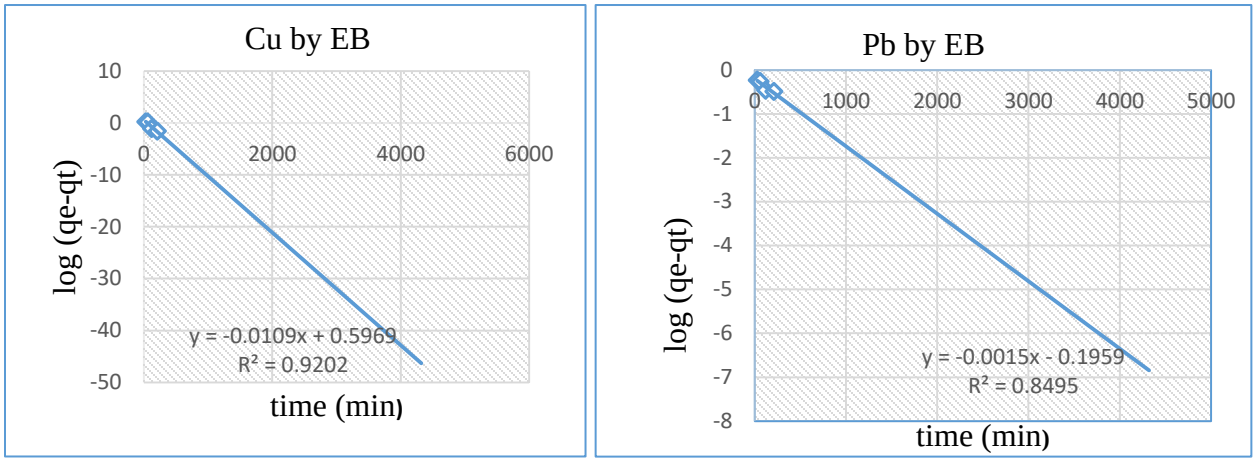


Figure 4.16: Pseudo-first order kinetic model fitting by EB (Cu, Pb)

4.6.2. Pseudo-second order kinetics

The conformity between experimental data and the model predicted values is expressed by the correlation coefficients (R^2, values close or equal to 1). A relatively high R^2 value indicated that the model successfully describes the second order kinetics of metal ions adsorption onto the adsorbents (Islam, 2011). By Integration of equation 2.9 and application of the conditions $q_t = 0$ *at* $t = 0$ and $q_t = q_t$ at $t = t$, gives the equation 2.10 in the above.

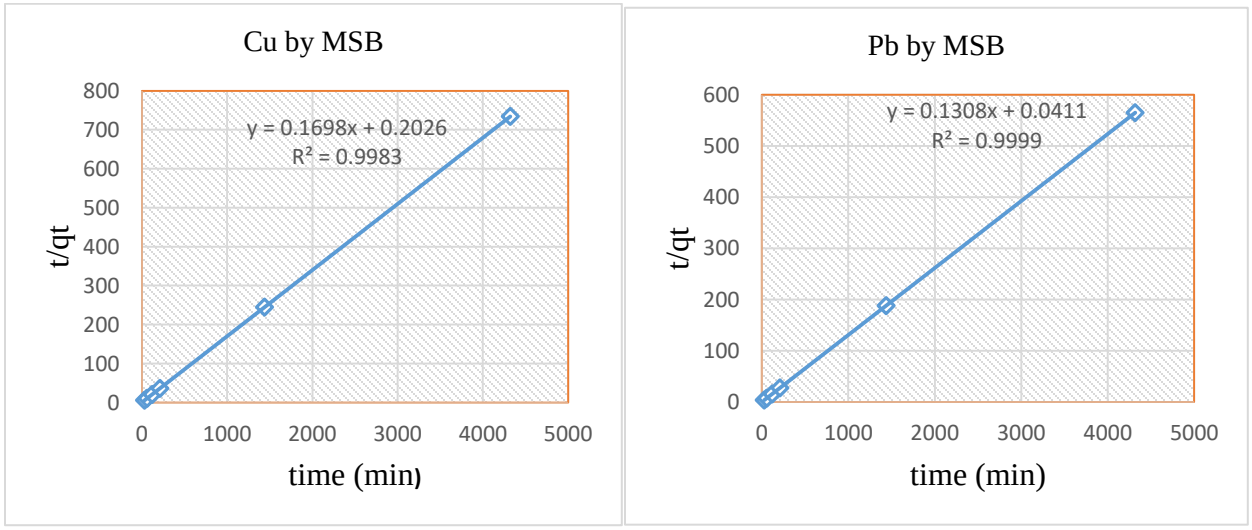


Figure 4.17: Pseudo-second order kinetic model fitting by MSB (Cu, Pb)

Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed an excellent linearity with high correlation coefficient ($R^2 > 0.99$) (A.O, 2012).

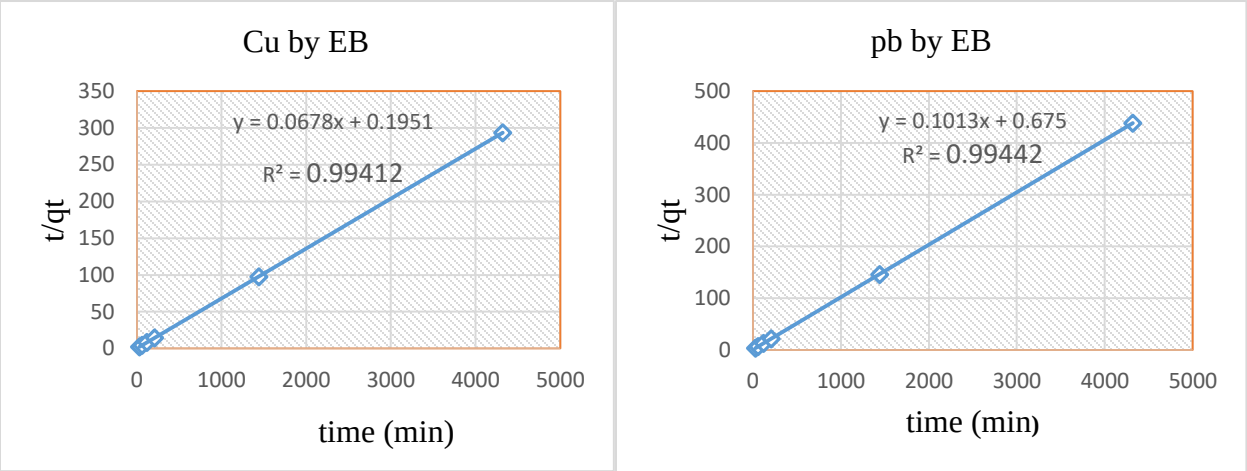


Figure 4.18: Pseudo-second order kinetic model fitting by EB (Cu, Pb)

So, it was inferred that the adsorption of Cu and Pb on to MSB and EB followed pseudo-second-order kinetics. The correlation coefficient for pseudo-second order kinetics is compared with correlation coefficient of pseudo first order kinetics and the best model that fits the experimental data is selected. The correlation coefficient (R^2) is found to be Cu by MSB (0.9983) and EB (0.99412), Pb by MSB and EB is 0.9999, 0.99442 respectively. From the given graphs shown above and the parameters, the best kinetic model that fits to the adsorption process is obtained to be pseudo second order kinetics model. Therefore, this model is selected to be the best model for the both adsorbent used. Hence, taking pseudo second order as best kinetics model, the parameters such as equilibrium mass of adsorption is found to be for Cu by MSB 5.9mg/g, by EB (14.6mg/g), for Pb by MSB (7.65mg/g) & by EB (15mg/g) these is the same as with report of the Langmuir model.

Table 4.9: Pseudo first-order and second order parameters

Adsorbent	Pseudo first-order						Pseudo-second-order					
	K_1*10^{-2} (min^{-1})		q_e (mg/g)		R^2		K_2 (mg/g/min)		q_e (mg/g)		R^2	
	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
MSB	0.6	221	0.17	0.11	0.8144	0.7521	0.14	0.42	5.9	7.7	0.9983	0.9999
EB	2.5	3.45	3.96	0.64	0.9202	0.8495	0.03	0.22	15	15	0.9941	0.9944

4.7. Desorption experiments

In the desorption studies deionized water was used as a desorbing agent. The dried adsorbent 4 sample of the combination of loaded with (Cu^{2+}), (Pb^{2+}) was collected and dried in electric, hot air oven at 105^{o}C for 6h. The MSB and EB samples loaded with different adsorbed amount of Cu (II), Pb(II) were placed in 25 ml deionized water and the amount of Cu (II), Pb(II) ions desorbed were measured by mixing of 1g of adsorbents after 2hrs contacted time. The mixtures so obtained were agitated in orbital shaker at 200rpm for MSB and 175rpm for EB in 2hrs at room temperature. The suspension was filtered through what man filter paper and the filtrate were analyzed for Cu^{2+} and Pb^{2+}. Similarly repeated with 2times H_2SO_4, HNO_3 and deionized water. It was observed the desorption efficiency, increased with an increase in the concentration from 0.1M of the agent (HCl, H_2SO_4 and HNO_3) but the bio sorbent deteriorating at higher concentration of the same and it was noticed that HCl gave maximum desorption (99%) as compared to H_2SO_4 (83%), HNO_3 (74%) and H_2O (Joginder Singh, 2013).

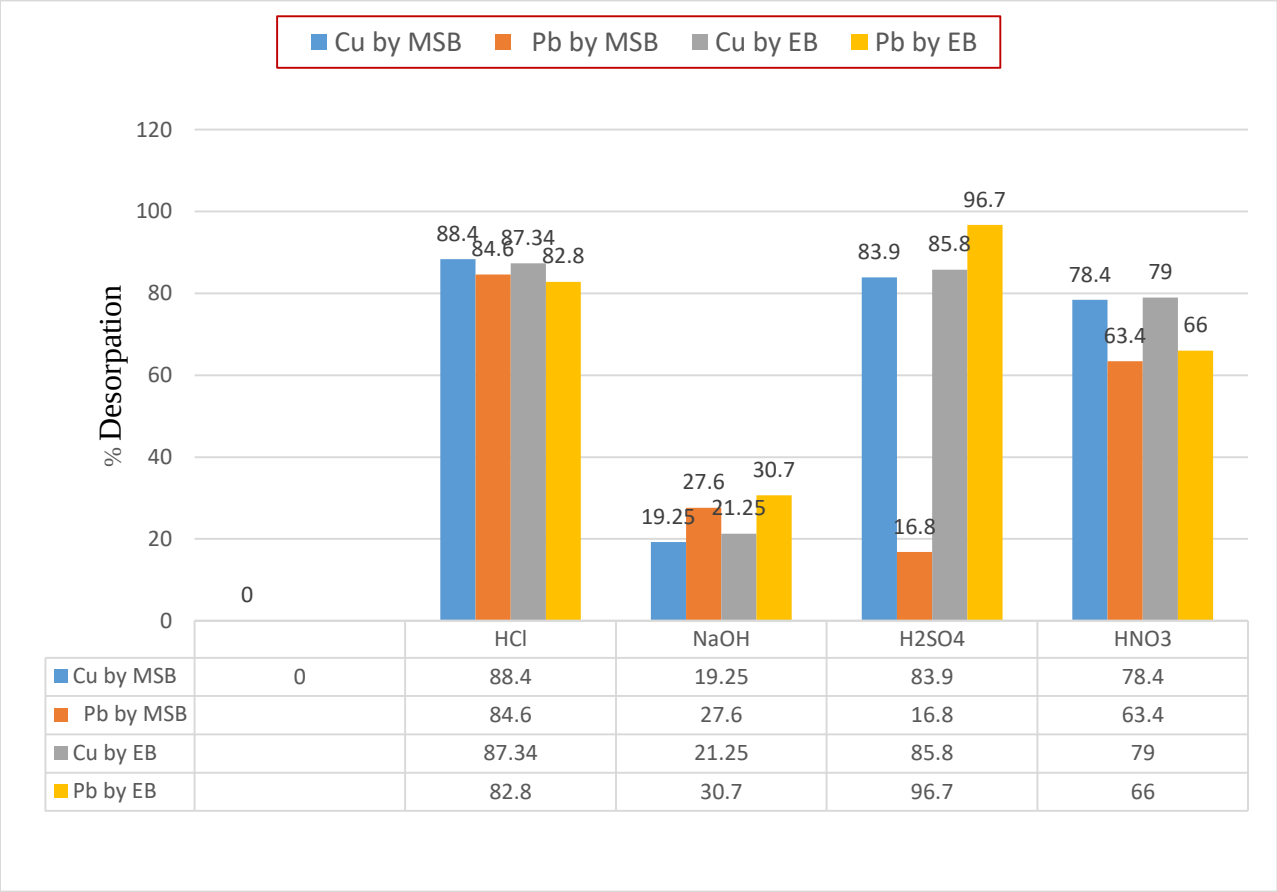
The desorption efficiency (DE) was determined using the following equation (4.7) (Studies, 2014):

$$DE = (\frac{C*V}{q*m})100 \quad \text{.....(4.7)}$$

Where, C (mg/L) is the concentration of Cu (36.2, 24.08, 55.15, 14.6), Pb (2.24,3.82,2.4,1.04) ions by MSB, Cu (43.7,39.4,21,11.7) and Pb (3.04, 4, 1.92, 0.8) ions by EB. The volume V(L) of the desorption solution is 25ml, q (mg/g) is the amount of Cu and Pb ions adsorbed on the adsorbents before desorption experiment. The m (g) is the amount of the adsorbent used in the desorption experiments was on the above given data obtained from adsorption result samples. The metal ion is releasing from MSB and EB adsorbent treated with 0.1M HCL acid for 2hrs in total volume of 25ml. The acid treated adsorbent were soaked in 0.1M NaOH solution to neutralize the acid, filtered, and washed with distilled water.

Then the adsorption process was conducted again according to the section on heavy metal ion adsorption by bagasse based adsorbent (Studies, 2014). Batch desorption experiments were carried out and efficiencies were compared. It conducted to explore the potential reusability of the hydrogels and recovery of metal ions. These contribute to elucidate the nature of adsorption process, it is necessary to examine the possibility to recover metal ions, to regenerate and recycle

the adsorbent. It can be easily known that desorption efficiency decreased with increasing cycle number due to the decrease of adsorption capacity as shown in figure 4.19. In eucalyptus bark H_2SO_4 acid showed the maximum desorption efficiency for Pb (II) (96.7%), Cu (II) (85.8%) and in MSB HCL for Cu (II) (88.4%), Cu (II) by EB (87.34%) showed the maximum desorption, whereas the minimum desorption from result was NaOH.



		HCl	NaOH	H2SO4	HNO3
Cu by MSB	0	88.4	19.25	83.9	78.4
Pb by MSB		84.6	27.6	16.8	63.4
Cu by EB		87.34	21.25	85.8	79
Pb by EB		82.8	30.7	96.7	66

Figure 4.19: Desorption efficiency using various solvents

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Low cost adsorbents offer a lot of promising benefits of commercial purpose in the future. Modified bagasse and eucalyptus bark was characterized using selected proximate analysis such as low % MC, low % VM, & a relatively low ash content, indicating that bulk density (g/cm^3) relatively small, high content FC, high C, low N_2 content and that biomaterials should be excellent raw material for adsorbents. The proximate analysis, % (C, N_2), high specific surface area (m^2/g) of EB than MSB, FTIR, XRD and the result obtained were comparable with other literature. Wastewater compositions analyzed were pH 8-8.5, EC (µs/cm) 2980, turbidity in (NTU) 7800, temperature (10-33°C), TDS (1213ppm), TSS (750ppm), COD (120ppm) and WAD CN^- with Temp<11ºC (0.025). There are high positive loading values/greater than permissible limit for EC, TDS, TSS & turbidity which is an indication of mixed sources of pollution. The heavy metals determined from effluent were Fe (313.11), Cu (71), Pb (16), Mn (0.94), Cr (VI) (0.43), Zn (0.34), Co (0.17), Ni (0.1) & Cd (0.02) ppm, except Cd and Zn all these elements were beyond permissible level.

Batch adsorption studies were carried out to evaluate the effects of pH, contact time and adsorbent dose. It was found that percent adsorption increases with an increase in pH (2 - 5), contact time (60 min – 90 min) and adsorbent dose (0.6g – 1.8g) for both metals. In this work, the maximum adsorption occurs 88.45% Cu (II), 94% Pb (II) by MSB and 92% Cu (II), 99%, Pb (II) was obtained at pH 5, 90 min and 1.8g/40ml of adsorbent dose. There is also decreasing trend with an increase three variables in the solution even if by taking one variable as fixed value beyond optimum value pH>5, contacting time>90min and similar result in the dosage value.

Langmuir model best fitted to the sorption data with a highest correlation factor R^2 describing the adsorption of Cu (II) and Pb (II) by both adsorbents. The coefficient of determinations R^2 were Cu (II) (0.9109), Pb (II) (0.9844) by modified bagasse and Cu (II) (0.9379), Pb (II) (0.9952) by eucalyptus bark. Kinetics of the adsorption process was best fitted to pseudo second order which indicates the presence of chemisorption. The value of R^2 was found to be Cu (II) by modified bagasse (0.9983) and eucalyptus bark (0.99412), Pb (II) by modified bagasse and eucalyptus bark was 0.9999, 0.99442 respectively.

From these comparison study that the eucalyptus bark (EB) is more effective than modified bagasse (MSB) in all selected conditions for removal of Cu (II) and Pb (II) including cost, locally abundant and more efficient in all case without using other treatment beyond acid treatment.

5.2. Recommendation

The following recommendations have been made for any future study on this important topic:

- ♥ Eucalyptus bark and modified bagasse have used as an alternative for the removal of other heavy metals due to its multi-functionality.
- ♥ It is also possible to study the thermodynamics of the system to get a fuller picture of the removal capacity of the bark and bagasse powder for heavy metal removal from gold mining wastewater.
- ♥ Various experiments with different experimental parameters like the concentration, temperature, particle size, agitation speed and ionic strength to increase the adsorptive efficiency.
- ♥ To get more information on the characteristics of the produced adsorbent, it is better to perform the BET tests to analyze the surface area including volume of the pores produced of sugarcane bagasse and eucalyptus bark. Because surface area of these studies are obtained by using titrimetric by acids and base instead of stop without working better to estimate the approximation not true value based on different report of literature review like gear method.
- ♥ Mining waste water may contain many ions more toxic from literature report that possible to remove by sesame husks the most locally available in Meli factory after MSB and EB, eucalyptus leaves, constructing wetland the most modern one, neem (leaves, bark) and activated carbon of corncob as adsorbent are needs further analysis.
- ♥ In the present's study the quality assessment of the tailings dam effluent characterization of are limited to other toxic heavy metals, NH_4^+, PO_4^{3-}, nitrates, sulphates due to availability of equipment, cost needs further analysis of wastewater.

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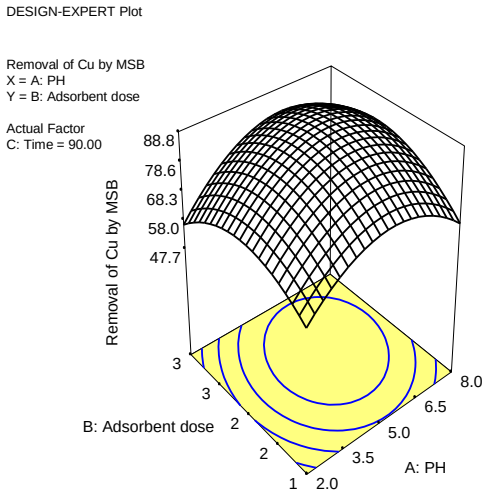
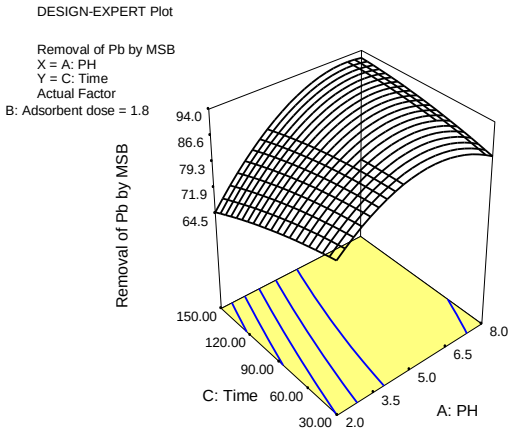
APPENDICES

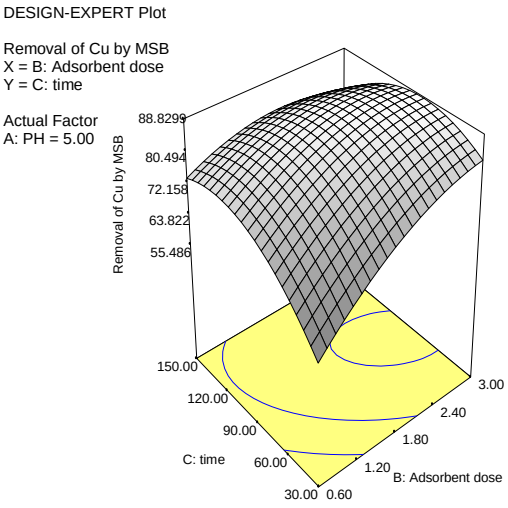
Appendix A: BBD matrix in a coded terms and actual terms with experimental and predicted values for adsorption

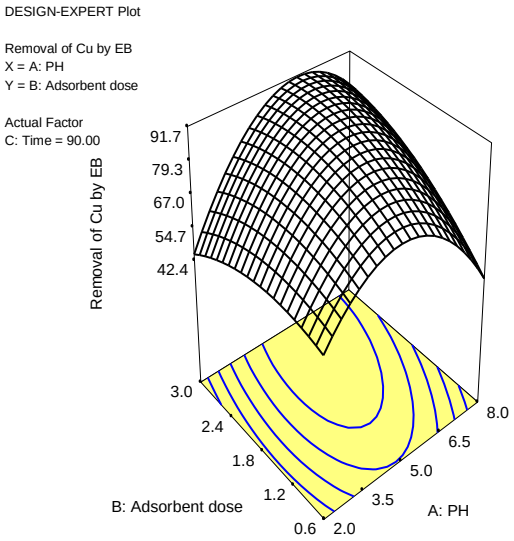
Std run	Parameters			Modified sugarcane bagasse (MSB)				Eyucalptus bark (EB)			
				η Cu(II) (%)		η Pb(II) (%)		η Cu(II) (%)		η Pb(II) (%)	
	A:X_1	B:X_2	C:X_3	Actual Value	Predicted value	Actual Value	Predicted value	Actual Value	Predicted value	Actual Value	Predicted value
1	2	0.6	90	49.00	47.72	64.5	64.31	52.7	53.54	79.98	79.30
2	8	0.6	90	49.00	49.39	86	84.31	38.5	42.36	81.00	82.70
3	2	3	90	56.75	56.36	72	73.69	48.5	44.64	86.00	84.30
4	8	3	90	72.00	73.28	86.89	87.08	79.75	78.91	91.67	92.35
5	2	1.8	30	66.09	64.37	76.09	78.28	44.5	49.52	75.00	77.65
6	8	1.8	30	77.50	74.12	81	84.68	56.5	58.51	82.40	82.67
7	2	1.8	150	67.50	70.88	68.5	64.81	58.9	56.89	84.60	84.33
8	8	1.8	150	78.00	79.72	93.5	91.81	76	70.97	93.40	90.75
9	5	0.6	30	50.50	53.49	85.09	83.09	70.5	64.63	88.00	86.03
10	5	3	30	79.50	81.61	94	89.62	83.5	82.33	95.60	94.65
11	5	0.6	150	73.50	71.40	76.5	80.38	77.25	78.42	93.75	94.70
12	5	3	150	78.80	75.81	84	86.00	82.5	88.37	98.75	100.72
13	5	1.8	90	88.45	87.27	92	89.70	92	88.60	98.50	97.17
14	5	1.8	90	85.50	87.27	90	89.70	89.75	88.60	99.00	97.17
15	5	1.8	90	86.90	87.27	89	89.70	87	88.60	96.00	97.17
16	5	1.8	90	87.50	87.27	88.5	89.70	89.6	88.60	97.60	97.17
17	5	1.8	90	88.00	87.27	89	89.70	84.67	88.60	94.75	97.17

Notes: η- Percent Removal effinciey, x_1-PH, x_2-Adsorbent dose, x_3-Contacting time, Max. concenteration of the waste water Cu (71mg/l), Pb (16mg/l), (mixing speed=200rpm to MSB and 175rpm to EB, at room temprature, Particle size 850µm for SB and 500µm for EB)









Appendix B: 3D plots for removal percentage of MSB (Cu, Pb) & EB (Cu)

Appendix C: Result of initial concentration on Cu, Pb by MSB & EB from selected sites Effect of initial concentration % adsorption at pH = 5, 1.8g, 90 min, MSB (200rpm, 850µm) EB (175rpm, 500 µm), at room temperature &100ml sample waste water)

Adsorbent	Samples sites dam	Co (ppm)		Final C_f (ppm)		(%)Removal efficiency		capacity of in mg/g	
		Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
MSB	1-South	30	3.8	3.43	0.3328	88.567	91.1	1.48	0.193
MSB	2-North	40	6.0	4.7	0.4974	88.25	91.7	1.96	0.306
MSB	3-west	51	10.2	5.6	0.6845	89	93.3	2.467	0.53
EB	1-South	30	3.8	2.98	0.2673	90.06	93	1.5	0.196
EB	2-North	40	6.0	4.3	0.2478	89.25	96	1.98	0.32
EB	3-west	51	10.2	3.58	0.3354	93	96.7	2.63	0.55

Appendix D: Effect of MSB & EB on % adsorption at temperature 45˚C (Co (Cu) =51ppm, Co (Pb) =10.2ppm) west site of the dam, 90 min, pH =5, 200 rpm for MSB and 175rpm for EB

Adsorbent dose	PH	Adsorbent dosage in g											
		0.6				1.8				3			
		Final concentration in ppm											
		Cu	η%	Pb	η%	Cu	η%	Pb	η%	Cu	η%	Pb	η%
MSB	2	25	51	5	51	16.7	67.3	2.5	75.5	18	64.7	4.2	58.8
EB	2	21	58.8	3.7	63.7	14	72.6	2.2	78.4	17	66.7	3.9	61.77
MSB	5	9	82.4	3.6	70.6	2.9	94.3	0.3	97.1	14.2	72	1.8	82.35
EB	5	7	82.7	3.4	66.7	2	96.1	0.02	99.8	11.6	77.25	1.9	81.4
MSB	8	26	49	6.2	64.7	13.8	73	2.7	73.5	18.7	63.3	4.4	56.9
EB	8	23	55	4.8	66.7	11.2	78	2	79.4	15	70.6	4.1	60

Appendix E: Result of experimental kinetic model

Time (min)	Initial Cu concentration by EB (75ppm)			Initial Pb by EB concentration (25ppm)		
	q_t(mg/g)	t/qt	Log(q_e-q_t)	q_t(mg/g)	t/qt	Log(q_e-q_t)
30	13	2.3077	0.238	4.37	3.6946	-0.2321
60	13.18	4.5524	0.1898	4.4	6.881	-0.2549
120	14.638	8.198	-1.0458	4.606	13.1579	-0.4559
210	14.7	14.2857	-1.553	4.63	21.784	-0.4868
1440	14.728	97.773	----	4.956	146.134	----
4320	14.728	293.319	----	4.956	438.402	-----

Appendix F: The flame AAS and wavelength analytic in Ezana analytical laboratory

Elements	Emission wavelength in nm	Atomize temperature in °C	Flame type
Cd	326.1	900	Air/acetylene
Cr(VI)	425	2500	Air/acetylene
Co	345.4	2100	Air/acetylene
Cu	324.8	2100	Air/acetylene
Fe	372	2100	Air/acetylene
Pb	405.8	1200	Air/acetylene
Mn	403	1800	Air/acetylene
Ni	341.5	2500	Air/acetylene
Zn	213.9	1100	Air/acetylene

- Volume total= 100ml, volume sample 50ml then dilution factor = by dividing total volume by volume of sample = 100/50= 2 then AAS value (mg//l)*dilution factor.
- Since, 2drop = 0.1ml, 1ml=1g, 1drop= 0.045ml, the base line reference 1g in 1000ml $AgNO_3$ is the quality control with PH between 10-10.5 using NaOH.

Appendix G: Some receipt obtained from AAU chemistry department (FTIR, XRD) and Ezana analytical laboratory for 42 samples

EZANA ANLYTICAL LABORATORY
TEL.: 251 344 40 87 79 FAX: 251 344 40 54 53
MEKELLE, ETHIOPIA

Invoice

(Sample preparation and analysis services)

Company:	AAU	Date: 29/01/2018	
Attn:	Mebrahtom Hagos	Client Code: EMD-005	
City:	A.A	Job No.: EAL-18A0458	
State:		Project:	
Country	Ethiopia	Order No.	
Phone:	914416349	Invoice No. - BEC/557/18	

Method Code	Description	No of analytes	Quantity	Unit Price (Birr)	Total Price (Birr)
AA46	HCLO4 digest-AAS finish, base metals HF digest -AAS finish, base metals	2	42	36.81	3,092.04
	Subtotal				3,092.04
	V.A.T				463.81
	Total				3,555.85

Prepared By

Alganesh Hadgu
Adiminstration Assistant

Approved By

Yirgaalem W. Gebriel
Laboratory Manager

Ezana Mining Development Pvt. Ltd. Co

Please remit the invoiced amount to:
Ezana Mining Development PLC

Commercial Bank of Ethiopia,
Mekelle Branch, Acco. No.1000012053766.