ADDIS ABABA UNIVERSITY

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MSC. THESIS ON:

REMOVAL OF HEAVY METALS FROM ELECTROPLATING WASTE WATER INDUSTRY USING ADSORPTION TECHINQUE(LIGNITE COAL)

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ACRONYM

AAS	Atomic absorption spectrophotometer
AC	Activated Coke
ACS	American chemical society
ANOVA	Analysis of variance
APHA	American Public Health Association
C_e	the concentration of the sorbate at equilibrium (mg/L),
Ci	initial concentration of the metal ion
Cf	final concentration of the metal ion
Conc.	Concentration
HCL	hydrochloric acid
K_f	Freundlich adsorption capacity
K_L	Langmuir equilibrium constant (l/mg).
k_f	Pseudo firstorder rate constant
k_s	pseudo second order rate constant
LAC	lignite activated coke
NaoH	Sodium hydroxide
n	Sorption intensity
pH	Power of hydrogen
q_e	Amount of sorbate sorbed at equilibrium per unit mass (mg/g),
q_m	Monolayer sorption capacity at equilibrium (mg/g)
R	Removal efficiency
R^2	correlation coefficient

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ABSTRACT

Wastewater from industry can lead to water pollution if untreated, especially due to its high concentration of heavy metals. Heavy metals are considered extremely harmful because they can cause illnesses, disorder and diseases to human. Therefore, industrial wastewater containing heavy metal should be treated before discharge to the water stream but its treatment is very costly. There are several techniques to remove heavy metals from wastewater such as biosorption, filtration and adsorption of heavy metal but there is some limitation such as long treatment time. The adsorption of copper and zinc from synthetic wastewater by lignite coal was investigated. The effect of different environmental conditions such as contact time, initial metal ion concentration adsorbent dosage and pH on metal ions removal has been studied by keeping stirring at 200rpm and solution temperature of 25^{o}c. Experiment results showed that maximum removal of Cupper ion by lignite coal at optimum condition (6 pH, 120 min. contact time, 2g adsorbent dose and 200ppm concentration) is 82.32% and for Zinc ion are 77.54% at optimum condition (4 pH, 90 min. contact time and 1.5g adsorbent dose, 150ppm concentration). These experimental studies on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated industrial effluents.The adsorption data of metal ions at temperature of 25°C have been described by the Freundlich and Langmuir isotherm models. The sorption process conformed to both Langmuir and Freundlich isotherms with maximum sorption capacities of 16.468 and 13.45mg/g for copper and zinc, respectively. The equilibrium time was found to be of the order of 120 minute for copper and 90 minute for zinc sorption by lignite coal. Sorption kinetics was determined using pseudo first-order, second order and, hence adsorption rate constants were calculated. The results revealed that sorption kinetics of copper and zinc followed pseudo second order with regration coefficients of 0.9994 and 0.9988 respectively. Optimum results were applied to remove copper and zinc from real electroplating wastewater. Optimum parameters for copper sorption were pH=6, contact time =120 mins, and lignite dosage of 2gm and for zinc batch sorption were; pH=4, contact time =90 minute, and lignite dosage of 1.5gm. The results showed lignite coal reduced copper ions from its initial concentration of 187.67 mg/l to 38.37 mg/l while zinc was reduced from 147.45 mg/l to 88.73 mg/l. Their respective removal efficiency was 63.45% and 59.65%

Introduction

1.1. Background

From different environmental issues, pollution by heavy metals of surface water, ground water and soil in urban areas are the major environmental problems. Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. The presence of heavy metal ions is of major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, paint, electroplating, smelting, alloy industries and storage batteries industries. The most common and harmful heavy metals are mercury, lead, copper, nickel, chromium and zinc. They are stable elements that cannot be metabolized by the body and get passed up in the food chain to human beings. When waste is disposed into the environment, a further long- term hazard is encountered. The increasing awareness of the environmental consequences arising from heavy metal contamination of the aquatic environment has led to the demand for the treatment of industrial Waste water before discharge into the aquatic environment (Fostner and Whittmann, 1979).

Heavy metals occur in immobilized form in sediments and as ores in nature. However due to anthropogenic activities these metals are mobilized and released and natural biogeochemical cycles are disrupted causing increased depositions of heavy metals in terrestrial and aquatic environment (Alluri et al., 2007 and Holant, 1995). Because of their non-biodegradable and persistent nature, heavy metals pollution poses a significant threat to the environment (Mahamood, 2010 and Fu & Wang, 2011). These toxic metals may be generated from different activities such as mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives (Kanamadi, 2003).

Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in different body parts. Heavy metals such as lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, silver, copper and nickel are given concerns and found in wastewaters (Kanamadi, 2003). Most of them (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.) are well known toxic and carcinogenic agents and when discharged into the wastewater represent serious threat to receiving water bodies and cause adverse effects on the environment (Orhan et al., 2006 and Ahluwalia&Goyal, 2007), Even low concentrations of heavy metals have damaging effects to man and animals because there is no good mechanism for their elimination from the body. Nowadays heavy metals are ubiquitous because of their excessive use in industrial applications (Arora et al., 2008.

The conventional treatment methods are commonly used for removal of metal ions from aqueous streams. This treatment includes chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and activated carbon adsorption. However, these conventional technologies are providing expensive due to non regenerable materials used, high cost, generation of toxic sludge often ineffective particularly for the removal of heavy metal ions at low concentrations as below 50 mg/l (Holan& Volesky, 1995, Ahluwalia&Goyal, 2007 and Shoba, 2013). Existing technologies for heavy metals' removal from waters and wastewaters are often ineffective (especially at environmental levels), expensive and unavailable in developing countries. The need to find alternative inexpensive and effective methods for heavy metals abatement from waters becomes inevitable (Opeolu et al., 2010). Adsorption in comparison with other methods appeared to be preferable in terms of its efficiency and ease with which it can be applied in its application in the removal of heavy metals in wastewater. An adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a byproduct of waste material from waste industry. Plant wastes are inexpensive as they have no or very low economic value (Bailey, 1999). Today, in this regard, biosorption is one of the main components of environmental and bio-resource technology due to its economical and efficient in removing of very diluted metal concentrations from waste water (Holan&Volesky, 1995).Adsorption is a surface process that occurs when a solute is selectively retained on the surface of an adsorbent forming a thin layer of the adsorbate. Thus adsorption finds its use in the removal of dissolved substances from water with careful choice of adsorbent and adsorbate. It involves selective retention of the adsorbate to the adsorption sites of the adsorbent. Disposal of industrial wastes with an appreciable concentration of heavy metal ions is a persistent environmental issue. Therefore, the conventional methods in practice for the removal of heavy metal ions from waste waters include precipitation by chemical methods, ion exchange and biosorption7. Although these methods are expensive they are also associated with several limitations such as the generation of sludge, low percentage retention of metal ions, energy consumption and low selectivity which makes the process less suitable for small scale industries. Thus adsorption is proposed as an economical and effective method for the retention of heavy metals ion..

1.2. Statement of Problems

The presence of high levels of heavy metal in surface water, ground water, and soil has become a major concern from industries. Several industrial wastewater streams may contain heavy metals such as Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. including the waste liquids generated by electroplating, metal finishing or the mineral processing industries. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, while the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment.Rapid urbanization and industrialization generates enormous volumes of partially treated and untreated waste water which consists of heavy metals. These heavy metals have potential health risks associated with metal uptake via food chain, dermal absorption or inhaling. High levels of exposure to heavy metals have been known to cause cancer, organ damage, joint diseases, and in extreme cases, death (Holan& Volesky, 1995).The purpose of this research is to improve the method to remove heavy metal from industrial wastewater. It’s important to ensure there are no harmful heavy metals in the water stream because it can accumulate in the environment elements such as food chain and pose a significant danger to human health. Adsorption technique was used because this method offers many potential advantage in energy saving, process enhancement and processing time to remove heavy metal. In this research, lignite coal was used as an adsorbent to assist adsorption process because of its cost and its efficiency to remove heavy metals. Therefore, the most important measure needed is to prevent further environmental pollution of heavy metals is to develop treatment processes for contaminated water and soils. In view of the above circumstances, the development of suitable treatment systems for heavy metals removal from industrial wastewater appears to be the most promising option. The treatment options should be effective, reliable, and affordable for heavy metals removal from wastewater. In Dejen aviation idustry (METC), found at Debre Zait, Ethiopian due to the indiscriminate discharge of waste waters containing heavy metal ions such zinc and copper and have posed a serious challenge to human as well as environment.

Adsorption processes have received significant attention due to several reasons, especially for those metal ions that cannot be removed efficiently by other technique.

Hence, it is expedient to device or seeks alternative methods of removing heavy metal ions from wastewaters by using locally available cheap raw material like lignite via the process of adsorption.

1.3. Objectives

1.3.1 General Objective

The main goal of this study is to determine the optimum condition to remove heavy metal from electroplating industrial wastewater by using adsorption technique using lignite coal (activated carbon) as adsorbent. And to evaluate the adsorption characteristics of heavy metals from aqueous systems using locally available cheap raw material lignite coal, in the management of metal poisoning.

1.3.2 Specific Objective

- To prepare and characterize lignite samples for adsorption processes.
- To determine the concentration of the heavy metal ions before and after adsorption,
- To examine the ability of Ethiopian lignite coal as an adsorbent in the adsorption of heavy metals ions from aqueous solution and therefore evaluate its potential in wastewater treatment systems.
- To investigation of the optimum adsorption behavior of heavy metals on the indicated adsorbents under various experimental conditions of PH, concentration of heavy metals ions, adsorbent dosages, and at different contact times for each heavy metal ionic strength,
- To analyze the data obtained from the adsorption experiment using the sorption isotherm models and determination of the adsorption kinetics on the sorbent investigate.

1.4 .Significance of the Study

Recently, new technologies involving the removal of toxic metals from wastewaters have directed attention to adsorption, based on metal-binding capacities of various materials. In comparison to conventional methods adsorption is simple and widely used in wastewater treatment due to the simplicity, versatility, and efficiency in extracting a variety of chemical compounds. The prerequisite for commercial adsorption is the suitable and economical adsorbent. Activated coke (AC) is produced from natural carbonaceous materials like lignite termed lignite activated coke (LAC), petroleum coke, biomass, and wastes or by-products.

Therefore, use of lignite for heavy metal removal is significant by most to be a very effective low techno logy solution. The main reasons to give much attention to this method is the major advantages of adsorption cost, the materials are cheap and widely available, minimization of chemical and/or biological sludge, no additional nutrient requirement, Simple process, no daily dosage of chemicals, and the possibility of metal recovery and recycling of adsorbent metals from adsorbent.

2. Literature Review

2.1. Overview of heavy metals and Removal Technologies

Advanced industrialization processes have provided comforts to human beings on one hand, and on the other, it has resulted in indiscriminate release of solid wastes, gasses and liquids, which polluted the environment of biological system. Of the various sources of pollutants industrial effluents containing heavy metals pose a threat to the ecosystem. Presence of pollutants in effluent is a common environmental hazard since the toxic metal ions dissolved can ultimately reach the top of the food chain and becomes a risk factor for human beings. Heavy metals are elements of high density, and they are toxic at even low concentrations. They can also be defined as the elements in the d-block in the periodic table such as Nickel(Ni), Zinc(Zn), Copper(Cu) etc. Heavy metals are natural components of the Earth’s crust. Some heavy metals are vital to maintain the metabolism in our bodies at certain concentrations such as zinc. However, the excess of these heavy metals can lead to poisoning *via* drinking water contamination, high ambient air concentrations, or eating contaminated food.

2.1.1. Copper

Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fiber production, pipe corrosion and metal plating industries. The other major industries discharging copper in their effluents are paper, pulp, petroleum refining and wood preserving. Agricultural sources such as fertilizers, fungicidal sprays and animal wastes, also lead to water pollution due to copper. Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and drink. Copper has been reported to cause neurotoxicity commonly known as “Wilson’s disease” due to deposition of copper in the ventricular nucleus of the brain and kidney failure. In some instances, exposure to copper has resulted in jaundice and enlarged liver. It is suspected to be responsible for one form of metal fume fever. Moreover, continued inhalation of copper-containing sprays is linked to an increase in lung cancer among exposed workers.

2.1.2. Zinc

Due to its remarkable resistant to atmospheric corrosion, zinc is commonly used to protect iron from rusting, in the process called galvanization. Zinc is widely used for the manufacturing of zinc white and several useful alloys such as brass, German silver, delta metal, for the preparation of gold and silver in the cyanide method, for the desilverization of lead in parks process and as an anode material in galvanic cells. Various zinc salts are used industrially in wood preservatives, catalysts, Photographic paper, and accelerators for rubber vulcanisation, ceramics, textiles, fertilizers, pigments, steel production and batteries. Zinc toxicity from excessive ingestion is uncommon but causes gastrointestinal distress and diarrhea.

Table 2.1 Common type of heavy metals and their toxic effects of human beings

H. metal	Major sources	Toxic effect	References	WHO limits (ppm)
Pb	Mining, paint, pigments, electroplating, manufacturing of batteries, burning of coal	Anemia, mental deficiency, nervous system disorders, decreased hemoglobin synthesis, cardio vascular diseases, disorders in bone metabolism, renal function and reproduction.	(Low et al., 2000) (Ravikumar & K, 2013 and Holan & Volesky, 1995)	0.1
Cu	Electroplating, Printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations	Reproductive and developmental toxicity, neurotoxicity, and acute toxicity, dizziness, Diarrhoea	(Farooq et al., 2010)	0.05
Cd	Electroplating, smelting, alloy manufacturing, pigments, plastic, mining, refining	Itai-itai disease, causes high blood pressure, sterility among males, kidney damage, flu disorders	(Ravikumar & K, 2013 and Farooq et al., 2010)	0.05

Zn	Electroplating, Galvanization, paint, batteries, smelting, fertilizers and pesticides, fossil fuel combustion, pigment, polymer stabilizers, etc.,	Zinc fumes have corrosive effect on skin, cause damage to nervous membrane	(Sao et al., 2014)	15

Nickel	Porcelain enameling, non-ferrous metal, paint formulation, electroplating	headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness	(Deepa & Suresha, 2014)	0.05
Chromium	plastic coatings, electroplating, leather tanning and finishing, pigments and wood preservative, metal finishing, and chromate preparation	Epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract, lungs carcinoma	(Sobhanardakani et al., 2013 and Venkateswarlu et al., 2007)	100 µg/L (EPA)
Arsenic	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis	(Sao et al., 2014)	0.05

Mercury	metallurgical industries, chemical manufacturing and metal finishing industries	In the vapor form mercury attacks the lungs, kidneys and the brain. The vapor crosses the blood-brain and blood stream. It also causes blindness, mental and emotional deterioration, involuntary mobilization, loss of consciousness, etc.	(Igwe et al., 2008 and Shafeeq et al., 2012)	0.001

The presence of copper, zinc, cadmium, lead, mercury, iron, nickel and others metals, has a potentially damaging effect on human Physiology and other biological systems when the tolerance levels are exceeded (Demirbas, 2008). Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain(Barakat, 2011). The poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the normal metabolic processes (Duruibe, 2007).

2.2. Conventional removal methods of heavy metals

Methods for removing metal ions from aqueous solution mainly consist of Physical, chemical and biological technologies. Conventional technologies, such as chemical precipitation, lime coagulation, solvent extraction, membrane filtration, reverse osmosis, on exchange and adsorption, are being used for the removal of heavy metal ions from aqueous wastes (Holan & Volesky, 1995). The process description of each method is presented below (Kanamadi, 2003 and Zabochnicka-świątek & Krzywonos, 2014)

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

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

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

iv. **Ion exchange:** An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials held by electrostatic forces on the exchange resin. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantages include; high cost, partial removal of certain ions, and it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater.

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

vi. **Phytoremediation:** Phytoremediation is the use of certain plants to clean up soil, sediment, and water contaminated with metals. The disadvantages include that it takes a long time for removal of metals and the regeneration of the plant for further bio sorption is difficult.

Due to the disadvantages mentioned above, like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require cost-effective alternative technologies or adsorbents for the treatment of metal containing wastewaters are needed. Natural materials that are available in large quantities, or certain waste products from agricultural operations, may have potential as inexpensive adsorbents. Due to their low cost, after these materials have been expended, they can be disposed of without regeneration. (Kadirvelu et al., 2001 and Kanamadi, 2003)

The adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams and activated carbon has been frequently used as an adsorbent (Khan et al., 2004). Recently, apart from activated carbon various low-cost adsorbents, derived from agricultural waste, industrial byproduct, natural material, or modified biopolymers, have been developed and applied for the removal of heavy metals from metal contaminated wastewater (Barakat, 2011).

Adsorption can be utilized in various processes such as technological, environmental and biological. This process has been applied practically in industry and environmental protection. The adsorption of substrates is the first stage in many catalytic processes. During the last 15 years' new classes of solid adsorbents have been developed, such as activated carbon fibers and carbon molecular sieves, fullerenes and hetero fullerenes, microporous glasses and nanoporous both carbonaceous and inorganic materials (Dabrowski, 2001).

Porous sorbent particles follow three steps during sorption process (Lazaridis & Asouhidou, 2003). The first step is (i) external mass transfer (boundary layer or film diffusion) between the external surface of the sorbent particles and the surrounding fluid Phase. The driving force is the concentration difference across the boundary layer around each particle; (ii) Intraparticle transport within the particle, which may be limited by pore and solid diffusion; (iii) Reaction kinetics at Phase boundaries. In general, there are three main steps involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle (Barakat, 2011) .

Generally, for adsorption to occur there must be forces that attract the adsorbate to the solid surface in a solution. One is due to force of Physical nature called van der Waals force. This adsorption is relatively weak and plays an important part in connection with surface reactions, since they are not sufficiently strong to influence appreciably the reactivity of the molecule adsorbed. The second type is chemisorption which is much stronger than the first one. In this case the adsorbed molecules are held to the surface by valence force of the same type as those occurring between bound atoms in molecules.

2.3. Adsorption

Adsorption is the formation of bonds between dissolved species or small particles and the surface of a solid. Usually the solid is in the form of granular media, and water is treated by passage through packed beds. Powdered adsorbents may also be used, and adsorption is a key process during coagulation. Ion exchange can be considered as a special form of adsorption, though it is often considered separately. The efficiency of adsorption depends primarily on the attraction of the contaminant for the media being used and the extent of contact between water and surfaces (controlled by particle size and loading rates). Water chemistry may also be important: positively charged species (like most metals) are more easily removed at high PH, while negatively charged species (like arsenate) are best removed at lower PH. Competition from other dissolved species or clogging of the media by particles can also greatly reduce adsorption of the target chemical. All adsorption media have a limited number of sites where adsorption occurs, and as these sites are filled the media becomes exhausted and must be replaced or regenerated. Water treatment with granular adsorption media is relatively easy to implement:

2.4. Factors affecting adsorption

The most important factors that should be taken into account when considering adsorption are: (i) the type and nature of the dosage; (ii) initial solute concentration; (iii) dosage concentration (adsorbent dosage/solution volume) in solution; (iv) Physicochemical factors like temperature, PH, and ionic strength (Chimie, 2014). Apart from the Physicochemical factors such as PH, the presence of other anions and cations, metal speciation, pollutant solubility and form, etc. may also have an influence. With living cell systems, the provision of nutrients and optimal growth conditions is an obvious requirement (Gadd, 2009).

2.4.1. Effect of solution PH:

The PH of the metal ion solution is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate (Ii et al., 2011).Therefore, PH of solution influences the nature of biomass binding sites and metal solubility; Metal adsorption has frequently been shown to be strongly PH dependent in almost all systems examined, including bacteria, cyanobacteria, algae, and fungi (Holan & Volesky, 1995).

It has been generally reported that in highly acidic medium (PH≈2) the removal of metal ions is almost negligible and it increases by increasing the solution PH up to a certain limit (Abdelghani & Elchaghaby, 2014). This can be explained that decreasing of adsorption levels by lowering PH can be due to competition between protons and metal ions for the capturing same sites (Igwe, 2006). On the other hand, too high PH value can cause precipitation of metal complexes, so it should be avoided during experiments. For different adsorption system of metal ions, the optimal PH is different.(Wang & Chen, 2006)

2.4.2. Effect of temperature:

The effect of temperature is fairly common and increasing the mobility of the metal cation (Malkoc & Nuhoglu, 2005).Temperature influence has more effect in a situation where by metal uptake increases within a temperature range of about 20-30^{0}C, but decreases with an increase of temperature above a critical value. (Sulaiman, 2015) Increase in temperature probably weakens the bond formed between the metal ions and the adsorption sites on the adsorbent thereby resulting in an increase in the amount of metal ions adsorbed on the adsorbent.

This implies that increase in temperature creates a wider surface area for adsorption at the adsorbent (Okafor et al., 2012). At high temperature, the thickness of the boundary layer was expected to decrease due to the increased tendency of the metal ion to escape from the surface of the adsorbent to the solution Phase hence there was bound to be weak adsorption interactions between the adsorbent and the adsorbate (Ojedokun & Solomon, 2016).

2.4.3. Effect of contact time:

Adsorption is also affected by contact time between biomass and the solution containing metals. Adsorption proceeds fast and most metals are adsorbed at the very beginning of the process (Zabochnicka & Krzywonos, 2014).In adsorption systems, contact time plays a vital role irrespective of other experimental parameters affecting the adsorption kinetics. The determination of the optimum contact time needed to achieve the highest removal of metal ions is very important in batch adsorption experiments. The study on removal of iron, nickel and zinc was analyzed by (Elmaghrabi, 2014) that the time-dependent behavior of metal ions was measured by varying the equilibrium time in the range of 30–240 min. Results showed that the equilibrium is reached quickly (~30 min), indicating that, the adsorption sites are well exposed.

2.4.4. Effect of Initial solute concentration:

It is generally agreed that the adsorption capacity increases as the initial metal ion concentration in the solution increases, whereas the metal removal percentage (also called removal efficiency) decreases by increasing the metal ion initial concentration (Abdelghani & Elchaghaby, 2014). As a rule, increasing the initial metal concentration results in an increase in the adsorption capacity because it provides a driving force to overcome mass transfer resistance between the adsorbent and adsorption medium (Pahlavanzadeh et al., 2010).

2.4.5. Effect of Adsorbent dosage:

The amount of biomass in the solution also affects the specific metal uptake. In principle, with more adsorbent present, the available adsorption sites or functional groups also increase (Mosbah & Sahmoune, 2013). At low biomass dosage, the amount of ions adsorbed per unit adsorbent weight is high. Adsorption capacity is reduced when the biomass dosage increases as a result of lower adsorbate to binding site ratio where the ions are distributed onto larger amount of biomass binding sites (Ojedokun & Solomon, 2016).

2.5. Adsorption Equilibrium model

Adsorption equilibrium is the basic requirement for designing a adsorption system (Chimie, 2014). The adsorption isotherms describe the relationship between the mass of the adsorbed component per adsorbent mass the concentration of this component in the solution (Abdelghani & Elchaghaby, 2014). Modeling equilibrium sorption is important for industrial applications of adsorption; it yields data that facilitates designing and optimizing the process.

The classical Langmuir and Freundlich sorption isotherm models consider sorption by free binding sites rather than ion exchange. Sorption isotherms are useful in quantitatively evaluating and predicting the process performance of the binding capacity and affinity for different metal concentrations and sorbent dosages (Isabel et al., 2014). These models can be applied only at a constant PH. These models are the most used for the modeling of adsorption equilibrium in the presence of one metal. These are plotted in a 2D plane, where the specific uptake, q, is reported as function of the metal residual concentration, C_e. In the case of multi metal systems, models should be modified in order to take into account all the metals (Veglio & Beolchini, 1997).

Equilibrium studies are described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity for the sorbent.

2.5.1. The Langmuir Model

According to Langmuir, the sorption occurs at the surface of the sorbent in a homogeneous way and the atoms/ions form a mono-layer, having no mutual interactions, on the sorbent surface. Although it gives no information about the mechanism, it is still used to obtain the uptake capacities of the sorbents (Farooq et al., 2010). The Langmuir isotherm which hints on homogeneity describes the monolayer coverage of a sorbate on a sorbent surface at constant temperature (Adelagun, 2014). The linear form of the Langmuir equation is:

$$Ce/q_e = 1/Kq_m + C_e/q_m \qquad (1)$$

Where C_e is the concentration of the sorbate at equilibrium (mg/L), q_e is the amount of sorbate sorbed at equilibrium per unit mass (mg/g), q_m is the monolayer sorption capacity at equilibrium (mg/g) and k is the Langmuir equilibrium constant (l/mg). The values of q_m and k are obtained from the slope and intercept respectively of the plot of straight line graph bof C_e/q_e against C_e.

2.5.2. The Freundlich Model

The Freundlich model is used in the process of sorption on heterogenic surface, i.e. energy heterogenic surface. Typical property of heterogenic surface is that the areas where adsorption occurs differ in terms of adsorption energy. In consequence, adsorption places with the highest adsorption energy are covered first, and then the places with lower energy are covered (Zabochnickaświątek & Krzywonos, 2014). The Freundlich isotherm, which is empirical in nature, can be interpreted to adsorption onto surfaces supporting sites of varied affinities, and has been used widely to fit experimental data of liquid-PHase adsorption (Oubagaranadin & Murthy, 2010).

The Freundlich isotherm has also been employed to quantify equilibrium adsorption systems. Like the Langmuir isotherm, the extent of adsorption/sorption is determined as a function of the equilibrium concentration of the metal in solution, without reference to PH or other ions in the same aqueous system(Davis et al., 2003).The Freundlich isotherm is regarded as an empirical isotherm. It indicates the surface heterogeneity of the sorbent. The linearized form of Freundlich equation is given by:

$$\ln(q_e) = (1/n) \ln(C_e) + \ln(K_f) \quad (2)$$

Where K_f and n are Freundlich adsorption constants, related to adsorption capacity and sorption intensity respectively obtained from the plot of $\ln(q_e)$ against $\ln(C_e)$ which gives a straight line graph with 1/n as slope and $\log(K_f)$ as intercept.

2.6. Kinetics of sorption

The prediction of the adsorption rate gives important information for designing batch adsorption systems (Abdelghani & Elchaghaby, 2014). The efficiency of the adsorbent is evaluated by studying adsorption kinetics. Kinetics is an adsorption dynamic which describes the solute uptake rate and evidently control the resident time of adsorbate and possibilities of desorption. The kinetic properties of adsorbate uptake are used in selecting optimum operating conditions for the full scale batch process. Several kinetic models have been applied to fit the adsorption data of different metal ions onto various adsorbents. These models include the pseudo first order, pseudo second order, Elovich, intraparticle diffusion, etc.(Abdelghani & Elchaghaby, 2014)

2.6.1. Pseudo first order model

The Lagergren rate equation is one of the most widely used sorption rate equations for the adsorption of a solute from a liquid solution (Holan & Volesky, 1995). It may be represented as: The pseudo-first-order equation is given as:

$$dq_t/d_t = k_f (q_e - q_t) \quad (3)$$

where q_t is the amount of adsorbate adsorbed at time t (mg/g), qe is the adsorption capacity at equilibrium (mg/g), K_f is the seudo first order rate constant (min^{-1}), and t is the contact time (min).

The integration of the above equation with for the boundary conditions; t = 0 to t = t and qt = 0 to qt= qt, gives:

$$\log (q_e - q_t) = \log(q_e) - (K_f/2.303) * t \quad (4)$$

The values of adsorption rate constant (K_f) for metals adsorption on activated coal (lignite coal) will be determined from the plot of $\log(q_e-q_t)$ against t.

2.6.2. Pseudo-second-order model

The pseudo-second-order model is given as:

$$(dq_t/d_t) = K_s(q_e-q_t)^2 \qquad (5)$$

Where K_s is the pseudo-second-order rate constant (g/mg min), q_e is the amount of metal ion adsorbed at equilibrium (mg/g), and q_t is the amount of metal ion adsorbed at time t (mg/g). Integrating for the boundary conditions t = 0 to $t = t$ and q_t=0 to q_t= q_t gives

$$q_t = \frac{q_e^2 * K_s * t}{1+q_e K_s * t} \qquad (6)$$

Eq. (5) is the integrated rate law for a second order reaction and can be rearranged to obtain

$$q_t = \frac{t}{\frac{1}{K_s q_e^2} + \frac{t}{q_e}} \qquad (7)$$

This has a linear form of

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{1}{q_e} t \qquad (8)$$

The initial adsorption rate, ***h*** (mg/g min) is defined as:

$$h=k_s q_e^2 \qquad (9)$$

The rate parameters k_s and $q_e$can be directly obtained from the intercept and slope of the plot (t/q_t) against t.

3. Experimental methods and materials

3.1. Experimental materials and chemicals

The major raw material used for adsorbent during the experimental works was lignite coal. It were obtained from **Yayu (Wittete and around Yayu)** which is Oromia Region, on South Western part of Ethiopia. Analytical grade reagents were used for heavy metal solution; ACS reagent grade concentrated sulfuric acid and NaOH were used to adjusted pH values of samples. In all experimental work, Distilled water/ De-ionized water, Standard buffer solution-For pH meter calibration , materials like Ethiopian Lignite coal (adsorbent) , copper zinc and equipment's such as PH meter/ PH paper ,Atomic Absorption Spectrometry (AAS), 250 ml Stopper Conical flask, what man number 42 filter paper , Furnace, Digital Weighing Balance, Glass Beakers, Measuring Cylinders ,Burettes & Pipettes are useful. The experimental work was started in January 2016 and ended in May 2016; a total of five months' ware spent for the laboratory works. Copper and Zinc metal analysis was done, at Addis Ababa University collage of natural science, school of chemical and bio-engineering lab, environmental science postgraduate Laboratory and at Defence university collage, mechanical unit operation and reaction engineering lab. Real waste water samples for column adsorption were obtained from dejen aviation industry (METEC) located in Addis Ababa, Ethiopia

3.2. Experimental methods

3.2.1. Preparation of Lignite Coal and it's characterization

The raw Lignite were collected from **Yayu (Wittete and around Yayu)** in Oromia Region, on South Western part of Ethiopia.Process of cleaning the raw lignite thoroughly were washed to rid them of adhering of soil and other impurity attached, Process of drying the lignite, using an oven temperature of 60°C for 2 hours, Process of burning the lignite, using a furnace temperature of up to 600°C. The dried samples were broken into smaller pieces, grind into powder using mortar and pestle. Before performing adsorption experiments, soluble materials including metals were removed from the ash through a washing process using distilled or deionized water. The sample was then heated at 105°C in an oven until completely dried (usually 24h). The dried sample were sieved, and then physical characteristics and surface properties analysis was carried out on the raw adsorbent.

Table 3.1.Characterization of Lignite coal as an adsorbent

Parameter Test	**Result**	
	Raw Lignite	Acid Treated LAC
Bulk density	0.72g/cm^3	1.65 g/cm^3
Moisture content	4.52%	4.15%
Volatile content	32.85%	30.25%
Ash content	39.9%	19.95%
Fixed carbon	22.73%	45.65%
Percentage of dry matter	95.48%	95.85%

3.2.2. Adsorption Procedures to Determine the Optimum Experimental Parameters

1. Determination of optimum pH: 2, 4, and 6 pH.

2. Determination of optimum lignite/adsorbent dosage: 0.5,1 ,1.5 & 2gm.

3. Time, 30, 60, 90 & 120 minute.

4. Determination of optimum initial Cu, Zn, initial concentration of heavy metals 100,150 and 200mg/l.

Hence we have 3 factors and 3 levels, i.e. 3^3 = 27, for 2 heavy metal is 2*27=54and replication is 2, total 54 * 2=108 experimental run.

3.3. Waste Water Sampling

Waste water samples of (50 ml) were digested with 10 ml of concentrated HNO_3 at 80°C until the solution became transparent (APHA 2005). These transparent solutions were then filtered through Whatman number 42 filter paper and diluted to 50 ml with distilled water. Copper and Zinc Stock solution was prepared by dissolving the accurately weighed amounts of each heavy metal salts, in 1000ml distilled water and working solutions for calibration were prepared by serial dilution of the stock solution. The initial and final concentrations of heavy metal, in the filtrate were determined by using atomic absorption spectrophotometer for both copper and zinc, fitted with a specific lamp of particular metal using appropriate drift blanks and standards.

3.4. Preparation of Stock Solution

$CuSO_4 \cdot 5H2O$, $NiSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot 7H_2O$ were obtained in analytical grade and used without further purification synthetic 1000ppm stock solution prepared for each metal.

i) Copper solution: 3.927 grams of $CuSO_4 \cdot 5H_2O$ was added in the 100ml of distilled water in 1000ml volumetric flask. It was dissolved by shaking and the volume was made up to the mark. Copper concentration of this solution was 1000 mg/l.

ii) Zinc solution: 4.395 grams of $ZnSO_4 \cdot 7H_2O$ was added in the 100ml of distilled water in 1000ml volumetric flask. It was dissolved by shaking and the volume was made up to the mark. Zinc concentration of this solution was 1000 mg/l.

3.5. Batch Adsorption Experiment

Different initial concentrations (100, 150 and 200mg/l) of each copper and zinc solutions were prepared by proper dilution from stock (1000 mg/L) metal ions standard solutions. PH (2-6) of the test solution was monitored by adding 0.1M HCl and 0.1M NaOH solution as required. Definite amount of adsorbent (2g) was then added to the metal ion solution (200ml) in a 250ml stopper conical flask and agitated for the desired contact time using orbital shaker at 200 rpm. The time (0, 30, 60, 90 and 120 minutes) required for reaching equilibrium condition was estimated by drawing samples at regular interval of time till the equilibrium was reached. The content of the metal ion in the test flask was separated from adsorbent by filtration through a filter paper and was analyzed by AAS for both copper and zinc. For all operating conditions, the solutions will be filtered, and filtrates will be stored in pre-cleaned and acid (HNO_3) washed airtight plastic bottles. Then metal concentrations were analyzed by an Atomic Absorption Spectrophotometer.

The structure of all experimental works and flows is shown in figure 3.1 below.
Amount of metal ions bound during the series of batch investigations was calculated by using the mass balance equation. This can be described as metal ions disappeared from the solution by adsorbent materials. The sorption capacity of metals can be calculated as(Ashraf, Mahmood, & Wajid, 2011): $Q_e = \frac{(C_0 - C_e) * V}{m}$, Where Q_e= adsorption capacity at equilibrium, V = volume of adsorbate solution (ml), m = mass of BSG (g) C_o = initial concentration in mg/L, C_e= concentration at equilibrium (mg/L). The removal percentage (R %) is defined as the ratio of difference in metal concentration before and after adsorption (C_o–C_e) to the initial concentration of the adsorbate in aqueous solution (C_o) shown below: $\%R = \frac{(C_0 - C_e) * 100}{C_0}$Where, C_o = initial concentration in mg/L, C_e= concentration at equilibrium (mg/L).

3.6. Experimental Design

The following conditions are experimental design for heavy metal removal by lignite coal for all varying conditions (PH, Initial concentration, time) with constant dose 2g for all varying conditions, particle size (250 micro meter) and Agitation speed(200rpm).

Table. 3.2. Removal of cupper for varying conditions

Std.	Run	Block	Time (minute)	pH	Initial cu(mg/l)	Final Cu(mg/l)	Efficiency (η)%
1	3	Block 1	30	2	100	22.91	71.09
2	27	Block 1	60	4	150	58.71	60.86
3	7	Block 1	90	6	200	47.67	76.16
4	20	Block 1	30	2	100	20.99	79.01
5	17	Block 1	60	4	150	39.07	73.95
6	1	Block 1	90	6	200	45.22	77.39
7	23	Block 1	30	2	100	24.06	75.94
8	26	Block 1	60	4	150	45.59	69.60
9	9	Block 1	90	6	200	51.80	74.10
10	25	Block 1	30	2	100	33.09	66.91
11	11	Block 1	60	4	150	40.69	72.87
12	8	Block 1	90	6	200	46.73	76.63
13	6	Block 1	30	2	100	28.82	71.18
14	5	Block 1	60	4	150	44.09	70.60
15	18	Block 1	90	6	200	44.08	77.96
16	14	Block 1	30	2	100	24.085	75.91
17	19	Block 1	60	4	150	44.24	70.50
18	4	Block 1	90	6	200	39.73	80.15
19	21	Block 1	30	2	100	32.21	67.79
20	22	Block 1	60	4	150	46.08	69.28
21	10	Block 1	90	6	200	52.15	73.92
22	12	Block 1	30	2	100	29.36	70.64
23	24	Block 1	60	4	150	48.62	67.58
24	2	Block 1	90	6	200	38.73	80.63
25	16	Block 1	30	2	100	59.55	41.00
26	13	Block 1	60	4	150	44.18	70.54
27	15	Block 1	90	6	200	35.32	82.34

Table 3.3.Removal of Zinc for varying conditions

Std.	Run	Block	Time (min.)	pH	Initial Zn(mg/L)	Final Zn(mg/l)	Efficiency (η)%
1	3	Block 1	30	2	100	24.40	75.60
2	27	Block 1	60	4	150	33.41	77.72
3	7	Block 1	90	6	200	80.26	59.87
4	20	Block 1	30	2	100	44.78	55.22
5	17	Block 1	60	4	150	40.88	72.74
6	1	Block 1	90	6	200	73.75	63.12
7	23	Block 1	30	2	100	43.77	56.23
8	26	Block 1	60	4	150	39.11	73.92
9	9	Block 1	90	6	200	68.53	65.73
10	25	Block 1	30	2	100	41.02	58.98
11	11	Block 1	60	4	150	35.5	76.33
12	8	Block 1	90	6	200	69.75	65.12
13	6	Block 1	30	2	100	52.40	47.6
14	5	Block 1	60	4	150	39.45	73.70
15	18	Block 1	90	6	200	49.72	75.14
16	14	Block 1	30	2	100	48.51	51.49
17	19	Block 1	60	4	150	40.17	73.22
18	4	Block 1	90	6	200	66.14	66.93
19	21	Block 1	30	2	100	32.60	67.40
20	22	Block 1	60	4	150	34.60	76.93
21	10	Block 1	90	6	200	68.10	65.95
22	12	Block 1	30	2	100	44.14	55.86
23	24	Block 1	60	4	150	37.33	75.11
24	2	Block 1	90	6	200	48.72	75.64
25	16	Block 1	30	2	100	46.77	53.23
26	13	Block 1	60	4	150	43.58	70.94
27	15	Block 1	90	6	200	77.30	61.35

Finally obtaining the final concentration of the heavy metals by using AAS instrument , and calculate the removal efficiency for each run, then the higher efficiency were give as the optimal condition , so taking this optimal condition which run is, apply it for waste water. $R\% = [\,(C_{in} - C_f)/C_i\,]\%$ Where, R = removal efficiency C_{in} = Initial concentration C_f = Final concentration After result found from the synthetic preparation using AAS was obtained the optimum varying condition from table 3.1.run 15 which has 82.3% removal efficiency and run 27 which has 77.72% removal efficiency for copper and zinc, respectively. Waste Sample was taken from dejen aviation industry (METEC) and the initial and final concentration was analyised using AAS by varying condition dosage at 05, 1, 1.5 and2 gram and Time at 30,60,90, and 120minute.Result for waste water was found 63.45 % removal efficiency and 59.65% removal efficiency for copper and zinc respectively.

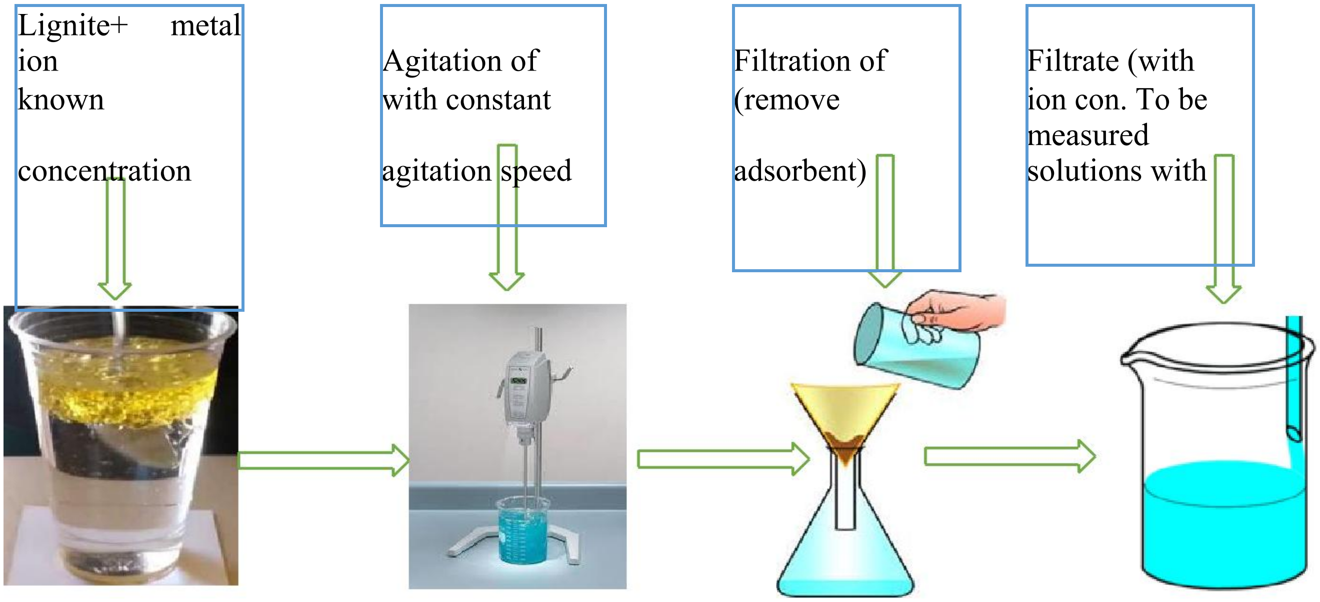

Fig 3.1 Diagram of heavy metal removal by lignite coal for all varying conditions

4. RESULT AND DISCUSSION

Adsorption experiments on Cu^{2+} and Zn^{2+} by lignite coal were done. The results obtained were replicated two times and it initiated to discuss about the effect of different environmental conditions such as PH, contact time, adsorbent dose and metal ions initial concentration on sorptive profile of copper and zinc by lignite coal. Adsorption isotherms and kinetics of metals removal were also discussed.

4.1. Effect of pH of Adsorbate Solution

PH effect on sorption of copper and zinc was conducted between the pH of solutions ranges of 2-6. This range was chosen because of the evidence that with an increase in pH, the amount of hydroxyl ions is increased in the solution. Metal ions react with OH^- ions and precipitate at higher pH values which results impossible the adsorption process (Chimie, 2014). Lowering the pH below 2 of the solution probably results in decreasing of adsorption levels and this can be explained due to competition between protons and metal ions for the capturing same sites of the adsorbent, which at low pHs, metal ions do not successful (Taghi ganji, 2005)

The influence of pH of metal in solution on the extent of sorption of copper and zinc ions on lignite coal is shown in Figure4.1 and table 4.1. From the plot, high amount of copper metal ion was adsorbed at pH 6 with maximum percentage removal of 82.34%, while maximum zinc sorption was observed at pH 4 with maximum percentage removal 77.72%. But as pH goes up from 2 to 6 its removal efficiency was increased. The maximum adsorption of zinc was observed at the basic range because at higher pH there is increase in OH^- ions on the adsorbent surface ,and the presence of zinc ions resulting significant strong electrostatic attraction (Agarwal & Gupta, 2015).

Table 4.1 Effect of metal solution PH on % removal and sorption capacity of lignite coal

Metals	**pH**	**% Removal**	**q_e(mg/gm)**
Cu^{2+}	2	79.01	15.8020
	4	80.15	14.7026
	6	82.34	16..4680
Zn^{2+}	2	75.60	15.1200
	4	77.72	15.5450
	6	75.64	15.1280

For zinc sorption onto lignite coal, maximum adsorption efficiency was obtained at pH 4. For sorption of zinc, as pH value increases from 4 to 6 slightly diminishing of removal efficiency was observed. This may be attributed to above optimum pH of 4, OH^- ions increment causes a decrease in adsorption of metal ions at adsorbent adsorbate interface (Thakur & Parmar, 2013).

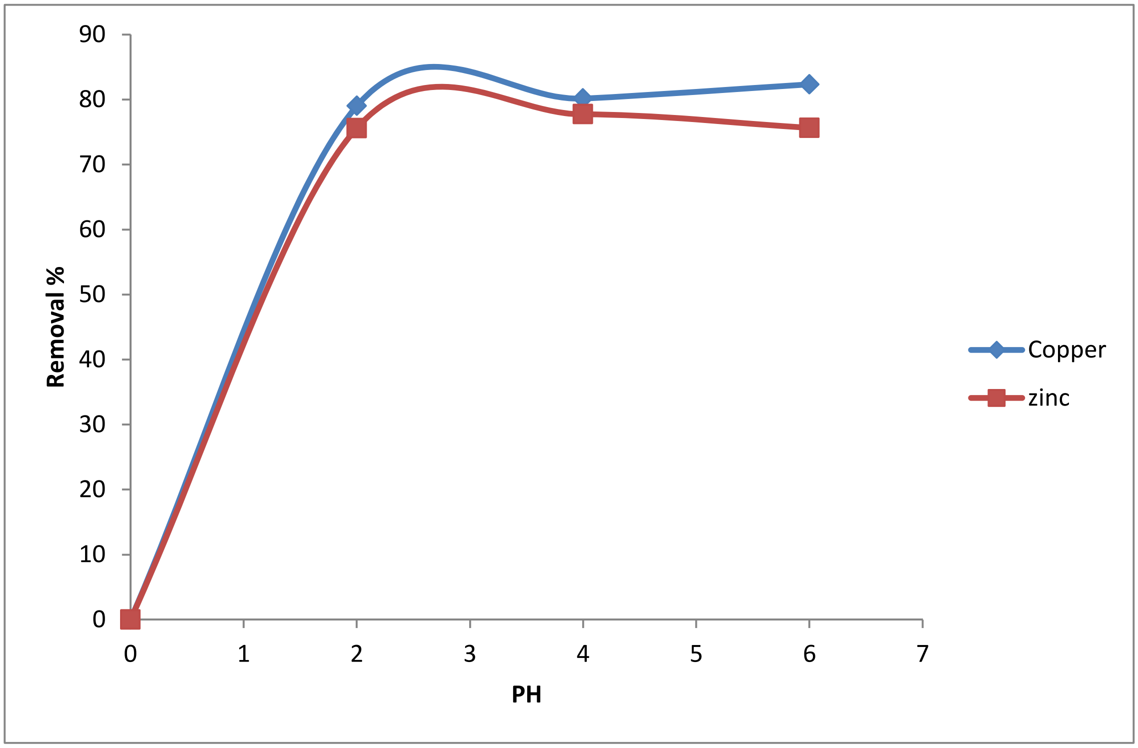

Fig 4.1 Effect of pH on Cu^{2+} and Zn^{2+} removal

4.2. Effect of Adsorbent Dosage

The effect of lignite coal dose (g) on sorptive removal of Cu^{2+} and Cn^{2+} was observed by varying its amount in 200 ml fixed volume of metal solutions. As shown in figure 4.2 results were obtained as lignite coal dosage was varied over the range 0.5-2 gm/200ml. Other constraints were kept constant at PH 6 for cupper and 4 for zinc and contact time of 120 min for both metal ions.

The removal efficiency of copper increased from 82.34% to 86.53% and that of Zn from 79.47% to 83.35% as the lignite coal dosage was increased from 0.5g to 2g in 200 ml of metal solution. This adsorption increment attributed to the fact that the increase in percentage removal of metal ions with increase in adsorbent dose is due to the availability of more and more adsorbent surfaces for the solutes to adsorb (Prabha & Udayashankara, 2014).

Table 4.2 Effect of lignite coal dose on % removal and sorption capacity of lignite coal

Metals	**Dose (g)**	**% Removal**	**q_e(mg/gm)**
Cu^{2+}	0.5	59.67	11.94
	1	68.84	13.768
	1.5	79.32	15..864
	2	86.53	17..306
Zn^{2+}	0.5	53.78	10.756
	1	63.63	12.726
	1.5	73.43	14.687
	2	80.52	16.104

Up to 2 gm of adsorbent dosage, both metals removal efficiency was rapid. Optimum dose was chosen for 2g of sorbent beyond which can change in the amount of metal removal was observed. This constant rate of adsorption is attributed to saturation of the adsorbent binding sites or equilibrium between liquid and solid phase (Deepa & Suresha, 2014). On the other hand, the adsorption capacity of lignite coal for both metals was increased as dose increased. Because this can be justified as that adsorption capacity is the ability of adsorbent (g) to capture metal ions (mg) in the fixed volume of wastewater (ml) (Itodo et al., 2014).

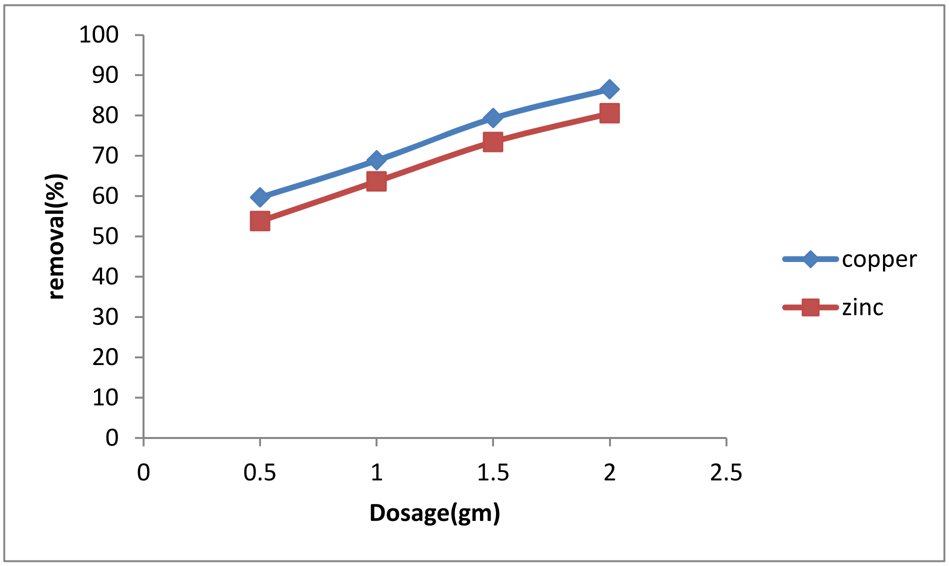

Fig 4.2. Effect of lignite coal dosage on $Cu^{2+}$and Zn^{2+} removal

4.3. Effect of contact time

Fig.4.3. shows the time profiles of lignite coal adsorption of Cu^{2+} and Zn^{2+}**.** Adsorption of $Cu^{2+}$and zn^{2+} showed an increasing trend up to a reaction time of 60min beyond which adsorption appeared to have approached equilibrium. After 90 min, the adsorption capacity of $Cu^{2+}$and Zn^{2+} by lignite coal was constant and % removal increment is almost negligible. After 120 min, all got equilibrium.

Table 4.3 Effect of contact time on % removal and sorption capacity of lignite coal

Metals	**Time (min)**	**Initial conc.(mg/l)**	**Final conc.(mg/l)**	**Dose (gm)**	**% Removal**	**qe(mg/gm)**
Cu^{2+}	0	0	0	0	0	0
	30	200	29.76	0.5	85.12	68.096
	60	200	28.22	1	85.89	34.356
	90	200	27.12	1.5	86.44	23.0506
	120	200	26.94	2	86.53	17.306
Zn^{2+}	0	0	0	0	0	0
	30	200	41.94	0.5	79.03	63.22
	60	200	41.10	1	79.45	31.78
	90	200	38.48	1.5	80.76	21.536
	120	200	38.36	2	80.82	2.3

Contact time required to attain equilibrium is dependent on the initial concentration of heavy metals. For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is attained (Thakur & Parmar, 2013). The result showed that the optimal contact time of Cu^{2+} and $Zn^{2+}$to attain equilibrium with lignite coal adsorbent was 120 and 90 minutes with removal efficiency of 86.44% for copper and 80.76% for zinc respectively.

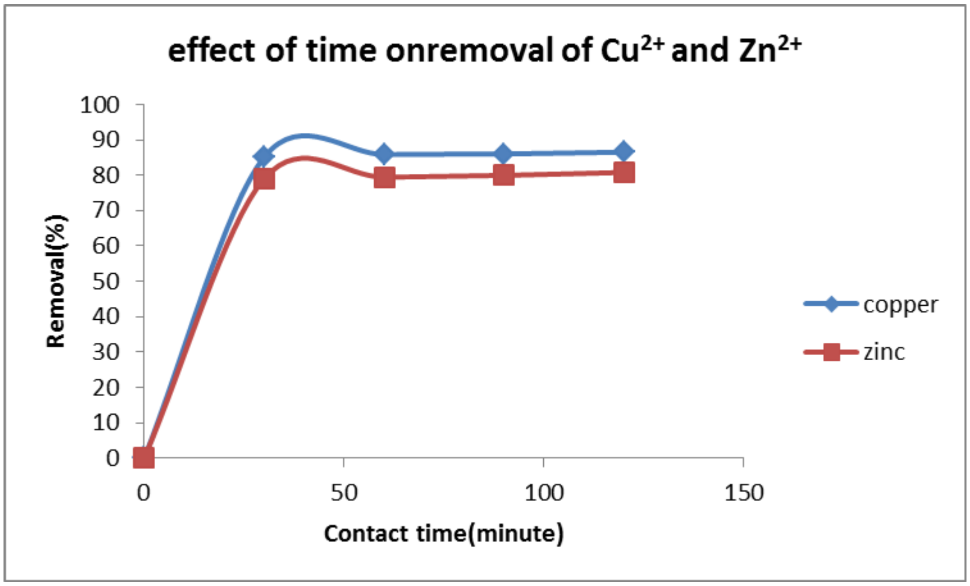

Fig.4.3. Effect of contact time on$Cu^{2+}$and Zn^{2+}removal

4.4. Effect of initial metal ions concentration

As the result showed infig.4.5 and table.4.4 that adsorption capacity increased with increasing concentration of adsorbate. For Cu^{2+}there is an increase from 8.67mg/g to 16.468mg/g when initial concentration was increased from 100mg/l to 200mg/l and for $Zn^{2+}$from 6.78mg/g to 13.41mg/g. For both metal ions adsorption capacity increased as their initial concentrations increase. This may be justified that increase in metal ions concentration results in increase in number of available molecules per binding sites of the adsorbent. Increase in initial metal ions concentration enhances the interaction between the metal molecules and the surface of the adsorbent (Itodo et al., 2014)

Table 4.4 Effect of initial conc. on % removal and sorption capacity of lignite coal

Metals	Initial con.	pH	% Removal	q_e(mg/gm)
Cu^{2+}	100	2	79.01	8.67
	150	4	80.15	12.52
	200	6	82.34	16.468

Zn^{2+}	100	2	75.6	6.78
	150	4	77.72	9.91
	200	6	75.64	13.41

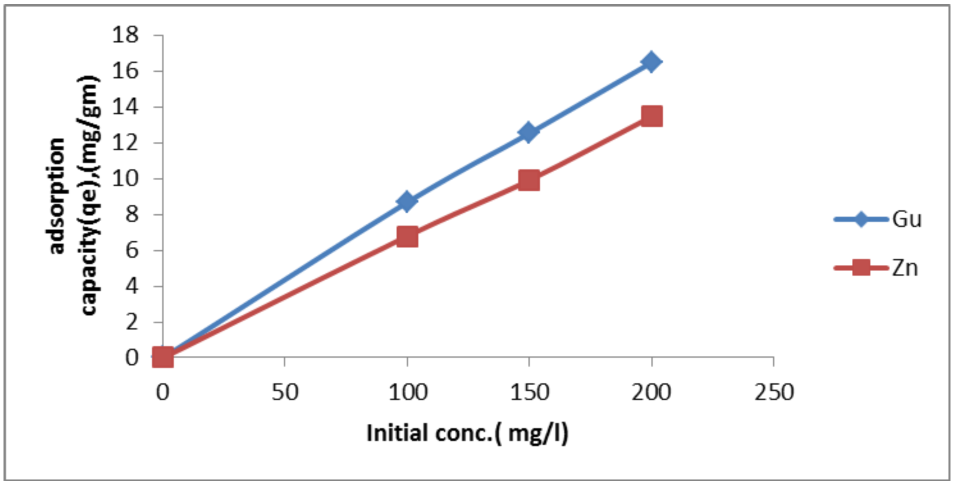

Fig.4.4. Effect of initial metal ions concentration on removal and adsorption capacity of $Cu^{2+}$and Zn^{2+}

Table. 4.5. Effect of pH on initial concentration and removal efficiency of lignite coal

PH	Initial con.	R%
0	0	0
2	100	68.69
2	150	68.9
2	200	68.9
0	0	0
4	100	73.54
4	150	73.54
4	200	73.54
0	0	0
6	100	81.74
6	150	81.74
6	200	81.74
0	0	0
2	100	50.76
2	150	50.76
2	200	50.76
0	0	0
4	100	77.09

4	150	77.09
4	200	77.09
0	0	0
6	100	62.65
6	150	62.65
6	200	62.65

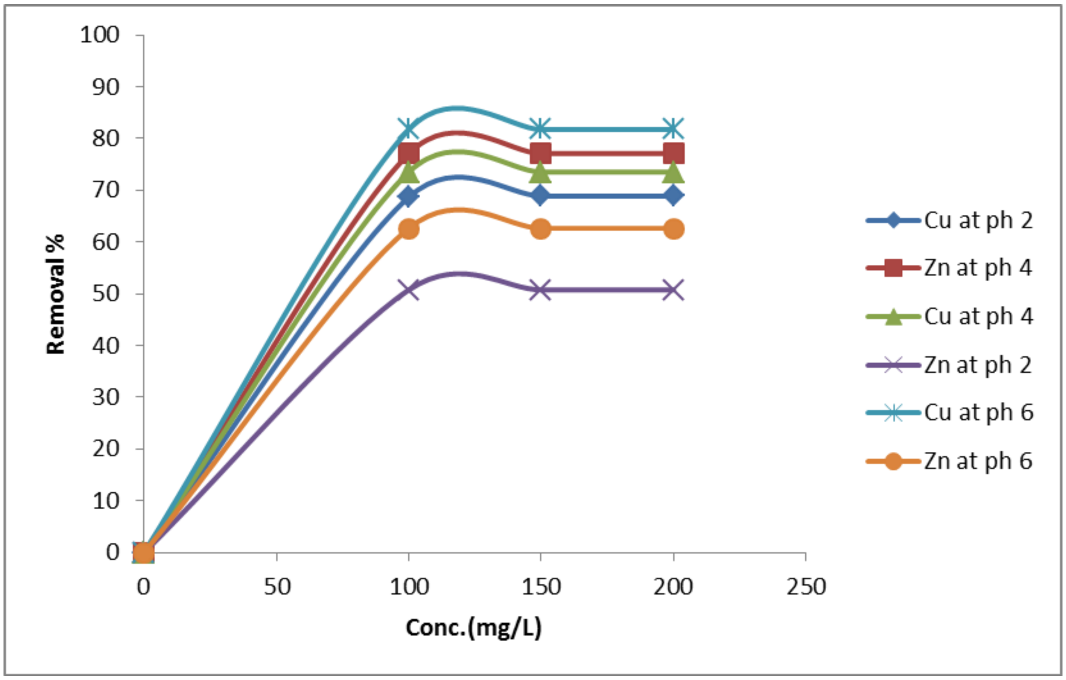

Fig.4.5. Effect of pH on initial concentration and removal efficiency of lignite coal

4.5. Adsorption Isotherms

The adsorption Isotherm for Cu^{2+} and Zn^{2+}metal ions was studied. The concentrations of the metal ions in their equilibrium pH and that in the lignite coal at a room temperature were studied to know the maximum sorption capacity of the lignite coal for the metal ions. To determine this maximum sorption capacity of lignite coal Langmuir and Freundlich isotherm models were used. Langmuir and Freundlich Isotherm Correlation coefficient and constants of the sorption of $Cu^{2+}$and Zn^{2+} lignite coal were obtained from the slope and intercept of the plot of amount of sorbed metal ions per unit mass, q_e against equilibrium concentration of metal ions remaining in solution, C_e shown in Fig 4.6-4.9. The different isotherm parameters from the different plots are tabulated in table 4.6 below.

Table.4.6.adsorption isotherm

Metals	Initial con.	pH	% Removal	q_e(mg/gm)	Ce/qe
Cu^{2+}	100	2	79.01	8.67	11.534
	150	4	80.15	12.52	11.98
	200	6	82.34	16.468	12.144
Zn^{2+}	100	2	75.6	6.78	14.74
	150	4	77.72	9.91	14.98
	200	6	75.64	13.41	15.10

The correlation coefficients (R^2) of Langmuir model and Freundlich isotherm models with a correlation coefficient (R^2) for the adsorption of and Zn^{2+} were 0.9945 and 0.9979, respectively, which were slightly higher than the R^2 values of Freundlich model for Zn. The result reveals that the adsorption of Zn on lignite coal is well fitted to the Langmuir model, meaning that lignite coal biomass surfaces are homogeneous sorption patches, on which monolayer coverage of Zn ions were formed on the outer surface of the sorbent i.e. lignite coal. Hence the uptake capacity of sorbent of the ion forms mono-layer, having no mutual interaction, on the sorbent surface. (Farooq et al, 2010)

On the other hand the correlation coefficients (R^2) on the sorption of cupper by lignite coal are well fitted to both Langmuir and Freundlich isotherm models with a correlation coefficient (R^2) 0.9995 and 0.9717 respectively.

Freundlich isotherm model constant parameters, K_f and n were determined by linear regression from the plot of log(q_e) against log(C_e). K_f is the degree of adsorption; when K_f value is low it indicates minimal adsorption of heavy metals whereas the higher K_f value suggests greater sorption ability(Oves et al., 2013). For this case, K_f value was highest for Cu^{2+}(0.0757) and it was lowest for Zn^{2+} (0.036) indicating a favorable adsorption according to Freundlich isotherm. The value of n from Freundlich Isotherm was determined for both metal ions. When n>1, the adsorbate is favorably adsorbed on an adsorbent and it indicates the situation of adsorption intensity (Itodo et al., 2014). From this it can be conclude that the two metal ions were favorably adsorbed on lignite coal. The value of n was lower for Cu^{2+} (13.21) but was highest forZn^{2+}

(27.7) suggesting a maximum sorption of $Zn^{2+}$and least of Cu^{2+} according to Freundlich model, but all values favored Freundlich isotherm.

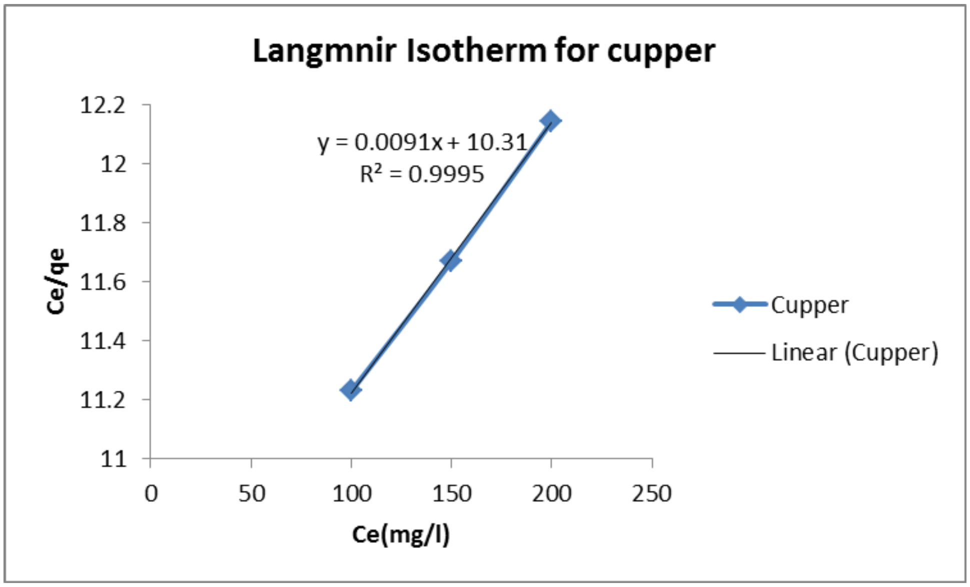

Fig 4.6 Langmuir Isotherm for Cupper adsorption by lignite coal

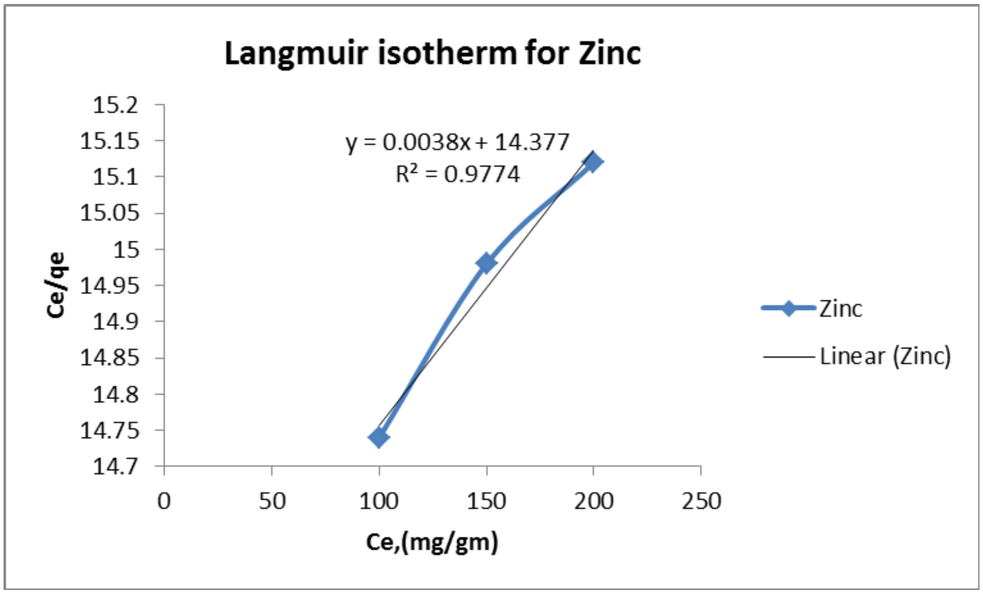

Fig.4.7 Langmuir Isotherm for Zinc adsorption by lignite coal

Tabel.4.7. Freundlich isotherm for cupper

ln(Ce)	ln(Ce/qe)	Ce	Ce/qe	qe
4.6051702	2.445301395	100	11.534025	8.67
5.0106353	2.483307928	150	11.980831	12.52
5.2983174	2.496898263	200	12.144766	16.468

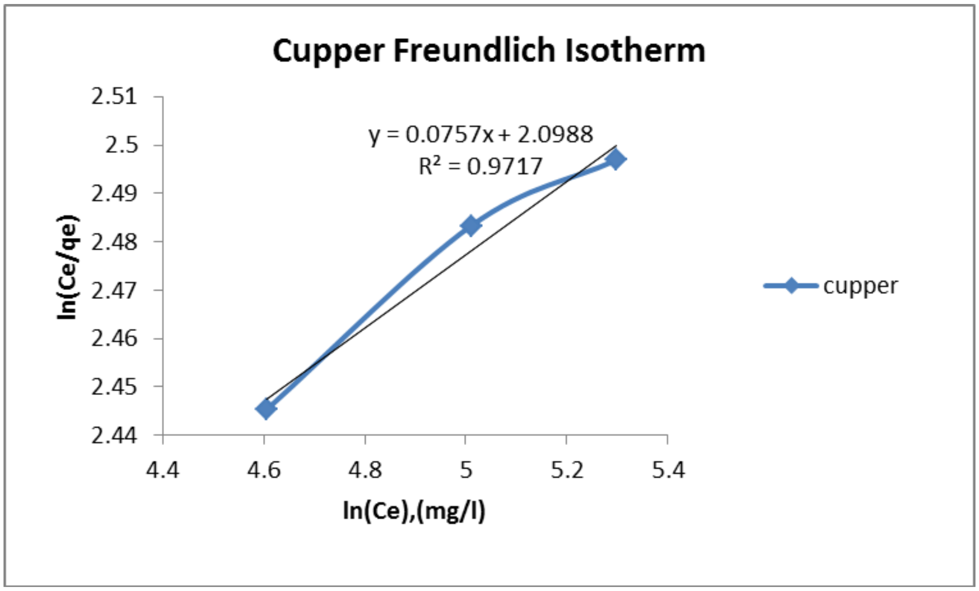

Fig.4.8.Freundlich Isotherm for Cupper adsorption by lignite coal

Tabel.4.8.Freundlich isotherm for cupper

ln(Ce)	ln(Ce/qe)	Ce	qe	Ce/qe
4.6051702	2.691193084	100	6.78	14.749263
5.0106353	2.706715978	150	9.91	14.98
5.2983174	2.716018371	200	13.45	15.12

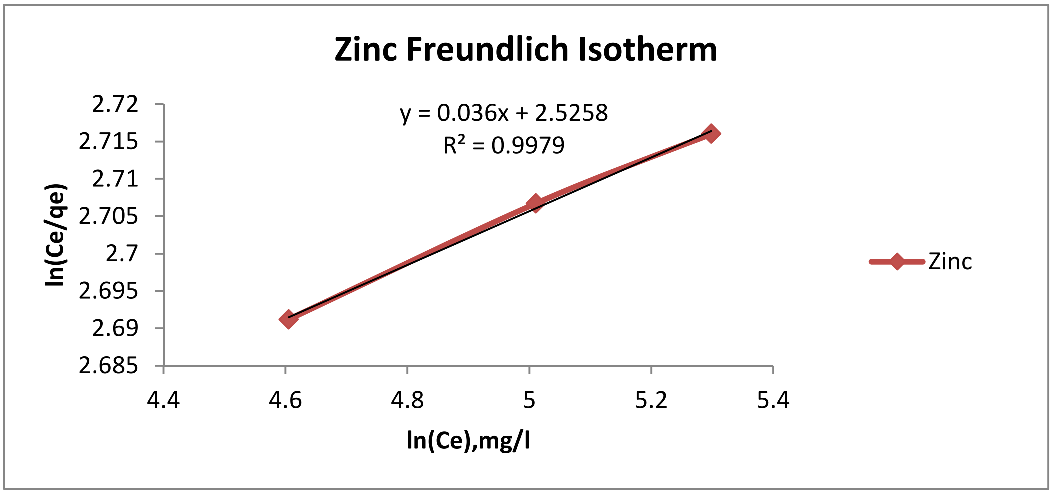

Fig.4.9.Freundlich Isotherm for zinc adsorption by lignite coal

Generally, from Langmuir Isotherm model the value of maximum sorption capacity, q_m of lignite coal for adsorption of Cu^{2+} were 16.468which is greater than for adsorption of Zn^{2+}, 13.45 mg/g. The constant parameter K_L in Langmuir equation is related to the energy of adsorption (Mehrasbi et al., 2009) and K_L values for adsorption of Cu^{2+} was greater thanZn^{2+}.

Table. 4.9. Langmuir and Freundlich Isotherm Correlation coefficient and constants of the Sorption of Cu^{2+} and $Zn^{2+}$by lignite coal.

Heavy metal ions	**Langmuir Isotherm**			**Freundlich Isotherm**		
	R^2	Q_m(mg/gm)	K_L(l/mg)	K_f (mg/g)	n	R^2
Cu^{2+}	0.9995	16.468	10.31	2.0988	13.21	0.9917
Zn^{2+}	0.9945	13.45	14.377	2.5258	27.77	0.9979

4.6. Adsorption kinetics

Pseudo first and second order kinetic models have been used to analyze data obtained from different sorption experiments of $Cu^{2+}$and Zn^{2+}onto lignite coal. The pseudo first order plots of $\ln(q_e/q_t)$ versus t for both metal sorption did not give approximate lines in figure 4.10 and the rate constants (k_f) can be calculated from the slope. The experimental and calculated qe values, pseudo-first order rate constants and regration coefficient of determination (R^2) values are given in table 4.11. Since the plots shown on linearity and the R^2values were found to be 0.9971 and 0.9852 for copper and zinc respectively, the calculated qe values (q_{cal}) we not in agreement with the experimental qe values (q_{exp}).

A pseudo second order kinetic model was applied to fit the experimental data. It was plotted t/q against t and constant parameters of k_s and h values were determined in for the slopes and intercepts. The linear pseudo-second order equation showed good agreement of experimental data with correlation coefficients 0.9994 and 0.9988 for copper and zinc respectively as shown in table 4.13 and figure 4.12.The experimental and calculated qe values, pseudo second order rate constants are in good agreement with those obtained experimentally. The applicability of this model suggested that sorption of Copper and Zinc on lignite coal was based on chemical reaction, between metals and active sites of the sorbent.

Tabel 4.10.pseudo first order for cupper

qe	qt	Time	ln(qe-qt)	C0
4.46	0.34	30	0.567	50
6.78	0.71	60	1.07	100
9.91	0.87	90	1.487	150
13.45	0.98	120	1.89	200

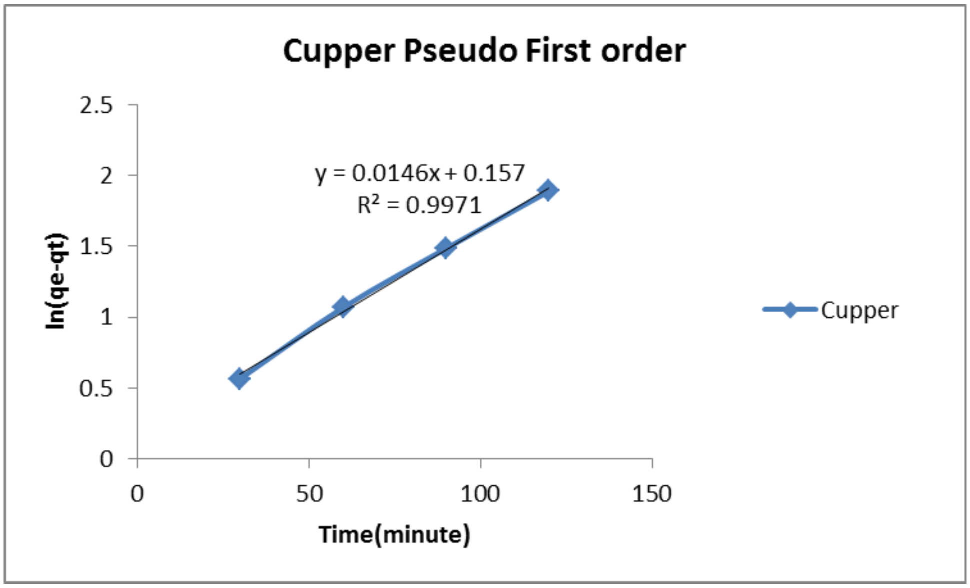

Fig 4.10 Pseudo first order for sorption of Cupper

Tabel.4.11. pseudo first order for zinc

qe	qt	Time	ln(qe-qt)
10.35	3.4	30	0.345
14.74	5.65	60	0.765
14.98	6.67	90	1.13
15.12	7.687	120	1.365

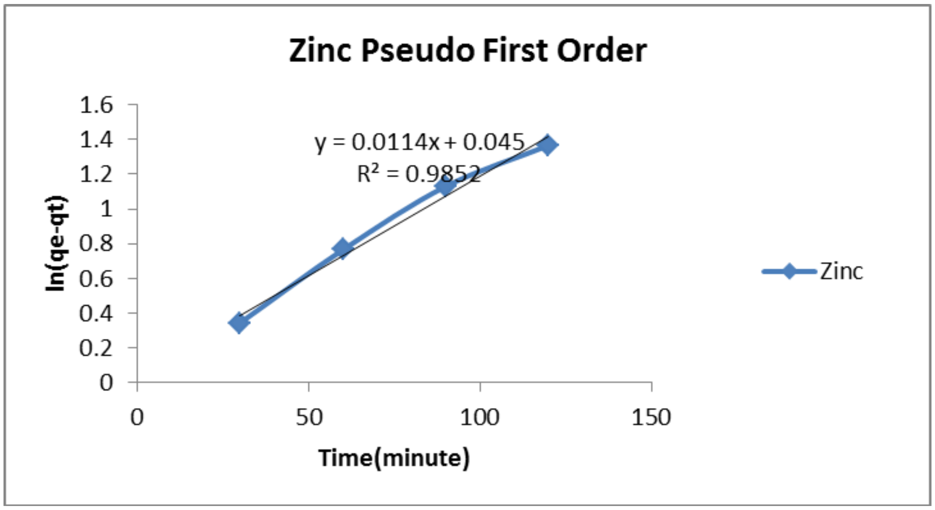

Fig 4.11 Pseudo first order for sorption of Zinc

The initial absorption rate, h was high for both metals. This is attributed to the fact that The initial rapid uptake could be ascribed to the concentration gradient, created at the start of the adsorption process, between solute concentration in solution and that at the lignite coal surface(Itodo et al., 2014).

Table 4.12.pseudo first order for zinc

qt	t	t/qt
Copper		
4.46	30	6.726457
6.78	60	8.5678
9.91	90	10.2346
13.45	120	11.8976
Zinc		
3.4	30	9.0234
5.65	60	11.0456
6.67	90	13.49325
7.687	120	15.61077

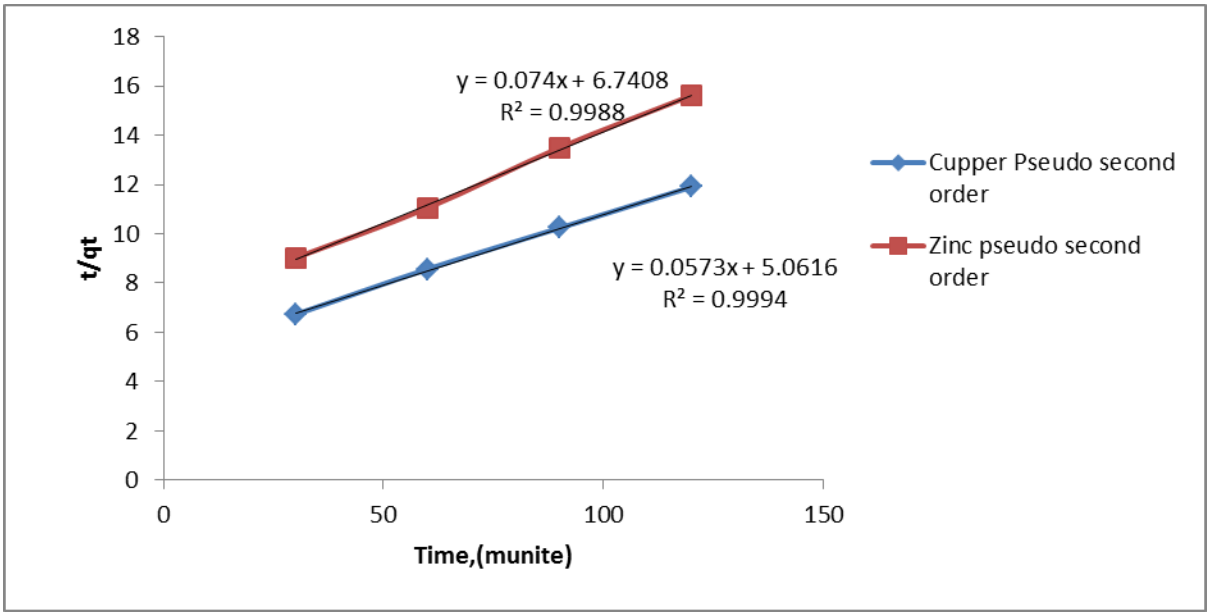

Fig 4.12 Pseudo second order for sorption of Cu and Zn onto lignite coal

Table 4.13Kinetic parameters for the adsorption of Cu and Zn onto lignite coal at temp. of298K.

Metal ions	Pseudo first order			Pseudo second order			
	$Q_{ep't}$(mg/gm)	R^2	K_f(min^{-1})	h(gm/mg/min)	$Q_{ex't}$(mg/gm)	Ks (g/mg/min	R^2
Cu^{2+}	0.0146	0.9971	0.157	0.01661	0.0573	5.0616	0.9994
Zn^{2+}	0.0114	0.9852	0.045	0.0369	0.074	6.7408	0.9988

4.7. Data analysis using Design expert 6.0.8 software

Three basic factors were selected for design expert to determine the total experiment runs. After finding their optimum values the fixed dose of 2gm lignite coal was varied over the range of 0.5gm, 1gm, 1.5gm and 2gm. Additional time level was selected for determining sorption equilibrium and kinetics up to 120 minutes. Initially three factors and three levels were selected to give a total experimental runs of 27 with a factorial design of 3^3 for each metals. The results were replicated two times to improve reliability of the data and that resulted to perform 108 experiments.

A planning matrix was set up to take account of the factors that could influence with responses, such as time, initial metal concentration, and PH of the solution of metals at different levels. Table 4.15 shows the factors and levels chosen for the planning matrix. Table 4.14 shown below the combinations of three levels of planning factors. The experiments were performed in batches at 25°C under constant stirring (200 rpm).

Table 4.14 Factors and levels for the adsorption experiments evaluated for each metal

Factors	Level	Level value	Representation
pH	1	2	0
	2	4	1
	3	6	2
Concentration	1	100mg/l	0
	2	1509mg/l	1
	3	200mg/l	2
Time	1	30min	0
	2	60min	1
	3	90min	2

The aim of applying a factorial design analysis was to identify the most significant factors affecting the metals removal percentages after the sorption process of batch experiments.

Table 4.15: Analysis of variance (ANOVA) - Influence of the factors studied in metal sorption. (A) Cu (R^2= 0.9995); (B) Zn (R^2 = 0.9774)

A)					
Source	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**F Value**	**Prob> F**
Model	22383.89	7	3197.698	13.06651	< 0.0001
A	21918.32	1	21918.32	89.56315	< 0.0001
B	37.05274	1	37.05274	0.151406	0.6990
C	319.5424	1	319.5424	1.305722	0.2591
AB	16.87756	1	16.87756	0.068966	0.7940
AC	91.37248	1	91.37248	0.373368	0.5442
BC	0.00241	1	0.00241	9.85E-06	0.9975
ABC	0.725549	1	0.725549	0.002965	0.9568
Residual	11257.34	46	244.7247		
Lack of Fit	11215.73	19	590.3018	383.1035	< 0.0001
Error	41.60272	27	1.540842		
Total	33641.23	53			
B)					
Source	Sum ofSquares	Degree of Freedom	MeanSquare	FValue	Prob> F
Model	6568.881	7	938.4116	54.71477	< 0.0001
A	5001.351	1	5001.351	291.6074	< 0.0001
B	147.5794	1	147.5794	8.604726	0.0052
C	16.08552	1	16.08552	0.937878	0.3379
AB	7.829728	1	7.829728	0.456518	0.5026
AC	1361.076	1	1361.076	79.35852	< 0.0001
BC	26.41843	1	26.41843	1.540346	0.2209
ABC	8.541276	1	8.541276	0.498005	0.4839
Residual	788.9448	46	17.15097		
Lack of Fit	626.797	19	32.98932	5.493208	< 0.0001
Error	162.1478	27	6.005474		
Total	7357.826	53			

A= pH, B= Time, C= Initial Concentration

The Model generated for both metals adsorption was significant that ANOVA analysis shown in the lower part of Table 4.8 proves the results discussed above at a confidence level of 95%. As shown from table 4.8 values of P less than 0.05 indicate model terms are significant. Results showed that the effect of PH (factor A) is of major importance for sorption of Cupper while A (PH), B(contact time) and combination of A*C(PH and concentration), are significant model terms for zinc removal.

For both metals adsorption the combination of three factors ABC (pH*time*initial concentration) did not affect their sorption efficiency onto lignite coal. As shown from the ANOVA results, PH was the dominant factor that affects cupper and zinc sorption. This result confirmed from many litratures that PH is the main factor influences the sorption pattern of metal ions. For cupper adsorption other main factors including their combination showed insignificant; meaning their contribution was very low. But in the case of zinc sorption, contact time had some significance for its removal. However, the interactions of pH with initial concentration AC (PH and initial concentration) significantly affect sorption of zinc next to pH.

Modeling equations show the removal efficiency of lignite coal in relation to different metals according to the factor levels. Note that the highest coefficients are related to the factors that most influence the efficiency of adsorption (Seolatto et al., 2012).

Cu Removal =+10.51314+14.51846* PH+0.042652* Time+0.17682* Initial con.-4.92349E-003* PH * Time-0.022804* pH * Initial con.+2.64048E-004 * Time *Initial con.-6.76025E-005 * pH * Time * Initial con.

Zn Removal=+107.80458-14.49287* PH+2.60074E-003* Time-0.46905 * Initial con.+0.021423 * PH * Time+0.12498* PH * Initial con.+2.61650E-004* Time * Initial con.-2.31948E-004 * pH * Time * Initial con.

As shown in Figure 4.13, the agreement between the experimental and the predicted values was good. This indicates that there is a linearity relationship between the removal efficiency and the three factors considered.

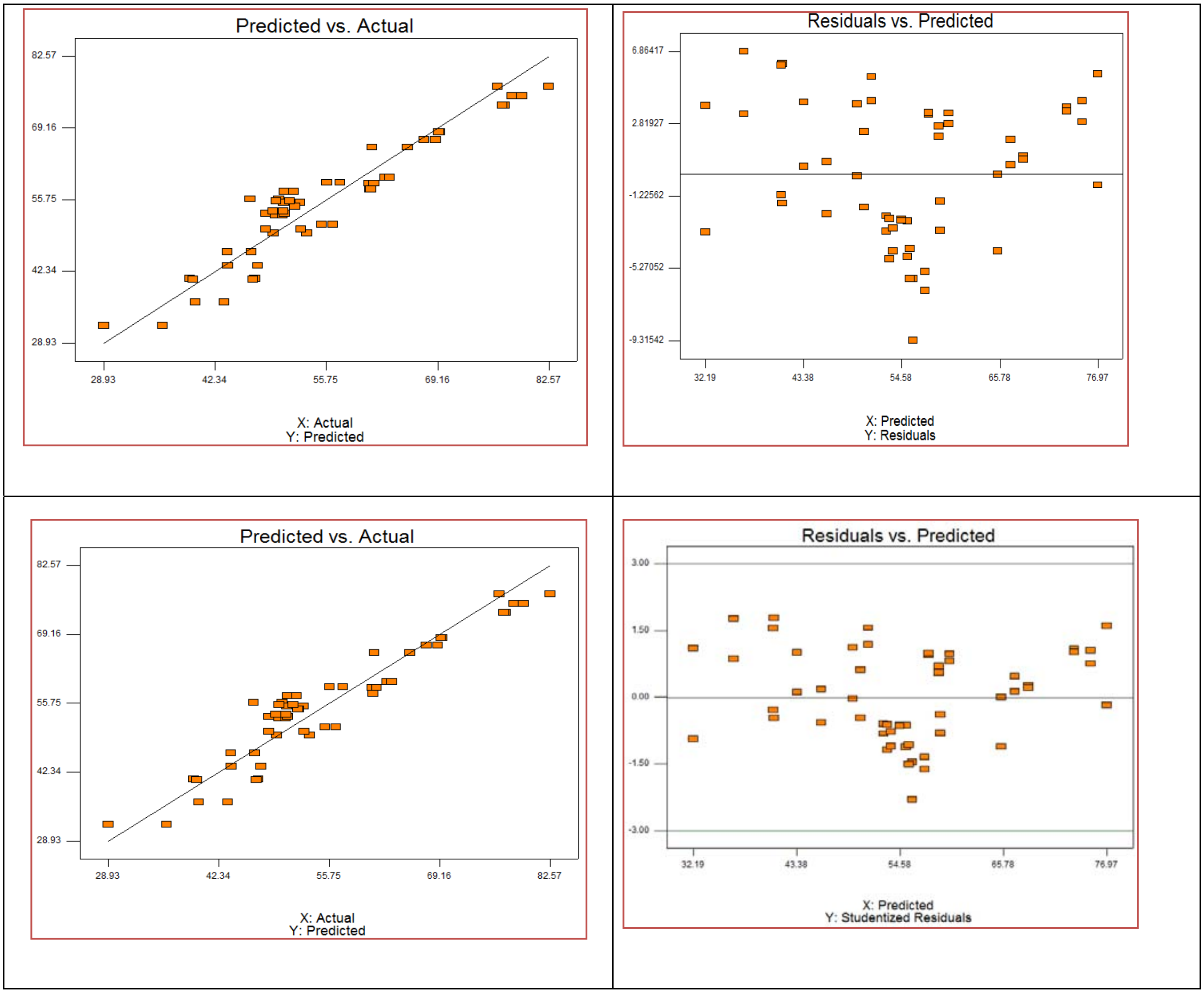

Fig. 4.13 metals sorption (Actual and residual vs. Predicted), for 3^3Factorial Design; A)

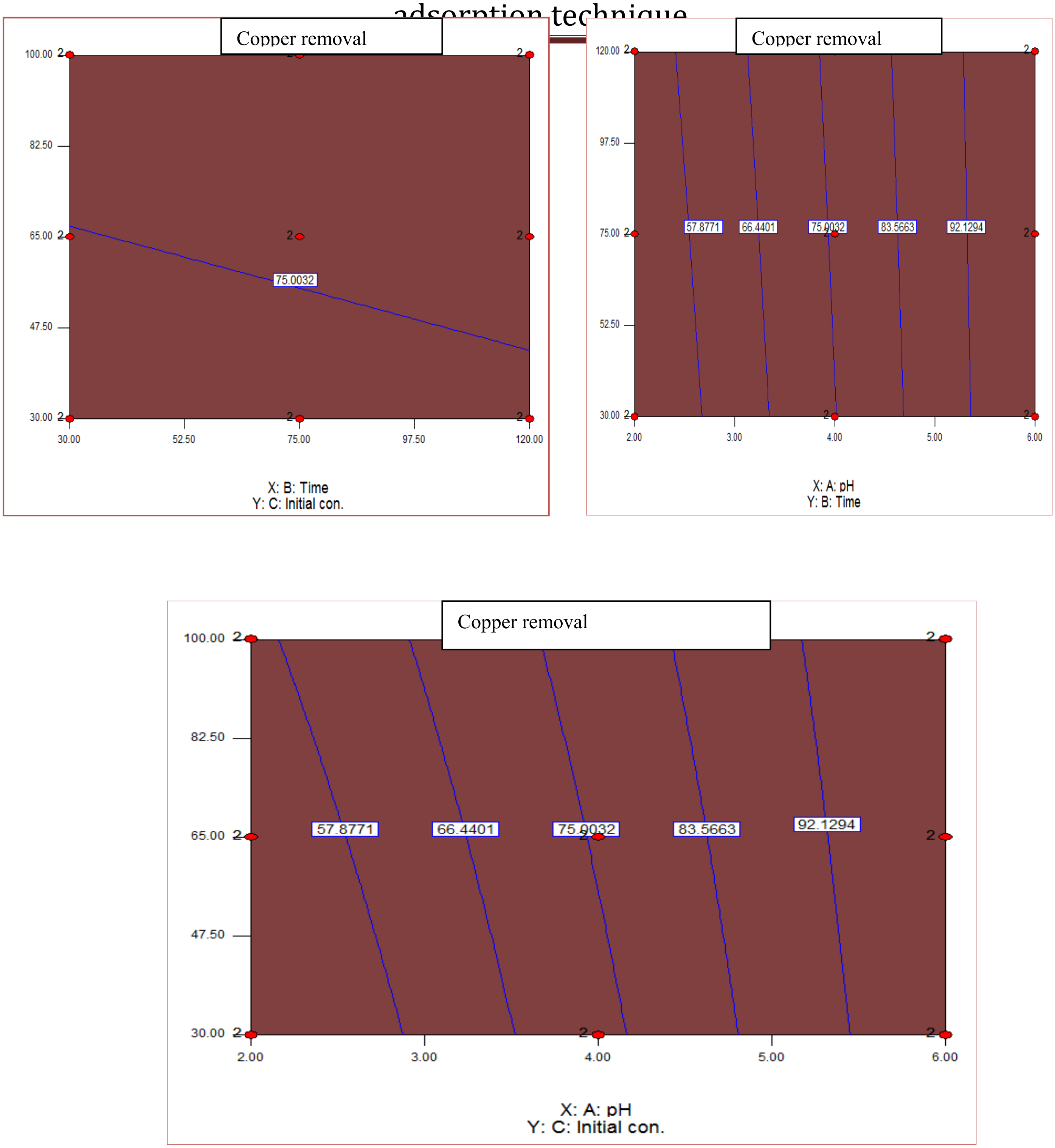

Figure 4.14 Contour Plots for cupper removal plot for 3^3Factorial Design, AB, AC, and BC interaction

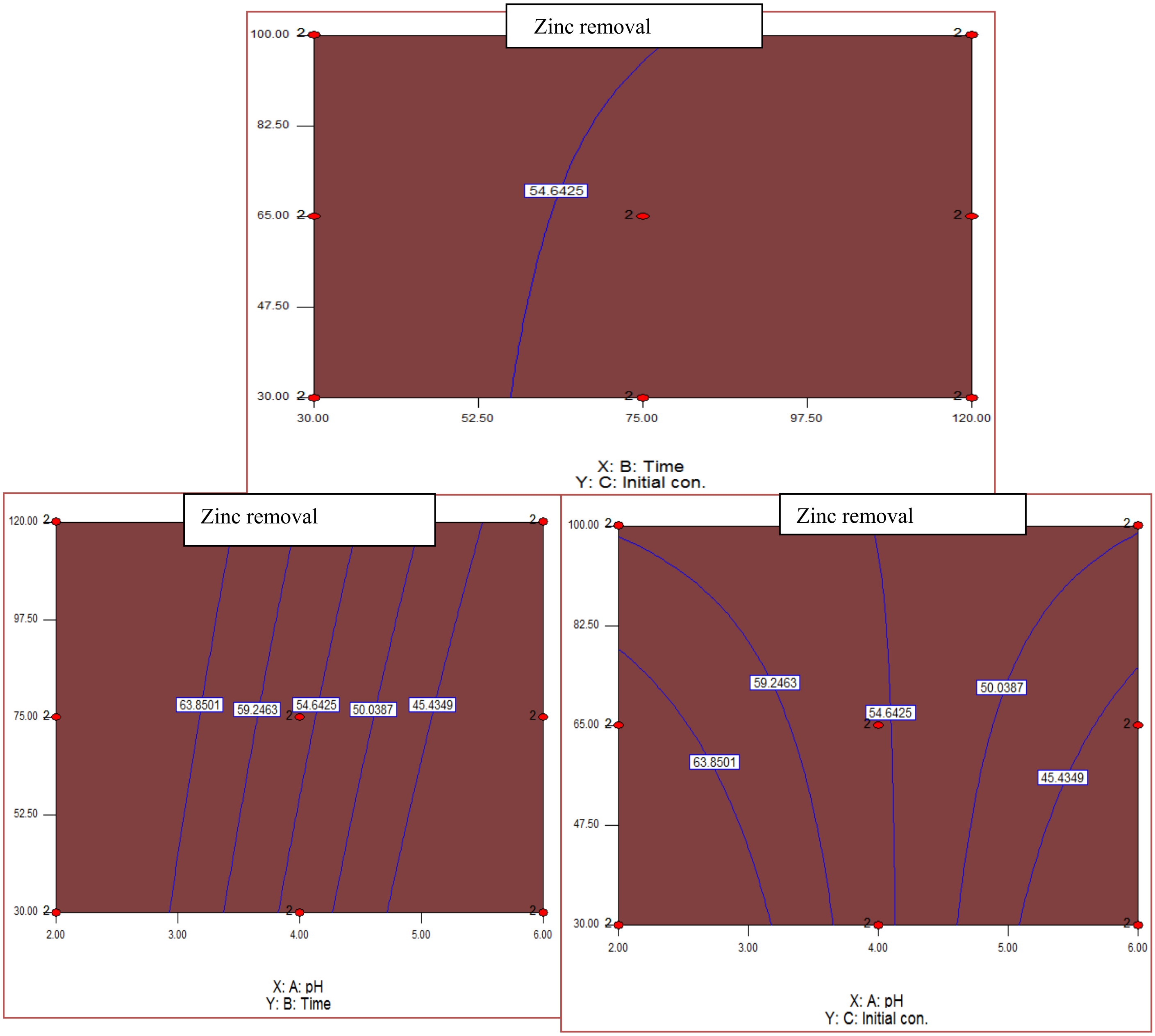

Figure 4.15 Contour Plots for zinc removal plot for 3^3Factorial Design, AB, AC, and BC interaction.

3-D surface plots for the three response variables were also generated and are shown in Figures 4.16 and 4.17. In the case of cupper sorptive removal, these graphs show that for the first response variable (PH); there is a slight interaction between the two factors and the interaction between time and concentration is week. Whereas, for zinc removal the first response variable (PH), the interaction between the two factors is significant, indicating that the two factors are PH dependent.

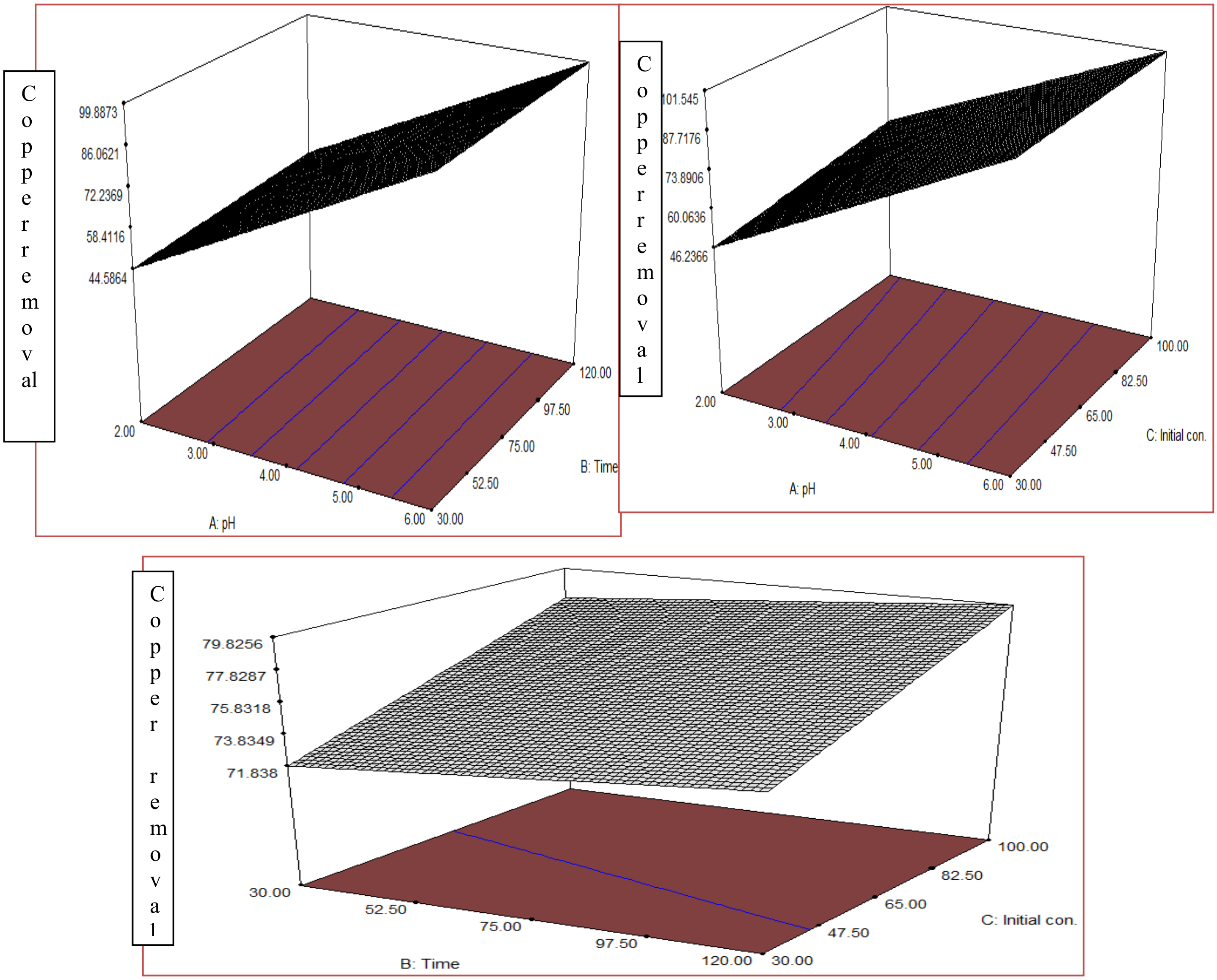

Figure 4.16. 3D surface Plots for cupper removal of 3^3 Factorial Design, AB, AC, and BC interactions.

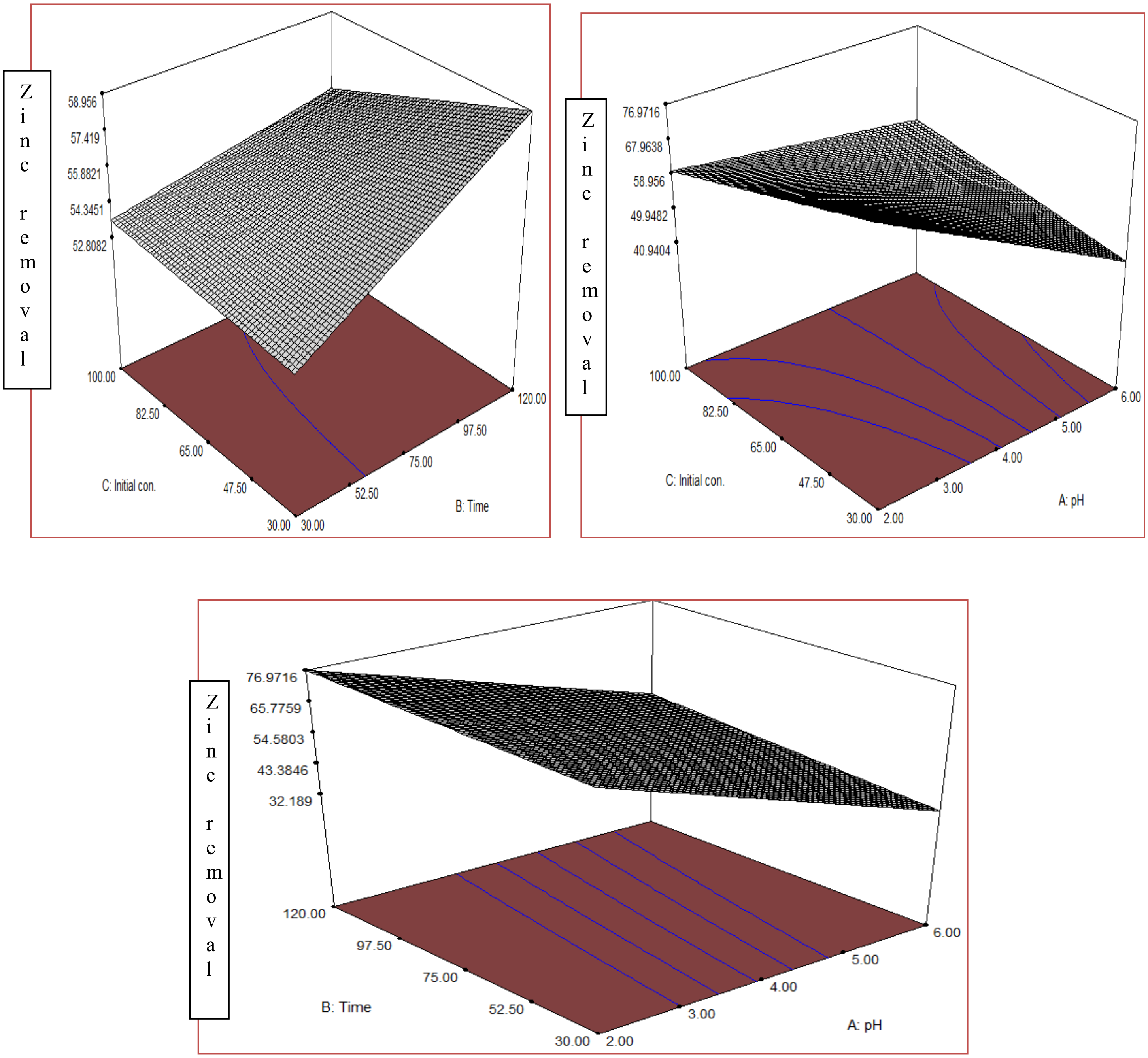

Figure.4.17. 3D surface plots for zinc removal of 3^3Factorial Design, AB, AC, and BC interaction.

4.8. Removal efficiency of lignite coal for real waste water

Attempts were made to apply laboratory experimental results to real wastewater samples in order to move from the experiment to the application in real world. Waste water samples containing copper and zinc were drawn from dejen aviation industry(METEC) electro plating section which is located debrezait, Ethiopia .Their waste is accumulated and finally discharged to the river without proper treatment and the effluent is not complying to the standard limits as it was measured for each metals ion.

Batch sorption was conducted for both metals at their optimum points obtained from prior synthetic waste water batch sorption experiment. The feasibility and efficiency of a sorption process depends not only on the properties of the sorbents, but also on the composition of the waste water (Kratochvil & Volesky, 1998).

For adsorption of wastewater containing Cu, optimum parameters from batch synthetic wastewater adsorption were selected as; PH=6, contact time =120 mins, and lignite coal dosage of 2gm. The initial measured concentration of cupper ions from the wastewater was taken 187.67mg/l. While optimum parameters for zinc batch sorption were; PH=4, contact time =120 mins, and lignite coal dosage of 2gm and its initial concentration in wastewater was 147.45mg/l

Table. 4.16. Optimum parameters chosen for batch copper and zinc adsorption onto lignite coal

Metal ions	Optimum parameters			Real waste water parameters	
	pH	Contact time (min)	Lignite coal dose (gm)	pH	Initial con. (mg/L)
Cu^{2+}	6	120	2gm	6 (after adjusting)	187.67
Zn^{2+}	4	120	2gm	4 (after adjusting)	147.45

After adsorption of waste water containing each metal ions onto lignite coal, it was found that cupper reduction was observed by 63.45% while zinc removal was 59.65%. The results were much lower than the removal efficiency of synthetic waste water containing individual metal ions. This can be justified to the fact that the presence other metal ions in the solution affect the removal efficiency by competing one another to the adsorbent site.

5. Conclusion and Recommendation

5.1. Conclusion

Lignite coal is a cheap and effective adsorbent for the removal of Cu and Zn ions from electroplating industrial waste water without requiring any pretreatment. Experiment results showed that maximum removal of Cupper ion by lignite coal at optimum condition (6 PH, 120 min. contact time, 2g adsorbent dose and 200ppm concentration) is 82.32% and for Zinc ion are 77.54% at optimum condition (4 PH, 90 min. contact time and 1.5g adsorbent dose, 150ppm concentration). These experimental studies on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated industrial effluents.

From the present work it can be conclude that lignite coal has been shown to be a potentially useful material for the removal of copper and zinc from aqueous solutions. Significant data were obtained through this study that showed lignite coal is attractive sorbent material because of its rapid uptake and high sorption capacity of metal ions. This high removal efficiency of lignite coal is attributed to the complex nature of its surface and broad ranges of functional groups present, according to AAS analysis.

Batch sorption study revealed that the adsorption of Copper and zinc ions onto lignite coal were heavily dependent on the amount of dosage, time of contact, initial concentration and PH of the metals solution. Among operational parameters, PH was found to be dominant factor as per analysis of ANOVA and optimal PH for copper and zinc was 6 and 4, respectively. Isothermal data of metal ions sorption by brewery spent grain indicated that, the sorption process followed to both the Langmuir and Freundlich models. Data analyzed from the models, showed the adsorption capacity of lignite coal for copper found to be higher than zinc. From this, it can be concluded that the affinity lignite coal for cupper was greater than zinc. The kinetics of sorption was well represented by pseudo second order kinetic model.

These experimental studies on lignite would be quite useful in developing an appropriate technology for the removal of contaminated industrial effluents containing heavy metal ions such as copper and zinc. Hence test was conducted in removing of copper and zinc from electroplating waste using lignite coal as adsorbent. The results showed that the removal efficiency for copper and zinc from electroplating waste was 63.45 and 59.65% respectively. This reduction of removal efficiency confirmed to the fact that the present of other metal ions inhibit the adsorbent site by competing one another to be sorbed. The affinity to the sorbent would be the governing mechanism for sorption of metals.

5.2. Recommendation

Based on the results gained from the study, the following suggestions have been made for future work.

Batch adsorption can be carried out by considering other excluded parameters such as various particle size, temperature and stirring rpm. In the present study the mentioned parameters effect was made to be constant.

Regeneration of the sludge can be done which involves the fate of the metal loaded biomass after the adsorption process. Regenerated the sludge can be used for another cycle of adsorption until it become exhausted. The final cycle of metal ions loaded with lignite coal disposal should be to the landfill or incineration.

Column adsorption can be developed to move laboratory batch adsorption results into practical real wastewater treatment containing heavy metal ions. The development of the adsorption processes by lignite coal requires further investigation in the direction of modeling, of regeneration of adsorbent material and of testing immobilized raw biomasses with industrial effluents.

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7. Appendix

Appendix A: Results for removal of cu and zn using AAS from bless Agri Food Laboratory Services PLC

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Test Report

Client Address
ADDIS ABABA INSTITUTE OF TECHNOLOGY
Tel: +251 910 017534
Addis Ababa,
Ethiopia

Bless Agri Food Laboratory Services P.L.C.
Client Ref No. : -
Letter Dated : -
Technical Signatory : Henok Ashagrie
Tel : +251 116 679224
Report No. : BLR1720516
Customer Sample Batch : -

Lab Reg. No:- 1190516 – 1270516
Date of Sampling:- -
Date Sample Received:- 17-05-16
Reference of the Sample:- Waste Water
Date Reported:- 24-05-16

Identification	Customer Sample Batch	Test Method Reference	Copper	Unit
BSC1657/16	Run 1	*FAAS*	22.91	*mg/l*
BSC1658/16	Run 2		58.71	*mg/l*
BSC1659/16	Run 3		47.67	*mg/l*
BSC1660/16	Run 4		20.99	*mg/l*
BSC1661/16	Run 5		39.07	*mg/l*
BSC1662/16	Run 6		45.22	*mg/l*
BSC1663/16	Run 7		24.06	*mg/l*
BSC1664/16	Run 8		45.59	*mg/l*
BSC1665/16	Run 9		51.80	*mg/l*

Remark:- Sample Prepared and Sampled by Client (Hile Hiluf)

Checked by: ____________ Approved by: ____________

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Ethiopia

Bless Agri Food Laboratory Services P.L.C.
Client Ref No. : -
Letter Dated : -
Technical Signatory : Henok Ashagrie
Tel : +251 116 679224
Report No. : BLR1730516
Customer Sample Batch : -

Lab Reg. No:- 1280516 – 1360516
Date of Sampling:- -
Date Sample Received:- 17-05-16
Reference of the Sample:- Waste Water
Date Reported:- 24-05-16

Identification	Customer Sample Batch	Test Method Reference	Copper	Unit
BSC1666/16	Run 10	*FAAS*	33.09	*mg/l*
BSC1667/16	Run 11		40.69	*mg/l*
BSC1668/16	Run 12		46.73	*mg/l*
BSC1669/16	Run 13		28.82	*mg/l*
BSC1670/16	Run 14		44.09	*mg/l*
BSC1671/16	Run 15		44.08	*mg/l*
BSC1672/16	Run 16		24.85	*mg/l*
BSC1673/16	Run 17		44.24	*mg/l*
BSC1674/16	Run 18		39.73	*mg/l*

Remark:- Sample Prepared and Sampled by Client (Hile Hiluf)

Checked by: ______________ Approved by: for ______________

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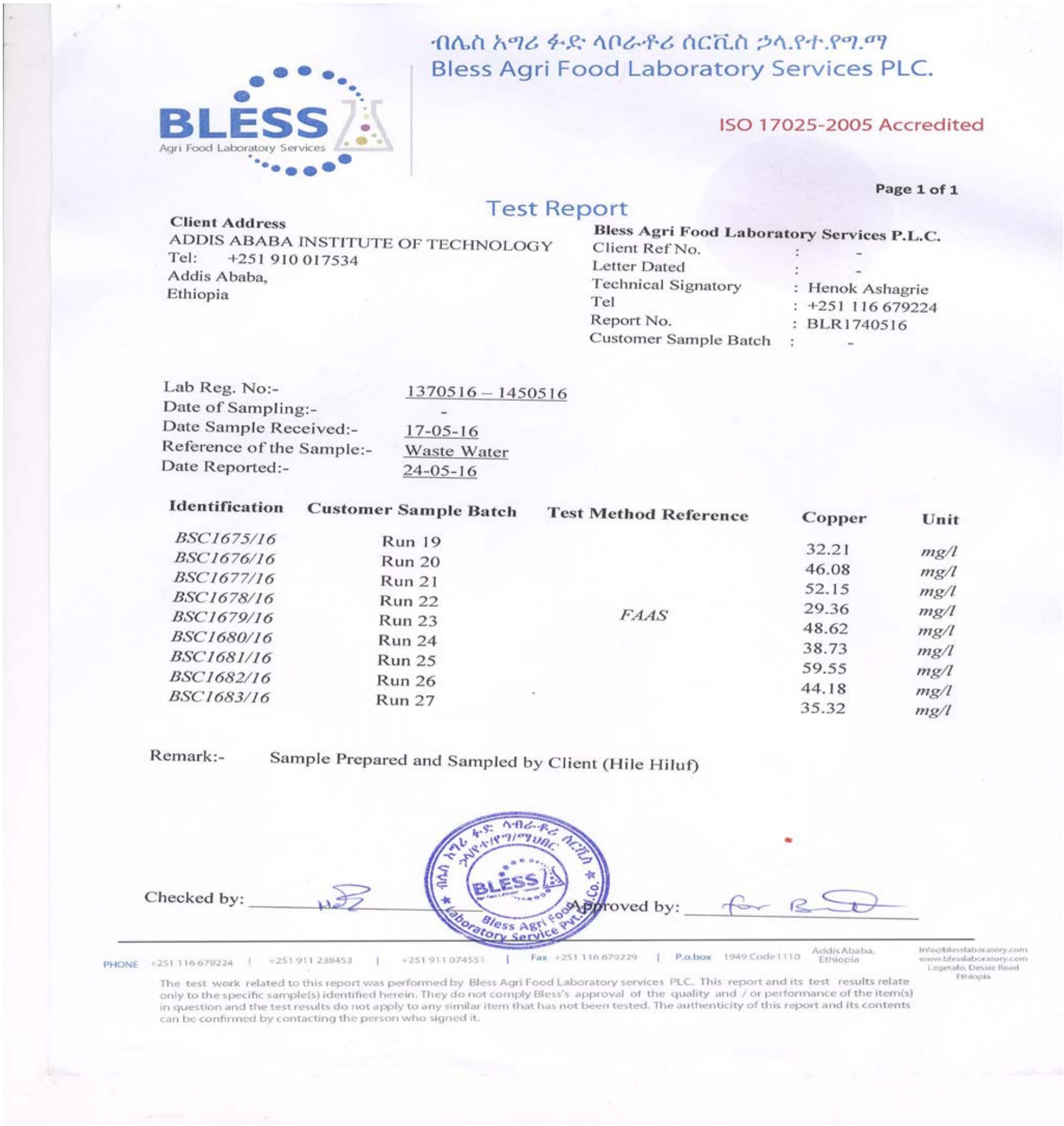

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Ethiopia

Bless Agri Food Laboratory Services P.L.C.
Client Ref No. : -
Letter Dated : -
Technical Signatory : Henok Ashagrie
Tel : +251 116 679224
Report No. : BLR1740516
Customer Sample Batch : -

Lab Reg. No:- 1370516 – 1450516
Date of Sampling:- -
Date Sample Received:- 17-05-16
Reference of the Sample:- Waste Water
Date Reported:- 24-05-16

Identification	Customer Sample Batch	Test Method Reference	Copper	Unit
BSC1675/16	Run 19	*FAAS*	32.21	*mg/l*
BSC1676/16	Run 20		46.08	*mg/l*
BSC1677/16	Run 21		52.15	*mg/l*
BSC1678/16	Run 22		29.36	*mg/l*
BSC1679/16	Run 23		48.62	*mg/l*
BSC1680/16	Run 24		38.73	*mg/l*
BSC1681/16	Run 25		59.55	*mg/l*
BSC1682/16	Run 26		44.18	*mg/l*
BSC1683/16	Run 27		35.32	*mg/l*

Remark:- Sample Prepared and Sampled by Client (Hile Hiluf)

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Client Ref No. : -
Letter Dated : -
Technical Signatory : Henok Ashagrie
Tel : +251 116 679224
Report No. : BLR1750516
Customer Sample Batch : -

Lab Reg. No:- 1460516 – 1540516
Date of Sampling:- -
Date Sample Received:- 17-05-16
Reference of the Sample:- Waste Water
Date Reported:- 24-05-16

Identification	Customer Sample Batch	Test Method Reference	Zinc	Unit
BSC1684/16	Run 1	*FAAS*	24.40	*mg/l*
BSC1685/16	Run 2		33.41	*mg/l*
BSC1686/16	Run 3		80.26	*mg/l*
BSC1687/16	Run 4		44.78	*mg/l*
BSC1688/16	Run 5		40.88	*mg/l*
BSC1689/16	Run 6		73.75	*mg/l*
BSC1690/16	Run 7		43.77	*mg/l*
BSC1691/16	Run 8		39.11	*mg/l*
BSC1692/16	Run 9		68.53	*mg/l*

Remark:- Sample Prepared and Sampled by Client (Hile Hiluf)

Checked by: ________ Approved by: ________

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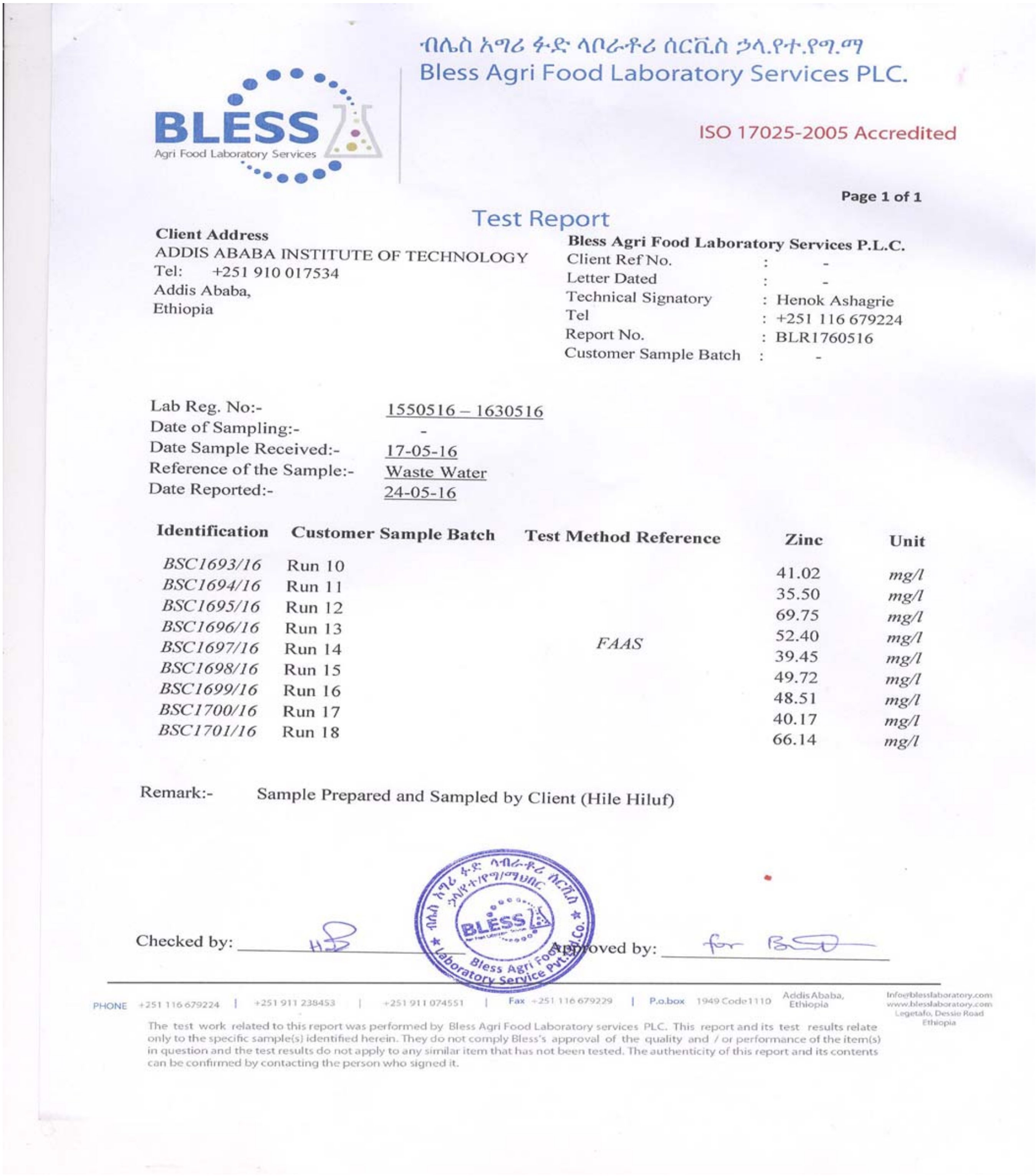

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Client Ref No. : -
Letter Dated : -
Technical Signatory : Henok Ashagrie
Tel : +251 116 679224
Report No. : BLR1760516
Customer Sample Batch : -

Lab Reg. No:- 1550516 – 1630516
Date of Sampling:- -
Date Sample Received:- 17-05-16
Reference of the Sample:- Waste Water
Date Reported:- 24-05-16

Identification	**Customer Sample Batch**	**Test Method Reference**	**Zinc**	**Unit**
BSC1693/16	Run 10	*FAAS*	41.02	*mg/l*
BSC1694/16	Run 11		35.50	*mg/l*
BSC1695/16	Run 12		69.75	*mg/l*
BSC1696/16	Run 13		52.40	*mg/l*
BSC1697/16	Run 14		39.45	*mg/l*
BSC1698/16	Run 15		49.72	*mg/l*
BSC1699/16	Run 16		48.51	*mg/l*
BSC1700/16	Run 17		40.17	*mg/l*
BSC1701/16	Run 18		66.14	*mg/l*

Remark:- Sample Prepared and Sampled by Client (Hile Hiluf)

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Client Ref No.	:	-
Letter Dated	:	-
Technical Signatory	:	Henok Ashagrie
Tel	:	+251 116 679224
Report No.	:	BLR1770516
Customer Sample Batch	:	-

Lab Reg. No:-	1640516 – 1720516
Date of Sampling:-	-
Date Sample Received:-	17-05-16
Reference of the Sample:-	Waste Water
Date Reported:-	24-05-16

Identification	Customer Sample Batch	Test Method Reference	Zinc	Unit
BSC1702/16	Run 19	*FAAS*	32.60	*mg/l*
BSC1703/16	Run 20		34.60	*mg/l*
BSC1704/16	Run 21		68.10	*mg/l*
BSC1705/16	Run 22		44.14	*mg/l*
BSC1706/16	Run 23		37.33	*mg/l*
BSC1707/16	Run 24		48.72	*mg/l*
BSC1708/16	Run 25		46.77	*mg/l*
BSC1709/16	Run 26		43.58	*mg/l*
BSC1710/16	Run 27		77.30	*mg/l*

Remark:- Sample Prepared and Sampled by Client (Hile Hiluf)

Checked by: ____________

Approved by: for ____________

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Appendix B: Adsorption Isotherms

- The linear form of the Langmuir equation:

$Ce/q_e = 1/Kq_m + C_e/q_m$

Where C_e is the concentration of the sorbate at equilibrium (mg/L), q_e is the amount of sorbate sorbed at equilibrium per unit mass (mg/g), $q_m$is the monolayer sorption capacity at equilibrium (mg/g) and k is the Langmuir equilibrium constant (l/mg).

- The linearized form of Freundlich equation is:

$Ln(q_e) = (1/n)\ ln(C_e) + ln(K_f)$

Where K_f and n are Freundlich adsorption constants, related to adsorption capacity and sorption intensity respectively.

Table B1: Langmuir models for sorption of Copper and Zinc onto lignite coal

Copper	
Ce	Ce/qe
100	11.23
150	11.66
200	12.144
Zinc	
100	14.74
150	14.98
200	15.12

Table B2: Freundlich models for sorption of Copper and Zinc onto lignite coal

Copper				
ln(Ce)	ln(Ce/qe)	Ce	Ce/qe	qe
4.6051702	2.445301395	100	11.534025	8.67
5.0106353	2.483307928	150	11.980831	12.52
5.2983174	2.496898263	200	12.144766	16.468

Zinc				
ln(Ce)	ln(Ce/qe)	Ce	qe	Ce/qe
4.6051702	2.691193084	100	6.78	14.749263
5.0106353	2.706715978	150	9.91	14.98
5.2983174	2.716018371	200	13.45	15.12

Table B3. Langmuir Freundlich adsorption constants

Heavy metal ions	Langmuir Isotherm			Freundlich Isotherm		
	R^2	Q_m(mg/gm)	K_L(l/mg)	K_f(mg/g)	n	R^2
Cu^{2+}	0.9995	16.468	10.31	2.0988	13.21	0.9917
Zn^{2+}	0.9945	13.45	14.377	2.5258	27.77	0.9979

Appendix C: Adsorption Kinetics

Pseudo first order kinetics equation

$$\log (q_e - q_t) = \log(q_e) - (K_f/2.303) * t$$

q_t is the amount of adsorbate adsorbed at time t (mg/g), qe is the adsorption capacity at equilibrium (mg/g), K_f is the pseudo first order rate constant (min^{-1}), and t is the contact time (min).

Pseudo first order kinetics equation

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{1}{q_e} t,$$

Where ks, pseudo second order rate constant(g/mg/min)

The initial adsorption rate, *h* (mg/g min) is defined as: $h = k_s q_e^2$

Table C1 Pseudo first order

Copper				
qe	qt	Time	ln(qe-qt)	Co
4.46	0.34	30	0.567	50
6.78	0.71	60	1.07	100
9.91	0.87	90	1.487	150
13.45	0.98	120	1.89	200
Zinc				
qe	**qt**	**Time**	**ln(qe-qt)**	**Co**
10.35	3.4	30	0.345	50
14.74	5.65	60	0.765	100
14.98	6.67	90	1.13	150
15.12	7.687	120	1.365	200

Table C2Pseudo second order

Copper		
qt	t	t/qt
4.46	30	6.726457
6.78	60	8.5678
9.91	90	10.2346
13.45	120	11.8976
Zinc		
3.4	30	9.0234
5.65	**60**	**11.0456**
6.67	**90**	**13.49325**
7.687	**120**	**15.61077**

Table C3: Pseudo first and second order kinetics and constant values

Metal ions	Pseudo first order			Pseudosecond order			
	$Q_{ep't}$(mg/gm)	R^2	K_f(min^{-1})	h(gm/mg/min)	$Q_{ex't}$(mg/gm)	Ks (g/mg/min	R^2
Cu^{2+}	0.0146	0.9971	0.157	0.01661	0.0573	5.0616	0.9994
Zn^{2+}	0.0114	0.9852	0.045	0.0369	0.074	6.7408	0.9988

Appendix D: AAS Calibration Curve And Standards

Analyst
Date Started 10:10 AM 5/17/2016 GMT: 7:10 AM 5/17/2016
Worksheet 201600517 Cu
Comment
Methods Cu

Method: Cu (Flame)
Element - Matrix: Cu -
Instrument Type: Flame
Conc. Units: mg/L
Instrument Mode: Absorbance
Sampling Mode: Manual
Calibration Mode: Concentration
Measurement Mode: Integrate
Replicates Standard: 3
Replicates Sample: 2

Expansion Factor: 1.0
Minimum Reading: Disabled
Smoothing: 7 point
Conc. Dec. Places: 4

Wavelength: 324.8 nm
Slit Width: 0.5 nm
Gain: 38 %
Lamp Current: 10.0 mA
Lamp Position: 4
Background Correction: BC On

STANDARD 1: 0.4000 mg/L
STANDARD 2: 0.8000 mg/L
STANDARD 3: 1.2000 mg/L
STANDARD 4: 1.6000 mg/L
STANDARD 5: 2.0000 mg/L
Reslope Rate: 50
Reslope Standard No.: 2
Reslope Lower Limit: 75.0 %
Reslope Upper Limit: 125.0 %
Recalibration Rate: 100
Calibration Algorithm: Linear Origin
Cal. Lower Limit: 20.0 %
Cal. Upper Limit: 150.0 %
SIPS: Off

Measurement Time: 5.0 s
Pre-Read Delay: 10 s
Flame Type: Air/Acetylene
Air Flow: 13.50 L/min
Acetylene Flow: 2.00 L/min
Burner Height: 0.0 mm

CuCAL ZERO
CuSTANDARD 1
CuSTANDARD 2
CuSTANDARD 3
CuSTANDARD 4
CuSTANDARD 5
Curve Fit = Linear Origin
Characteristic Conc = 0.0408 mg/L
r = 0.9994
Calculated Conc = -0.0059 0.4244 0.8352 1.2206 1.6031 1.9662

Residuals = 0.0059 -0.0244 -0.0352 -0.0206 -0.0031 0.0338
CuCAL ZERO
CuSTANDARD 1
CuSTANDARD 2
CuSTANDARD 3
CuSTANDARD 4
CuSTANDARD 5
Curve Fit = Linear Origin
Characteristic Conc = 0.0402 mg/L
r = 0.9992
Calculated Conc = -0.0037 0.4266 0.8353 1.2287 1.6011 1.9625
Residuals = 0.0037 -0.0266 -0.0353 -0.0287 -0.0011 0.0375
CuCAL ZERO
CuSTANDARD 1
CuSTANDARD 2
CuSTANDARD 3
CuSTANDARD 4
CuSTANDARD 5
Curve Fit = Linear Origin
Characteristic Conc = 0.0406 mg/L
r = 0.9995
Calculated Conc = -0.0032 0.4190 0.8305 1.2221 1.6056 1.9663
Residuals = 0.0032 -0.0190 -0.0305 -0.0221 -0.0056 0.0337

Analyst
Date Started 10:06 AM 5/17/2016 GMT: 7:06 AM 5/17/2016
Worksheet 20160517 Zn
Comment
Methods Zn

Method: Zn (Flame)
Element - Matrix: Zn -
Instrument Type: Flame
Conc. Units: mg/L
Instrument Mode: Absorbance
Sampling Mode: Manual
Calibration Mode: Concentration
Measurement Mode: Integrate
Replicates Standard: 3
Replicates Sample: 2

Expansion Factor: 1.0
Minimum Reading: Disabled
Smoothing: 7 point
Conc. Dec. Places: 4

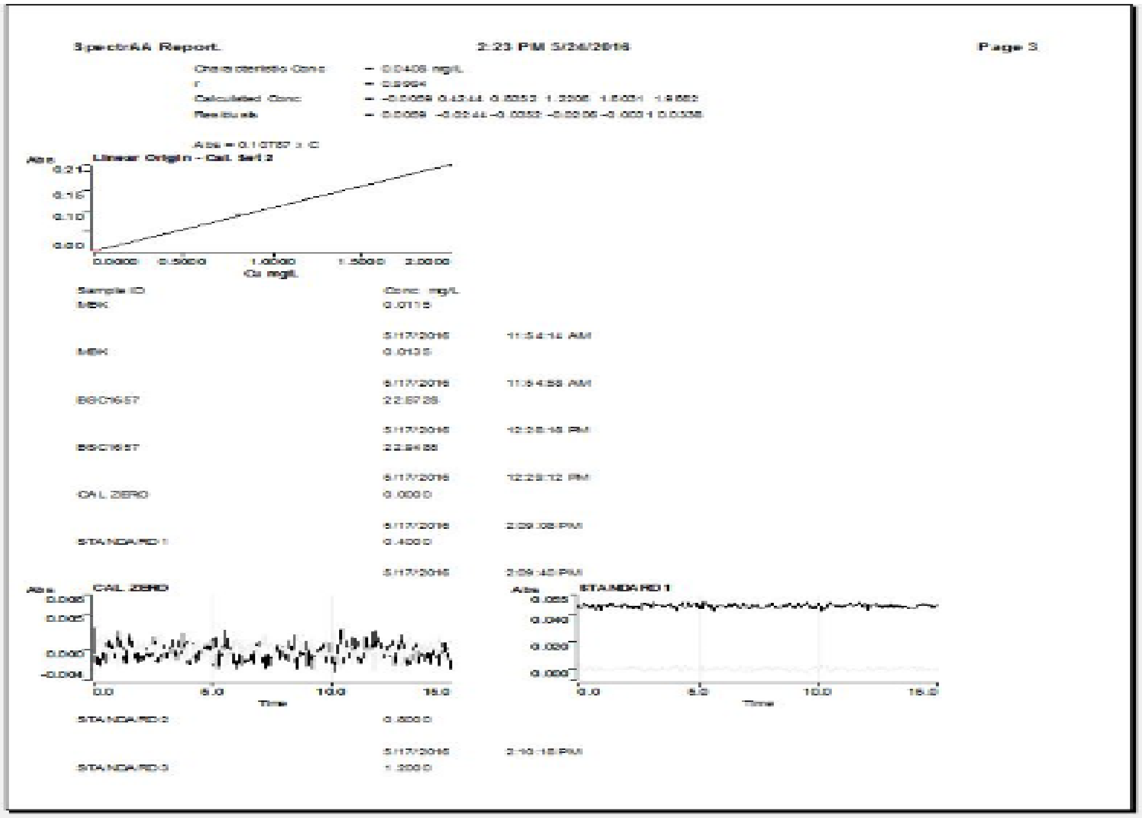
```
Wavelength:                 213.9 nm
Slit Width:               1.0 nm
Gain:                   53 %
Lamp Current:               5.0 mA
Lamp Position:              3
Background Correction:        BC On

STANDARD 1:                  0.2000 mg/L
STANDARD 2:                  0.4000 mg/L
STANDARD 3:                  0.6000 mg/L
STANDARD 4:                  0.8000 mg/L
STANDARD 5:                  1.0000 mg/L
Reslope Rate:               50
Reslope Standard No.:         2
Reslope Lower Limit:          75.0 %
Reslope Upper Limit:          125.0 %
Recalibration Rate:          100
Calibration Algorithm:       Linear Origin
Cal. Lower Limit:            20.0 %
Cal. Upper Limit:            150.0 %
SIPS:                   Off

Measurement Time:             5.0 s
Pre-Read Delay:              10 s
Flame Type:                 Air/Acetylene
Air Flow:                 13.50 L/min
Acetylene Flow:              2.00 L/min
Burner Height:               0.0 mm

ZnCAL ZERO
ZnSTANDARD 1
ZnSTANDARD 2
ZnSTANDARD 3
ZnSTANDARD 4
ZnSTANDARD 5
Curve Fit                              = Linear Origin
Characteristic Conc                        = 0.0167 mg/L
r                                  = 0.9909
Calculated Conc                          = 0.0000  0.2607          0.6590  0.8173  0.9386
Residuals                              = 0.0000  -0.0607         -0.0590 -0.0173 0.0614
ZnCAL ZERO
ZnSTANDARD 1
ZnSTANDARD 2
ZnSTANDARD 3
```

ZnSTANDARD 4
ZnSTANDARD 5
Curve Fit = Linear Origin
Characteristic Conc = 0.0156 mg/L
r = 0.9841
Calculated Conc = -0.0016 0.2637 0.4734 0.6535 0.8083 0.9192
Residuals = 0.0016 -0.0637 -0.0734 -0.0535 -0.0083 0.0808



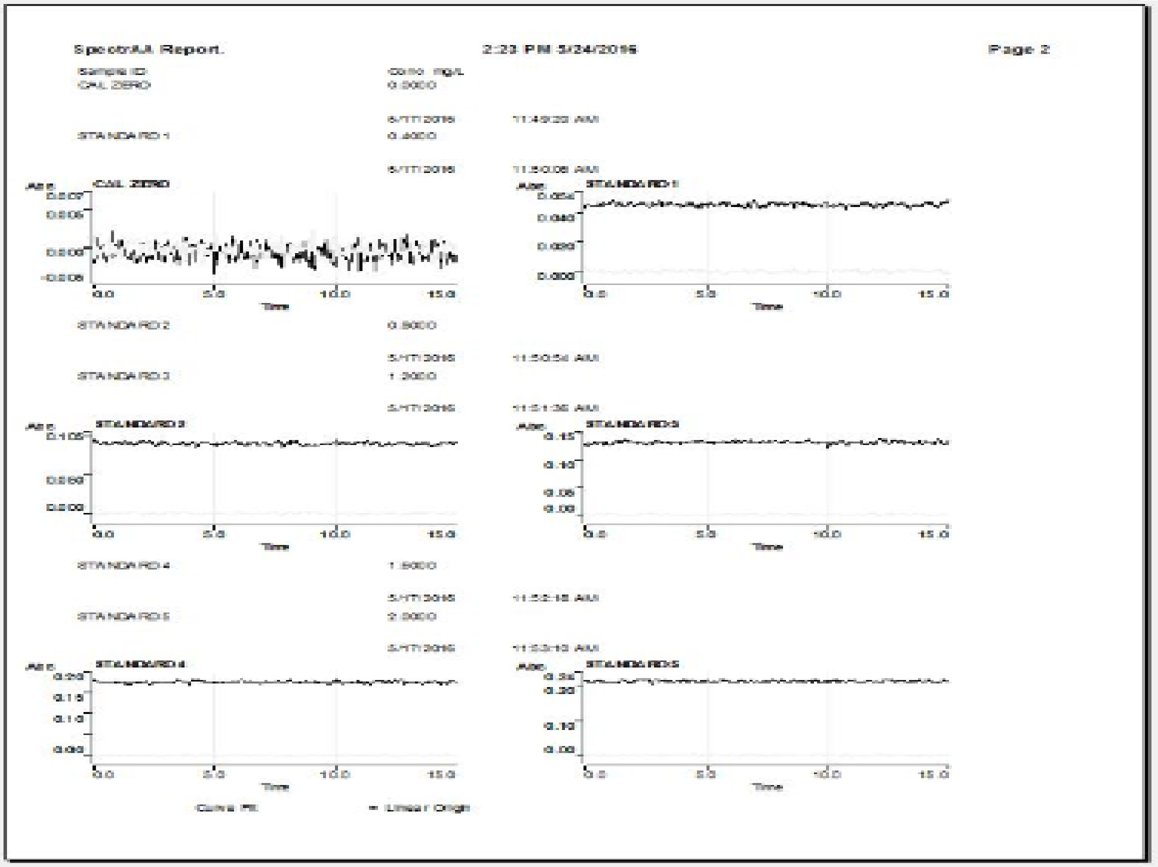
SpectrAA Report. 2:23 PM 5/24/2016 Page 3

Characteristic Conc = 0.0408 mg/L
r = 0.9994
Calculated Conc = -0.0059 0.4244 0.8052 1.2206 1.6031 1.9662
Residuals = 0.0059 -0.0244 -0.0052 -0.0206 -0.0031 0.0338

Abs = 0.10787 x C

Sample ID Conc mg/L
MBK 0.0115
5/17/2016 11:54:14 AM
MBK 0.0135
5/17/2016 11:54:58 AM
BSC1657 22.8728
5/17/2016 12:28:18 PM
BSC1657 22.9488
5/17/2016 12:29:12 PM
CAL ZERO 0.0000
5/17/2016 2:09:08 PM
STANDARD 1 0.4000
5/17/2016 2:09:40 PM

STANDARD 2 0.8000
5/17/2016 2:10:18 PM
STANDARD 3 1.2000



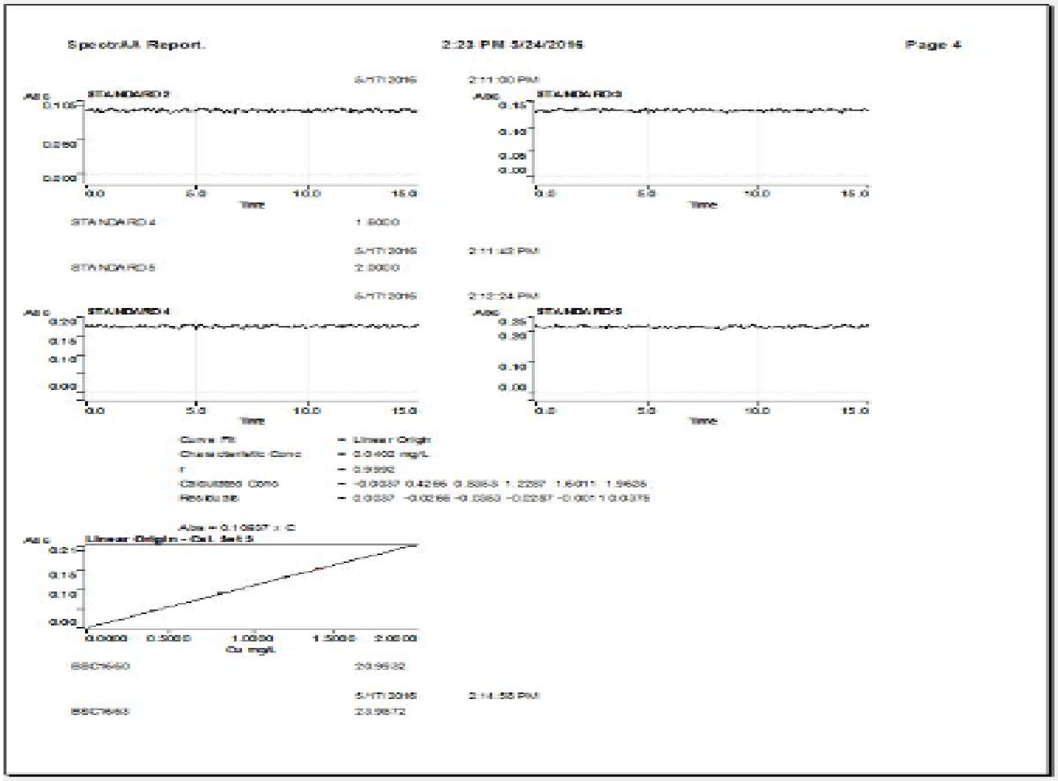
SpectrAA Report. 2:23 PM 5/24/2016 Page 2

Sample ID Conc mg/L
CAL ZERO 0.0000
5/17/2016 11:49:20 AM
STANDARD 1 0.4000
5/17/2016 11:50:08 AM

STANDARD 2 0.8000
5/17/2016 11:50:54 AM
STANDARD 3 1.2000
5/17/2016 11:51:36 AM

STANDARD 4 1.6000
5/17/2016 11:52:18 AM
STANDARD 5 2.0000
5/17/2016 11:53:10 AM

Curve Fit = Linear Origin



SpectrAA Report. 2:23 PM 3/24/2016 Page 4

5/17/2016 2:11:00 PM

STANDARD 4 1.6000

5/17/2016 2:11:42 PM

STANDARD 5 2.0000

5/17/2016 2:12:24 PM

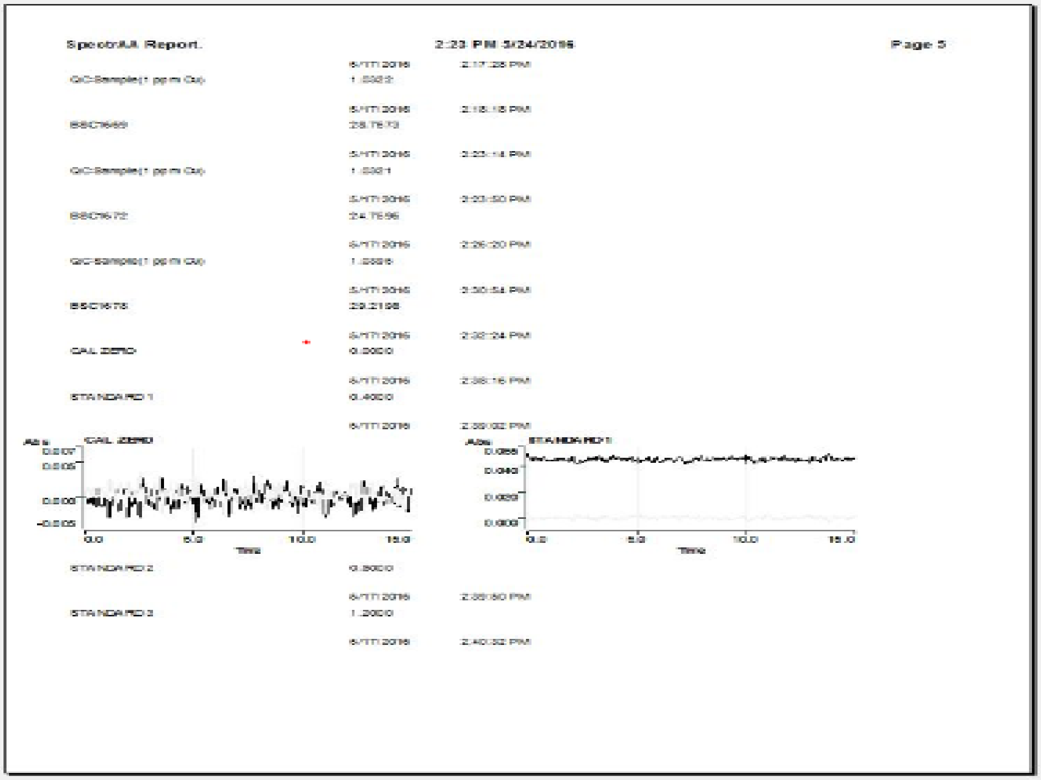
Curve Fit = Linear Origin
Characteristic Conc = 0.0400 mg/L
r = 0.9992
Calculated Conc = -0.0037 0.4266 0.8363 1.2287 1.6011 1.9625
Residuals = 0.0037 -0.0266 -0.0363 -0.0287 -0.0011 0.0375

Abs = 0.10607 x C

BSC1660 20.9532

5/17/2016 2:14:58 PM

BSC1663 23.9872



SpectrAA Report. 2:23 PM 3/24/2016 Page 5

5/17/2016 2:17:28 PM

QC-Sample(1 ppm Cu) 1.0322

5/17/2016 2:18:18 PM

BSC1669 28.7573

5/17/2016 2:23:14 PM

QC-Sample(1 ppm Cu) 1.0321

5/17/2016 2:23:50 PM

BSC1672 24.7596

5/17/2016 2:26:20 PM

QC-Sample(1 ppm Cu) 1.0326

5/17/2016 2:30:54 PM

BSC1678 29.2196

5/17/2016 2:32:24 PM

CAL ZERO 0.0000

5/17/2016 2:38:16 PM

STANDARD 1 0.4000

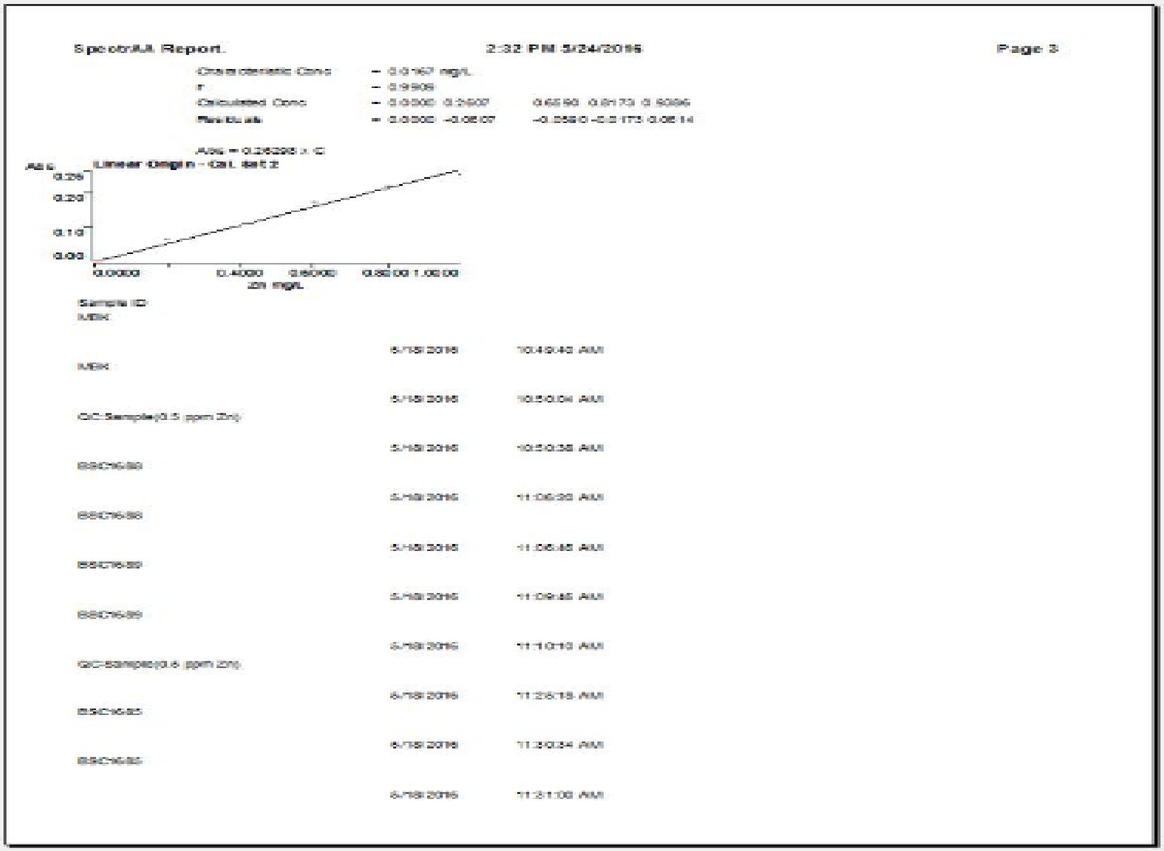
5/17/2016 2:39:02 PM

STANDARD 2 0.8000

5/17/2016 2:39:50 PM

STANDARD 3 1.2000

5/17/2016 2:40:32 PM

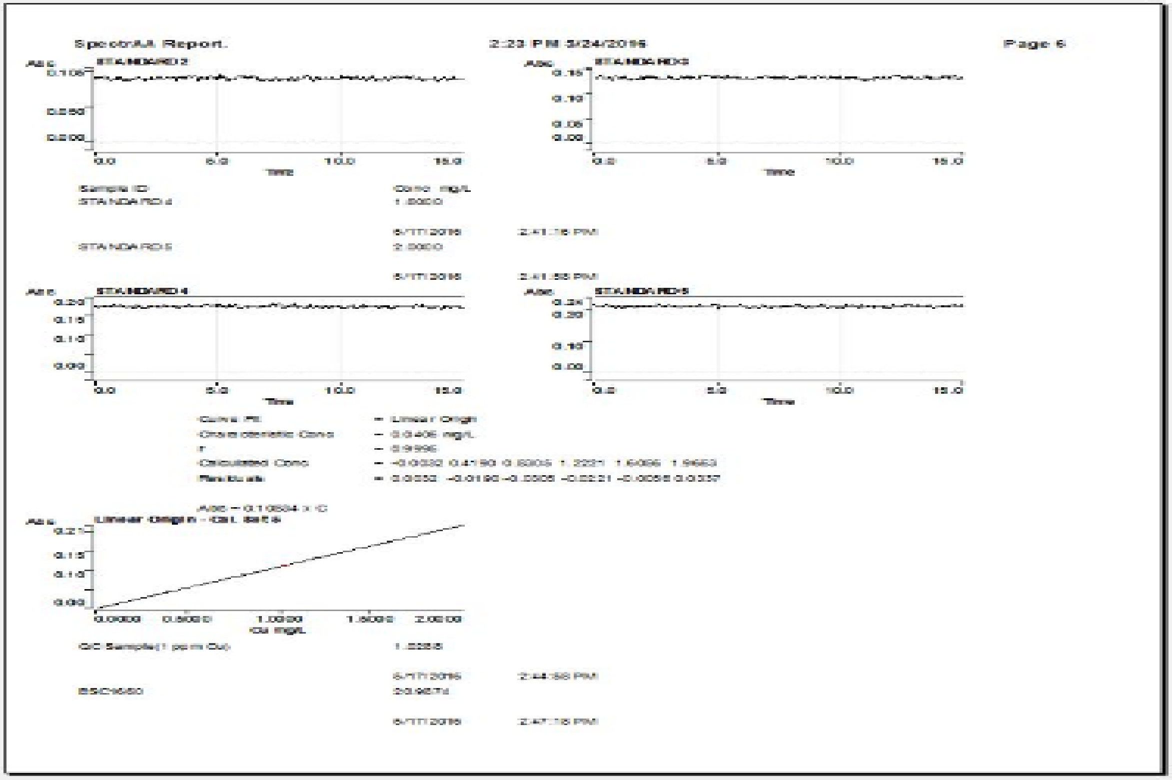


SpectrAA Report. 2:32 PM 5/24/2016 Page 5

Characteristic Conc = 0.0167 mg/L
r = 0.9909
Calculated Conc = 0.0000 0.2607 0.6590 0.8173 0.5086
Residuals = 0.0000 -0.0607 -0.2590 -0.0173 0.0814

Abs = 0.26298 x C

Sample ID
MBK
5/18/2016 10:49:40 AM
MBK
5/18/2016 10:50:04 AM
QC-Sample(0.5 ppm Zn)
5/18/2016 10:50:38 AM
BSC1680
5/18/2016 11:06:20 AM
BSC1688
5/18/2016 11:06:45 AM
BSC1689
5/18/2016 11:09:45 AM
BSC1689
5/18/2016 11:10:10 AM
QC-Sample(0.5 ppm Zn)
5/18/2016 11:26:15 AM
BSC1685
5/18/2016 11:30:34 AM
BSC1685
5/18/2016 11:31:00 AM



SpectrAA Report. 2:23 PM 5/24/2016 Page 6

Sample ID Conc mg/L
STANDARD 4 1.5000
5/17/2016 2:41:16 PM
STANDARD 5 2.0000
5/17/2016 2:41:55 PM

Curve Fit = Linear Origin
Characteristic Conc = 0.0405 mg/L
r = 0.9996
Calculated Conc = -0.0032 0.4190 0.8305 1.2221 1.6056 1.9663
Residuals = 0.0032 -0.0190 -0.0305 -0.0221 -0.0056 0.0337

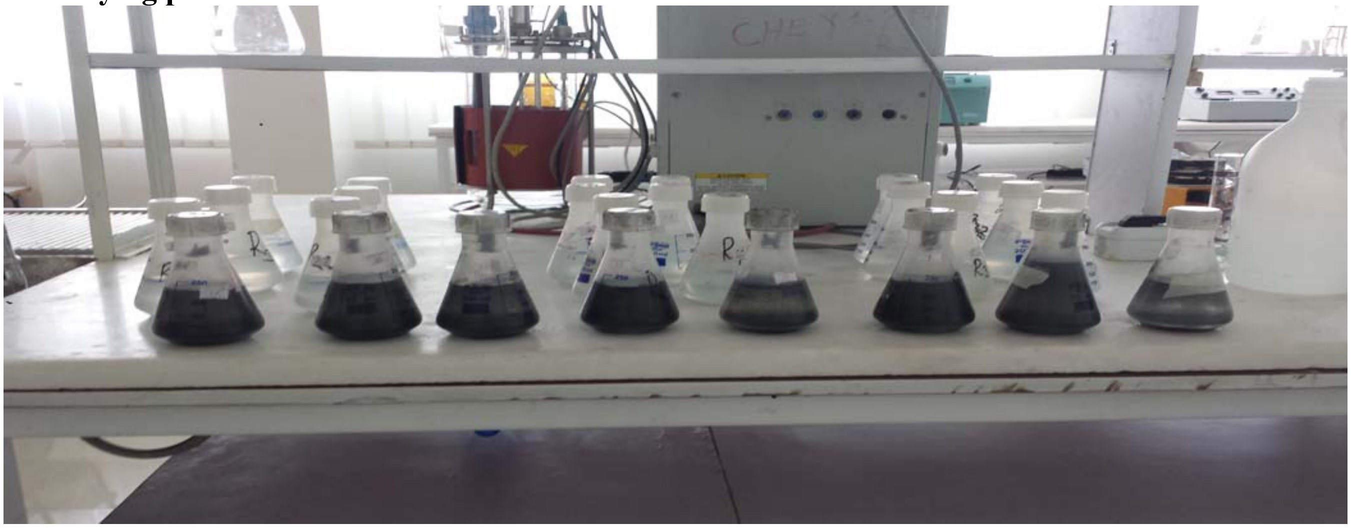
Abs = 0.10834 x C

QC-Sample(1 ppm Cu) 1.0288
5/17/2016 2:44:55 PM
BSC1680 20.9874
5/17/2016 2:47:15 PM

Appendix E: Laboratory pictures

Stock solution preparation and PH Adjustment

All varying parameters for different runs



Shaker

Filtration

Ready for AAS