ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

**M.Sc. Program in Environmental Engineering**

# ADSORPTION OF HEAVY METAL FROM CONSTITUENT WASTE WATER BY TEA WASTE ADSORBENT

A Thesis Submitted to Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in Partial Fulfillment of the Requirements for the Degree of Masters of Science in Environment Engineering.

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**JUNE, 2016**

**ADDIS ABABA, ETHIOPIA**

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This is to certify that the thesis is prepared by Lalise oljira, entitled: **Adsorption of heavy metal from constituent waste water** and submitted in partial fulfillment of the requirements for the Degree of Master of Science in Environmental Engineering obeys with the regulations of the University and meets the accepted standards with respect to originality and quality.

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# List of abbreviations

| | |
|---|---|
| AAS | Atomic Absorption Spectrometer |
| AC | Activated Carbon |
| ASTM | American Standard Testing Method |
| ANOVA | Analysis of Variance |
| BOD | Biological Oxygen Demands |
| CCD | Central Composite Design |
| DAF | Dissolved-Air Flotation |
| EPA | Environmental Protection Authority |
| ED | Electro dialysis |
| FDRE | Federal Democratic Republic Of Ethiopia |
| FTIR | Fourier Transform Infrared Spectroscopy |
| GDP | Great Domestic Product |
| RSM | Response Surface Methodology |

# *Abstract*

*Most industries such as electroplating, textile, fertilizer, batteries, leather, and others in less developed countries discharge huge volumes of untreated wastewater into water bodies. The industrial wastewater may contain toxic chemicals in excess of the threshold level when released into the environment, particularly to the aqueous environment and soil; significantly degrade the quality of the water thereby affecting river health substantially and subsequently human health. There are several techniques for removing toxic chemicals such as ion exchange, membrane filtration, adsorption, irradiation and chemical and biological treatments. However, the adsorption method is believed to be the better option because it is cost-effective, efficient, simple and easy to operate, and environmentally friendly according to many studies. Accordingly, this method can be a preferable option for developing countries like Ethiopia, where advanced treatment technologies for high volumes of toxic industrial waste water are unaffordable. The aim of this work was to determine the potential of tea waste (TW) as a useful adsorbent for the removal of copper and zinc ions from aqueous systems. The study was conducted using batch experiments with constituted wastewater having copper and zinc ion concentration of 1000* $mg \cdot L^{-1}$*. The effects of initial concentration, contact time and pH on adsorption efficiency were investigated. Adsorption isotherm was also studied. Generally, the result showed an increase in removal efficiency with increase in contact time, pH and decrease of initial concentration. The adsorption equilibrium data correlate well with Freundlich model and Langmuir model respectively for zinc removal and copper removal with regression coefficient (*$R^2$=0.9913, $R^2$=0.981*). The results showed that efficiencies of (TW) for the removal of copper and zinc ion were 95.98% and 99.80% respectively at optimum point of 5pH, 10ppm, and 120min. These results clearly indicate the efficiency of tea waste (TW) as a low-cost adsorbent for treatment of wastewater containing copper and zinc ions. Therefore, it is recommended that tea waste can be used, as a low cost and abundant source for the removal of heavy metals as an alternative to more costly materials.*

***KEY WORDS****: Copper, zinc, toxicology, adsorption, tea waste, batch study, atomic adsorption spectrometer.*

# 1 INTRODUCTION

## 1.1 Back Ground

Water is important for life and for processing various materials in industry. Living organisms cannot exist without water, and almost all industries require water to operate. However, in the 21st century the growing population and industrial sector have contributed significantly to a reduction in quality of water and its availability as result of discharge of untreated wastewater to the environment. Thus becoming the concern of many nations across the world (Kapanji, 2009; Sato *et al.*, 2013).

Globally, every day more than two million tons of liquid wastes are released from point(industrial area) and non-point sources like agricultural areas into both subsurface and surface water bodies without treatment (Corcoran, 2010). Considering some African country, for example, Egypt has generated $8.5 \times 10^9$ $m^3$ of waste water in 2011, out of which 56% was treated, while the rest of it was discharged without treatment (Sato *et al.*, 2013). Ghana and Morocco have each treated about 7% of their wastewater generated per year (Sato *et al.*, 2013). Similarly, Ethiopia has used 18% of 49 million $m^3$ of its wastewater generated in volume per annum without treatment for agricultural production and other purposes, while the remaining wastewater is discharged into nearby water bodies such as rivers, springs, streams, and lakes (Corcoran, 2010; GTP-MoFED, 2010; Sato *et al.*, 2013). In Addis Ababa, around 390 hectares of land for vegetable farming is irrigated with the contaminated Akaki river, reported to contain high amounts of toxic heavy metals (Ni, Cd, Cr, Zn, Cu, Mn and Pb), and found in the tissues of vegetables (lettuce, swiss chard, cauliflower, cabbage and kale). This shows that, industrial wastewater needs to be treated before being used for irrigation purposes (Itanna, 2002; Beyene and Banerjee, 2011).

The sustainability of the environment has become a critical global issue (Dişli, 2010) and the protection of fresh water bodies from various contaminants has become a major challenge facing the planet earth (Chaturvedi and Sahu, 2014). National values for the water poverty index Figure indicated that Ethiopia is the third of lowest countries of the world, according to five various indicators such as environmental impact, use, capacity, access and resources (Lawrence *et al.*, 2002). Among the major causes of environmental pollution is the discharge of untreated industrial wastewater containing toxic chemicals such as heavy metals (Park *et al.*, 2010; Kulkarni and Kaware, 2014). A direct industrial wastewater discharge into fresh water bodies is a usual practice particularly in less developed countries like Ethiopia, where no stringent environmental regulations have been enacted (Asfaw, 2007; Padanilly *et al*., 2008; Zinabu, 2011; Tong, 2012; Belay and Sahile, 2013; Mekuyie, 2014; Wosnie and Wondie, 2014). The release of toxic chemicals from industrial wastewater into the environment degrades water quality and is hazardous for human beings, as well as, other living organisms such as aquatic life (Ahluwalia and Goyal, 2007).

The composition of heavy metals from industrial wastewater is a major concern for the environment, based on the rich of copper (Cu), lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn), nickel (Ni), arsenic (As), and mercury (Hg) (Bhattacharyya and Gupta, 2008; Naiya *et al.*, 2009; Zwain *et al.*, 2014).

Population growth, an increase in development and the expansion of investment in the industrial sector has led to the rise in demand for industrial products. The expansion and development of various types of industries can result in generating huge volumes of wastewater along with complex toxic chemical compositions which demand advanced technological treatment techniques (Corcoran, 2010; Keng *et al.*, 2013; Zwain *et al.*, 2014). Subsequently, most industries in Ethiopia and other less developed countries discharge huge volumes of raw wastewater to water bodies, causing environmental and health damage to the local population and ecosystem.

Due to industrialization the volume of wastewater generated from the Ethiopian industrial sector has increased rapidly. From 1980 to 1990, the toxic load discharged per unit of industrial output increased by 1.8, which was about 1.3 times higher than sub-Saharan African countries such as Swaziland, Seychelles and others (UNIDO, 2001; Sato *et al.*, 2013; Tegegn, 2014).

Investment inflow into Ethiopia to establish industries is increasing for example, the contribution to Gross Domestic Product (GDP) from industry is expected to increase to 19.1% at the end of the Growth and Transformation Plan (GTP) 2014/15 from 8.1% in 2004/05 (GTP-

MoFED, 2010; FDRE-CRGE, 2011). As a consequence to prevent increasing environmental and health related problem, Ethiopia faces a challenge to effectively treat the industrial wastewater discharge. As with other developing countries, Ethiopia cannot afford to use advanced technologies for the treatment of contaminated water. Accordingly, it is crucial to explore low-cost, locally available materials for the treatment of industrials wastewater. Bearing in mind that, the adsorption principles should be cost-effective, simple to design and operate using locally available materials such as tea waste will be investigated for single and multicomponent adsorptive removal of $Cu^{2+}$ and $Zn^{2+}$ from industrial wastewater under batch experimental setup.

The findings of the study will used an input for the exploring and development of low-cost adsorptive removal techniques for the effective treatment of industrial wastewater.

## 1.2 Statement of the problem

Presence of heavy metals in wastewater has toxic effects on the receiving environment and human health. Industrial processes produce multicomponent wastewater that requires advanced treatment technologies in developed countries toxic heavy elements discharged from different industrial areas along with polluted liquid waste; have been successfully removed by high resolution and costly treatment methods. However, in developing countries the application of such advanced technologies for wastewater treatment is technically complex and expensive.

Similar to other developing countries, in Ethiopia also, such advanced treatment method are not widely used due to their high cost, non-feasibility and economic disadvantage, difficult to operate and also these processes involve use of chemicals and synthetic polymers whose impact on the environment has not been entirely studied.

Heavy metals, especially copper and zinc, present in many industrial wastewaters such as general industry and mining, pipe corrosion, paper products, fertilizers, steel works, metal finishing and electroplating are known to have toxic effects such as arthritis/rheumatoid arthritis, mental disorders, anemia, insomnia, liver damage and heart problems to human health. Wastewater containing Heavy metal causes detrimental effects on all forms of life upon direct discharge to the environment (Aksu *et al.,* 2005).

According to different information sources Krishna, (2011); Kaur (2012) 49 million $m^3$ $year^{-1}$ wastewater was generated in Ethiopia (2009). About 18% of this wastewater was used for agricultural production and other purposes without treatment; the rest of the water is released to adjacent surface water bodies. According to Kebena and Krishna (2011) in 2009, 161,668 $m^3.day^{-1}$ liquid waste was generated, and from this only 6,728 $m^3$. $day^{-1}$ (4%) was treated. These show that advanced wastewater treatment technologies are expensive and unaffordable, and the literature shows that as yet, there is no available wastewater treatment in the country. However, it is important that low-cost adsorptive technologies are developed for a sustainable environment and healthy life.

Therefore, it is urgently needed to develop cost effective and efficient treatment technology, by increasing research interest by using alternative low cost adsorbent and effective removal of heavy metal from waste water. Thus this project is stemmed by realizing the above interest and aimed to achieve effective and efficient method by optimizing the parameters.

## 1.3 Objectives of the study

### 1.3.1 The General Objective of the Study

The main aim of the research was to investigate the efficiency and the practical applicability of locally abundant low-cost adsorbents tea waste for the single or/and multicomponent removal of heavy metals ($Cu^{2+}$ and $Zn^{2+}$) from constituted wastewater.

### 1.3.2 Specific Objectives

The specific objectives of the study are:

- To prepare locally available adsorbent media (tea waste).
- To study and optimize the effect of contact time duration, dosage of the adsorbent, initial concentration of the adsorbate, pH of the solution and adsorption isotherm by using a batch adsorption technique.
- To investigate effect of tea waste treatment for adsorption.

## 1.4 Verified Outcomes

- Physicochemical composition of tea waste was characterized to observe suitability for treatment.
- Effect of contact time duration, dose of adsorbent, initial concentration of the adsorbate, pH and other factors were determined and optimized.
- Adsorption capacity and equilibrium isotherm of tea waste was evaluated and verified the possibility for scale up.
- It also contributes in reduction pollution related health problems in a sustainable and environmentally friendly way.
- Improve current research by increasing the percentage of heavy metal degradation from wastewater by using tea waste adsorbent.
- Prevent the heavy metal concentration release to the water stream which can causes foul odor and toxicity that can be potential hazard to human health and environment.

Therefore, the beneficiaries of the present study results were:

- ✓ Those who engaged in the environmental management;
- ✓ Those who are responsible in industry waste water treatment;
- ✓ The society, researcher and the government.

# 2 LITERATURE REVIEW

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and agriculture and can encompass a wide range of potential contaminants and concentrations.

According to Mahvi *et al*., (2008), water used in industries creates a wastewater that has a potential hazard for our environment because of introducing various contaminants such as heavy metals into soil and water resources. If there is no low cost, effective and efficient technology, wastewater can be reversed to the environment. Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of water bodies, soil and air. Industrial waste constitutes the major source of various kinds of metal pollution in natural waters. The important toxic metals found in industry water includes: Cd, Zn, Ni, and Pb which find its way mainly to the water bodies through waste waters. Heavy metals can accumulate in the environment and reach to liking organism through chain elements such as food chain, and thus may pose a significant health danger to liking organisms.

## 2.1 Wastewater

Wastewater is used water generated from homes, public and private institutions, rural areas, urban areas, farms, industries and others point and non-point sources (Majeed *et al.*, 2014). Billions of gallons of liquid waste from agricultural, industrial, domestic and commercial sources are discharged into fresh surface water bodies every day (Renge *et al.*, 2012). Worldwide, between 300 to 400 million tons of liquid, hazardous waste to living organisms is discharged annually into nearby surface water bodies from industries (Palaniappan *et al*., 2010; Pizano *et al*., 2010; UNEP, 2010). Similarly, approximately two million tons of liquid wastewater is released each day from non-point sources like agricultural areas and from point sources like industries to surface water bodies across the globe (Corcoran *et al*., 2010). The release of untreated wastewater into the environment can lead to the contamination of rivers, streams and other surface water bodies. Industrial wastewater contains harmful suspended and dissolved matter, like heavy metals, and inorganic matters, which when released untreated greatly affects the environment and causes serious health problems to living organisms. According to available evidence, including the World Health Organization, (WHO, 1984; El-Gendy *et al.*, 2011;

Shahmohammadi *et al.*, 2011; Isah and Lawal, 2012; Sonde and Odoemelam *et al*., 2012; Muiruri *et al.*, 2013), heavy metals of urgent environmental concern are lead, chromium, mercury, cadmium, copper, zinc, and iron. The industrialization drive of most developing countries like Ethiopia has attracted foreign investments but has led to heavy pollution of water bodies due to the discharge of untreated industrial waste. This pollution has been of great concern to governments and other stakeholders, and therefore, exploring low-cost and effective treatment techniques is the focus of many researchers and scientists across the globe.

## 2.2 Heavy metals pollution

Heavy metals are toxic chemicals that have specific gravity greater than 5 $g.cm^{-3}$ and consistence 5 and five times greater than specific gravity of water at 4 $^{o}C$ (Abas *et al.*, 2013). In addition, the atomic number and atomic weight of heavy metals is high (Srivastava, 1995; Al-Farraj *et al.*, 2013). Heavy metal pollution is a quickly growing problem in oceans, lakes, and rivers (aquatic). But only a relatively small number of heavy metals such as cadmium, lead, zinc, copper, iron, cobalt, mercury, vanadium, nickel, chromium, manganese, molybdenum, silver, and tin as well as the metalloids arsenic and selenium are associated with environmental, plant, animal, or human health problems.

Even though the chemical forms of heavy metals can be changed, they are not subject to chemical or biological destruction. Therefore, after release into the environment they are persistent contaminants. Natural processes such as bedrock and soil weathering, wind and water erosion, volcanic activity, sea salt spray, and forest fires release heavy metals into the environment. While the origins of anthropogenic releases of heavy metals are lost in antiquity, they probably began as our prehistoric ancestors learned to recover metals such as gold, silver, copper, and tin from their ores and to produce bronze.

The modern age of heavy metal pollution has its beginning with the industrial revolution. The rapid development of industry, intensive agriculture, transportation, and urbanization over the past 150 years, however, has been the precursor of today's environmental contamination problems (El-Awady Sami *et al*., 1997). Anthropogenic utilization has also increased heavy metal distribution by removing the substances from localized ore deposits and transporting them to other parts of the environment. Heavy metal by-products result from many activities including: ore extraction and smelting, fossil fuel combustion, dumping and landfilling of industrial wastes, exhausts from leaded gasoline's, steel, iron, cement and fertilizer production, refuse and wood combustion.

Water sources that are near factories and manufacturing plants may be contaminated with heavy metals like mercury, zinc, copper, nickel, lead, cadmium, iron, magnesium and aluminum. If the metals attach to the sediment, they may find their way into the food chain via plants and aquatic animals. The end result is heavy metal poisoning if the concentration in the water is high enough.

In a global context, the major problem of surface water pollution is heavy metal discharge from industrial activities (Narain *et al.*, 2011; Alfarra *et al.*, 2014; Pawar *et al.*, 2014). The development of industrial sector in the African continents is the primary cause of heavy metals being released into water, air and soil in all countries, including Ethiopia.

Most industries are the point source of heavy metals (Pehlivan *et al.*, 2008); these industries include electroplating, chemical and petrochemical, metal and mining, leather, textile, ceramic, cement, fertilizer, tanneries, batteries, paper, pesticides and others. These industries release their wastewater containing various harmful heavy metals without treatment into the environment (Fasinu and Orisakwe, 2013). These harmful toxic chemicals include elements such as uranium (Ur), selenium (Se), zinc (Zn), silver (Ag), gold (Au), nickel (Ni), cadmium (Cd), mercury (Hg), copper (Cu), chromium (Cr), arsenic (As), lead (Pb) and others (Ahalya *et al.*, 2003). The presence of these harmful heavy metal elements, even at low concentrations, affects the health of humans and other living organisms (Srivastava *et al*., 1995; Duruibe *et al.*, 2007). The fact that these elements are highly soluble in water and not easily degradable by soil, makes their presence in water bodies more alarming (Kurniawan *et al.*, 2006b).

## 2.3 Health effects of heavy metals

Excess levels of heavy metals in the environment are harmful to the health of human beings and other living organisms. The gradual accumulation of toxic chemicals in the body of a living organism can result in bioaccumulation. Bioaccumulation happens when an organism uptakes toxic substance at a higher concentration than its release (Renge *et al.*, 2012). Therefore, the storage of these chemicals in the body of a living organism is greater than their release may occur gradually. As these elements cannot biodegrade or break down easily, the negative effects are worsened by the ecosystem of the environment (Abas *et al.*, 2013). For example, Cd can be accumulated in the human body for up to 30 years, without being destroyed or becoming soluble like organic matter (Mohod and Dhote, 2013). According to the study conducted by Biney and Ameyibor, (1992) untreated industrial wastewater containing heavy metals (Cd, Cu, Zn, Pb, Hg and Fe) released into fresh water bodies can also be stored in the bodies of aquatic organisms, for example in Pink Shrimp. Therefore, the need to treat wastewater is of great importance in order to safeguard the environment and reduce associated health problems. According to the World Health Organization (WHO) reports and other studies (WHO, 1984; El-Gendy *et al.*, 2011; Sahniet, 2011; Shahmohammadi *et al.*, 2011; Isah and Lawal, 2012; Sonde and Odoemelam ,2012; Muiruri *et al.*, 2013), the heavy metals which are of greatest concern with regard to human health are Pb, Cd, Hg, Cr, Cu, Zn and Fe. Most products such as pharmaceutical products and dental products, some drugs, and Unani drugs, cosmetic products like shampoos, lipsticks, hair colors and others contain heavy metals (Sahni *et al*., 2011; Bocca *et al.*, 2014).

The metals are transferred from these products and the environment to humans and other living organisms by the food chain or food web and by coming in contact with the skin. In the food chain process, heavy metals are absorbed into the body of the organism through eating food that contains high levels of heavy metals, or by drinking water, inhalation, skin and eye contact and through other sense organs (Yadanaparthi *et al.*, 2009). Small amounts of these elements, beyond allowable limits, have serious effects and are unsuitable for living organisms because of their high energy particle output (Kara, 2005; Arora *et al.*, 2008; Memon and Schröder, 2009; Ali *et al.*, 2013; Ghiloufi *et al.*, 2014). Due to this, wellbeing of living organisms' is compromised (Ghiloufi *et al.*, 2014; Pawar *et al.*, 2014), and living organisms are easily exposed to different diseases and associated problems such as carcinogens, schizophrenic like behavior, dyspnea, mental disorders, kidney damage, lung fibrosis, liver disease, high blood pressure, headaches, intestinal problems and others (Renge *et al.*, 2012). Therefore, it is important to eliminate heavy metals from contaminated water.

## 2.4 Waste water treatment

Wastewater treatment is the method of purifying wastewater. This operation is highly important due to the fact that some contaminants or pollutants are difficult to manage after release from point source pollution to environments (Handa, 1983; Wang, 2011b). A conventional wastewater treatment process is divided into three various stages; primary, secondary and tertiary. These stages depend on the characteristics of wastewater discharge, and the amount of harmfulness, and cost effectiveness. Accessibility of land for construction of treatment plants is main factors in the process. Making polluted water fit for consumption and use again is not an easy process. No one purification or filtration method works for all types of water pollution. In order to make water usable again after water pollution, it must be treated with a variety of filtration and purification methods. Therefore, it is important to treat heavy metals discharge from industrial wastewater, with affordable and technically feasible methods. This initiates the need for exploring cost-effective, simple and efficient removal techniques.

### 2.4.1 Primary wastewater treatment

Primary wastewater treatment eliminates large particles in solid waste that has come from different point and non-point source pollutants. The purpose of the primary treatment is to eliminate large suspended solid waste materials (grit and gravel), that settle down at the bottom of the tanks by gravitational force (Mihelcic *et al*.,2010). The design of primary treatment tanks may be rectangular or circular in shape and in this process 30% of Biological Oxygen Demand (BOD), and 60% of Total Suspended Solids (TSS) can be eliminated (Mihelcic *et al*., 2010). The primary wastewater treatment supports the secondary stage of treatment (Metcalf *et al*., 2004; Kapanji, 2009; El Zayat, 2014).

### 2.4.2 Secondary wastewater treatment

At this treatment stage, biologically broken down materials can be reduced into residual organic matter. For example, the remaining 70% biological oxygen demands (BOD) of the organic compounds from primary wastewater treatment stages are treated by microorganisms (bacteria). Other small particles of suspended solids pass through the first stage, and settle at the bottom of the tank by using a coagulant (alum). The coagulant encourages the colloidal materials in the wastewater to join together into small aggregates (Metcalf, 2004; Kapanj, 2009; Mihelcic *et al.*,2010; El Zayat *et al.*, 2014).

Generally, the secondary stage of wastewater treatment does not remove non-biodegradable toxic contaminants such as heavy metals that are being discharged from industries (Santhy and Selvapathy, 2004).

### 2.4.3 Tertiary wastewater treatment

This is the final stage of conventional wastewater treatment. Most of the time at these stage different disinfectants like chlorine, ozonation and ultraviolet radiation are used to treat wastewater (Metcalf, 2004; Chenet, 2009; Kapanji, 2009; Mihelcic *et al.*, 2010). In various developed countries, the treatment of water contaminated by heavy metals is performed using different technologies such as chemical precipitation, as in Thailand (Charerntanyarak *et al.*, 1999) and Turkey (Tünay and Kabdaşli *et al.*, 1994); coagulation-flocculation in China (Kurniawan *et al.*, 2006b); flotation in Greece (Kurniawan *et al.*, 2006b) and USA (Lazaridis *et al.*, 2002); ion exchange in Italy and Spain (Pansini *et al.*, 1991); and membrane filtration in Taiwan (Juang and Shiau, 2000) and South Korea (Ahn *et al.*, 1999). These techniques are promising technologies for the wastewater treatment having toxic heavy metals; however, they are expensive (Rao *et al.*, 2010).

## 2.5 Technologies for heavy metal removal

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

### 2.5.1 Chemical precipitation

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

$$M^{2+} + 2(OH)^{-} = M\,(OH)^{-} \qquad (2.1)$$

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage (Ahalya *et al*., 2003). Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, in expensive equipment requirement, and convenient and safe operations. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Baraket, 2011). In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Bose *et al*., 2002).

### 2.5.2 Ion exchange

Ion exchange is a reversible chemical reaction where in an ion (an atom or Molecule that has lost or gained an electron and thus acquired an electrical charge) from Solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. An organic ion exchange resin is composed of High-molecular weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin. Most of the resins Used are synthetic because their characteristics can be tailored to specific applications. Synthetic resin made by polymerization of organic compounds in a porous three dimensional Structure. Ion exchange resins are classified as cat ion exchangers, whom it has positively charged mobile ions available for exchange, and anion exchangers (Yang *et al*., 2001). Both anion and cat-ion resins are produced from the same basic organic polymers. They differ in the ionisable group Attached to the hydrocarbon network. It is this functional group that determines the Chemical behavior of the resin. Resins can be broadly classified as strong or weak acid Cat-ion exchangers or strong or weak base anion exchangers.

Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluent. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to the pH of the solution. Electrolytic recovery or electro-winning is one of the many technologies used to remove metals from process water streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantage was that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced (Pendiasetal *et al*.,1992).

### 2.5.3 Electro dialysis

Electro dialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cat-ions toward the cathode, crossing the anion exchange and cat-ion exchange membranes (Chen, 2004). The disadvantage is the formation of metal hydroxides, which clog the membrane. In the electro-dialysis process, ionic components of a solution are separated through the use of semipermeable ion-selective membranes. This process may be operated in either a continuous or a batch mode.

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

### 2.5.4 Membrane filtration

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

### 2.5.5 Reverse osmosis process

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

### 2.5.6 Ultra filtration

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

### 2.5.7 Coagulation–flocculation

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

### 2.5.8 Flotation

Flotation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment (Wang 2004). The attached particles are separated from the suspension of heavy metal by the bubble rise. Flotation can be classified as: (i) dispersed-air flotation, (ii) dissolved-air flotation (DAF), (iii) Vacuum air flotation, (iv) Electro flotation and (v) Biological flotation.

Among the various types of flotation, DAF is the most commonly used for the treatment of metal contaminated wastewater. Adsorptive bubble separation employs foaming to separate the metal impurities. The target floated substances are separated from bulk water in a foaming phase.

Although it is only a kind of physical separation process, heavy metal removal by flotation has the potential for industrial application (Jokela and Keskitalo1999). Low cost materials such as zeolite and chabazite have been found to be effective collectors with removal efficiency of higher than 95% for an initial metal concentration ranging from 60 to 500 mg/L. Flotation can be employed to treat inorganic effluent with a metal concentration of less than 50 mg/L or higher than 150 mg/L. other advantages such as a better removal of small particles, shorter hydraulic retention times and low cost make flotation one of the most promising alternatives for the treatment of metal-contaminated wastewater (Matis *et al*.,2003).

However the data shows that these techniques are not widely used because they are less feasible for small scale industries, as well as having high expenses (Ghiloufi *et al.*, 2014). They also produce a harmful sludge and have been found to be not ecologically-friendly mainly because the technology requires high energy for operation (Abas *et al.*, 2013) In addition, these technologies were reported to be complex to control (Alfarra *et al.*, 2014; Habuda *et al.*, 2014; Zwain *et al.*, 2014), and do not completely remove the heavy metals from the contaminated water (Ahalya *et al.*, 2003;).

In contrast, due to it being inexpensive, environmentally friendly and efficient, the adsorption technique has been chosen as a method of wastewater treatment with a special interest in the removal of heavy metals from contaminant water (Li *et al.*, 2007). The adsorption technique is also found to be simple and easy to operate, effective and efficient in eliminating heavy metals (Tajrishy, 2012).

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

This is attributed to the fact that handling wastewater requires technically skilled manpower and sufficient funds as the process is so costly. Therefore, the adsorption method has the potential to treat wastewater and remove heavy metals using low-cost locally available materials (Renge *et al.*, 2012).

### 2.5.9 Adsorption

Adsorption has emerged as promising technique for metal removal. The processes can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, or liquid-solid interfaces (Barakat, 2011). Moreover, adsorption is coming to be regarded as a practicable separation method for purification or bulk separation in newly developed material production processes of, for example, high- tech materials and biochemical and biomedical products.

Surface characteristics and pore structures of adsorbents are the main properties in determining adsorption equilibrium and rate properties which are needed for plant design. New adsorbents are continuously being developed, introducing new applications for adsorption technology. Adsorption equilibrium is the fundamental factor in designing adsorption operations. When adsorption takes place with suspended adsorbent particles in a vessel, adsorb ate is transported from the bulk fluid phase to the adsorption sites in the adsorbent particle. In this type of situation, changes in the amount adsorbed or concentration in the fluid phase can be predicted by solving the set of differential equations describing the mass balances in the particle, at the outer surface and between the particle and the fluid phase. Determination of diffusion parameters should be done with a simple kinetic system. These discussions are also applicable to the analysis and design of adsorption operation in a vessel or differential reactor. Another powerful technique for determining the rate parameters involved in an adsorption packed column gives the basic relations used for calculation of breakthrough curves.

Advantages of adsorption:

- Metals at low concentration can be selectively removed.
- Effluent discharge concentration meets the govt. regulation.
- System operates over the broad pH ranges (2-9).
- System is effective over a temperature ranges of 4-90$^{o}$C.
- System offers low capital investment and low operation cost.
- Convert metal pollutant to metal product.
- System offers simple design, easy operation

Adsorption is a good weapon in the fight against toxic metals threatening our environment.

### 2.5.10 Types of adsorption

At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed.

- Physical adsorption: It is a result of intermolecular forces of attraction between molecules of the adsorbent and the adsorbate. In this case the molecular attractive forces that retain the adsorbent on the surface are purely physical are called Vander Walls forces. This is a readily reversible phenomenon. The energy of interaction between the adsorbate and adsorbent has the same order of magnitudes as, but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed.
- Chemical adsorption: It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption, irreversible and it is particularly important in catalysis. Therefore, the energy of chemisorption's considered like chemical reaction. It may be exothermic or endothermic processes ranging from very small to very large magnitudes. The elementary step in chemisorption often involves large activation energy (Activated adsorption).

## 2.6 Low cost adsorbents

There is increasing research interest in using alternative low-cost adsorbents. Many such materials have been investigated, including microbial biomass, peat, compost, leaf mold, palm press fiber, coal, sugarcane bagasse, straw, wool fiber and by products of rice mill, soybean and cottonseed hulls etc. . The low cost agricultural waste by-products such as sugarcane bagasse, rice husk, sawdust, coconut husk. Oil palm shell, neem bark etc., for the elimination of heavy metals from wastewater has been investigated by various researchers. Tea waste is most cost-effective adsorbent because it is available easily and it has more adsorption capacity to other natural adsorbents, Tea waste biomass can serve as a good and cheap substitute for conventional carbon- based adsorbents, Moringa oleifera (Drum sticks) seeds are a low cost adsorbent.

## 2.7 Type of low-cost materials

There are various types of adsorbents such as natural (soil and/or ore) material, industrial by-products (waste), agricultural waste (products) are some adsorptive unwanted toxic metals from polluted water bodies such as rivers, streams, lakes and others.

Heavy metal adsorption capacity with natural materials like clay is either better or equivalent to other low-cost adsorbents, and it takes as scavengers Cu, Pb, Cd, Zn, Cr, As, Co, Fe from wastewater (Bhattacharyya and Gupta, 2008).

### 2.7.1 Industrial wastes

Coffee husk, Bagasse fly ash, tea industry waste, Blast furnace slag and Red mud are some of the byproducts of industrial waste. The removal of $Cu^{2+,}$ $Pb^{2+,}$ $Cr^{6+,}$ Hg2+ and $Cd^{2+}$ has been done. The efficiency of coffee husk adsorption was shown to be 7.5, 6.96, 5.57 and 6.85 mg g-1 for $Pb^{2+}$, $Cr^{6+,}$ $Zn^{2+}$ and $Cd^{2+}$, respectively.

Bagasse fly ash is an example of the industrial byproducts made from the sugar processing industries displaying good sorptive abilities. In 2003, the uses of bagasse fly ash to eliminate $Pb^{2+,}$ $Cr^{6+}$, $Zn^{2+}$ and $Cd^{2+}$ from wastewater was investigated (Gupta *et al*., 2003). The adsorption capacity of bagasse fly ash has been shown to be 285-566, 4.25, 13.21 and 1.24-2 mg.g-1 for $Pb^{2+,}Cr^{6+}$, $Zn^{2+}$and $Cd^{2+}$,respectively followed both Freundlich and Langmuir’s isotherm adsorption model. These all show that an industrial waste by product adsorption treatment was easily accessible, technically applicable and economically feasible.

### 2.7.2 Agricultural wastes

Cotton seed hulls are an example of agricultural waste or by-product (Marshall *et al*., 1995). The removal efficiency of heavy metals with a cotton seed hull adsorbent was indicated to be high from the literature.

# 3 MATERIALS AND METHODS

## 3.1 Materials and Reagent or Chemicals used

### 3.1.1 Equipment used

All glass wares (Conical flasks, Pipette, Measuring cylinders, Beakers, Petri plates and Test tubes etc. The instruments and apparatus used throughout the experiment are listed in table (3.1).

Table 3.1 List of Instruments used during the whole experiment

| S. No. | Instrument | Model and uses | labs |
|---|---|---|---|
| 1 | Atomic adsorption spectrophotometer | Perkin Elmer model 3110, to measure residual metal ion concentrations | Haramaya university chemistry department lab |
| 2 | Digital Weight Balance | model Mettler Toledo (PB 602-S): to weigh the samples | AAiT Environmental Engineering lab |
| 3 | What man filter paper no.1 | To filter or separate adsorbent from solution | |
| 4 | Orbital shaker | Excella E 24 incubator Used to agitate the adsorbent with aqueous metal ion mixtures. | AAiT Food Engineering Lab |
| 5 | pH meter | Precisa model 900, to measure the pH of the solution | AAiT environmental Engineering lab |
| 6 | spoons | | |
| 7 | sieve analyzer | Particle size determination | AAiT, Mechanical unit operation lab |
| 9 | FTIR instrument | To determine the varies functional groups on the surface of the tea waste. | Science faculty, chemistry department lab |

### 3.1.2 Reagent or Chemicals used

All chemical used were analytical grade for heavy metal solution; reagent grade concentrated sulfuric acid and NaOH were used to adjusted PH values of samples, Nitric acid conc.was used . In all experimental work, distilled demineralized water is used.

## 3.2 Adsorbent collection and preparation

Tea waste were collected from home, restaurants and washed by distilled water repeatedly at (85°C) up to color removal. Then it is dried in hot oven at 105°C for 18 hours. The dried material was soaked by phosphoric acid ($H_3PO_4$) activating agent for 12hrs, this help to make pore on the surface of tea waste, then washed up to pH neutral . Again dried it at 105°C for 12 hours and then stored in plastic bags at room temperature. Now it was ready to use as an adsorbent. The activation method of the adsorbent was done as follows, 100gram of tea sample was crushed manually then dilute phosphoric acid solution was prepared 70ml of acid was utilized to digest tea waste this kept at 30°C for 12 hr. Then wash the digested sample using distilled water up to make pH neutral.

Figure 3.1 Tea waste (Adsorbent) collected and oven dried

## 3.3 Experimental procedures

The overall experimental activities carried out in the study were illustrated by the following Figure (3.2).

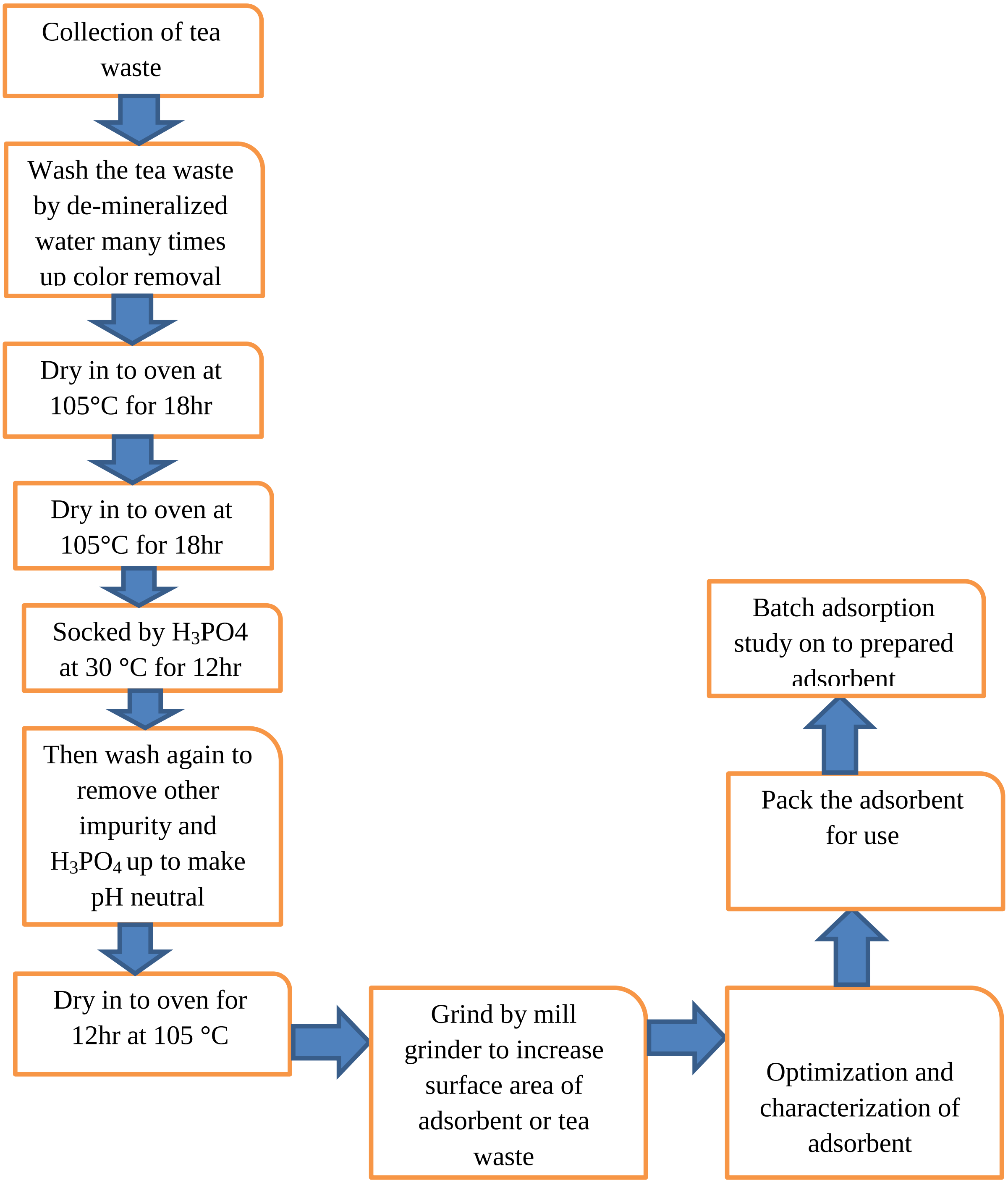


Figure 3.2 The overall experimental procedures

## 3.4 Characterizations of Adsorbent

The physical analysis of tea waste was conducted according to an American Standard Testing Method (ASTM). Proximate analysis of the adsorbent constituted determination of moisture content, volatile matter, fixed carbon, ash content and Fourier transform infra-red (FTIR) spectral analysis were used to study the structural and morphological characteristics of adsorbents.

### 3.4.1 Ash content determination

A crucible was washed and dried in a hot air oven for 30min at a temperature of $105^0$C. After heating, it was then cooled in a desiccator for 30 min. The crucible was weighed using analytical balance. So that 1g of sample was weighed into the crucible and its weight was recorded. It was transferred to a muffle furnace maintaining a temperature of $500^0$C for one hour, for complete de-carbonization to obtain white ash. The crucible and ash were cooled and the weight was recorded. The result was expressed as percentage of the weight of ash over the original weight of sample as shown in equation (3.1).

$$\text{Ash content (\%)} = \frac{Wf}{Wi} \times 100\% \qquad (3.1)$$

Where

$w_i$ = Weight of original sample and $W_f$ = weight of sample after drying.

### 3.4.2 Moisture content

This method was used to determine the percentage of water in a sample by drying the sample to a constant weight. The moisture content of the tea waste was calculated by using digital moisture analyzer at 105°c for 30 min. Three samples, weighting 1 g each, were used to determine the moisture content with the use of the digital moisture analyzer, the mean value of the three results is reported. The moisture was also analyzed with the use of oven drying method and reveals the same results. The result was expressed using the following equation (3.2)

$$Mc = \frac{\text{wo}-\text{w1}}{\text{wo}} * 100\% \qquad (3.2)$$

Where

wo= initial weight of dry sorbent, w1= weight of sorbent after dry

### 3.4.3 Porosity

The porosity of the tea waste was determined based on the particle size of the tea. The porosity of the tea was analyzed by simply read from the data graph by using particle size range. The porosity of the tea waste also shows the active surface area of the adsorbent.

### 3.4.4 Particle size determination

- To weigh the known amount tea waste, and put on the sieve shaker with different sieve size.
- After shaking or vibrating the sieve, collect the tea which remains on the range of usable.
- After that weighing the usable range tea waste and preserve it for adsorption purpose.

### 3.4.5 Surface area

The surface area of the tea waste was computed compared to its porosity and particle size, the surface area is the surface per volume ratio of one tea waste particle that was the basic physical parameter for the adsorption capacity of the adsorbent

The surface area of the tea particle is calculated by using equation (3.3)

$$s = \frac{Ss * \sqrt{T}}{\sqrt{T}\ s} \qquad (3.3)$$

Where: Ss =surface volume of the bed, constant value for tea = 3974 $cm^3$.

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

$T_s$ = time determined for dropping the fluid, constant value for tea =50.2 sec.

S = surface area of the particle.

### 3.4.5 Volatile matter determination

Empty Crucible was weighed at the first; 1g of sample was added in the crucible and weighed then after it was kept in the muffle furnace at a temperature of 600°C for 10 minutes. Then taken out and kept in the desiccators for half an hour to cool down. The weight of the sample in crucible was measured again. Percent volatile matter was then calculated by using equation (3.4).

$$V = \frac{(w0-wa)}{wo} * 100 \qquad (3.4)$$

Where

wo – initial weight of dry sorbent, wa- weight of tea after cooling

### 3.4.6 Bulk Density determination

The mass of Psychomotor was measured at the first, fill the sample up to 50% volume of the psychomotor and take the weight then fill the remain volume with distilled water, then calculate the bulk density.

Determination of bulk density is important as it ensures sufficient mechanical strength, thereby reducing weight losses during treatment process. It depends not only on the characteristics of the starting materials but also then activation method (Zahangir *et al*., 2008).

### 3.4.7 Fourier Transformation Infrared Spectroscopy (FTIR)

The FTIR studies were performed to determine the varies functional groups on the surface of the material (tea waste). The instrument used to record the FTIR spectra by FTIR instrument with kBr as reference. The spectrum was recorded by using FTIR (Ahmaruzzaman.and Laxmi Gayatri) spectrophotometric in a spectral range of 400-4000cm$^{-1}$.

## 3.5 Preparation of copper and Zinc (Adsorbate) stock solution

Copper sulphate bihygdrate and zinc sulphate bihygdrate were used as the source for copper and zinc stock solution respectively. All the required solutions were prepared with analytical grade reagents and distilled water. The ($CuSO4.5H2O$), ($ZnSO4.7H2O$) stock solution (1000mg/L) were made by dissolving 3.927g of 98% $CuSO4.5H2O$ and 4.395 grams of $ZnSO4.7H2O$ in1.0L distilled water. Synthetic samples of different concentrations of CuSO4.5H2O, ZnSO4.7H2O were prepared from this stock solution by appropriate dilutions.

To prepare stock solution for the calibration of an Atomic Adsorption spectrophotometer we are required to use Atomic adsorption spectrophotometer (AAS) to measure the concentration of cupper with in a test solution .To Produce standard solution, prepare 1000ppm of an initial stock solution with an approximate cupper concentration of about 1000ppm which kept for later use the reason for prepare strong solution was that small amount of cupper was leach in the container wall over time but the effect on the concentration was proportionally less.

The following analysis describes the type of calculation that we made:

Frist calculate mass of cupper that must be present in 1000ppm of solution to produce cupper concentration of 1000ppm was 1g.

We have calculated that it require 1.0g of cupper in 1000ml solution to obtain a concentration of 1000ppm .

Then calculate the mass of $CuSO_4$.5H2O that were contain 1.0g of cupper by using the following atomic masses Cu: 63.5, S: 32.1, O: 16 and H : 1

The molar mass of $CuSO_4$.5H2O was calculated by combining the relative atomic masses to give: 1*63.5+ 1*32.1+5*(2*1+1*16)=249.6, the molar mass of 249.6g of $CuSO_4$.5H2O was contain the atomic mass of 63.5g of cupper ,hence to get 1.0g of cupper we must divide the total amount by 63.5, 249.6/63.5=3.931g,so we have calculated that 3.931g of $CuSO_4$.5H2O contain 1.0g of cupper, then we weighed out accurate 3.931g of $CuSO_4$.5H2O and dissolve it in to nitric acid in 1.0liter volumetric flask solution to prevent sedimentation of cupper.

To obtain 200ml of 10ppm of solution directly from an initial concentration of 1000ppm would require taking a volume vi of the stock solution given by dilution equation : vi(ml)*1000ppm = 200ml *10ppm :VI= (200*10ppm) /1000=2ml.

So we follow the same procedure for, $ZnSO_4$.7H2O.

## 3.6 Full factorial design

Factorial design is used to test the effect of each factor. In factorial experiment, all possible combination of factor levels was tested. And it was determined the effects of individual factors and assessed the effect of change of variables for copper and zinc removal full factorial design with three factor with each three level described in table (3.2).

Table 3.2 full factorial deign experimental methods

| Independent factors | Factors level |
|---|---|
| Concentration of copper and zinc | Three (10ppm, 30ppm,50ppm) |
| Contact time | Three (60min,120min,180min) |
| pH | Three (4,5,6) |
| No of run | 27 |
| Replicate(two times) | 2*27=54 |
| Total experiment | 128 |
| Response | %removal=$((C_o-C_e)/C_o))*100$ |

## 3.7 Heavy metal ion Adsorption procedure

A series of duplicate single adsorbate or competitive batch adsorption experiments were conducted at 30°C grade in acid washed polyethylene plastic bottles with blank (only with the adsorbent media) and control (only with the heavy metal ions) experiments. A 200mL constituent wastewater solution containing a known heavy metal ions concentration and a desired adsorbent dose were agitated at a fixed revolution per minute (110 rpm) on a horizontal shaker for a predetermined contact time. Afterwards the adsorbent were separated by filtration using what man filter paper no.1. Then, the heavy metal concentration (Cu and Zn in the filtrate were analyzed on Atomic Absorption Spectrometers (AAS) at 324.8 nm and 213nm respectively. The average of duplicate measurements was reported.

### 3.7.1 Batch Mode Adsorption Experimental Studies

The adsorption of heavy metals on tea waste was studied by batch technique. The general method used for this study was described as follows:

A known weight of tea waste adsorbent (e.g. 1 g adsorbent) was equilibrated with 200 ml of the each heavy metals (namely Cu and Zn ions) solution of known concentration (10, 30 and 50 ppm) in different stoppered borosil glass flask at a fixed temperature ($30^oC$) in an orbital shaker for a known period (60–180 Min.) of time. Then 10ml of sample were collected from each flask in time interval of 60, 120 and 180 minutes and the suspension of the adsorbent were separated from solution by filtration using what man No.1 filter paper. The concentration of heavy metal ions remaining in solution were measured by Atomic Adsorption spectrometer (AAS). The effect of several parameters, such as pH, concentrations and contact time on the adsorption were studied. The pH of the adsorptive solutions was adjusted using sulfuric acid, sodium hydroxide and buffer solutions when required. The percentage of heavy metal removal was calculated using equation (3.5).

$$\%E = \frac{\mathrm{Co - Ct * 100}}{\mathrm{Co}} \qquad (3.5)$$

Where *C*o: initial metal ion concentration of test solution, mg/l; Ct is heavy metal concentration [mg.l-1] at time t [min] .

The quantity of toxic heavy elements adsorbed in locally available material (tea waste) can be assumed using equation (3.6) (Volesky, 2003; Argun *et al.*, 2007).

$$\mathrm{qe} = \frac{\mathrm{(Co - Ce) * v}}{\mathrm{w}} \qquad (3.6)$$

Where qe the adsorption efficiency [mg.g-1], $C_o$ is amount of heavy metal before process [mg.l1], Ce is equilibrium amount of heavy metal [mg.l-1], v is volume of waste water, and w is adsorbent weight [g].

## 3.8 Analyze concentration of copper and Zink

The concentrations of the adsorbate under investigation were measured using an atomic adsorption spectrophotometer (Model Perkin Elmer 3100). The basic principle for single element quantitative analysis using atomic adsorption spectrophotometer is the Beer- Lambert or Beer’s Law. The calibration curves were developed by using an Atomic Absorption Spectrophotometer (Perkin Elmer 3100). It was obtained by aspirating the standard solution into the flame; standard solutions containing known five concentrations; 10, 20, 30, 40 and 50 mg/l of Cu (II) and Zn (II) cat-ions solutions respectively. The calibration curves are shown in Appendix (fig.1 and 2). The absorption of each solution was determined and the water samples were analyzed against the calibration curve prepared by the standard solutions of the metals (Cu, and Zn). A blank reagent, i.e., distilled water was also run before the development of the calibration curve and during the interval of each sample. Copper specific hollow cathode lamp (wavelength 324.8 nm), and Zink specific hollow cathode lamp (wavelength 213 nm) were used.

## 3.9 Adsorption isotherm

The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm; adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity or homogeneity of adsorbents, the type of coverage, and possibility of interaction between the adsorbate species.

Adsorption isotherm study was carried out by fitting the equilibrium data to two isotherm models: the Langmuir and Freundlich isotherm models. The applicability of the isotherm equation to the equilibrium data was explained by observing the values of the correlation coefficients, $R^2$. According to the regression analysis, the higher the $R^2$ value (closer to unity), the better is the model for depicting the isotherm parameters (Ahmad, 2006; Tan, 2008).

### 3.9.1 Langmuir isotherm

Langmuir isotherm is a monolayer type adsorption (Langmuir, 1916; Abas *et al.*, 2013). Irving Langmuir reported the data regarding adsorption between gases and solids.

The formula of isotherm comes from the following theories
(a) Collect similar surface of adsorbent material

(b) Molecules of adsorbent material do not attract each other

(c) Uniform mechanisms of adsorption

(d) Monolayer made at the highest adsorption process and

(e) Molecule of adsorbate adsorbed at the open place of adsorbent.

Langmuir isotherm model was derived from the above mentioned hypothesis that the relation between the highest adsorption with a monolayer of adsorbent materials, without an attraction amongst the adsorbed metals. The Langmuir adsorption is efficiently used for the attraction of metals ions from solution (Langmuir, 1916; Kırbıyık, 2012) and is defined as follows:

$$qE = \frac{\mathrm{qM*kL*CE}}{\mathrm{1+kLCE}} \qquad (3.7)$$

Linear equation of Langmuir written equation (3.8)

$$\frac{1}{\mathrm{qE}} = \frac{1}{qE} + \frac{1}{qMkL}\,\frac{1}{CE} \qquad (3.8)$$

Where $q_E$ is a mass of heavy metal adsorbed per gram of local available materials CE is equilibrium of heavy metal concentration in wastewater, milligram of heavy metal per liter $K_L$ is Langmuir constant, liter per milligram of heavy metal, and $q_M$ is maximum coverage, milligram of heavy metal per gram of local available materials.

The important features of Langmuir stated in the forms of dimensionless separation factor (Moreno and Giraldo, 2012), RL is defined as equation (3.9).

$$RL = \frac{1}{(1+\mathrm{KLCo})} \qquad (3.9)$$

Where $K_L$ is constant of Langmuir [L.mg$^{-1}$], and *Co* is primary concentration of heavy metal ions [mg.L$^{-1}$], $R_L$ a value indicating the shape of the isotherms: $R_L$ >1 shows disapproving adsorption, $R_L$ = 1 is shows linear, $R_L$ values between 0 and 1 shows approving adsorption, and $RL$= 0 shows irreversible adsorption.

### 3.9.2 Freundlich isotherm

The Freundlich isotherm is a multilayer type adsorption equation (Freundlich, 1906). The Freundlich model depends on a multilayered/heterogeneous surface among liquids and solid equilibrium linkages. The Freundlich equation is described according to the following equation (PMDFEU, 2009; Kırbıyık, 2012).

$$qe = \frac{\mathrm{K_F}\ \ \mathrm{Ce}^{\frac{1}{n}}}{2a} \qquad (3.10)$$

Freundlich linear formula stands:

$$\log(qe) = \ \log k_F + \frac{1}{n}\log C_e \qquad (3.1)$$

# 4 RESULTS AND DISCUSSION

This chapter provides result of laboratory analysis made for tea waste characterization, study of effects of parameters such as pH, concentration of heavy metal and contact time on heavy metal removal capacity of tea waste from constituent waste water are presented. The constituent waste water loaded with heavy metal was treated with tea waste and performance of the tea waste was evaluated by varying the parameters to optimize those factors which affect the performance of tea waste for specific metal ion.

## 4.1 Treatment of Tea waste to remove heavy metal

### 4.1.1 Characterization of Tea waste

Table 4.1 Physicochemical properties of tea waste

| Characteristics | Unit | Present Value | Comparisons with other investigation (Malkoc et al.,2007,Amarasingheand Williams,(2007) |
|---|---|---|---|
| Ash content | % | 2.99 | 2.97 |
| Carbon Content | % | 70 | 68 |
| Volatile matter | % | 79.9 | 80.24 |
| Bulk density | $g/cm^3$ | 0.602 | 0.36 |
| Moisture content | % | 4.91 | 11.2 |
| Pore size | nm | 1.92 | 1.92 |
| Particle size | µm | 50-80 | - |

The various physicochemical composition of tea waste was characterized and compares present value with other investigations (Table 4.1). As show in table the moisture content of tea waste was tended to be low (4.91%) showing that this adsorbent was properly prepared and handled. Moisture content, according to Aziza *et al*., (2008) has a relationship with porosity of a given adsorbent. Adsorbent with high moisture content was expected to swell less, thus retarding pore size expansion for adsorbate uptake. Volatile matter of 79.9% was recorded in the study. This was responsible for decomposition of the organic materials to release volatiles and development of micro porous structures (Malik *et al*., 2006). Ash is a measure of inorganic impurities in the carbons (Bansode *et al*., 2003). The ash content has lower value that indicates the good adsorbent characteristics; Carbon content is the residual amount of carbon present in the sample. The result obtained shows that carbon content was 70%. This is in concord with the findings of Malik *et al*., (2006) who reported that most of the carbon composition of adsorbent falls within 50-90%. Sometimes there is variation of surface area of a material if a different mode of activation is followed.

### 4.1.2 The FTIR spectrum of tea waste

The adsorption mechanism of $cu^{2+}$ and $zn^{2+}$ on tea waste can be better understood from a FTIR study of tea waste before adsorption. The infrared (IR) spectrum of the adsorbent was shown in Figures 4.1. The complex nature of the adsorbent was displayed by the number of adsorption peaks in the spectra. The recorded FTIR spectra of tea waste before adsorption showed a sharp bend at 3429.4 $cm^{-1}$ due to asymmetric stretching of the N-H group confirming the existence of an amino group. The peak at 3333.0 $cm^{-1}$ is due to OH stretching of the COOH group, while the peak at 2970.4 $cm^{-1}$ is likely due to the C-H normal mode. The OH stretching of the COOH group is responsible for the band near 2630 $cm^{-1}$. The spectrum also showed a strong peak at 2904.8 $cm^{-1}$ due to the C-H group. The peak at 1726 $cm^{-1}$ may be due to a carbonyl ester group. The peak generated at 1612 $cm^{-1}$ is due to the aromatic ring vibration. The peak at 1502 $cm^{-1}$ is due to symmetric stretching of double bonds. The presence of these bands confirmed the adsorption of $cu^{2+}$ and $zn^{2+.}$

FTIR analysis of the spectra showed that the H-bonded O-H stretch, C-C=C symmetric stretch and C-O stretch of esters may be held responsible for the adsorption of $Cu^{2+}$ and $Zn^{2+}$ on the tea waste surface.

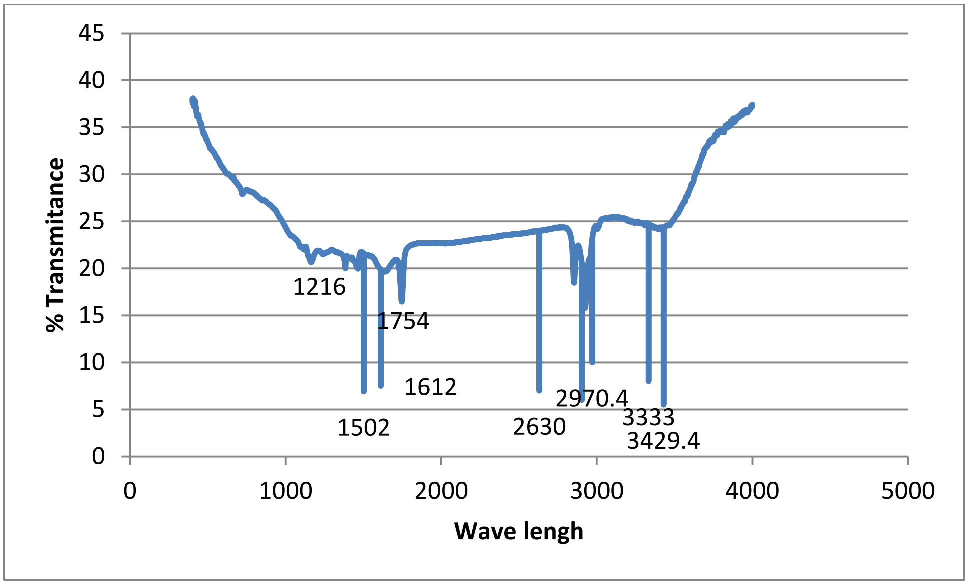


Figure 4.1: a, FTIR Analysis of tea waste before adsorption

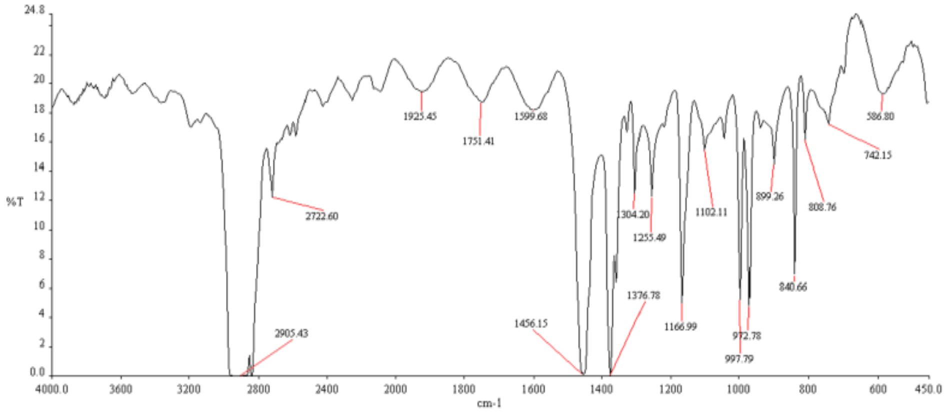


Figure 4.1b, Compazine with another investigation of the FTIR of Activated carbon

The difference in the nature of chemical reagents affects the porosity development of adsorbent. Comparative adsorption data were obtained for the char, NaOH, $ZnCl_2$, KOH, $H_3PO_4$, $H_2O_2$, and $MnO_2$ treated other adsorbent as (26.73, 39.18, 78.63, 77.28, 94.60, 28.42, and 8.19) mg· $g^{-1}$, respectively (Ahmaruzzaman and Laxmi 2010). The result showed that $H_3PO_4$ was the best activating agent for the adsorbent for the adsorption of heavy metal from aqueous solution. In present study also the, H3PO4 socked tea waste was used as the adsorbent for the effective removal $Cu^{2+}$ $Zn^{2+}$ from waste water.

## 4.2 Optimum Conditions for copper and Zink Removal by the Tea waste adsorbent

### 4.2.1 Effect of adsorbent dose

The results, of adsorbent dose study are given in Figure (4.2). The removal efficiency increases from 64.36% to 92.45% with an increase in adsorbent dose from 0.4 to 1.0g/200ml. This can be attributed to increased number of sorption sites available for sorbent solute interaction. With further increase of adsorbent dose from 1.0 to 2.0 g, the percent adsorption increases less significantly. Thus, the adsorbent dose was maintained at 1.0 g in all the subsequent experiments, which was considered to be sufficient for the removal of copper and zinc. According to, (Wasewar *et al*. 2009) increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites.

In some cases the amount of metal ions adsorbed per unit weight of adsorbent decreases with the adsorbent dose. This is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value and the system reaches equilibrium at lower values of indicating the adsorption sites remain unsaturated ( Bose *et al*., 2002).

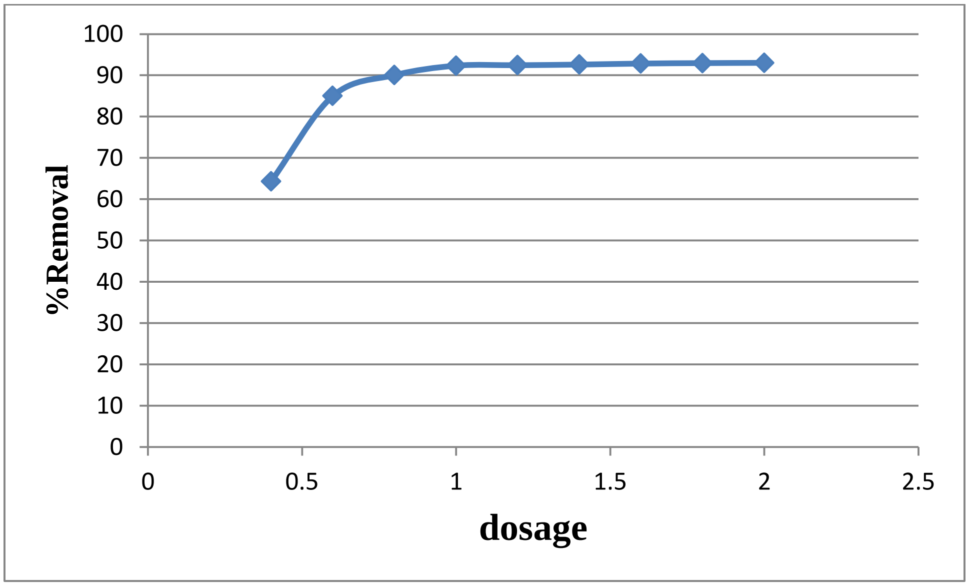


Figure 4.2 Effect of adsorbent dose on the % removal of copper (Co = 30ppm, pH = 3, agitation speed = 110 rpm and contact time = 3hr)

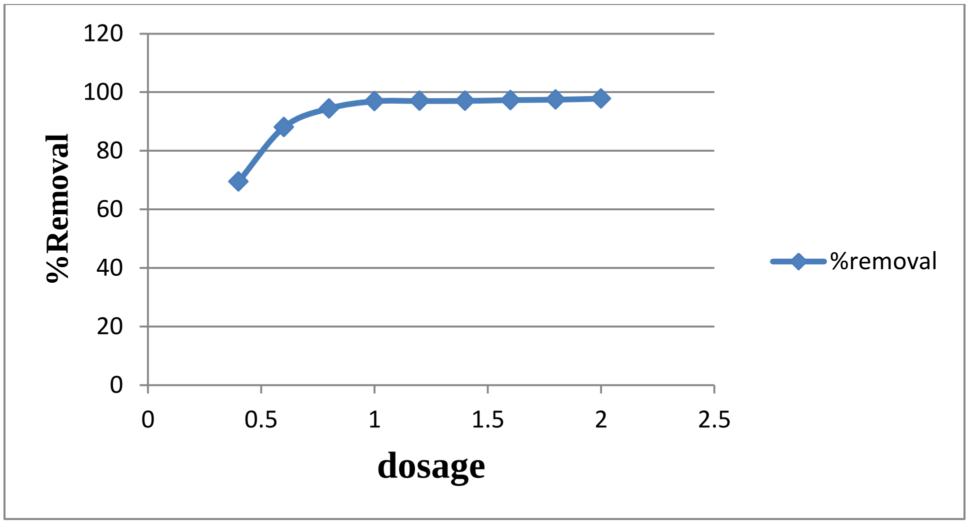


Figure 4.3 Effect of adsorbent dose on the % removal of Zinc (Co = 30ppm, pH = 3, Agitation speed = 110 rpm and contact time = 3hr)

#### 4.2.1.1 Effect of contact time

The variation in the percentage removal of heavy metals with contact time using 1g/200ml of tea waste adsorbent at 5pH for varying initial metal ions concentration of 10ppm, 30ppm and 50ppm was shown in Fig.4.4 and Fig.4.5The maximum percent removal of copper and zinc ions are 95.98% and 99.8% respectively at 120 minutes and concentration of 10ppm in each case.

This was achieved by varying the contact time from 60min to 180 min. in separate experimental runs. As expected, the amount of ion adsorbed into adsorbent increases with time, and at some point, reaches a constant value beyond which no more is removed from solution. At this point, the amount of the ion desorbing from the adsorbent is in a state of dynamic equilibrium with the amount being absorbed to the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. Equilibrium was reached at 120 min. in all cases. This can be explained by the fact that initially, the rate of ion uptake was higher because all sites on the adsorbent were vacant and ion concentration was high, but decrease of adsorption sites reduced the uptake rate. Similar results were found in the study of (Mousavi, 2010).

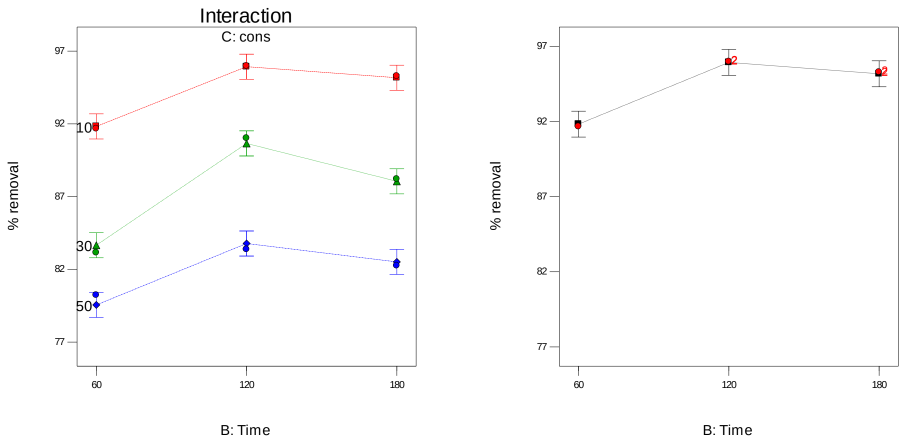


Figure 4.4 Effect of contact time on % removal of cupper ion by Tea waste adsorbent at 5pH

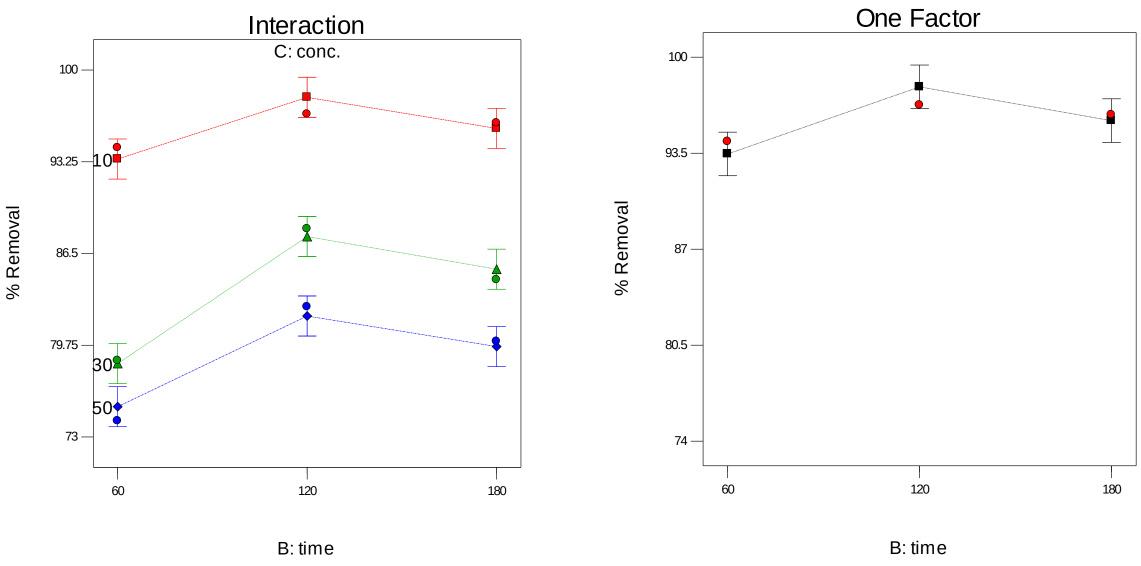


Figure 4.5 Effect of contact time on % removal of zinc ion by tea Waste Adsorbent

### 4.2.1.2 Effect of pH

Variations of pH are one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Fig.4.6 and Fig 4.7 show the effect of pH on heavy metals removal efficiencies of tea waste adsorbent. These studies were conducted at an initial metal ions concentration of 10, 30 and 50ppm in 200ml solution, and constant adsorbent dose 1 g/200ml solution and agitation period of 120 minutes for both heavy metal ions at varying the pH in each solution.

The percentage adsorption increases with pH. The maximum adsorption was attained at 5pH and thereafter it decreases with further increase in pH. Maximum removal efficiency at optimum pH is about 95.98% and 99.8% metal from solution with initial copper and zinc concentration of 10ppm. This may be because at pH values below 4.0, the electrostatic force of repulsion between adsorbent (tea waste) and adsorbate ($Cu^{2+,}$ $Zn^{2+}$) is prominent. At pH above 6.0, there is a possibility of adsorbate precipitation on the surface of the adsorbents by nucleation ( Agrawal *et al.*,2004).

In Fig.4.6 and Fig 4.7 higher pH, that is, above optimum pH of 5, increase in $OH^{-}$ ions cause a decrease in adsorption of metal ions at adsorbent adsorbate interface. Lower solubility's of hydrolyzed metal ions species may be another reason for the maximum adsorption at 5 pH. Since, in lower pH range, metal is present predominantly as metal ions in the adsorptive solution, there is a competition between $H^{+}$ and $M^{+}$ ions for adsorption at the ion exchangeable sites, leading to a low removal of metal. The extensive repulsion of metal ions due to protonation of the adsorbent surface at lower pH may be another reason for decrease in adsorption of metal in lower pH range.

The mechanism of metal ion adsorption may also be explained based on ion exchange model. In carbon aerogel, carbon–oxygen complexes are presented by Equations 4.1 and Equation 4.2. The surface oxygen complexes hydrolyzed water molecules are shown below:

$$2COH + M^{+} \rightarrow (CO)_2 M^{+} + 2H^{+} \quad (4.1)$$

$$COH2^{2} + M^{+} \rightarrow COM_{2+} + 2H^{+} \quad (4.2)$$

The above mechanism has been confirmed by an increasing initial metal ion concentration in aqueous solution as the final pH of solution decrease. This clearly indicates that uptake of more metal ions causes release of more $H^{+}$ ions. The increase in metal removal as the pH increases can be explained on the basis of a decrease in competition between proton and metal cat-ions for the same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between the surface and the metal ions. Decrease in adsorption at higher pH (above 5 pH) is due to the formation of soluble hydroxyl complexes.

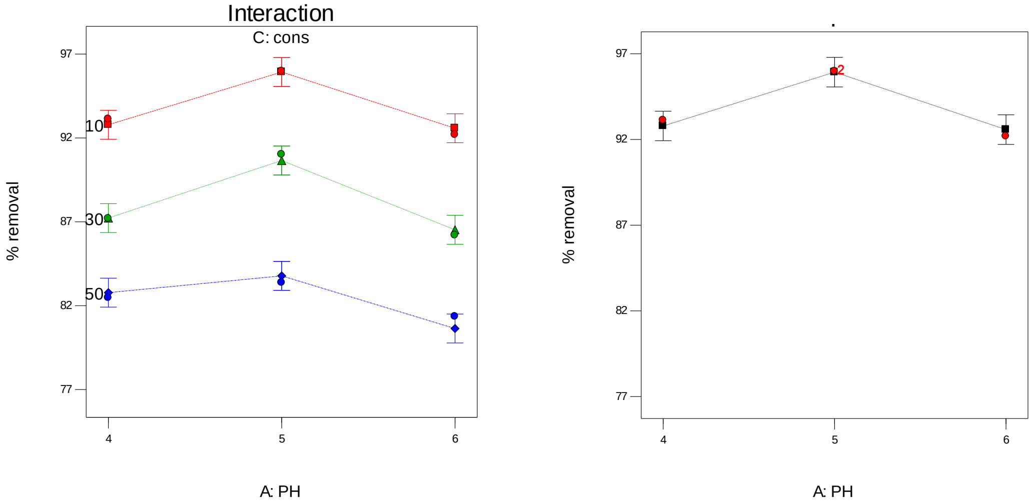


Figure 4.6 Effect of pH on % removal of copper ion by tea waste adsorbent at 2hr.

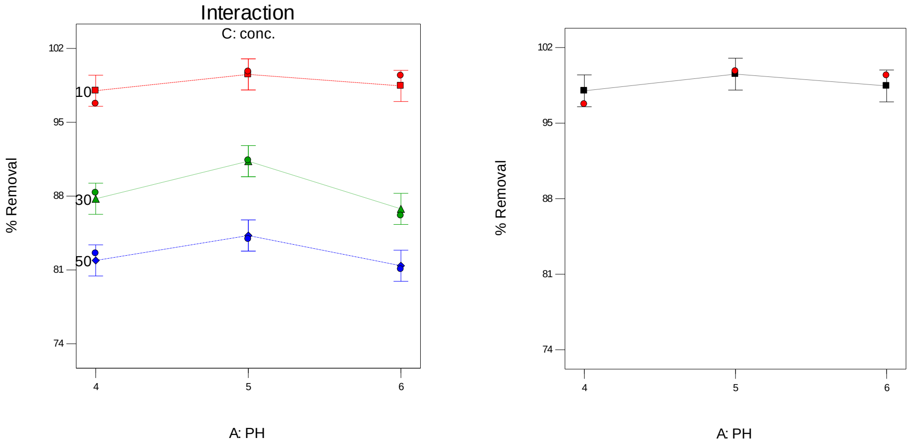


Figure 4.7 Effect of pH on % removal of zinc ion by tea waste adsorbent at 2hr.

### 4.2.1.3 Effect of initial concentration of heavy metal

The effect of initial ion concentrations on the adsorption efficiency of the studied tea wastes at optimum point of pH 5, 120 contact time and 110 rpm agitation speed shown in Fig. 4.8 and Fig 4.9, Adsorption experiments were carried out at different initial ion concentrations ranging from

10ppm to 50ppm. It was observed as a general trend that there was decrease of the removal percentage with increase in initial concentration. These results may be explained on the basis that the increase in the number of ions competing for the available binding sites and also because of the lack of active sites on the adsorbent at higher concentrations. Therefore, more metal ions were left un-adsorbed in solution at higher concentration levels (Krishnan & Anirudhan, 2003).

According to Bose *et al*.,(2002), at low ion concentrations the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact with the adsorbent and be removed from the solution. However, amount of metal adsorbed per unit weight of adsorbent (adsorption capacity) is higher at high concentrations.

At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, the fractional adsorption is independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. The maximum %removal of copper and zinc ions are 95.98% and 99.81% respectively at 10ppm concentration.

Hence, the percent removal of heavy metals depends on the initial metal ions concentration and decreases with increase in initial metal ions concentration. The difference in percentage removal of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent.

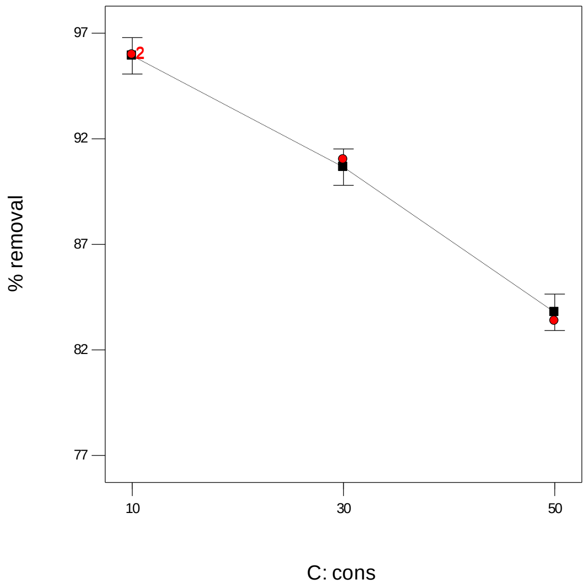


Figure 4.8 Effect of concentration on the % removal of cupper at (pH = 5 agitation speed = 110 rpm and contact time = 2hr)

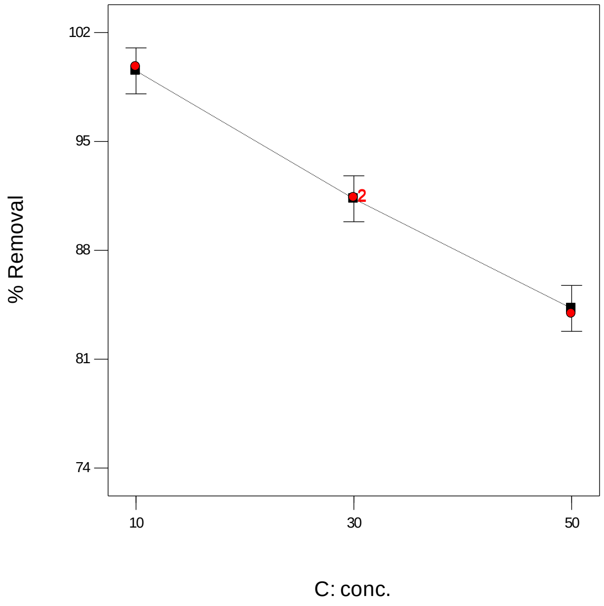


Figure 4.9 Effect of concentration on the % removal of zinc at (pH = 5 agitation speed = 110 rpm and contact time = 2hr)

### 4.2.2 Combined effect of independent variables (concentration and pH) verses % removal

In order to study the interaction among different independent variables and their corresponding effect on the response variable, contour plots were drawn. A contour plot is a graphical representation of a three dimensional response surface as a function of two independent variables, maintaining all other variables at fixed or different level. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response variable. Interaction effect of initial $Cu^{2+}$; $Zn^{2+}$ concentration and pH was shown in contour and 3D plot of Fig. 4.10 and Fig 4.11. Removal percentage increases with decreasing initial concentration and pH increase.

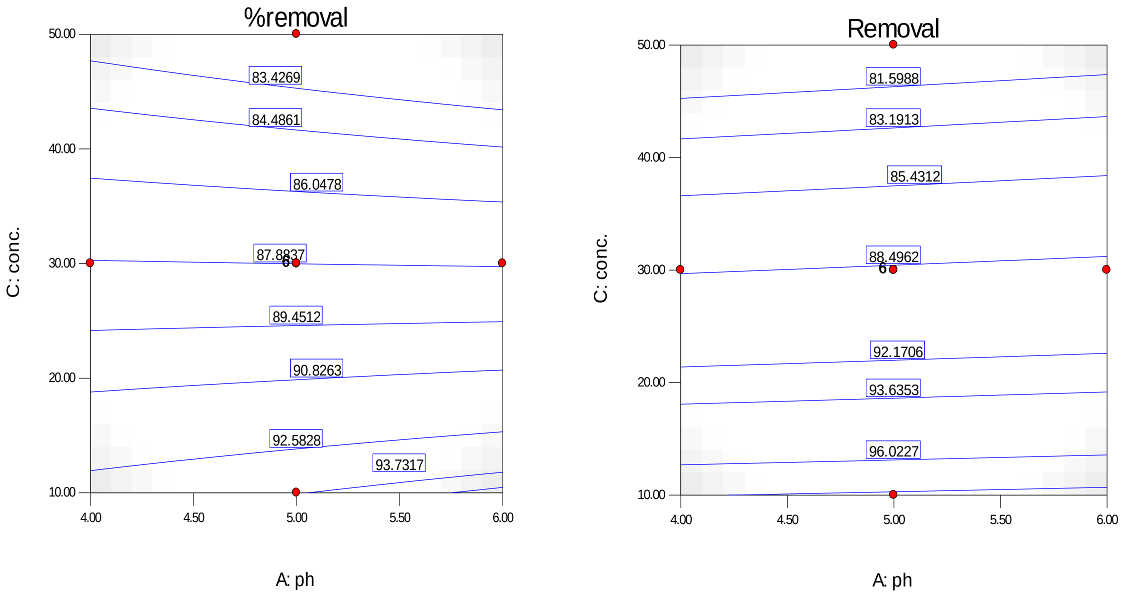


Figure 4.10 Contour plots showing the combined effect of $Cu^{2+}$ and $Zn^{2+}$ concentration and pH, at optimized adsorbent dose of 1g, shaking time 2hr

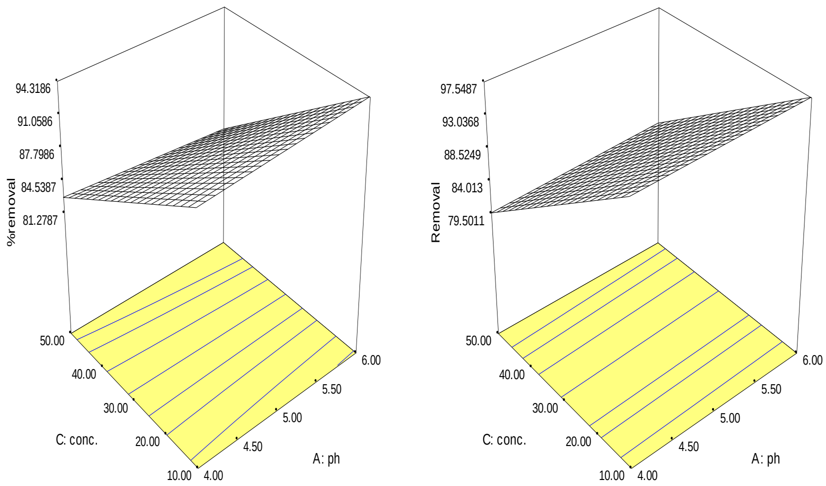


Figure 4.11 3D plots showing the combined effect of $Cu^{2+}$ and $Zn^{2+}$ concentration and pH, at optimized adsorbent dose of 1g, shaking time 2hr

In general, at higher $Cu^{2+}$ and $Zn^{2+}$concentration, the % removal decreased with pH decrease from 6 to 4, while at lower concentration, removal increases. Possible explanations may lie in the states of the copper and zinc ion, protonation level and surface charge of the adsorbent.

### 4.2.3 Combined Effects of concentration and time on %removal of $Cu^{2+}$ and $Zn^{2+}$

Fig. 4.12 and Fig 4.13 shows the simultaneous effects of concentration and time on $Cu^{2+}$ and $Zn^{2+}$ removal by tea waste is shown in contour and 3D plots**.** From the obtained result, it is evident that the removal of metal ions increased as contact time increases and concentration decrease. It is clear from Fig.4.12 and Fig 4.13 that as time increase concentration decrease removal efficiency increase, as concentration increase time decrease removal efficiency decrease.

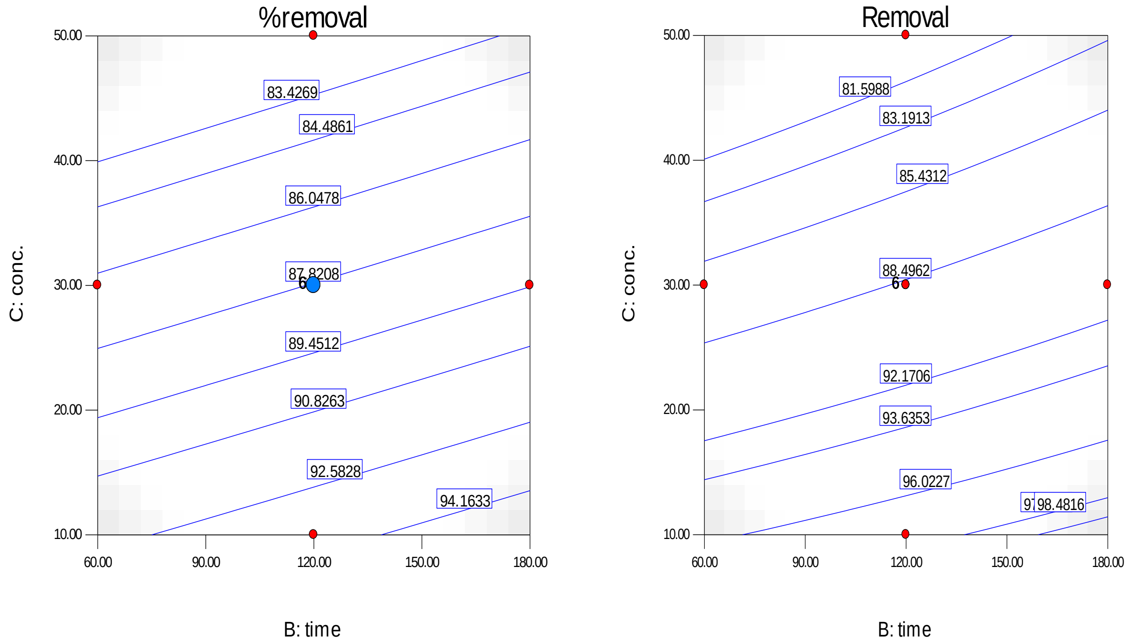


Figure 4.12 Contour plots showing the combined effect of $Cu^{2+}$ and $Zn^{2+}$concentration and time, at optimized adsorbent dose of 1g, and pH 5

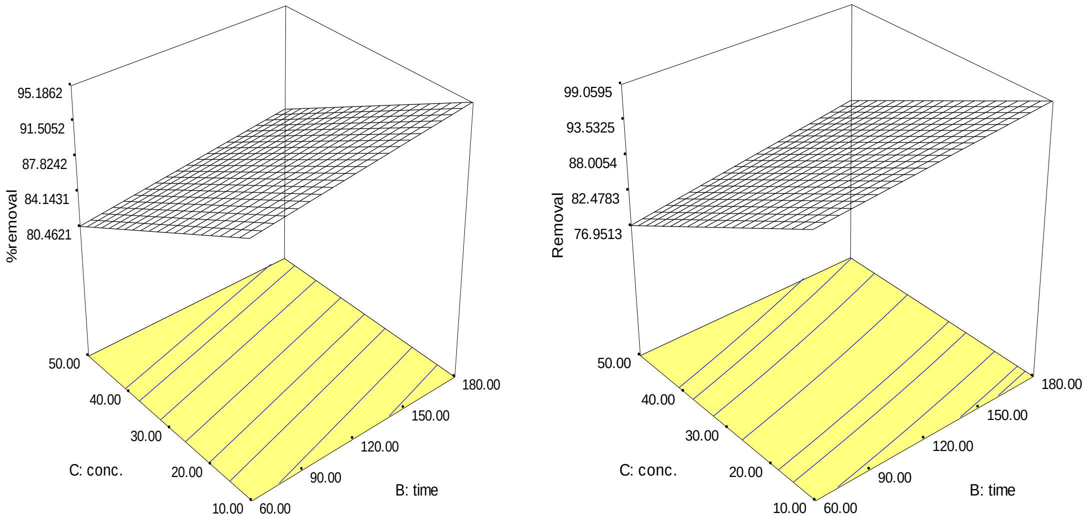


Figure 4.13 3D plots showing the combined effect of $Cu^{2+}$ and $Zn^{2+}$concentration and time, at optimized adsorbent dose of 1g and at pH 5

### 4.2.4 Combined Effects of pH and time on %removal of $Cu^{2+}$ and $Zn^{2+}$

The simultaneous effects of pH and time on $Cu^{2+}$ $Zn^{2+}$ removal by tea waste shown in contour and 3D plots of Fig 4.14 and Fig 4.15. As shown on the graph % removal increase as time increase from 60min-180min and also pH increase from 4 to 6.

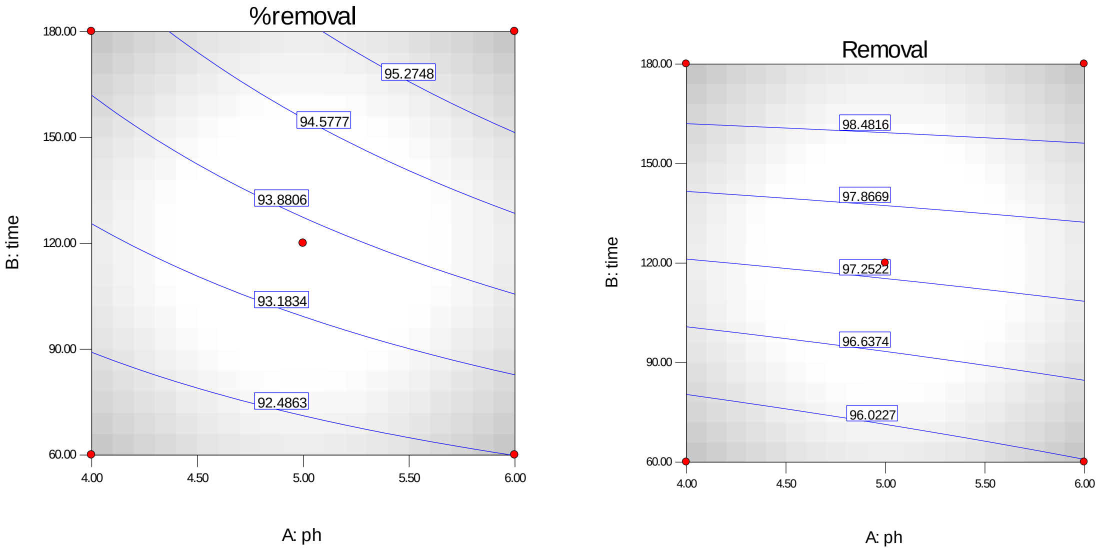


Figure 4.14 Contour plot showing the combined effect of pH and time for $Cu^{2+}$ and $Zn^{2+}$ respectively, at optimized adsorbent dose of 1g, and concentration10ppm

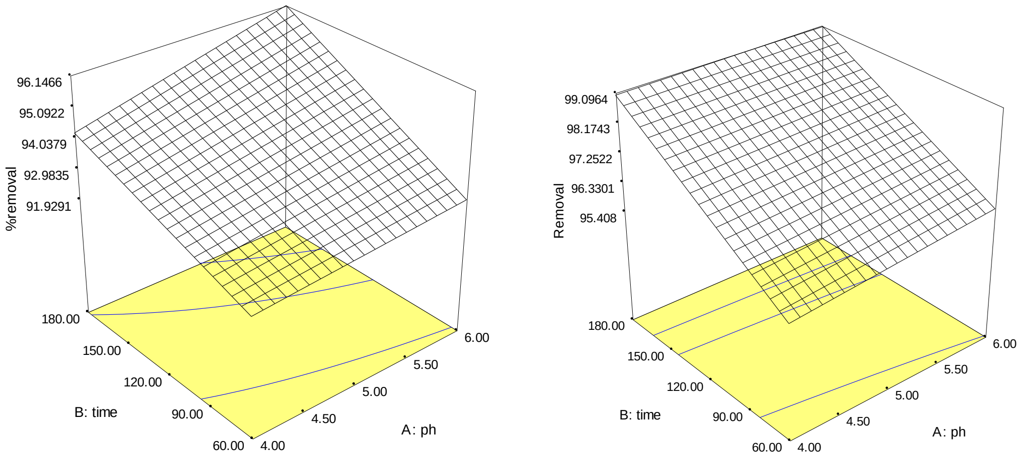


Figure 4.15 3D plots showing the combined effect of PH and time for $Cu^{2+}$ and $Zn^{2+}$ respectively, at optimized adsorbent dose of 1g and concentration 10ppm

### 4.2.5 Development of Regression model analysis

Statistical analysis by response surface methodology (RSM) was used to determine a well-fitted regression model of adsorption process. The experimental data of each adsorbate $Cu^{2+}$and $Zn^{2+}$ were fitted with linear, interactive, quadratic and cubic models. The significance of suggested regression models for each adsorbate could be determined through the ANOVA.

The results in Table 4.2 showed that the treatment method of copper and zinc using tea waste were effective at concentration of 10ppm, 5pH and contact time of 120min. The maximum removal efficiency of copper and zinc at optimum point were 95.98% and 99.8% respectively

Table 4.2 CCD design metrics for three variables and response value

| Run | pH | Time(min) | Cu and Zn conc.(ppm) | % removal of Cu | % removal of Zn |
|---|---|---|---|---|---|
| 1 | 5 | 120 | 10 | 95.98 | 99.8052 |
| 2 | 6 | 120 | 30 | 86.2 | 91.3853 |
| 3 | 6 | 180 | 10 | 93.8202 | 97.5325 |
| 4 | 4 | 180 | 50 | 81.7978 | 80.026 |
| 5 | 5 | 120 | 30 | 91.0112 | 91.3853 |
| 6 | 5 | 120 | 30 | 91.0112 | 91.3853 |
| 7 | 6 | 60 | 10 | 90.8764 | 94.9351 |
| 8 | 5 | 120 | 50 | 83.3708 | 83.9221 |
| 9 | 4 | 180 | 10 | 91.9101 | 96.1039 |
| 10 | 5 | 120 | 30 | 91.0112 | 91.3853 |
| 11 | 6 | 60 | 50 | 77.7528 | 76.7792 |
| 12 | 6 | 180 | 50 | 81.3483 | 80.8052 |
| 13 | 5 | 120 | 30 | 91.0112 | 91.3853 |
| 14 | 4 | 120 | 30 | 87.191 | 88.3117 |
| 15 | 5 | 60 | 30 | 83.1461 | 81.645 |
| 16 | 5 | 120 | 30 | 91.0112 | 91.3853 |
| 17 | 5 | 120 | 30 | 91.0112 | 91.3853 |
| 18 | 4 | 60 | 10 | 89.8876 | 94.2857 |
| 19 | 4 | 60 | 50 | 80 | 74.1818 |
| 20 | 5 | 180 | 30 | 88.2022 | 90.9524 |

#### 4.2.2.1 Analysis of variance

Table 4.3 ANOVA results of the regression model for optimization of cu$^{2+}$ adsorption

| ANOVA for selected factorial model | | | | | | |
|---|---|---|---|---|---|---|
| Analysis of variance table [Classical sum of squares - Type II] | | | | | | |
| Source | Sum of Squares | df | Mean Square | F Value | p-value Prob > F | |
| Model | 741.17 | 18 | 41.18 | 103.57 | < 0.0001 | significant |
| A-pH | 27.19 | 2 | 13.59 | 34.19 | 0.0001 | |
| B-Time | 77.79 | 2 | 38.89 | 97.83 | < 0.0001 | |
| C-cons | 615 | 2 | 307.5 | 773.43 | < 0.0001 | |
| AB | 6.81 | 4 | 1.7 | 4.28 | 0.0003 | |
| AC | 6.09 | 4 | 1.52 | 3.83 | 0.00502 | |
| BC | 8.3 | 4 | 2.07 | 5.22 | 0.00029 | |
| Residual | 3.18 | 8 | 0.4 | | | |
| Cor Total | 744.35 | 26 | | | | |

The Model F-value of 103.57 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.Values of "Prob > F" less than 0.0500 indicate model terms are significant.In this case A, B, C, AB, BC are significant model terms.Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Table 4.4 ANOVA results of the regression model for optimization of Zn adsorption

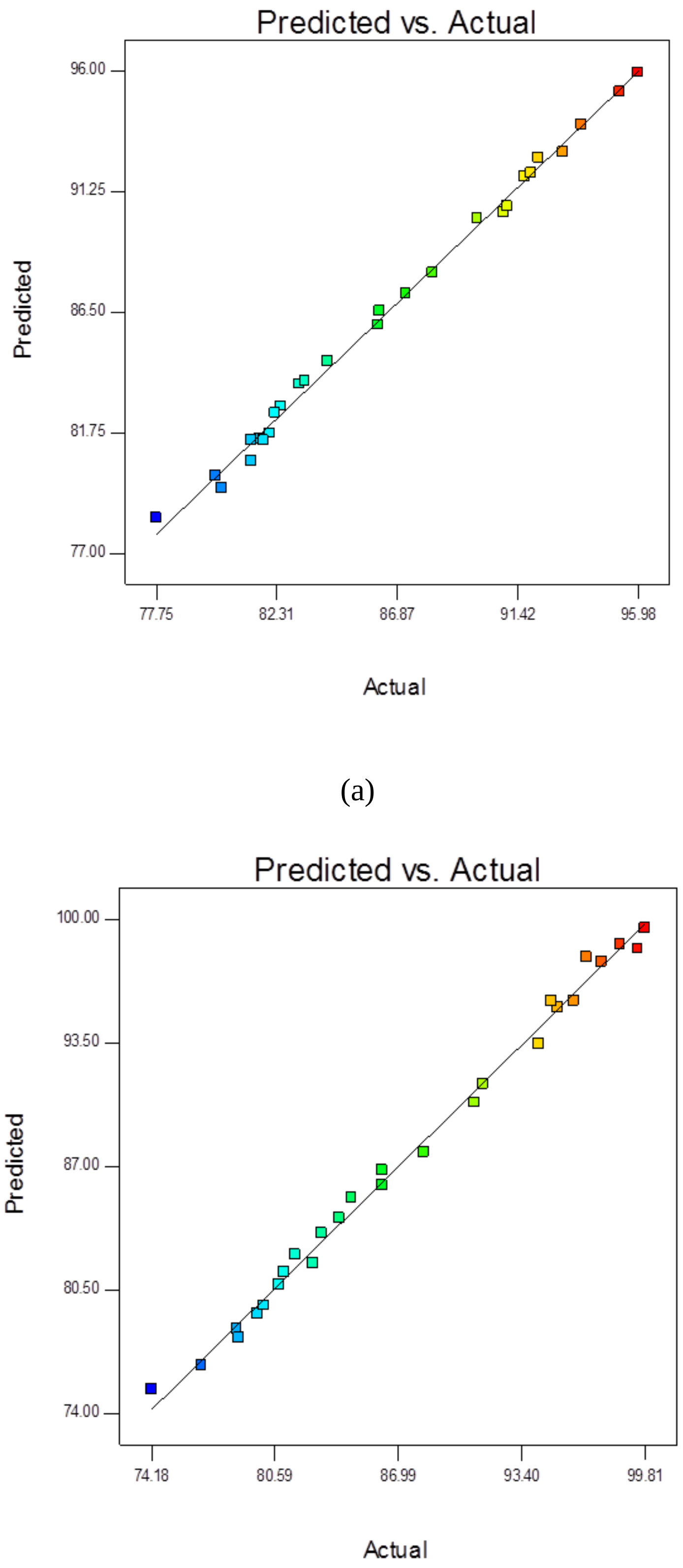
| ANOVA for selected factorial model | | | | | | |
|---|---|---|---|---|---|---|
| Analysis of variance table [Classical sum of squares - Type II] | | | | | | |
| | Sum of | | Mean | F | p-value | |
| Source | Squares | df | Square | Value | Prob > F | |
| Model | 1609.64 | 18 | 89.42 | 76.84 | < 0.0001 | significant |
| A-PH | 46.36 | 2 | 23.18 | 19.92 | 0.0008 | |
| B-time | 188.33 | 2 | 94.16 | 80.91 | < 0.0001 | |
| C-conc. | 1339.16 | 2 | 669.58 | 575.33 | < 0.0001 | |
| AB | 4.24 | 4 | 1.06 | 0.91 | 0.502 | |
| AC | 9.01 | 4 | 2.25 | 1.93 | 0.01981 | |
| BC | 22.56 | 4 | 5.64 | 4.85 | 0.0279 | |
| Residual | 9.31 | 8 | 1.16 | | | |
| Cor Total | 1618.95 | 26 | | | | |
| | | | | | | |

The Model F-value of 76.84 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AC BC are significant model termsValues greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

### 4.2.2.2 Predicted verses Actual

The performance of the model can be also visualized by observing the plots of predicted versus experimental percentage yield and removal as shown in Figures 4.4. As estimated, the predicted values for copper and zinc yield are the closest to their experimental values.

Figure 4.16 proves that the predicted response from the empirical model is in agreement with the observed ones



(a)

Figure 4.16 predicted verses actual for cupper (a) and zink (b) respectivel

## 4.3 Evaluation of Adsorption capacity

The driving force for adsorption is the concentration difference between the solute on the sorbent and the solute in the solution. High concentration difference provides a high driving force for the adsorption process and this may explain why higher adsorption capacities were achieved in the column fed with a higher $Cu^{2+}$ and $Zn^{2+}$ concentration.

An increase of the initial copper and zinc concentration from 10ppm to 50ppm, when other experimental conditions are kept constant, the corresponding adsorption bed capacity appears to increase from 1.9 to 8.34, 1.996 to 8.4 mg/g respectively. Higher initial copper and zinc concentrations caused a faster breakthrough. A decreased inlet copper and zinc concentrations gave delayed breakthrough curves, since the lower concentration gradient caused slower transport due to decreased diffusion coefficient (Aksu, 2005).

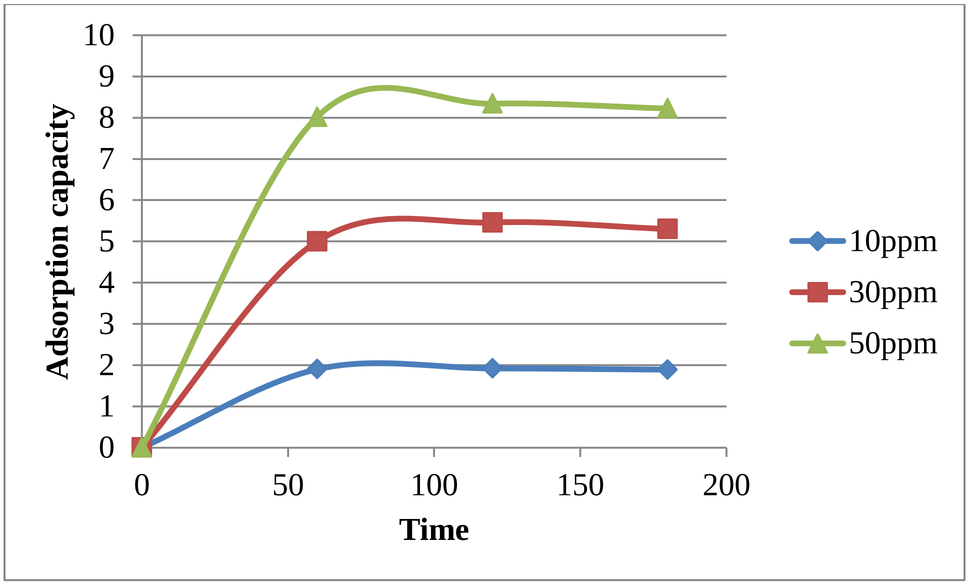


Figure 4.4 Adsorption capacity of tea waste at different concentration for copper at 1g/200ml of dosage and 5pH.

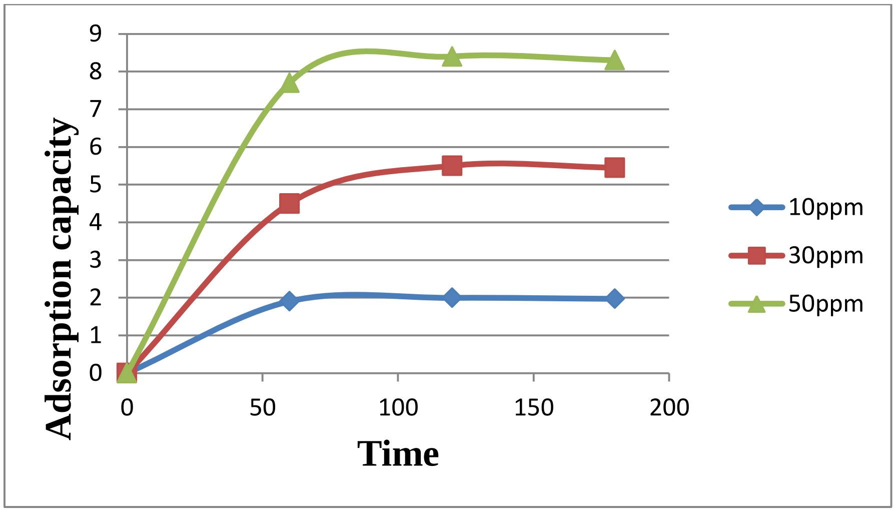


Figure 4.5 Adsorption capacity of tea waste at different concentration of zinc at 1g/200ml of dosage and 5pH.

## 4.4 Adsorption Isotherm

**Langmuir isotherm:** Value of Langmuir parameters and correlation coefficients $R^2$ are summarized in Table 4.7. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter ($R_L$) (Weber and Chakkravorti, 1974), which is defined by Equation (4.3).

$$RL = \frac{1}{(1+KLCo)} \qquad (4.3)$$

where; $K_L$ is the Langmuir constant, $C_0$ is the highest metal concentration ($mg.L^{-1}$). The value of RL indicates the type of the isotherm to be either unfavorable $R_L > 1$, linear $R_L = 1$, favorable $0 < R_L < 1$ or irreversible $R_L = 0$ (Fytianos, 2003 and others). Values of $R_L$ are summarized in Table (4.6).

Table 4.5 values of $R_L$ for removal of copper ions

| Concentration in ppm | $R_L$ for $Cu^{2+}$ | $R_L$ for $Zn^{2+}$ |
|---|---|---|
| 10 | 0.167 | 0.0625 |
| 30 | 0.06297 | 0.022 |
| 50 | 0.04 | 0.0132 |

It will be seen that the value of $R_L$ are between 0 and 1 indicating the adsorbents prepared are favorable for adsorption of the metal ions under conditions used in the study.

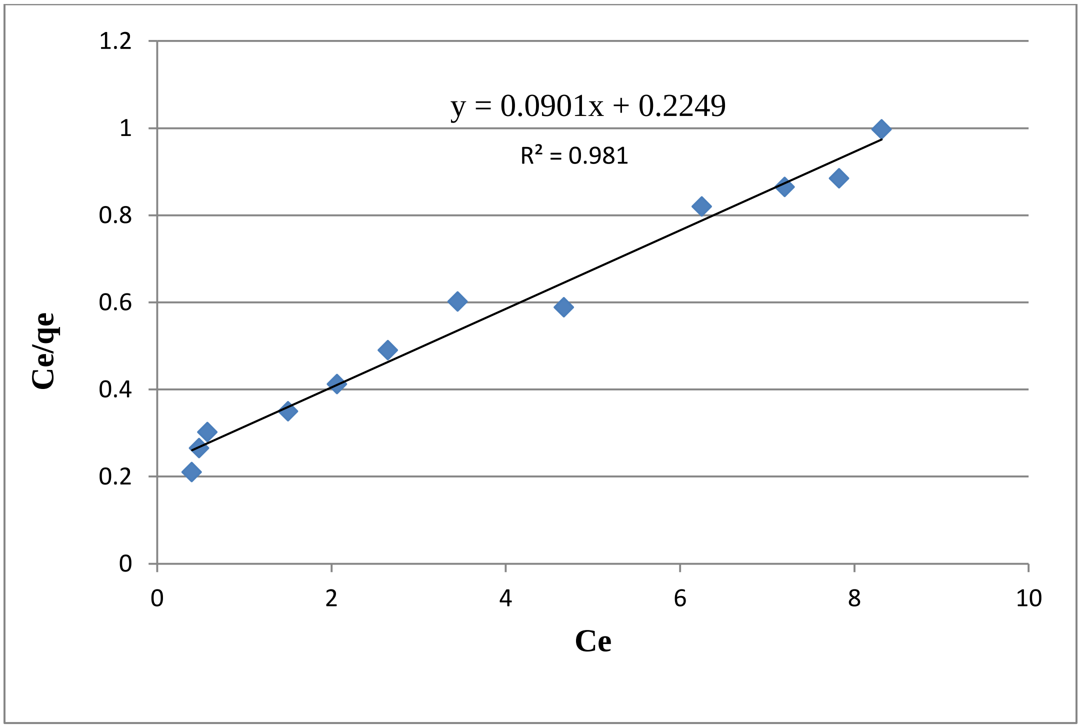


Figure 4.6 Langmuir plot for copper adsorption at pH 5

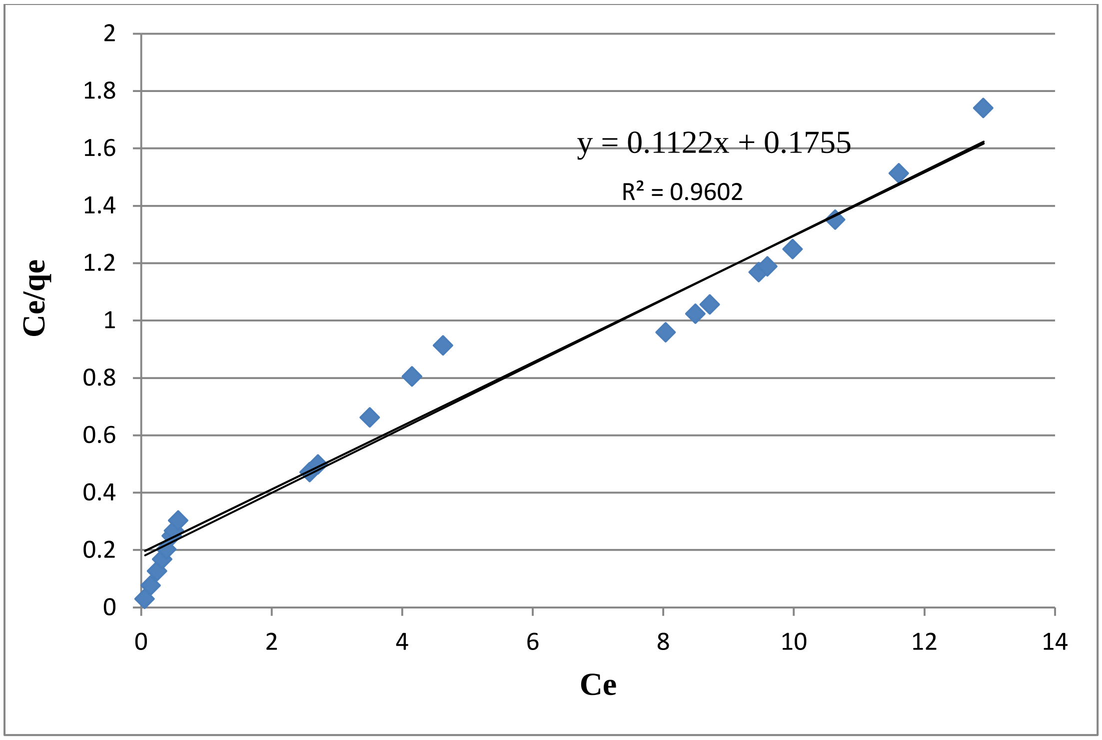


Figure 4.7 Langmuir plot for zinc adsorption at pH 5

**Freundlich model:** The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghseresht and Lu, 1998). A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption (Fytianos and others, 2003). Values of 1/n for copper and zinc were 0.4922 and 0.229 respectively. It will be noted that the value of 1/n was between 0 and 1 indicating the adsorbents prepared are favorable for adsorption of the metal ions under conditions used in the study.

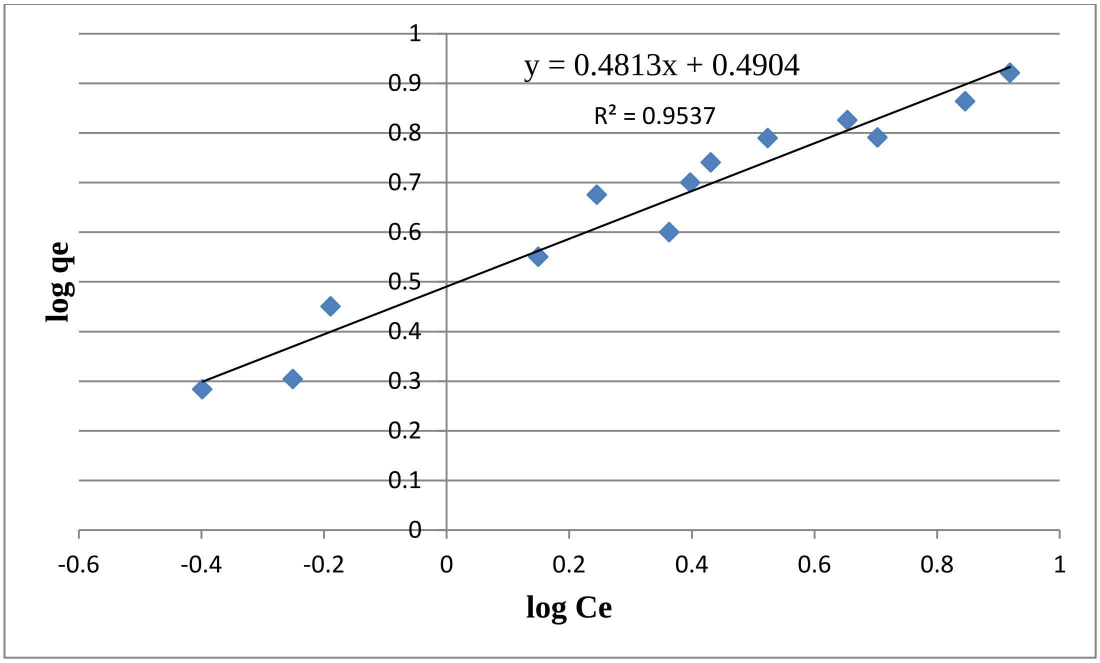


Figure 4.8 Freundlich plot for copper adsorption at PH 5

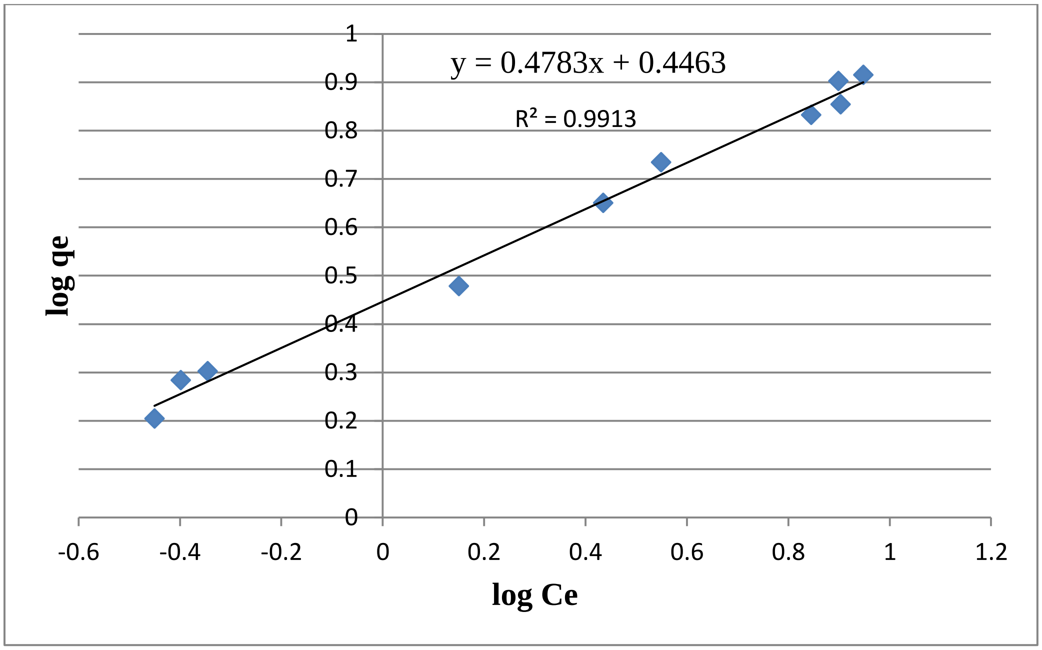


Figure 4.9 Freundlich plot for zinc adsorption at pH 5

Table 4.6 Isotherms parameter of copper and zinc removal by tea waste adsorbent

| Isothermal model | Parameter | Copper | Zinc |
|---|---|---|---|
| | Adsorption constant($k_L$) | 0.496 | 1.5 |
| Langmuir | Adsorption capacity(Qmax) | 8.34 | 8.4 |
| | Correlation coefficient($R^2$) | 0.981 | 09602 |
| Feundlich | Adsorption intensity(i/n) | 0.4922 | 0.22 |
| | Adsorption capacity $k_F$ | 3.11 | 4.334 |
| | Correlation coefficient($R^2$) | 0.9537 | 0.9913 |

**Better-fit Isotherm models**: As can be seen from Table: 4.7, the adsorption of Zn ions onto tea waste, the Freundlich model presents greater $R^2$ value (0.9913) than the Langmuir model (0.9602). In this case, Freundlich model fitted better to the adsorption data and thus it is more suitable used to describe the relationship between the amounts of $Zn^{2+}$ adsorbed by tea waste and its equilibrium concentration in the solution (Adamson, 2001). On the other hand, adsorption of Cu ions onto tea waste, fitted better to the Langmuir model $R^2$ value (0.981) than Freundlich model under the same conditions.

# 5 CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

In this study, low cost adsorbents were successfully prepared from agricultural tea waste. Further, the adsorption of recalcitrant compounds from synthetic wastewater using these locally available low cost adsorbents was studied. Additionally, response surface methodology was used to investigate the interactive effect of the operating parameters namely; adsorbent dose, initial concentration and solution pH and dosage of adsorbent.

Tea waste may be cheap and effective adsorbent for the removal of Cu and Zn ions from waste water. Experiment results showed that maximum removal of copper and zinc ion by tea waste at optimum condition (5 pH, 120 min. contact time, 1g/200ml adsorbent dose and 10ppm concentration) is 95.98%and 99.8% respectively. 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.

## 5.2 Recommendations

The result of the tea waste adsorbent indicates that the adsorbent is capable of removing copper and zinc ions from aqueous solution. Therefore, the following recommendations are made as a result of the outcome of the study.

It is recommended that tea waste can be used, as a low cost and abundant source, for the removal of heavy metals and it may be an alternative to more costly materials.

Carry out the research on the ability of the adsorbent for its simultaneous uptake of Copper and zinc along with other toxic heavy metals such as cadmium, lead, mercury etc.

Carry out the research on the ability of the adsorbent selectivity with ionon.

It is recommended to conduct a research on other toxic waste such as dye.

Optimize the removal efficiency of the tea waste adsorbent through continuous column experiment, and try to immobilize the adsorbent on materials to improve its recovery.

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# APPENDIXES

## Calibration Curves

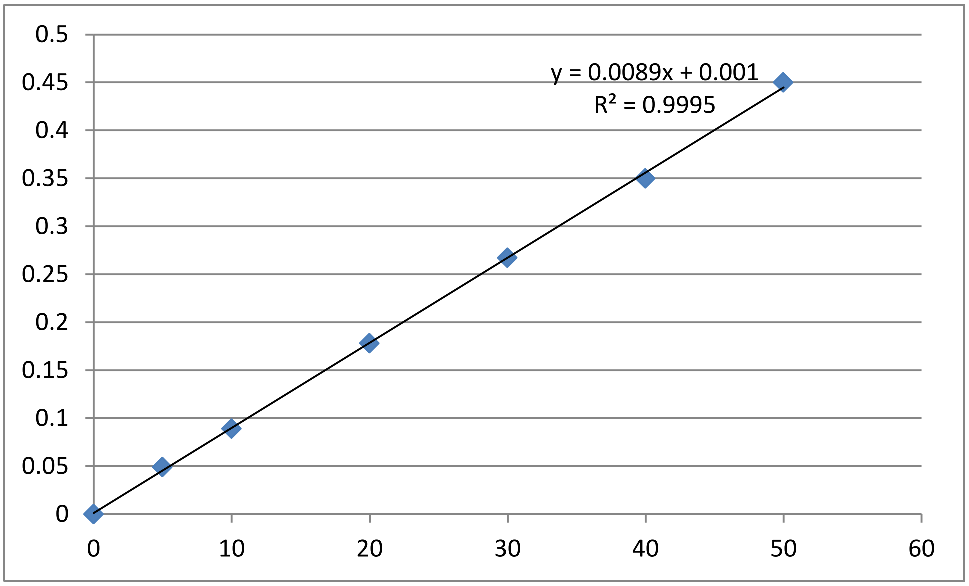

Figure 1: Calibration curve for cupper

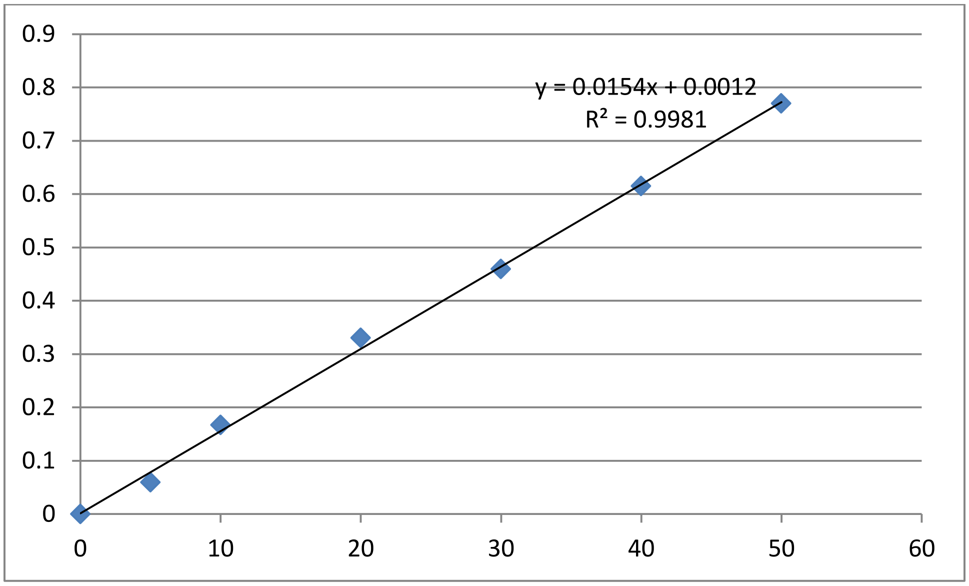

Figure 2: Calibration curve for zinc

Tables 1: Effect of pH, concentration and time on adsorption capacity of cupper

| run | pH | time | conc. | %removal |
|---|---|---|---|---|
| 1 | 5 | 180 | 50 | 82.2472 |
| 2 | 5 | 120 | 50 | 83.3708 |
| 3 | 6 | 180 | 50 | 81.3483 |
| 4 | 6 | 180 | 10 | 93.8202 |
| 5 | 4 | 180 | 30 | 84.2322 |
| 6 | 4 | 120 | 10 | 93.1236 |
| 7 | 6 | 180 | 30 | 86.1423 |
| 8 | 5 | 180 | 10 | 95.2809 |
| 9 | 5 | 120 | 10 | 95.9775 |
| 10 | 4 | 120 | 30 | 87.191 |
| 11 | 4 | 120 | 50 | 82.4719 |
| 12 | 4 | 180 | 50 | 81.7978 |
| 13 | 6 | 120 | 10 | 92.191 |
| 14 | 6 | 60 | 50 | 77.7528 |
| 15 | 5 | 60 | 10 | 91.6629 |
| 16 | 6 | 120 | 50 | 81.3483 |
| 17 | 4 | 60 | 50 | 80 |
| 18 | 6 | 60 | 30 | 81.6479 |
| 19 | 6 | 120 | 30 | 86.2 |
| 20 | 5 | 120 | 30 | 91.0112 |
| 21 | 5 | 180 | 30 | 88.2022 |
| 22 | 6 | 60 | 10 | 90.8764 |
| 23 | 4 | 60 | 10 | 89.8876 |
| 24 | 5 | 60 | 30 | 83.1461 |
| 25 | 4 | 60 | 30 | 82.0599 |
| 26 | 5 | 60 | 50 | 80.2247 |
| 27 | 4 | 180 | 10 | 91.9101 |

Tables 2: Effect of pH, concentration and time on adsorption capacity of zinc

| run | pH | time | conc. | %removal | $C_e$ |
|---|---|---|---|---|---|
| 1 | 5 | 60 | 10 | 95.2597 | 0.474026 |
| 2 | 6 | 180 | 10 | 97.5325 | 0.246753 |
| 3 | 6 | 120 | 50 | 81.0649 | 9.467532 |
| 4 | 6 | 180 | 50 | 80.8052 | 9.597403 |
| 5 | 4 | 120 | 30 | 88.3117 | 3.506494 |
| 6 | 6 | 180 | 30 | 86.1472 | 4.155844 |
| 7 | 4 | 60 | 30 | 78.6147 | 6.415584 |
| 8 | 4 | 60 | 10 | 94.2857 | 0.571429 |
| 9 | 5 | 180 | 30 | 90.9524 | 2.714286 |
| 10 | 5 | 180 | 10 | 98.5065 | 0.149351 |
| 11 | 5 | 60 | 50 | 78.7273 | 10.63636 |
| 12 | 6 | 120 | 10 | 99.4156 | 0.058442 |
| 13 | 4 | 180 | 10 | 96.1039 | 0.38961 |
| 14 | 5 | 120 | 50 | 83.9221 | 8.038961 |
| 15 | 6 | 60 | 10 | 94.9351 | 0.506494 |
| 16 | 5 | 60 | 30 | 81.645 | 5.506494 |
| 17 | 4 | 180 | 50 | 80.026 | 9.987013 |
| 18 | 5 | 120 | 10 | 99.8052 | 0.019481 |
| 19 | 6 | 60 | 30 | 79.697 | 6.090909 |
| 20 | 4 | 180 | 30 | 84.5671 | 4.62987 |
| 21 | 4 | 120 | 50 | 82.5714 | 8.714286 |
| 22 | 4 | 60 | 50 | 74.1818 | 12.90909 |
| 23 | 5 | 180 | 50 | 83.013 | 8.493506 |
| 24 | 6 | 60 | 50 | 76.7792 | 11.61039 |
| 25 | 5 | 120 | 30 | 91.3853 | 2.584416 |
| 26 | 4 | 120 | 10 | 96.7532 | 0.325 |
| 27 | 6 | 120 | 30 | 86.1472 | 4.15584 |

Tables 3: Results for cupper adsorption isotherms.

| $C_o$ | $C_e$ mg/l | $Q_e$ (mg/g) | $C_e/q_e$ | log $C_e$ | Log $q_e$ |
|---|---|---|---|---|---|
| 10 | 0.4 | 1.92 | 0.21 | -0.398 | 0.833 |
| 30 | 2.64 | 5.46 | 0.494 | 0.431 | 0.74 |
| 50 | 8.314 | 8.34 | 0.997 | 0.919 | 0.921 |

Tables 4: Results for zinc adsorption isotherms

| $C_o$ | $C_e$ mg/g | $C_e/q_e$ | $\log C_e$ | $\log q_e$ |
|---|---|---|---|---|
| 10 | 0.0195 | 0.009759 | -1.7164 | 0.3 |
| 30 | 2.5844 | 0.4713 | 0.4123 | 0.74 |
| 50 | 8.04 | 0.96 | 0.91 | 0.924 |

Tables 5: $R_L$ values for cupper adsorption at different concentration.

| initial concentration in mg/l | $R_L$ |
|---|---|
| 10 | 0.167 |
| 30 | 0.06297 |
| 50 | 0.04 |

Tables 6: $R_L$ values for zinc adsorption at different concentration.

| initial concentration in mg/l | $R_L$ |
|---|---|
| 10 | 0.0625 |
| 30 | 0.022 |
| 50 | 0.0132 |

Figure below discribe stock solution prepared, AAS analysis of copper and zinc concentration after adsorption.