STUDIES ON THE POTENTIAL APPLICATION OF BIO-WASTE FOR HEAVY METALS REMOVAL FROM AQUEOUS SOLUTION

A THESIS SUBMITTED TO THE
CENTRAL DEPARTMENT OF CHEMISTRY
INSTITUTE OF SCIENCE AND TECHNOLOGY
TRIBHUVAN UNIVERSITY
NEPAL

FOR THE AWARD OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY
BY
BINDRA SHRESTHA RAGHUBANSHI
OCTOBER, 2014

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Declaration

Thesis entitled **“STUDIES ON THE POTENTIAL APPLICATION OF BIO-WASTE FOR HEAVY METALS REMOVAL FROM AQUEOUS SOLUTION"**which is being submitted to the Central Department of Chemistry, Institute of Science and Technology (IOST), Tribhuvan University, Nepal for the award of the degree of Doctor of Philosophy (Ph.D.), is a research work carried out by me under the supervision of Prof. Dr. Kedar Nath Ghimire, Central Department of Chemistry, Tribhuvan University and co supervised by Prof. Dr. Megh Raj Pokhrel.

This research is original and has not been submitted earlier in part or full in this or any other form to any university or institute, here or elsewhere, for the award of any degree.

[Bindra Shrestha Raghubanshi]

Recommendation

This is to recommend that **BINDRA SHRESTHA RAGHUBANSHI** has carried out research entitled ***"*STUDIES ON THE POTENTIAL APPLICATION OF BIO-WASTE FOR HEAVY METALS REMOVAL FROM AQUEOUS SOLUTION*"*** for the award of Doctor of Philosophy (Ph.D.) in **CHEMISTRY** under my/our supervision. To our knowledge, this work has not been submitted for any other degree.

She has fulfilled all the requirements laid down by the Institute of Science and Technology (IOST), Tribhuvan University, Kirtipur for the submission of the thesis for the award of Ph.D. degree.

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LETTER OF APPROVAL

Date: 19/11/2014

On the recommendation of Prof. Dr. Kedar Nath Ghimire and Prof. Dr. Megh Raj Pokhrel, this Ph.D. thesis submitted by Bindra Shrestha Raghubanshi**,** entitled **"STUDIES ON THE POTENTIAL APPLICATION OF BIO-WASTE FOR HEAVY METALS REMOVAL FROM AQUEOUS SOLUTION"** is forwarded by Central Department Research Committee (CDRC) to the Dean, IOST, T.U.

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(Bindra Shrestha Raghubanshi)

October, 2014

ABSTRACT

An efficient and effective biosorbents were investigated by using waste tealeaves. It was prepared by amination with three different aminating reagents to introduce amino groups onto the surface of biosorbent. The biosorbent was aminated by using ethylenediamine, dimethylamine and hydrazine monohydrate. They are called CATL-1, CATL-2 and CATL-3, respectively. The prepared biosorbents were characterized with elemental analysis, analysis of cellulose, hemicelluloses and lignin, SEM images, FTIR spectra, XRD analysis, TG/DTA analysis and zeta potential analysis.

These aminated biosorbents were used for sequestration of heavy metals like lead, copper, cadmium and zinc. Their metal uptake perfomance were also elucidated by using batch experiments. The adsorption capacities of biosorbents were studied as the function of solution pH, initial concentration of metal ions and contact time of adsorption. The effect of pH on adsorption were studied by varying the solution pH from 1-7. The results indicated that the uptake performance of biosorbents significantly change with pH of solution and optimum pH for adsorption was also determined. The initial concentration of metal ions varying from 25-800 mg/L were used to calculate the optimum loading capacity of biosorbents. The optimum time for adsorption were determined by contacting the adsorbent with metal solution at different interval of time.

The experimental data were found to be well fitted with langmuir isotherm model. From the isotherm plots the maximum adsorption capacities for lead was found to be highest for all of the three adsorbents while the values were lowest for zinc. Among the three biosorbents, CATL-3 is found to be having highest adsorption capacity for all metal ions used in this study. In CATL-3, the maximum adsorption capacity for Pb (II), Cu (II), Cd (II) and Zn (II) are found to be 120.8, 90.4,114.3 and 79.76 mg/g, respectively. The optimum contact time for metal ions are found to be between 120 - 150 min for all the biosorbents. The kinetic data were well fitted with pseudo - second order model.

Hence the biosorbents prepared from waste tealeaves can be potentially applied for treatment of waste water contaminted with toxic heavy metals.

Keywords: adsorption, biosorbents, heavy metals, Langmuir isotherm, pseudo- second order model.

LIST OF ACRONYMS AND ABBREVIATIONS

µg	microgram
AAS	Atomic absorption spectrometry
C	Centigrade
CATL-1	Charred aminated tealeaves by ethylenediamine
CATL-2	Charred aminated tealeaves by dimethylamine
CATL-3	Charred aminated tealeaves by hydrazine monohydrate
cm	Centimeter
DTA	Differential Thermal Analysis
FTIR	Fourier Transform Infrared Spectroscopy
g	gram
K	Kelvin
L	Liter
m	meter
mg	milligram
mL	milliliter
mm	millimeter
pH	power of hydrogen ions concentration
rpm	rotation per minute
RTL	Raw tealeaves
SEM	Scanning Electron Microscopy
TGA	Thermo Gravimetric Analysis
XRD	X-Ray Diffraction

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CHAPTER 1

1. INTRODUCTION

1. 1 Introduction

Industrial waste water streams containing heavy metals are produced from different industries like electro-plating, electrolytic deposition, conversion coating, anodizing, cleaning, milling, etching and printed circuit board manufacturing. Other sources of heavy metals are the waste from leather tanning industries, wood processing industries, inorganic pigment manufacturing industries, petroleum refining industries and photographic operation (Volesky, 1990a, Demirbas, *et al*., 2005). Similarly heavy metals enter into the water system by agricultural chemicals and solid waste from animals. A huge amount of heavy metals also comes from acid rain, which breaks down soils and rocks releasing heavy metals into lakes, ground water and streams (Pastircakova, 2004).

Heavy metal is a collective term representing a group of metals and metalloids which have molecular weight above 20 and atomic density greater than 5 g/cm^3. They include antimony, bismuth, cadmium, chromium, cobalt, copper, gallium, gold, iron, lead, mercury, nickel, vanadium and zinc. Most of these heavy metals are associated with pollution and toxicity problems. The heavy metals cannot be degraded into harmless end products and they accumulate in living organisms (Babel & Kurniawan, 2003). The toxicity of heavy metals has become one of the most important environmental problems in the world especially in developing countries. They have tendency to transport with sediments and they persist in the environment due to non biodegradable nature and can bioaccumulate in food chain (Garg, *et al*., 2007, Igwe & Abia, 2006).

Manganese, iron, cobalt, copper, zinc, molybdenum and selenium are essential heavy metals. They exist in our body at much lower level. Any metal would become hazardous to living organisms and human beings, if its concentration is above the acceptable level. Toxic heavy metals including As, Pb, Hg, Cd and Ni are nonessential. Their negative effect is less observed when their concentration is less than toxic level. However, they become harmful when their concentration exceeds toxic level and may be lethal toxicant above the lethal level (Nurchi & Villaescusa, 2008, Singh, 2011). A group of three elements including Hg, Pb and Cd are called 'big - three' and they are in lime light due to their impact on the environment (Volesky, 2003).

Heavy metals in higher level than critical value can cause a series of health problems. The toxicity may damage or reduce mental and central nervous functions, lower energy levels, damage blood composition, lungs, kidneys, liver and other vital organs. Long time exposure to these toxic metals may cause various cancers, muscular dystrophy and neurological degenerative processes (Babel & Kurniawan, 2003).

Heavy metals express their toxicity to human beings by different mechanisms. They can easily form precipitates with anionic substances like CO_3^{--}, SO_4^{--},S^{--} and PO_4^{---}, which stay in human body. Some of the heavy metals are adsorbed onto organic functional group of enzymes which force the essential metal to detach from that enzyme and replace them with harmful heavy metals e.g. copper displaces zinc and cadmium displaces calcium. It results in change in biological activity of that enzyme. Some of the heavy metals may cause forceful redox reaction of basic elements like carbon to change their chemistry. Chromium (VI) causes oxidation of carbon in tissues of human body (Ademorati, 1996, Seiler & Sigel, 1988, Friberg, 1986).

Lead is one of the most useful metals and used since antiquity. However, it has the most damaging effect on human health. It can enter to human body through food, water and air (Shotyk, *et al.*, 2005, Friberg & Elinder, 1985). It is a neurotoxin metal. Exposure to this metal causes the development of autoimmunity, in which person's immune system attacks its own cells. It causes joint diseases such as rheumatoid arthritis and diseases of kidneys, circulatory system, nervous system and damage of the fetal brain. It forms complex with oxo-group in enzymes to affect virtually all the steps in process of haemoglobin synthesis and prophyrin metabolism, (Zulkali, *et al.*, 2006, Lo, *et al.*, 1999, Ho & Ofomaja, 2005). The main sources of lead contamination are fuel combustion, industrial processes and solid waste combustion. Its concentration in soil and water increases through the corrosion of pipelines in water transportation system (Scumann, 1990). One of the main sources of lead contamination is corrosion of paints. It comes to the environment from plastics, ceramics, solders, pieces of lead flashing and cable reclamation. It binds strongly to oils, sediments and sewage sludge (Babel & Kurniawan, 2003, Lai, *et al*., 2006, Tunali, *et al*., 2006).

Copper is another most widely used heavy metals. However in large scale it is highly toxic to living organisms. Copper is known as one of the highest mammalian toxic metal. It deposits in brain, skin, liver, pancreas and myocardium causing different disorders. Inhalation of its compounds causes lung cancer (Ahmed, 2011, McKay, *et al*., 1999, Bowen, 1979). The copper contamination in water body increases from copper mining, manufacture of alloys containing copper and electroplating industries. Its compounds are also used in agriculture. Copper sulphate is widely used as an algaecide in water reservoirs affected by blue green algae (Masri, *et al*., 1974, Asku, 1991).

Cadmium accumulates in human body especially in kidneys leading to dysfunction of kidneys. Other health hazards due to cadmium in humans are hepatic damage and hypertension. Itai-itai disease characterized by extensive pain in the bone is caused due to cadmium toxicity. Cadmium and its compounds are relatively more soluble in water as compared to other heavy metals. So they are highly mobile in soil and tend to bioaccumulate (Volesky & Holan, 1995, Montanher, *et al*., 2005, Singh, *et al*., 2005, Butter, 2009). The long life time PVC window frames, plastics and plating on steel generates cadmium in the environment, It is also generated as the waste during steel production, nonferrous alloy production, refining, cement manufacture, cadmium plating, battery manufacture, phosphate fertilizers and plastic industries (Ajmal, *et al*., 2006, Seki, *et al*., 1997, Kumar & Bandyoppadhyay, 2006, Blazquez, 2005).

Zinc is an essential element and relatively non toxic. It is second most abundant trace metal found in human body. It is a cofactor of many enzyme systems and found in active sites of various enzymes (Chergui, 2007). Zinc and its compounds are widely used in alloy production, electrical devices, rubber and tyre industries and paints. It is also used as anticorrosion coatings of steel and iron during galvanization. Its compounds are used as pesticides (Pavasant, 2006, Igwe, 2005, Long, 2003).

Due to better understanding of heavy metal toxicity, frequently occurring environmental accidents from anthropogenic sources as well as natural geochemical processes and public awareness of environmental pollution, there requires an enactment and enforcement of stricter legislation on the discharge of toxic heavy metal contaminants (Eckenfelder, 2000). Waste water regulations were established to minimize human and environmental exposure to these hazardous heavy metals. This includes limits on the type of concentration of heavy metals that may be present in discharged waste water. Consequently development of cost effective treatment technologies become paramount (Friberg, 1985).

Remedies: Plausible options

Several conventional treatment technologies have been developed to remove heavy metals from waste water. They are chemical precipitation, ion - exchange, membrane separation, ultra filtration, floatation, electro - coagulation, solvent extraction, sedimentation, electrochemical precipitation, soil - flushing and washing, electro kinetic extraction, phytoremediation, reduction, reverse osmosis, dialysis and electrochemical dialysis, evaporation and flocculation (Gardea- Torresdey, *et al.*, 1998, Patterson, 1985, Zhang, *et al.*, 1998). The chemical precipitation has been the most widely used traditional method for removal of heavy metals. The most commonly used precipitation processes include hydroxide precipitation, sulphide precipitation, carbonate precipitation and phosphate precipitation (Wang, *et al.*, 2004).

The precipitation can be represented as

$$M^{2+} + 2(OH)^- \rightarrow M(OH)_2 \downarrow$$

Where M^{2+} is divalent metal ion, OH^- is the precipitant and $M(OH)_2$ is insoluble metal hydroxide. Lime and limestone are the most commonly used precipitants due to their availability and low cost. Lime precipitation can be used for the treatment of effluent with metal concentration higher than 1000 mg/L. The process is simple, convenient, safe operation and requires inexpensive equipments (Aziz, *et al.*, 2008). However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. The excessive sludge production during the process, slow metal precipitation and poor settling are drawbacks of the process. Another disadvantage of the process is leakage of toxic metal back to environment (Zulkali, *et al.*, 2006, Cabuk, *et al.*, 2007, Malkoc & Nuhoglu, 2005).

Ion - exchange is another common heavy metal removal method in which ion exchangers are used. They are solid substances which are capable of exchanging other ions from their surroundings. Synthetic organic ion exchange resins are commonly used. But such exchangers are not suitable for concentrated metal solutions as the exchanger is fouled by impurities. In electrolytic metal removal process the electricity is used to pass a current through an aqueous metal solution containing a cathode plate and an insoluble anode. In this process positively charged metal ions are attracted towards the negatively charged cathode to deposit the metal (Kurniawan, *et al.*, 2006). In this process the electrodes would frequently have to be replaced due to their corrosion.

Recently, adsorption has become one of the most promising alternative treatment techniques for waste water containing heavy metals. Adsorption is a mass transfer process by which a substance is transferred from liquid phase to surface of a solid and becomes bound by physical and chemical interaction. It is now recognized as an efficient, effective and low cost method for decontamination of waste water (Kurniawan, & Babel, 2003, Cochrane, 2006). The adsorbent may be of mineral origin like zeolites , clays, silica beads, alumina, metal oxides and may be of organic or biological origin like activated carbon, low cost industrial byproducts, agricultural wastes, organic polymers and resins (Grant, *et al.*, 1987, Gupta & Tiwari, 1985, Pandey, 2009, Naseem, 2001).

Activated carbon: Activated carbons are used as versatile adsorbent in waste water treatment application throughout the world (Horikoshi, *et al.*, 1981, Hosea, *et al.*, 1986). It shows the maximum adsorption capacity to remove pollutants from aqueous solutions. It is due to their highly porous texture which gives them a large surface area. The effectiveness of activated carbon obtained from various sources has been evaluated by several researchers for removal of metal ions from waste water (Kadirvelu, *et al.*, 2003, Hu, *et al.*, 2003, Pereira, *et al.*, 2003). Many cheap and easily available plant based materials like coconut coir, straw, sawdust (Vinodhini & Das, 2010), rice husk, rice bran, silk and cotton seed hulls, jute fiber, palm kernel shell, corncob waste have been used as sources of activated carbon (Kadirvelu & Namasivayam, 2000). Activated carbons were found highly effective for adsorptive removal of heavy metals from aqueous solution (Jia, 2002). However the adsorbent is non - regenerable and they also require complexing agent to improve their removal performance. Hence the process becomes quite expensive for waste water treatment. In such regards biological methods like biosorption provides an attractive alternative and it emerges as a new cost effective technology for removal of heavy metals from waste water for last few decades (Volesky, 1995, Bailey, 1999, Homagai, 2010).

Biosorption: Biosorption is defined as the removal of metals, metalloids, compounds and particulates from solution by using biological materials (Volesky, 1990a). The property of certain bio - molecules to bind and concentrate selected ions or molecules from aqueous solution is biosorption (Volesky, 2007, Alluri, 2007).

Biosorption is a biological method for treatment of heavy metals containing waste water and it involves physiochemical interaction between metal species and microbial cells (Wang & Chen 2006, Davis, 2003C). It offers several advantages over conventional treatment methods including cost effectiveness, efficiency and minimization of chemical or biological sludge and regeneration of biosorbent with possibility of metal recovery (Southichak, 2006).

Biosorption involves an interaction between a solid phase (sorbent) and a liquid phase (solvent) containing dissolved species to be sorbed (sorbate i.e. metal ions). Due to higher affinity of the sorbent for sorbate species, the latter are attracted towards the sorbent and removed by different mechanism. This process continues till equilibrium is established between the amount of solid, bound sorbate species and its portion remaining in the solution. The degree of affinity of sorbent for the sorbate determines its distribution between solid and liquid phase.

The adsorptive removal of toxic heavy metals by using biosorption produces close to drinking water quality. The initial concentration of 1 - 100 mg/L can be reduced to final concentration of 0.01 - 0.1 mg/L. If metal concentration in waste water to be treated is high (more than 100 mg/L), the n pretreatment by using other techniques like precipitation or electrolytic removal is used to reduce bulk of the metal ions.

Biosorbents: In last few decades, the study of low cost biosorbents that have efficient metal binding capacity has been intensified. In this regards, different biosorbents have been explored for removal of heavy metals. They include algae, fungi, bacteria, agricultural waste and waste from industries (Ayyappan, 2005, Kapoor, 1995, Kuyicak, 1990, Tan, 2003, Gupta, 2000).

Various species of algal biomass are emerging as attractive, economic and effective biosorbents. Algae have low nutrient requirement, production of large biomass because of autotropic nature and they do not produce toxic substances. The metal binding capacity on algal surface depends on the algal species, ionic charge of metal ions and chemical composition of metal solution (Ghimire, 2007, Yun, 2001).

Fungal biomass has been used as efficient and economic biosorbent for removal of toxic heavy metals. The fungal biomass has a high percentage of cell wall material which has excellent metal binding properties (Deng, 2005). Large quantities of fungal biomass are obtained from antibiotic food industries. Hence it also provides ecofriendly environment.

Bacteria of different species have been identified as having high potential for removal of heavy metals. They are widespread, abundant and geochemically reactive components of aquatic environment. They have ability to grow under controlled condition and their smaller size leads to high surface area and fast rates for metal removal (Vijayaraghavan, 2008).

Recently, the research work has been focused on removal of heavy metals from waste water by the use of agricultural biowaste as adsorbent (Sud, 2008). The process utilizes inactive biowaste to bind and concentrate heavy metals from waste water by purely physic - chemical process. New resources such as orange and apple residue (Ghimire *et al.*, 2003, Dhakal, 2005), banana peel, sugarcane bagasse (Homagai *et al.*, 2011, Frederic, 2007), waste tealeaves(Hossain, 2005, Mahvi, 2005), rice bran(Oliveira, 2005, Kumar, 2006), rice husk (Chien, 2000), wheat bran (Chen, 2010), saw dust of various plants (Sciban, 2006, Memon, 2007), cotton seed hulls, maize corncob (Buasri, 2012), bark of trees, groundnut shells, soyabean hulls, grapes stalk, sugarbeet pulp, sunflower stalk (Sun & Shi, 1998, Jain, 2009), coffee beans, cotton stalk, coconut husk, olive cake, almond shells (Witek-Krowiak, 2011) and many others have been used for heavy metals uptake from waste water (Dhakal, 2005, Anandkumar, 2009, Ahalya, 2005, Vijayaraghavan, 2006) . These agricultural biowaste are inexhaustible, cost - effective and nonhazardous materials which can be easily disposed by incineration (Garg, 2007).

Lignocellulogic substance: The major constituents of agricultural biowaste are cellulose, hemicelluloses and lignin. The polar functional groups including alcohols, aldehydes, ketones, carboxylic acids, phenolic and ether groups present on the surface of these natural polymers are responsible for sequestration of heavy metals from waste water (Basso, 2002, Fang, 2003). These groups have ability to bind heavy metals by donation of electron pair to form complexes with metal ions in solution.

In lignocellulosic materials, lignin with wide variety of functional groups has been reported as the most active component for metal binding process. Lignin is very complex natural polymers with no precise single structure. Figure 1(c) is a representation of lignin, illustrating typical chemical linkages and functional groups. It has aromatic, three dimensional and highly branched polyphenolic structures with high molecular weight. It is amorphous cross linked resin which serves as main binder for the agglomeration of fibrous cellulosic components. It also provides a shield against rapid microbial or fungal destruction of cellulosic fibers. Lignin is not soluble in water but it is mechanically cleavable to relatively low molecular weight substance. It has strong resistance to chemical reaction and has high surface area (180 m^2/g). Due to these properties it can be used as biosorbent to remove heavy metals from waste water.

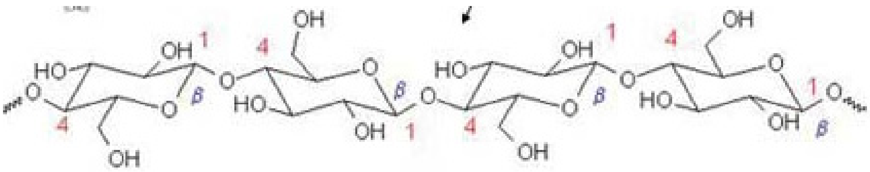

Figure 1(a): Structure of cellulose

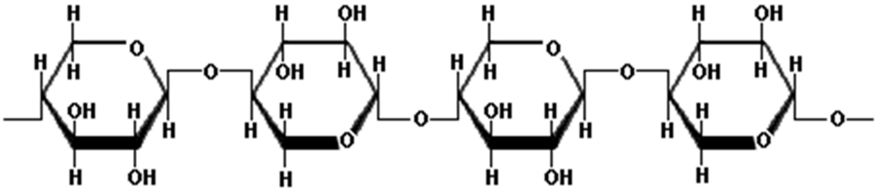

Figure 1(b): Structure of Hemicellulose

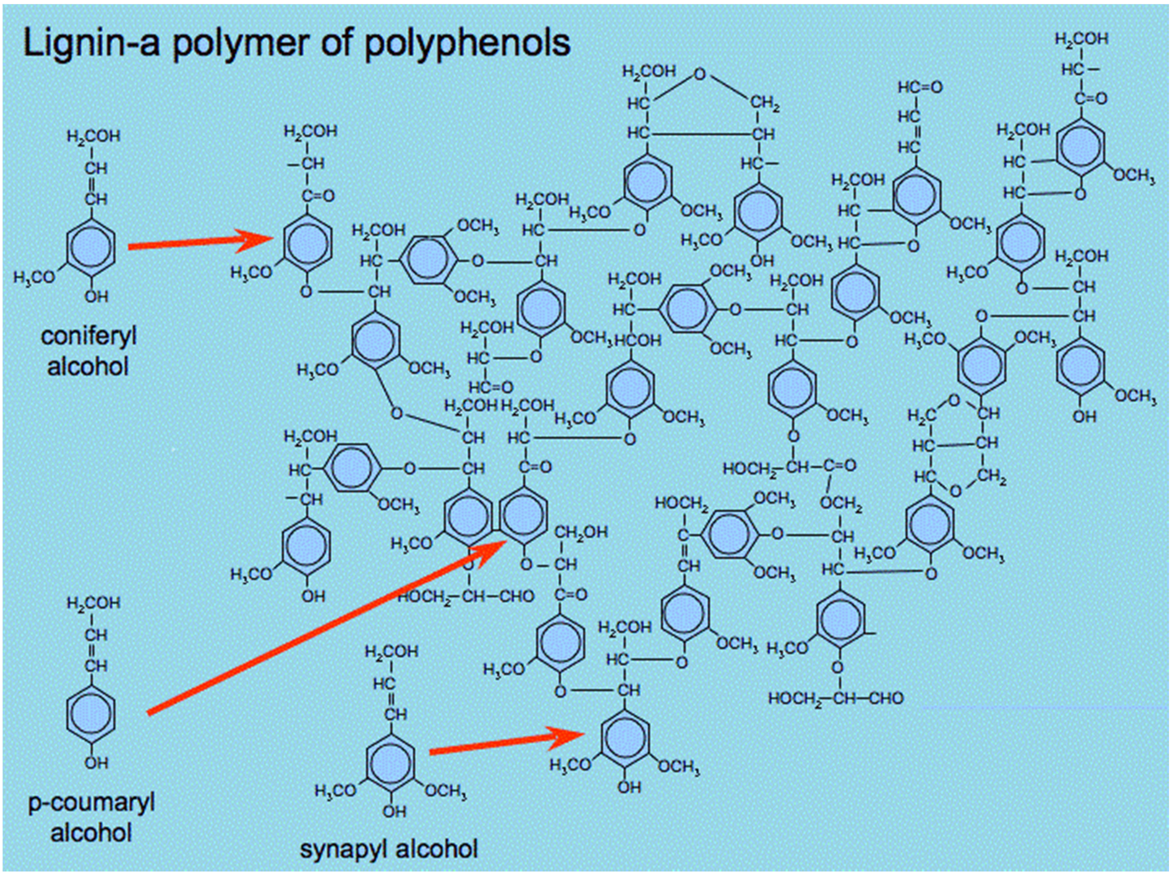

Figure 1(c): Structure of Lignin

Cellulose is an organic polymer consisting of units of anhydroglucose held together in a giant straight chain molecule as shown in Figure 1(a). These glucose units are linked together by β - (1,4) - glycosidic linkages. Inter - and intra - molecular hydrogen bonds are formed between the - OH groups within the same cellulose chain or the surrounding cellulose chain, forming a crystalline super molecular structure. Cellulose is insoluble in most of the solvents and has low accessibility to acids and enzymatic hydrolysis (Thirumavalavan,2010, Tsioptsias, 2010).

Hemicelluloses consist of different monosaccharide units as shown in figure 1(b). The polymer chains of hemicelluloses have short branches and are amorphous. They are swellable and partially soluble in water. They act as cement material holding together the cellulose fibers.

These promising agricultural lignocellulosic biowaste in their natural forms were used by many researchers to remove heavy metals from waste water (Sukla & Pai, 2005a). These native biosorbents have unsatisfactory results due to their poor mechanical strength and low sorption capacity. In recent years, research interest has been focused on increasing the sorption capacity of the biosorbent by physical and chemical modification. They can be modified by heat treatment, acid or alkali treatment, treatment with zinc chloride, calcium chloride etc. which enhance their metal binding capacity (Ghimire, 2002). The physical strength as well as binding capacity can be increased by cross linking by glutaraldehyde and epichlorohydrin. The surface of biosorbents can be altered by chemical treatment processes. The target of such modifications are to increase the density of effective functional groups such as carbohydrates, hydroxyl, sulphate, xanthate, phosphate, amine and amide groups on the surface of biosorbent (Paudyal, 2013). The increase in sorption active sites on the surface of biosorbent is an effective approach to enhance the sorption capacity. The common chemical treatment processes which alter the surface of biosorbent by introduction of various functional groups are amination, carboxylation, xanthation (Kumar, 2000) and phosphorylation. After introduction of effective functional groups on the surface of biosorbent, obviously their metal binding capacity increases significantly (Deng, 2003). Among different functional groups amine functional group has been found to be very effective in removing heavy metal pollution (Deng, 2003, Tang, 2003). It not only can chelate with cationic metals but also adsorbes anionic pollutants through the electrostatic interaction.

In present study waste tealeaves - a biowaste, has been used as biosorbent. After water, tea is the most widely consumed beverage in the world. The tealeaves *(Camellia sinensis)*, once the beverage has been brewed, becomes a waste. The waste tealeaves were then chemically modified to introduce amino functional group by using ethylenediamine, dimethylamine and hydrazine monohydrate.

Figure 2 (a): Tealeaves in Tea Garden

Figure 2 (b): A woman collecting tealeaves

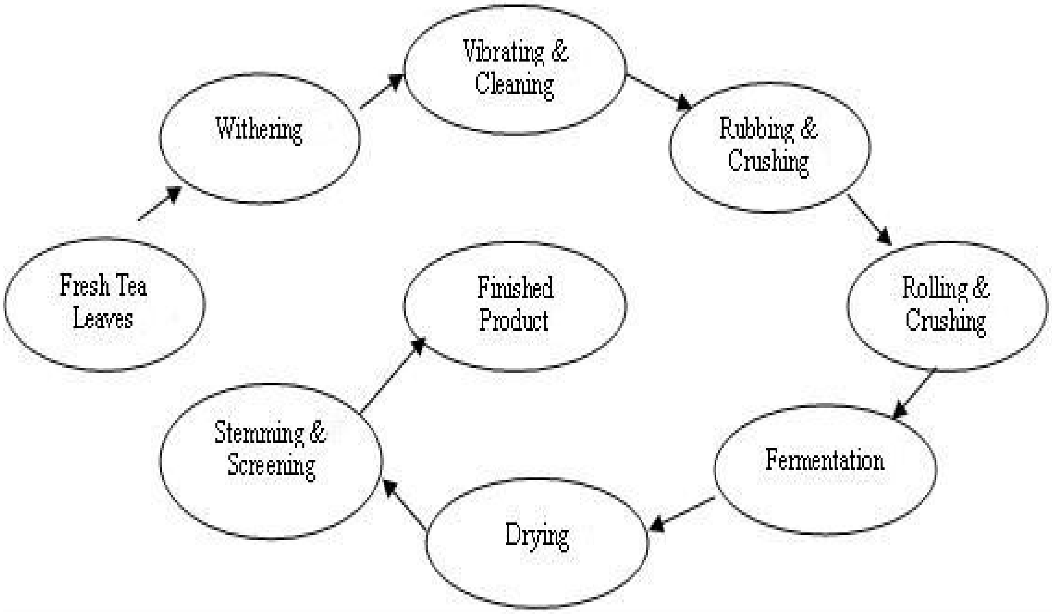

Figure 2 (c): Schematic diagram for preparation of CTC tea from fresh tealeaves

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Figure 2 (d): CTC tea

1.2 Rational

Most of the developing countries suffer from water pollution. In view of treatment of heavy metals into consideration, several schemes and technologies have been adopted. In this regard, new technologies have to be developed or more than one process has to be coupled with other, depending on the nature of complexity of the waste water. In order to meet water quality standard, various synthetic materials are quite often used to reduce the concentration of heavy metals in waste water. Such processes are quite expensive.

The main rational behind this study is to develop a cost effective and environmental friendly adsorbent that can be incinerated without releasing dioxane to the environment as it happens with the synthetic materials. This research work is focused on the development of waste tealeaves as an efficient and cost effective biosorbent, which can be potentially used to remove heavy metals from waste water.

1.3 Objectives

The continuous increasing demand of most of the known metals, the decrease in grade of available ores and stricter environmental regulations, force to find effective and efficient methods for treatment of waste water containing metal ions even at very low concentration. In this regard adsorptive removal of metal ions becomes an attractive alternative. Recently, research works are focused on the use of appropriate low cost technology for treatment of waste water in developing countries. The treatment processes by using biosorbents, which are technically feasible and economically viable are gaining importance. In this study, an efficient and cost effective biosorbent is investigated using naturally abundant waste material i.e. waste tealeaves. The adsorption efficiency of the biosorbent is enhanced by introducing amino functional groups onto the surface of biosorbent.

Main objectives of this study are following :

Introduction of amino groups on the surface of biosorbent i.e. waste tealeaves by using three different reagents to enhance adsorption capacity of biosorbent.

Elemental analysis of raw and aminated biosorbents.

To analyze the percentage of cellulose, hemicelluloses and lignin in biosorbents.

Characterization of functional groups present on the surface of biosorbents through FTIR spectroscopy.

Determination of optimum pH, equilibrium time and effect of initial metal ion concentration.

Determination of maximum loading capacity using Langmuir and Freundlich isotherm models.

Desorption study of metal loaded biosorbent using various eluting agents.

Reuse of the biosorbent after desorption of adsorbed metal ions to decrease the cost of adsorbent.

Comparison of adsorption capacity of the biosorbents with those found in the literatures.

CHAPTER 2

2. LITERATURE REVIEW

To develop an inexpensive, highly available, effective metal ion adsorbent a plentiful sources of natural wastes (or byproducts) were applied as replacements for existing commercial adsorbents. From our literature survey various naturally abundant bio-waste were developed as biosorbent for sequestration of heavy metals. Biosorbents are of following categories: bacteria, fungi, algae, agricultural waste and industrial waste. Various waste materials were investigated as adsorbents for sequestration of toxic heavy metals. Some of them are plant roots, tree leaves, tree bark, sawdust, coconut husk, walnut waste, peanut skin, soybean hulls, onion skin, apple waste, rice bran, rice straw, maize cob, sugarcane bagasse, sugar-beet pulp, cottonseed hulls, exhausted coffee grounds, waste tealeaves, fish scales, linseed flax straw and others.

Bacteria are most abundant and versatile microorganisms. Different species of bacteria were used as biosorbent due to their smaller size, their ubiquity and their ability to grow under controlled conditions. Bacterial species such as Bacillus, Pseudomonas, Streptomyces, Escherichia and Micrococcus have tested for their metal sequestration capacity. Many researchers evaluated the adsorption capacity of bacterial species and provided the basic information to evaluate the possibility of using this bacterial biomass for removal of metal ions.

The yeast biomass, a type of fungi has been successfully used as biosorbent for removal of various heavy metals from aqueous solution. Wang & Chen (2006) studied the selectivity and competitive biosorption of *Saccharomyces cerevisiae* in detail. *Aspergillus niger* is commercially and economically essential fungus for citric acid production by fermentation. The waste product of this fungus was utilized as biosorbent to remove toxic heavy metals by (Dursun, 2006). *Aspergillus niger*, pretreated with sodium hydroxide showed good sorption capacity than untreated biomass for adsorption of Cu (II) and Pb (II).

Algae are group of lower plants ranging from unicellular to multicellular forms. They are used in waste water treatment to reduce hazardous metals. The seaweed *Laminaria japonica* was investigated as biosorbent for removal of heavy metal ions. The adsorbent was prepared by cross linking with epichlorohydrin in basic medium to increase the metal uptake capacity (Ghimire, *et al.*,2008).

Pavasanta, *et al.* (2006) and his coworkers investigated the adsorption of Cu (II), Cd (II), Pb (II) and Zn (II) onto dried algae *Caulerpa lentillifera*. They evaluated the adsorption capacity at different pH and particle size. The functional groups like carboxylic acid, amines, amides, sulphonyl and sulphonate were identified as the groups responsible for metal sorption by using FTIR analysis.

Chromium adsorption onto cross linked chitosan was investigated by Rojas, *et al.* (2005). Effect of pH, particle size, adsorbent weight, concentration and chromium oxidation state on adsorption was studied. The optimum adsorption pH was 4, while chromium (VI) is partially reduced in the range pH ≤ 3. The lower chitosan affinity for chromium (III) (6 mg/g) differs with chitosans very high capacity for chromium (VI) (215 mg/g). This high capacity is due to the large stoichiometry of protonated amine sites in the acidic range pH. Equilibration data fitted to both Langmuir and Freunlich isotherms.

Marshall & Champagne (1995) evaluated byproducts of soybean and cottonseed hulls, rice straw and sugarcane bagasse as metal ion adsorbents in aqueous solution. Adsorption capacities were determined by adsorption isotherms using the Langmuir model. Capacities for Zn^{2+} varied from 0.52 to 0.06 meq/g dry weight of byproduct. Rice straw and sugarcane bagasse had low adsorption capacities (0.12 meq/g). At a subsaturating concentration of metal ion (100mg/l), soybean and cottonseed hulls adsorbed high levels of Cr^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}.

Vazquez, *et al.* (1994) reported the ambient temperature adsorption of the metal cation Zn^{2+}, Cu^{2+} and Pb^{2+} on *Pinus pinaster* bark pretreated with acidified formaldehyde solution. It was suggested that bark tannins (polyhydroxy polyphenols) were the active species in this process, where the metal ion is displacing the protons of two adjacent phenolic hydroxyl groups to form a chelate. The influence of pretreatment conditions and pH of the cation solution on the adsorption capacity of the bark was investigated. Adsorption of Pb^{2+} peaked between pH 6.2 and 6.8, Cu^{2+} adsorption increased steadily throughout the range studied (5.9-7.6) while Zn^{2+} adsorption was practically independent of pH. The slight influence of pretreatment conditions on the adsorption process was clearer for Cu^{2+} than for Pb^{2+} and Zn^{2+}. The values obtained for the adsorption capacity decreased in the same order as the fractions of metal ions adsorbed (Pb^{2+}>Cu^{2+}>Zn^{2+}). The equilibrium data were satisfactorily fitted by Freundlich isotherms.

Yang & Zall (1984) investigated binding of Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+} and Pb^{2+} to naturally occurring polymers obtained from seafood processing wastes. The five adsorbents tested were chitin, chitosan and scales from three different species of fish: porgy, flounder and cod. Chitosan was shown to be more active adsorbent of metals than chitin. The selectivity sequence in uptake of metals was Cu>Cr>=Cd>Pb>Zn. The effectiveness for removing metals with fish scales was relatively lower than with chitosan, where porgy scales showed a higher percentage of removal and selectivity sequence was very similar to chitosan. To avoid solubility in acid environment chitosan was crosslinked with glutaraldehyde or hexamethylene diisocyanate. In both cases, a large drop of adsorption capacity as well as affinity toward the metals was observed at the small amount of crosslinked reagents added. The study indicated that column operation is preferred to the batch system.

Sharma & Forster (1994), presented the use of certain cellulosic materials such as sugar cane bagasse, sawdust, sugar beet pulp and maize cob for the removal of hexavalent chromium. Adsorption capacities were found to be 39.7, 17.2, 13.4 and13.8 mg/g for sawdust, sugar beet pulp, sugar cane bagasse and maize cob, respectively. Chromium concentrations up to 10mg/litre were best treated with sawdust at pH_{adj} 3.0; between 40 and 100 mg/liter, the maxima were attained at pH 2.5 and higher concentrations showed the best removal at pH 2.0.Sugar cane bagasse demonstrated the best performance at

pH_{adj} 2.0, when concentrations of up to 100 mg/liter were treated. At concentrations above 100 mg/liter, pH_{adj} of 1.5 gave the best removal. The behavior of sugar beet pulp was very similar to that of sugar cane bagasse. The maize cob data also showed that pH 2.0 was the optimum for concentrations above 40 mg/liter. However, pH 2.5 or greater was better for low concentrations. It was concluded that cellulosic materials that had been subjected to some degree of anaerobic biodegradation are better adsorbents than fresh cellulosic material. In other words, humification reactions can produce polymeric structures, which have polyfunctional groupings with a strong binding capacity.

Adeyiga, *et al.* (1998) tested twelve different kinds of tree leaves for Pb, Ni and Zn adsorption. The adsorption of different metal ions on the same tree leaves had different removal rates, Pb had the highest removal rate, and Ni had the lowest removal rate. The experiments showed that the equilibrium is reached within the first 30 minutes of adsorption.

Periasamy & Namasivayam (1994) reported a use of activated carbon prepared from peanut hulls (PHC) for the adsorption of Cd^{2+} from synthetic wastewater. An almost quantitative removal of 20mg/l Cd^{2+} by 0.7 g of PHC/l of aqueous solution was observed in the pH range 3.5-9.5.A comparative studies with commercial granular activated carbon (CAC) showed that the adsorption capacity of PHC was 31 times larger than that of CAC.

Orhan & Buyukgungor (1993) examined adsorbents such as waste tea, Turkish coffee, exhausted coffee, nut and walnut shells to remove heavy metals from wastewater. Batch studies were conducted at room temperature and adsorption experiments were carried out by shaking 0.3 g of adsorbent with 100 ml of synthetic wastewater containing Cr^{6+}, Cd^{2+} and Al^{3+} metal ions. These adsorbents exhibited a good adsorption potential for Al^{3+} metal. Decaying leaves of *Plantanus orientalis* can remove Cr and Ni from solution. The root biomass of tobacco and tomato plants has been shown to adsorb Sr from solution. Trace concentration of Pb and Zn were successfully removed from solution by processed oil residue of olive mill products. A recent paper examined the binding of Cr to oat byproducts. Considering the diversity of tested materials and the variations in experimental conditions, the quoted efficiencies are relatively homogeneous. As a rule, however, materials of marine origins (seaweeds, chitin/chitosan) offer a high metal-binding potential whereas modified materials (sawdust, apple residue) display higher biosorption capacities than raw counterparts.

Maranon & Sastre (1991) demonstrated the removal of copper, zinc and nickel ions in packed beds. To improve their physico-chemical properties, they submitted AW to phosphorylation by treatment with phosphorus oxylchloride and crosslinking by epichlorohydrin with subsequent xanthation reaction. The cation exchange capacity of the original residues (0.3-0.4 meq/g) considerably increased in xanthated residues (up to 1.1 meq/g) and phosphorylated residues (up to 1.6meq/g). The unmodified residues as well as the chemically modified residues showed higher selectivity for Cu (II) ions and similar selectivity for Zn (II) and Ni (II) ions. A decrease in particle size of adsorbent had a favourable effect on the heavy metal exchange. Swelling was very high in the unmodified apple sresidues; an important decrease was obtained by phosphorylation which may be due to the fact that phosphorus oxylchloride can also act as a crosslinking agent. The residues submitted to crosslinking and xanthation showed only a slight decrease in swelling. The yield of crosslinking, which greatly depends on the reaction conditions, was obviously low.

Lee & Yang (1997) studied an effect of ionic strength, co-ions and ligands on copper removal by phosphorylated apple residue (P-AW). The optimal pH range was shown to be from pH 5.5 to 7.0.A divalent cation Cu^{2+} and monovalent cation $Cu(OH)^+$ are dominant metal species at this pH range. Equilibrium was established very rapidly initially and decreased markedly after 1 hour. Copper uptake capacities were 10.8mg Cu/g AW and 36.2mg Cu/g P-AW. Increasing ionic strength up to 0.1 N had little effect on metal uptake. The presence of co-ions such as lead and nickel decreased the removal capacity of copper where influence of lead was more significant. The presence of ligands such as EDTA and ammonia also reduced metal removal efficiency due to a metal-ligand complexation in the solution.

Lee & Jung (1998) tested AW and P-AW for copper, lead and cadmium removal. The optimal pH ranges were from 6.0 to 7.0 for copper, 6.5 to 8.0 for lead and 8.0 to 9.5 for cadmium, respectively. These results indicated that the binding of copper and cadmium is more pH-dependant than that of lead. Both AW and P-AW showed higher selectivity for lead ions compared to copper and cadmium ions. The most remarkable result was that the dynamic removal capacity for cadmium with P-AW had increased by six times by phosphorylation. Recently, a much more significant bio-sorbent having better metal loading capacity as compared to commercially used synthetic materials has been investigated [20,37]. The research results conducted in last ten years indicated that plastic synthetic materials as a means of wastewater treatment will be replaced by the biomaterials in the near future.

Basso, *et al*. (2002) studied the adsorption capacity of Cd (II) and Ni (II) by activated carbons developed from *Arundo donax*, a rapid growing plant. The plant was converted to activated carbons by phosphoric acid activation under four different activation atmospheres. They are flow of air, carbon dioxide, self generated atmosphere and nitrogen. The carbons derived under flowing air have the largest total content of polar and acidic surface oxygen functional groups and showed the best adsorption effectiveness of above 90% for both ions. The adsorption kinetic data obtained were properly described with pseudo - second order rate model. Equilibrium isotherm was well fitted with Langmuir isotherm model. They also investigated the effect of pH on metal uptake studied desorption from metal loaded carbon for recovery of adsorbent. They also studied binary system of equimolar concentration of Cd (II) and Ni (II). The adsorption of Ni (II) was found more affected by competitive presence of Cd (II).

Wan Ngah & Hanafiah, (2008) reviewed the application of low cost adsorbents, which are obtained from plant waste as replacement for costly conventional methods for removing heavy metals from waste water. They found that cellulosic waste materials can be obtained and employed as cheap adsorbents. Their performance was improved by chemical treatments with mineral and organic acids, bases, oxidizing agents and other organic compounds. Such chemically modified adsorbents have good adsorption capacities for Cd, Cu, Pb, Zn, Ni and Cr (IV). The chemical modification might change the properties of adsorbents and they recommend characterizing the adsorbents by measuring surface area, pHpzc and spectroscopic analysis.

Thirumavalavan, *et al.*, (2010) explored a viable and cost effective technology for the removal of Cu (II), Ni (II), Zn (II), Cd (II) and Pb (II). They used adsorptive removal of these metals by using orange peel (OP), lemon peel (LP) and banana peel (BP). These cellulosic materials were chemically modified by acid and alkali treatment. The modified adsorbents were characterized by FTIR, BET and SEM. The Langmuir isotherm model was used to describe the adsorption equilibrium process. Adsorption of Cu (II) and Ni (II) was found to be more than that of other metal ions. The chemically modified adsorbents were found to have enhanced adsorption capacity.

Antonio & Roberto (2010) evaluated the adsorption properties of tea waste. They evaluated the removal efficiency of Pb (II) by spent tea leaves of green and black tea. Batch adsorption experiments were performed at 25 and 40^{o}C at initial lead concentration between 0.01 and 2 g/L. The equilibrium data were analyzed by Langmuir equation to evaluate the maximum adsorption capacity and equilibrium constant. The removal efficiencies were found to be within 94 - 99% depending on the solution concentration and adsorption condition. The adsorption properties of these adsorbents were found more effective than conventional adsorbents like activated carbon and Fuller's earth.

Tajmeri, *et al.* (2009) performed batch experiments using used black tea leaves as low cost adsorbent for removal of lead from aqueous solution. They conducted the adsorption experiment as the function of contact time, initial metal concentration, solution pH and temperature. The adsorption of lead was increased with increase in initial pH of solution upto pH 5. The adsorption isotherm followed Langmuir equation better and it was found more applicable at higher temperature. A probable mechanism was also proposed on the basis of surface charge of adsorbent and the change of charge of Pb (II) with pH of solution.

Thakur & Parmar (2013) used tea waste as a cheap and effective adsorbent for the removal of Cu (II), Zn (II) and Ni (II) from waste water without any pretreatment. The maximum removal of Ni (II) was found to be 94% at optimum condition of pH 5,contact time 120 min, adsorbent dose 0.5 g/100 mL and concentration 20 ppm. For Cu (II) and Zn (II) maximum removal were 89% and 91% respectively, at their optimum condition of pH 5, contact time 120 min, adsorbent dose 0.5 g/ 100 mL and concentration of metal solution 10 ppm.

Bajpai & Jain (2010) used spent tea leaves for the removal of Cu (II) from aqueous solution in Batch experiment. The adsorbent was characterized with respect to surface area, pore volume and density. The equilibrium sorption data were fitted to various sorption isotherm models and the order of fitness was Langmuir > Temkin > Freundlich. The maximum sorption capacity evaluated using Langmuir isotherms at 27°C and 37°C were found to be 90.9 and 68.4, respectively. The decreased sorption capacity with increasing temperature indicated the exothermic nature of metal uptake process. The kinetic uptake data were best interpreted with by pseudo second order kinetic model. They also evaluated the thermodynamic parameters like ΔG_o, ΔH_o and ΔS_o were also evaluated.

Dadhich, *et al*. (2004) investigated the rice husk as non-conventional adsorbent for removal of nickel. The effects of contact time, adsorbent dosage, pH, concentration of the metal ion and isotherm models for adsorption were studied using batch process. A steady trend was observed for all these variables. The adsorption percentage increased with increase in contact time, adsorbent dosage and pH, but there was a decrease in adsorption with increase in concentration of the metal ion.

Kaushik, *et al*. (2005) reduced the color of cotton fabric dyeing effluent containing direct dyes using commonly available adsorbents. The extent of adsorption efficiency of these adsorbents with variable doses was studied and compared with activated carbon. It was found that adsorption efficiency of wood ash was better than the others. Effect of pH was also examined in decolourisation of dyes effluent, which shows variable impact with regard to the nature of dyes and the adsorbent used.

Rao, *et al*. (2004) investigated the potentiality of commercially available activated carbon as an effective adsorbent to remove the dyes from aqueous solutions. The effects of pH of the solution, dose of adsorbent, concentration of solutes and temperature on activated carbon for azo dyes such as acid orange 7 and direct red 31 have been evaluated. The percentage removal of the dyes has been found to be high at neutral pH.

Revathi, *et al*. (2005) investigated the removal Ni (II) from industrial effluents by using activated alumina as the adsorbent. The optimum pH for the adsorption process was found at 9. The adsorption data were fitted with suitable adsorption isotherm. The optimum conditions for the best adsorption have been evaluated for the following factors: dose of adsorbent, contact time, pH of solution, initial concentration of nickel ions and temperature. The process of regeneration of the adsorbent has also been studied.

Singh & Rastogi (2004) prepared activated carbon from used tea leaves impregnated with H_3PO_4 (50%, w/v) and carbonized at 300ºC. The adsorption capacity of the adsorbent was determined for the decolourisation of wastewater containing malachite green and methylene blue. The optimum pH range was 8-10 and dosage required was 1.2 g/L for 100% removal of both malachite green and methylene blue (100 mg/L).

Srivastava, *et al*. (2005) investigated the removal of cadmium from aqueous solution using sawdust available in plenty in every saw mill. The effects of concentration of cadmium ions, temperature, amount of adsorbent and contact time were studied in batch experiments. Maximum removal was obtained in the pH range of 6-9 and removal of metal increased with increase in temperature. The results were found to be encouraging and 99% removal of cadmium was obtained.

Yun, *et al*. (2001) utilized protonated *Ecklonia sp.* for Cr (III) adsorption. The Algal species contained at least three different types of functional groups. FT- IR spectroscopy showed that carboxyl group was chromium (III) binding site within the pH range of 1 - 5.

Cr (III) did not precipitate in this range. The pka value and number of carboxyl groups were estimated at 4.6 and 2.2mmol/g, respectively. A model describing chromium biosorption was also developed incorporating known chromium aqueous hydrolysis reaction.

Deng & Ting (2005) modified *Penicillium chrysogenum* fungal biomass by grafting polyethylenimine (PEI) onto the biomass surface in a two step reaction. This adsorbent acquires a positive charge due to protonation of amine functions at low pHs. The presence of PEI on the biomass surface was verified by FT-IR and XPS analysis. The high density of amine groups in PEI chains bound to the surface possessed a positive zeta potential at pH below 10.4. This led to a high sorption capacity for anionic Cr (VI). The maximum sorption capacity for Cr (VI) at pH 4.3 - 5.5 was 5.37 mmol/g. XPS confirmed Cr (III) on the biomass surface in the pH range 2.5 - 10.5, suggesting that Cr (VI) anions were reduced to Cr (III) during the sorption. Electrostatic interaction, chelation and precipitation were likely to be involved in chromium sorption on the PEI- modified biomass.

Nourbakhsh, *et al*. (2002) reported Cr (VI), Pb (II) and Cu (II) biosorption on *Bacillus* species in single and multi-component systems. In multi component solutions, lead biosorption increased widely while Cr (VI) Cu (II) biosorption decreased versus their amount in single metal ion systems. Loukidou et al. [245] explored aqueous Cr (VI) removal by *Aeromonas caviae* biomass particles, isolated from potable ground water supplies. The optimum pH was 2.5 and the maximum adsorption capacity was 284.4 mg/g.

Hasan, *et al*. (2003) investigated Cr (VI) remediation using chitosan coated perlite beads. Chitosan coated perlite beads were prepared by addition of chitosan and perlite liquid slurry to an alkaline bath. The beads were characterized by SEM and EDS X-ray microanalysis. The chitosan content of the beads was 23%. The chitosan coated perlite adsorption capacity was 104mg/g using batch determination method. The Cr (VI) capacity 452 mg/g of chitosan. This large capacity was considerably higher than that of natural and modified chitosan, which ranged from 11.3 to 78 mg/g of chitosan. The beads loaded with chromium were regenerated with sodium hydroxide solution.

Chemical modification of cellulose fiber to improve its removal performance and adsorption capacity for Cu (II), Ni (II) and Zn (II) ions using ethylenediamine was conducted by Torres, *et al.* (2006). Cellulose consist of active hydroxyl groups present on each monomeric unit of cellulose, therefore cellulose can react with carboxyl and amine groups of organic compounds. Based on the isotherm study, it was found that ethylenediamine modified cellulose fiber adsorbed Zn (II) more efficiently than Ni (II) and Cu (II) ions. The reported values of maximum adsorption capacities were 104.1, 308.2 and 69.3 mg/gfor Cu, Ni and Zn, respectively. The modified adsorbent was also capable to adsorb metals 100 times more than unmodified cellulose. Adsorption of heavy metal ions occurred through complexation mechanism in which the amine groups of ethylenediamine take part in the chelation process.

Rehman, *et al*. (2006) reported the removal of Ni (II) ions by using sodium hydroxide treated sawdust of *Dalbergia sissoo*, a byproduct of sawmills. The treatment of sawdust with NaOH results in the conversion methyl esters which are the major constituents in cellulose, hemicelluloses and lignin to carboxylate ligands. The adsorption time study revealed that nickel ions were removed fast in the first 20 min due to extra-cellular binding. The maximum adsorption capacity of Ni (II) ions was found to be 10.47 mg/g at 50^{o}C. Adsorption was more favourable at higher temperature and adsorption followed both Langmuir and Freundlich isotherm models.

Amarasinghe & Williams (2007) developed a potential biosorbent from tealeaves of Srilankan tea. They studied the adsorption capacity of teawaste based activated carbon. The adsorbent was used for removal of Cu (II) and Pb (II) from waste water.

Wang, *et al*. (2006) used rice bran, which is a by-product of rice milling process as an alternative adsorbent for removal of zinc from waste water. The effects of various parameters such as pH, temperature and particle size and adsorption time on the adsorption capacity were studied. They concluded that pH of the solution played an important role on adsorption of zinc and particle size

The solid waste of commercially available tea leaves were used in the adsorption of metal ions by Tee, *et al.* (1988). The extent of adsorption depends on pH, ionic strength, metal concentration, substrate concentration, and the presence of interfering ions and surfactants. Among the various types of surfactants studied, cetyl trimethylammonium bromide severely hindered the metal uptake while Triton XlOO interfered mildly. Initial enhancement of Pb(II) and Zn(II) uptake was observed in the presence of small amount of sodium dodecyl sulphate. The enhancement effect decreased as the anionic surfactant concentration increased. Metal concentration dependence curves can be described by a Langmuir isotherm. Adsorption capacities of tea leaves were found to be 0.38, 0.28 and 0.18 mmole/g for Pb, Cd and Zn respectively. Column experiments revealed near 100% efficiency for metal removal of as much as 100 ppm Pb(II) ion at pH 6, using 1.8 g waste tea leaves and flow rate of 25 mL / min. The relative affinities of metal ions towards waste tea leaves is in the order of Pb > Cd > Zn.

CHAPTER 3

3. MATERIALS AND METHODS

3.1 Chemicals

1000 mg/L stock solution of Pb (II), Cu (II), Cd (II) and Zn (II) were prepared by dissolving calculated amount of lead nitrate, copper sulphate, cadmium nitrate and zinc sulphate in 0.1 M HNO_3. Working solutions of various concentrations were prepared by diluting the stock solution with 0.1 M HNO_3. In all the experimental works pH of the solutions were maintained by using 0.1 M HNO_3 and 0.1 M NaOH. The 0.1 M solution of 2-[4-(2-hydroxymethyl)-1-piperazinyl] ethanesulphonic acid [HEPES] was used as buffer. Fisher Scientific chemicals with analytical grade (AR) were used and double distilled water was used wherever necessary for the experimental works.

3.2 Preparation of biosorbent

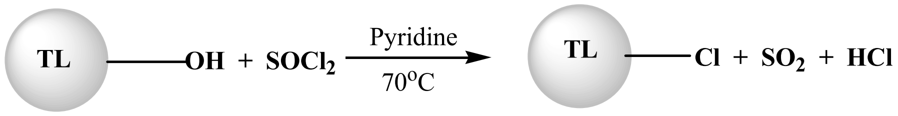
In this study the biosorbent selected was waste tealeaves. It was prepared from Tokla tea. About 150 g of tealeaves was washed several times with hot water to obtain clear and colorless filtrate. It was dried in an air oven at 70°C for 24 h. This dried tealeaves was powdered in mortar and sieved through 212 μm sieve.

The biowaste was pretreated with concentrated H_2SO_4, which is known as charring process. About 150 mL of concentrated H_2SO_4 was added to 100 g waste tealeaves, drop by drop with constant stirring and left for 24 h. The charred biowaste was washed several times with distilled water till the neutrality. It was dried in an air oven at 70°C for 24 h. Such acid treatment extracts lower molecular weight soluble organic compounds from the material and also creates a suitable environment for the breakdown polymeric chain of biopolymers like lignin or ring opening in cellulose and hemicelluloses (Morrison & Boyd, 1994). It causes the exposure of the biosorbent for further chemical modification. The charred biowaste was chemically modified to introduce amine functional group on its surface by using following methods.

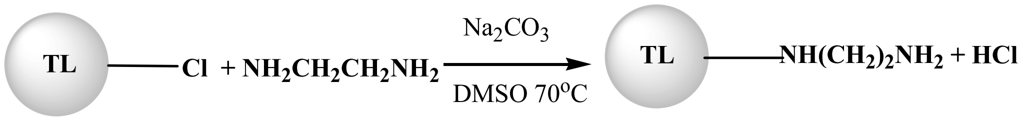
3.2.1 Chemical modification with ethylenediamine:

In the first method the charred biowaste was aminated in two steps. The first step is chlorination by using thionyl chloride, in which the – OH group is substituted with – Cl group. In the second step the –Cl group is substituted with amino group by using ethylenediamine. The reaction schemes are represented in scheme 1.

Step I



Step II



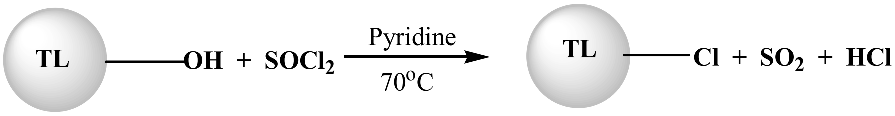
Scheme 1: Amination of tealeaves by using ethylenediamine

In a three necked flask, a weight of 20 g charred tealeaves was mixed with 100 mL of thionyl chloride in presence of 250 mL of pyridine at 0°C using an ice bath. The mixture was heated at 70°C for 90 min. After cooling the sample, it was washed with distilled water followed by propanol and dried in an air oven. This chlorinated sample was mixed with 90 mL ethylene diamine and 32 g of solid sodium carbonate in presence of 300 mL dimethyl sulphoxide. The mixture was heated at 70°C for 6 h. After cooling down to room temperature, the sample was washed with 4 L of 0.1 M HCl followed by distilled water till the filtrate became neutral. Finally, the aminated biosorbent was washed with propanol and dried in an air oven at 70°C for 24 h. The sample is referred as charred aminated tealeaves with ethylenediamine [CATL – 1 or T-1].

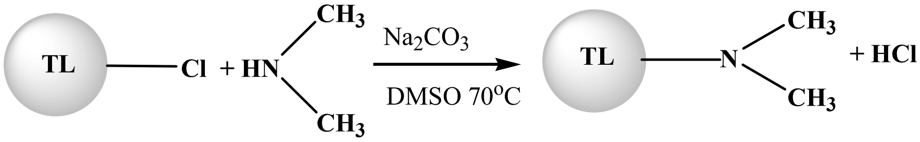
3.2.2 Chemical modification with dimethylamine:

In the second method, the biosorbent was aminated by using dimethylamine. All the processes are same as in method (A). In this method dimethylamine is used instead of ethylenediamine. The reaction can be represented as in scheme 2. This sample is termed as charred aminated tealeaves by dimethylamine [CATL – 2 or T-2]

Step I



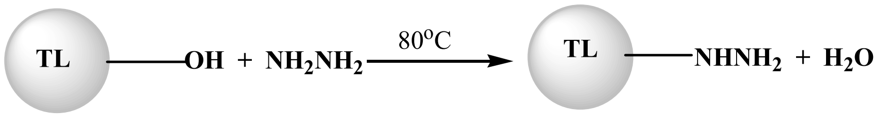
Step II



Scheme 2: Amination of tealeaves by using dimethylamine

3.2.3 Chmical modification with hydrazine monohydrate:

In this method the biowaste was chemically modified by using hydrazine monohydrate.A volume of 20 ml charred biosorbent was mixed with 160 mL distilled water and left for swelling over night. To the mixture 8 g of hydrazine monohydrate was added dropwise with constant stirring and heated in a water bath at 80°C for 4 h. The mixture was cooled and washed with distilled water for several times. Finally, the sample was washed with methanol and dried in an air oven at 70°C for 24 h. Thus obtained adsorbent is charred aminated tealeaves with hydrazine monohydrate [CATL – 3 or T-3]. The reaction can be represented as in scheme 3.



Scheme 3: Amination of tealeaves by using hydrazine monohydrate

3.3 Elemental analysis

The percentage of constituent elements C, N and S present in the biosorbent were analyzed by using Elementar Vario Macro elemental analysis instrument.

3.4 Scanning Electron Microscope (SEM) analysis

Scanning Electron Microscope (SEM) image was used to study the surface morphology of biosorbent. In SEM analysis the samples are bombarded by focused, high energy electron beams and the secondary electrons ejected from the samples are detected. SEM can achieve higher magnification than optical microscopes. SEM characterization of RTL, CATL-1, CATL-2 and CATL-3 were recorded using an S-3000N Scanning Electron Microscope of HITACHI, Japan, type instrument in vacuum environment. As the samples are non-conductive, they are coated with electrically conductive coatings during analysis. SEM images of different magnification at different areas were recorded.

3.5 Diffuse reflectance infrared spectroscopy (DFTIR) analysis

FTIR measurement is primarily used for determination of certain types of bonding structure and functional groups. It measures the absorption of infrared radiation by materials as their atoms vibrate about their bonds. When a material is illuminated by IR-radiation of approximate frequencies the atoms, ions and functional groups in the molecules will vibrate about their bonds and energy will be absorbed. Each bending and stretching vibrational mode in a molecule will absorbs a particular frequency, which appears as peaks in the spectrum. Hence functional groups present in the biosorbent can be identified by observing the FTIR spectrum. The functional groups in RTL, CATL-1 CATL-2 and CATL-3 were characterized by their FTIR spectra obtained at frequency range of 4000 to 500 cm-1 using FTIR – Harrick scientific corporation [Diffuse reflectance infrared spectroscopy – DFTIR].

3.6 Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry (AAS) is widely used technique to determine trace level of elements in a sample with good accuracy and acceptable precision. This technique uses the absorption of radiation by free gaseous atoms in order to achieve qualitative detection and quantitative determination of elements. It measures the logarithm of rate of incident light power (Po) to transmitted light power (P).

$$A = \log P_o/P \qquad (1)$$

The relation between P_o and P, when a light beam is absorbed by the medium through which it passes is given by equation 2.

$$P = P_o \exp(-kL) \qquad (2)$$

where k is absorption coefficient which is a function of wavelength of light, number of atoms in the ground state per unit volume and L is path length of the medium.

3.7 Adsorption Experiments

The adsorption behavior of metal ions onto the biosorbents was determined by batch experiment method. A volume of 20 mL metal solution was added in 50 mL conical flask containing 25 mg of biosorbent. The flasks were shaken in a mechanical shaker at 150 rpm for 24 h to attain equilibrium. After 24 h, the mixtures were filtered and filtrates were analyzed for equilibrium concentration of metal ions using AAS. The decrease in concentration of metal ions in solution was used to calculate the amount of adsorbed metal ions onto the biosorbents.

The filtrates obtained in batch experiment were analyzed using flame AAS. The instrument of type Agilent technologies, AAS, model – 240FSAA, USA was used. During the measurement hollow cathode lamps of corresponding metals were used to determine the subsequent metal content of filtrates.

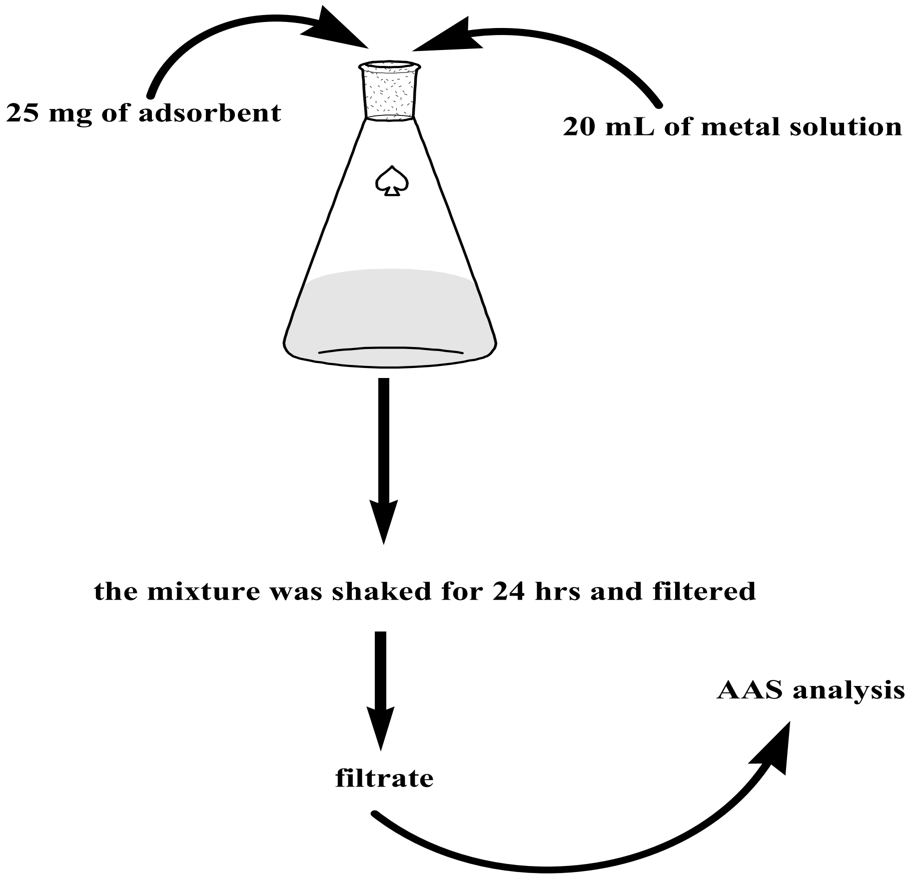


Figure 3: Batch adsorption experiment

3.7.1 Effect of pH on metal adsorption

The adsorption of metal ions depends on the pH of the solution. The pH of the solution has great influence on the surface charge of the biosorbent and degree of ionization of metal ions. The effect of pH of the solution for the adsorption of metal ions was studied by using batch experiment, keeping the concentration of metal ions constant. In this experiment, the optimum value for the adsorption of metal ions can be obtained.

A volume of 20 mL of 50 mg/L metal solution with varying pH from 1 – 7, were kept into 50 mL conical flask each with 25 mg of biosorbent. The pH of the solution was maintained by using either 0.1 M HNO_3 or 0.1 M NaOH as appropriately. The flasks were shaken for 24 h in a mechanical shaker at 150 rpm at 25°C to attain equilibrium. After shaking the mixtures were filtered. In the filtrate, the equilibrium pH of the solution and residual concentration of metal ions were measured.

The adsorption efficiency i.e. adsorption percentage (A %) can be calculated by using equation 3.

$$A\% = \frac{C_i - C_e}{C_i} X 100 \qquad (3)$$

where C_i and C_e are the initial and equilibrium concentration of metal ions.

3.7.2 Zeta potential

The zeta potential measurement indicates the stability of colloidal system. In a colloidal system one of the three states of matter – gas, liquid and solid are finely dispersed in one of the other (except gas – gas system). One of the prime concerns could be the solid dispersed in a liquid system (Langmuir, 1916). Many colloidal particles acquire an electrical charge through the ionization of surface functional group. Ionization of these groups is pH dependent and the particles may acquire a net positive charge at low pH, a negative charge at high pH and a net charge of zero at some intermediate pH, which is known as isoelectric point.

Net charge at the surface of the particle affects the distribution of ions in its surrounding interfacial region, which causes accumulation of oppositely charged ions (counter ions) close to the surface of the particles. Hence, the charge on the colloidal particles is counterbalanced by counter ions of dispersing phase, resulting in the formation of an electrical double layer. It is the cause for the electro neutrality of colloidal dispersion.

The distribution of electrical potential near the colloidal particle can be described by a model proposed by Stern as shown in Figure 4.

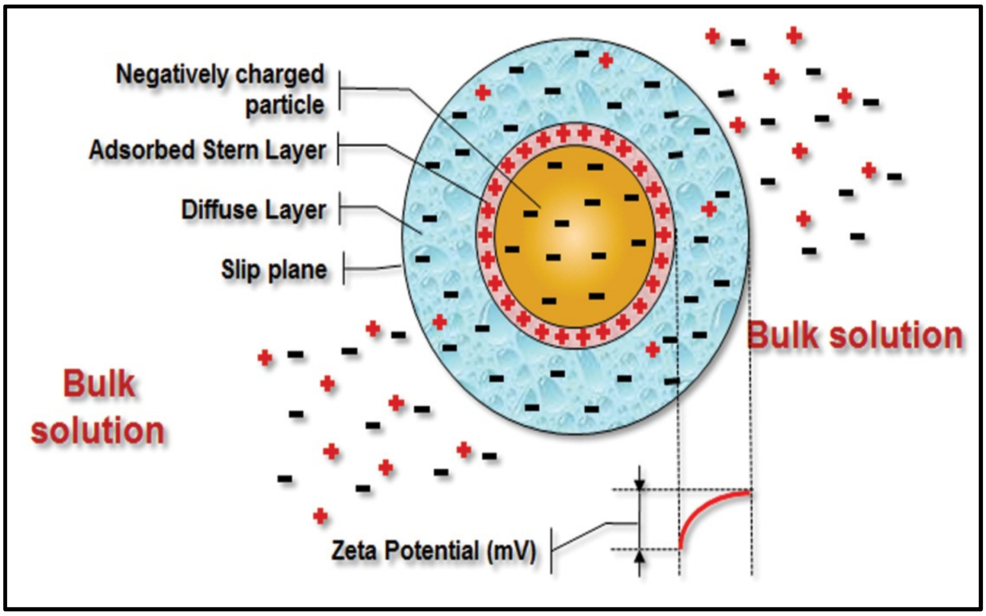


Figure 4: Schematic representation of zeta potential

The electrical potential developed due to charge on the surface of particles will attract the counter ions towards the particle. These ions are strongly bound in inner layer of the liquid layer surrounding the particle which is called stern layer. Beyond the stern layer is diffuse layer in which ions are less firmly attracted. Within the diffuse layer there is a boundary, inside which the particle forms a stable entity with ions. These ions inside the boundary moves with the particle but other ions beyond the boundary do not move with the particle. This boundary within the diffuse layer is called shear or slipping plane. The potential that exists at the plane of shear between the bulk liquid and an envelope of liquid phase which moves with the particle is called zeta potential.

The stability of colloidal particles is measured in terms of zeta potential. Higher zeta potential indicates the strong forces of separation and stable colloidal system, whereas lower value indicates the less stable system i.e. the particles come together and flocculate. Generally the particles with zeta potential more positive than +30 mV or more negative than -30 mV are considered as stable system. In the plot of zeta potential versus pH of the solution the point where the plot passes through zero zeta potential is called isoelectric point or point of zero charge as in Figure 5. It is the point where the system becomes least stable and important for further practical consideration.

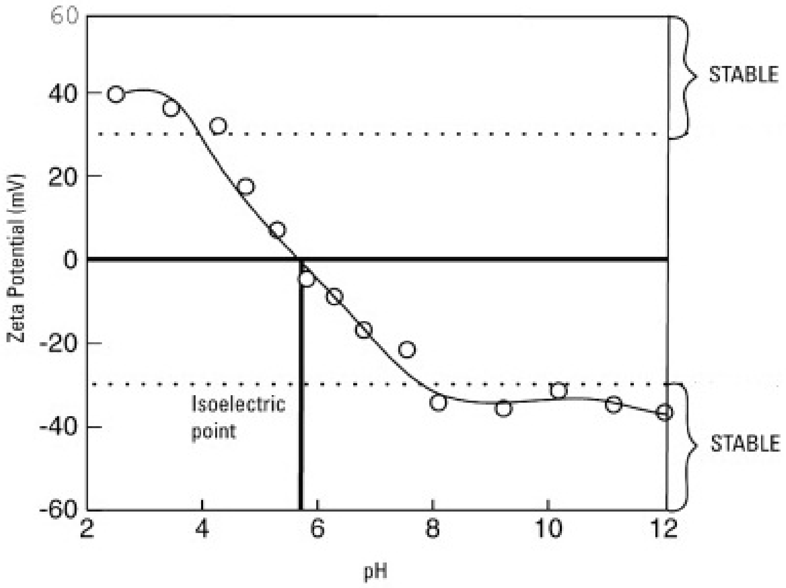


Figure 5: A typical plot of zeta potential curve

For pHpzc measurement, 20 mL of distilled water at varying pH from 1 – 12 was stirred with 25 mg of biosorbent in 50 mL conical flask in a mechanical shaker at 150 rpm for 2 h. After shaking the mixtures were filtered and used to conduct zeta potential measurement.

3.7.3 Effect of concentration on adsorption: Adsorption isotherm

The adsorption isotherm helps to evaluate the loading capacity of biosorbent. In this scheme the effect of initial concentration of metal ions in the adsorption was studied. The test solution of metal ions of varying concentration, 25, 50, 100, 200, 400, 600 and 800 mg/L, respectively, were prepared by proper dilution of stock solution of 1000 mg/L. A concentration of 0.1 M nitric acid was used for dilution and 0.1 M HEPES solution was used as buffering agent.

The effect of initial concentration of metal ions in the adsorption of metal ions was studied by using 20 mL of test solution of varying concentration. The metal solution ranging from 25 – 800 mg/L was added to 50 mL conical flasks, each containing 25 mg of biosorbent. During the experiment, the optimum pH was maintained by using 0.1 M HNO_3 and 0.1 M NaOH. The flasks were agitated in a mechanical shaker at 150 rpm for 24 h to attain equilibrium. After shaking the mixtures were filtered and the filtrates were analyzed for equilibrium concentration of metal ions.

The loading capacity of an adsorbent is the accumulation of metal ions onto the adsorbent at equilibrium. It can be calculated on the basis of mass balance principle as given in equation 4.

$$q = \frac{C_i - C_e}{W} X \frac{L}{1000} \qquad (4)$$

where q is amount of metal ions adsorbed per unit mass of the adsorbent, L is volume of metal solution, W is dry mass of adsorbent and C_i and C_e are initial and equilibrium concentration of metal ions, respectively.

3.7.4 Effect of contact time on adsorption – Kinetic study

The kinetic study of adsorption helps to calculate the optimum contact time for adsorption as well as the rate of adsorption. The kinetics of adsorption of metal ions was determined by using 20 ml of 50 mg/L metal solution and 25 mg of the bioadsorbent in 50 mL conical flask. The optimum pH was maintained by using 0.1 M HNO_3 and 0.1 M NaOH and 0.1 M HEPES was used as buffering agent. The flasks were shaken in a mechanical shaker at 150 rpm. The flasks were taken out from the shaker after each predetermined intervals of time and filtered. The filtrates of different contact time (5 – 240 min) were analyzed for concentration of metal ions by using atomic absorption spectrometer (AAS).

3.7.5 Desorption studies

The desorption studies of biosorbent explores the possibility of reuse of the biosorbent and recovery of metal ions. Desorption studies was carried out by using batch experiment. A concentration of 0.1 M HCl, 0.1 M HNO_3 and 0.1 M NaOH were used for desorption of metal ions. Among which HNO_3 was found to be more effective. Further the metal loaded adsorbent was desorbed with 0.1 HNO_3 by shaking in a mechanical shaker at 150 rpm for 1 h. The mixture was filtered and the filtrate was analyzed for desorbed metal ions. After the adsorption desorption cycle the biosorbent was washed with distilled water and dried in an air oven at 70°C for 24 h. This regenerated biosorbent was reused for another 5 adsorption/ desorption cycles, which determines the potential for reusability of the adsorbent.

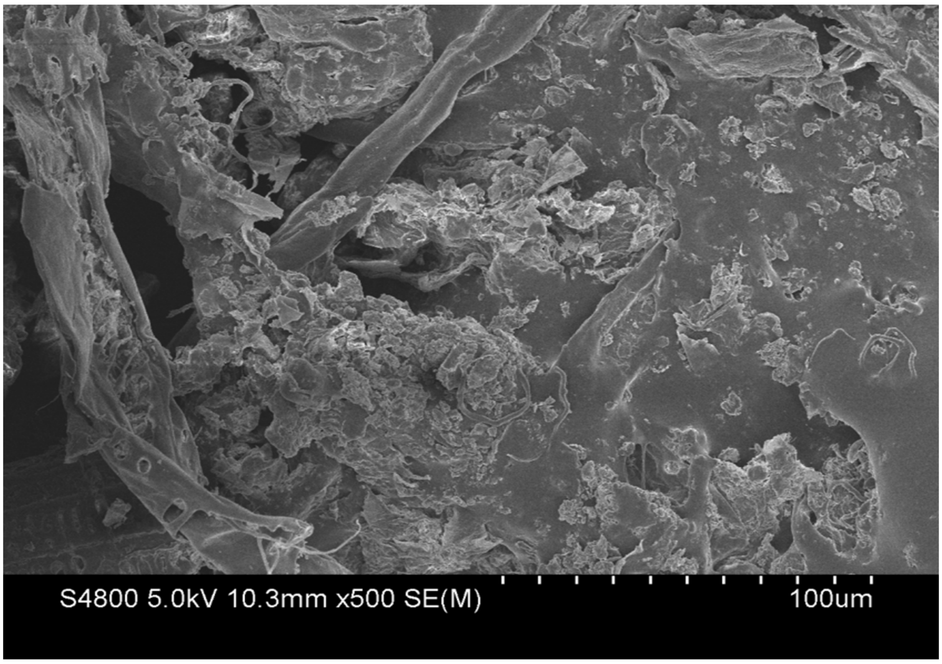
CHAPTER 4

4. RESULTS AND DISCUSSION

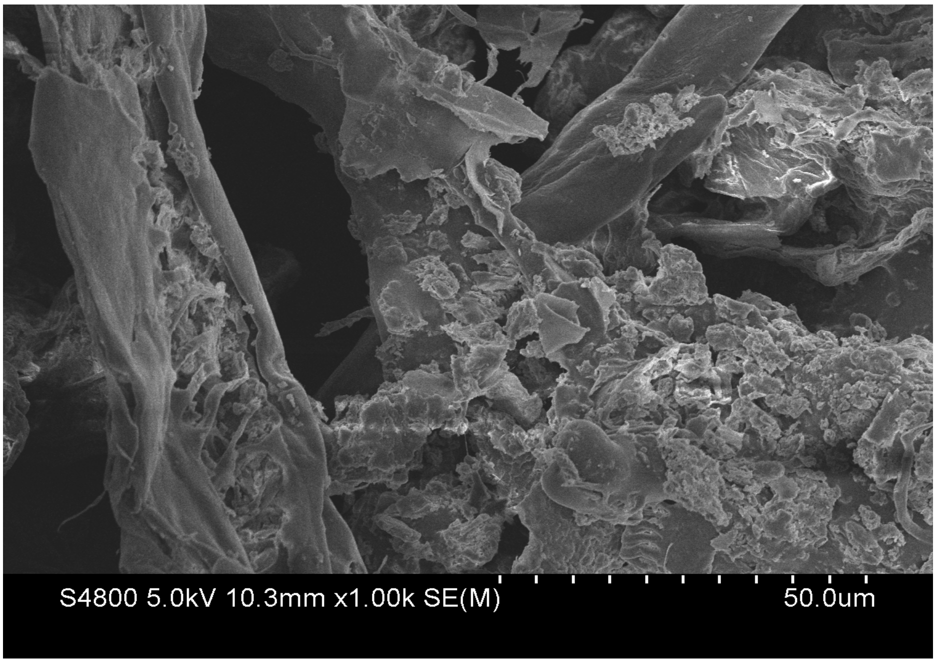
4.1 SEM analysis

Scanning Electron Microscope [SEM] images are used to examine the surface morphology of the biomaterials. SEM images of raw tealeaves were shown in Figure 6 (a) and (b). The biomaterial, waste tealeaves contain cellulose, hemicelluloses and lignin as the main constituent of biopolymers and its surface morphology was fibrous in nature. The biomaterial under study was chemically modified to introduce amine groups on its surface by using three different methods. After chemical modification, the fibrous nature of the biomaterial surface was destroyed and apparently isolated and irregularly distributed pores were formed in all of the three modified biomaterials CATL-1, CATL-2 and CATL-3. Such pores were supposed to be formed due to the increased effective diffusion surface area derived from pore formation and the surface of biomaterial became rough as shown in Figure 7, 8 and 10, respectively. This morphological change revealed to indicate required chemical modification onto the biomaterials. The surface of biomaterials after amination was full of cavities that are essential to enhance the metal binding capacity of the adsorbent.

The SEM images of aminated tealeaves CATL-2 and CATL-3 after adsorption of Cd (II) are shown in Figure 9 and 11, respectively. In the SEM images after metal adsorption, morphological changes were seen. After metal loading the heterogeneous rough and porous surface of adsorbent was changed into homogenous or smooth surface which can be seen especially in the images with high magnification.

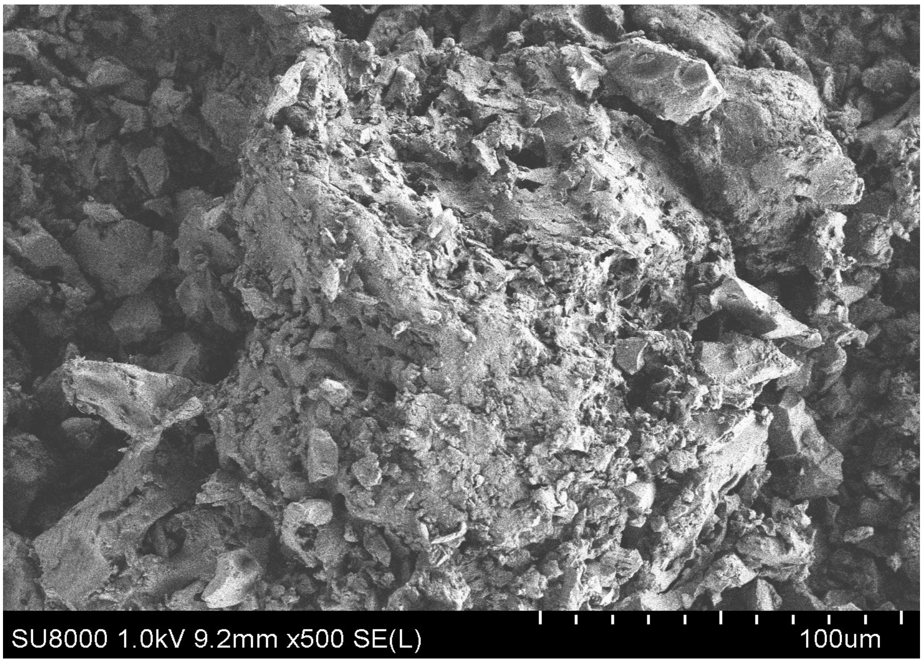


6 (a)

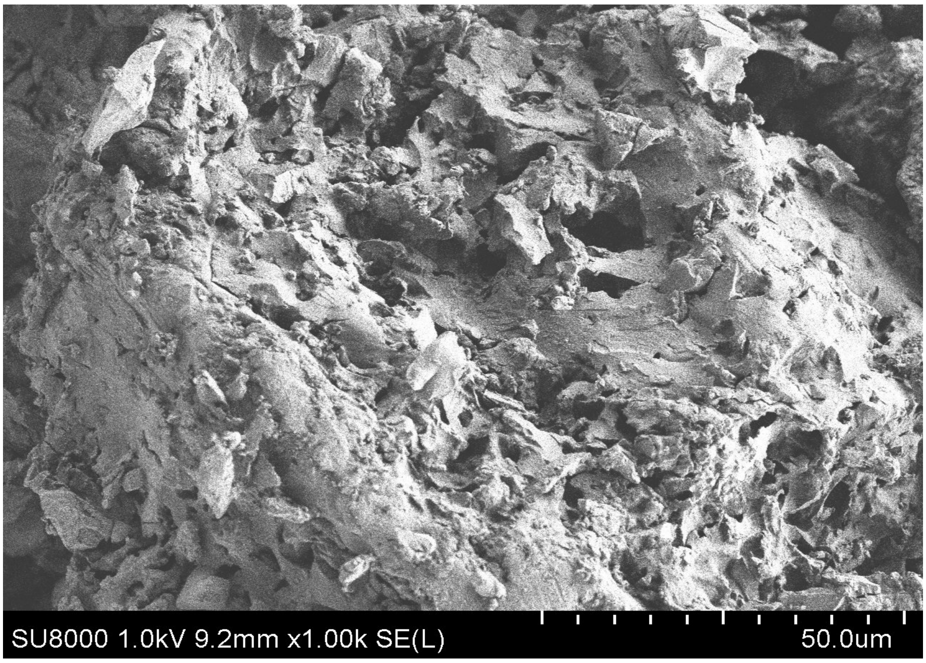


6 (b)

Figure 6: (a) and (b): SEM images of RTL

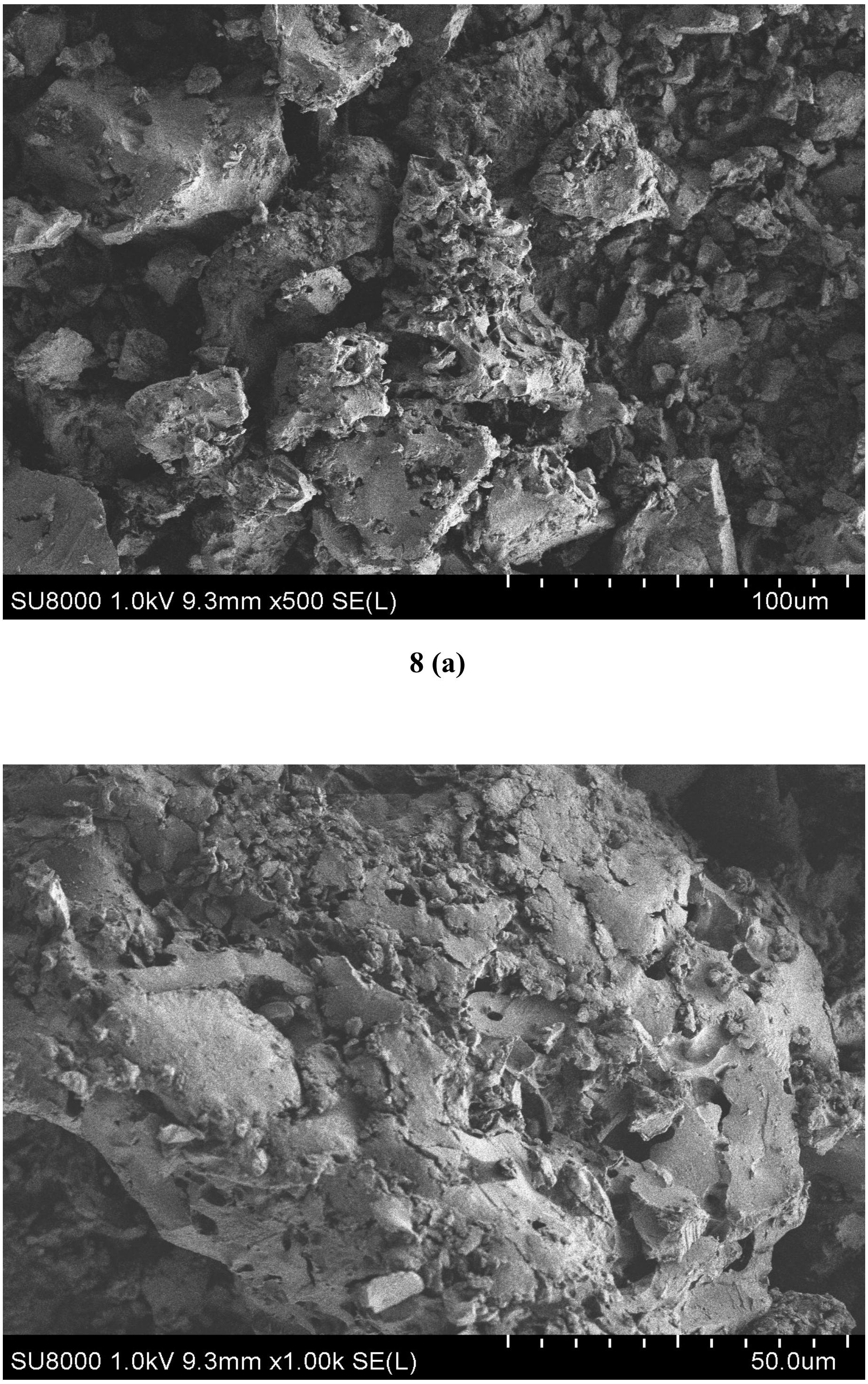


7 (a)



7 (b)

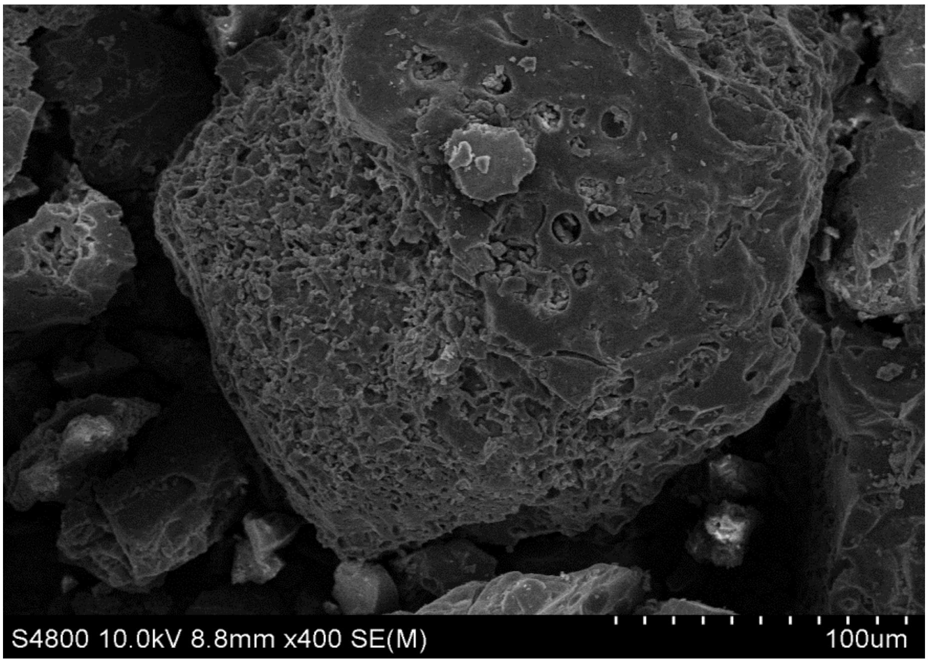
Figure 7 (a) and (b): SEM images of CATL-1



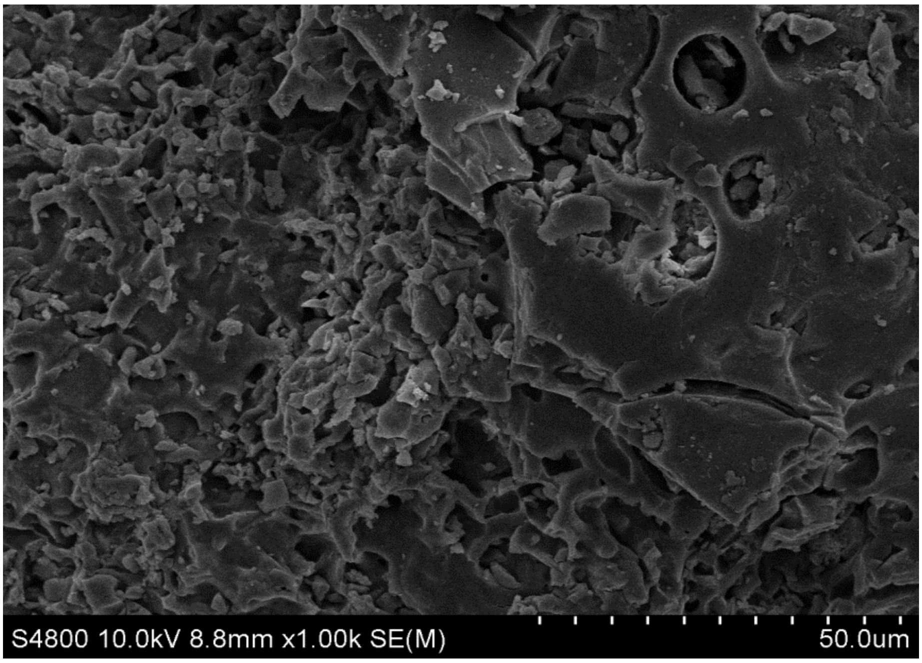
8 (a)

8 (b)

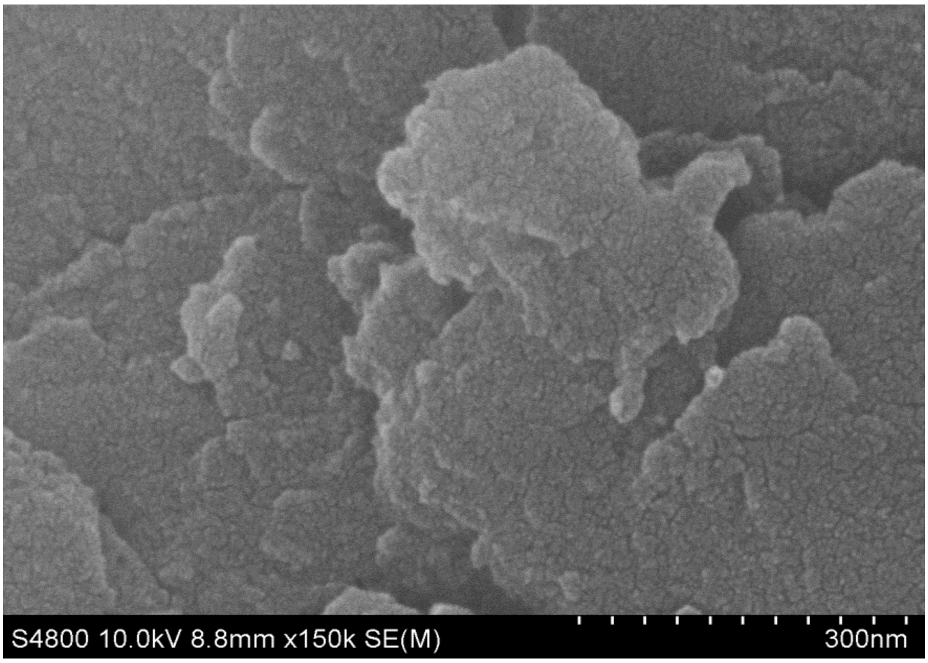
Figure 8 (a) and (b): SEM images of CATL-2


S4800 10.0kV 8.8mm x400 SE(M)
100um

9 (a)

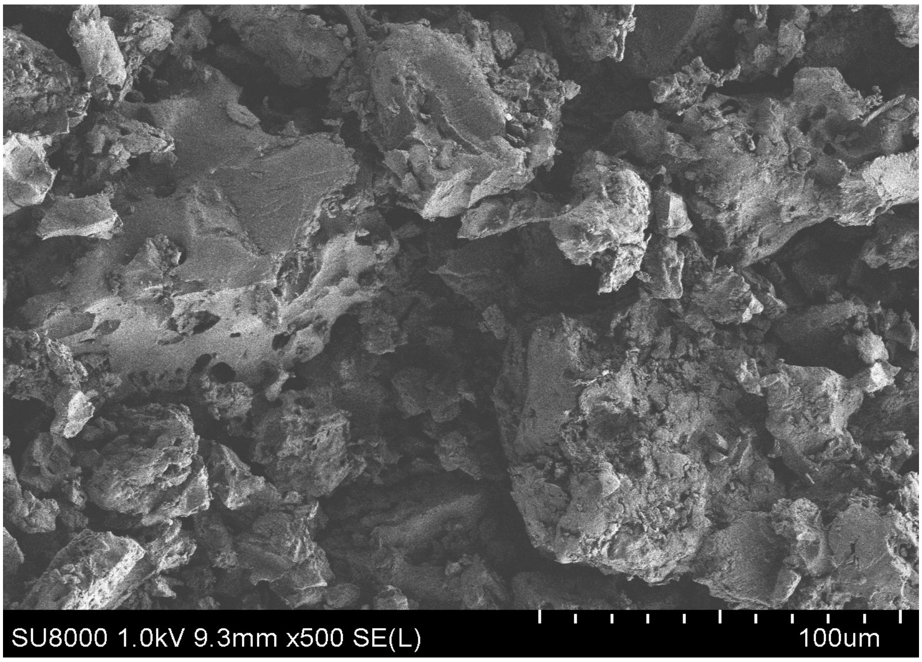

S4800 10.0kV 8.8mm x1.00k SE(M)
50.0um

9 (b)

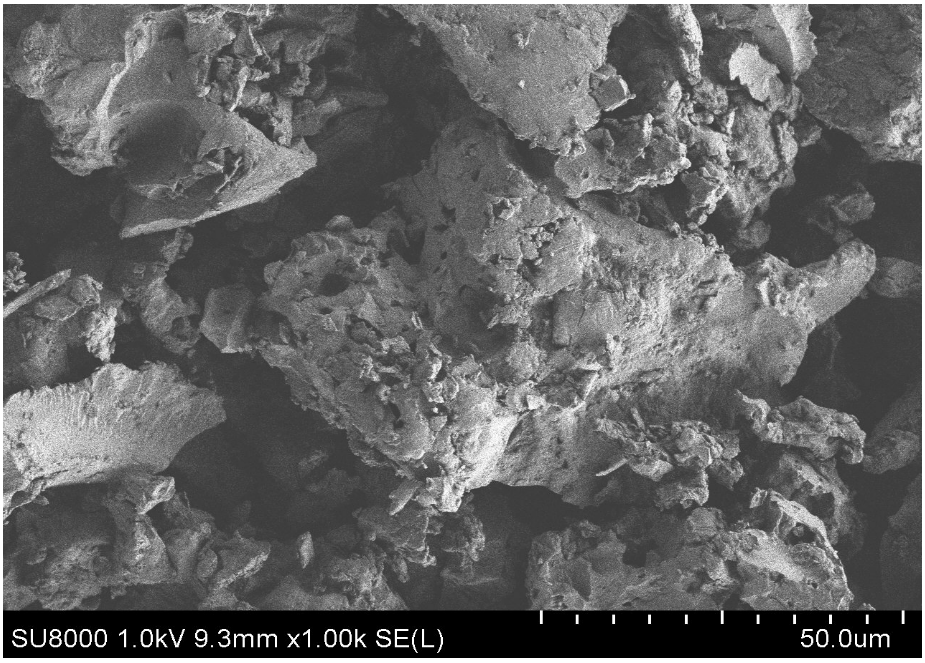


9 (c)

Figure 9 (a), (b) and (c): SEM images of Cd loaded CATL-2

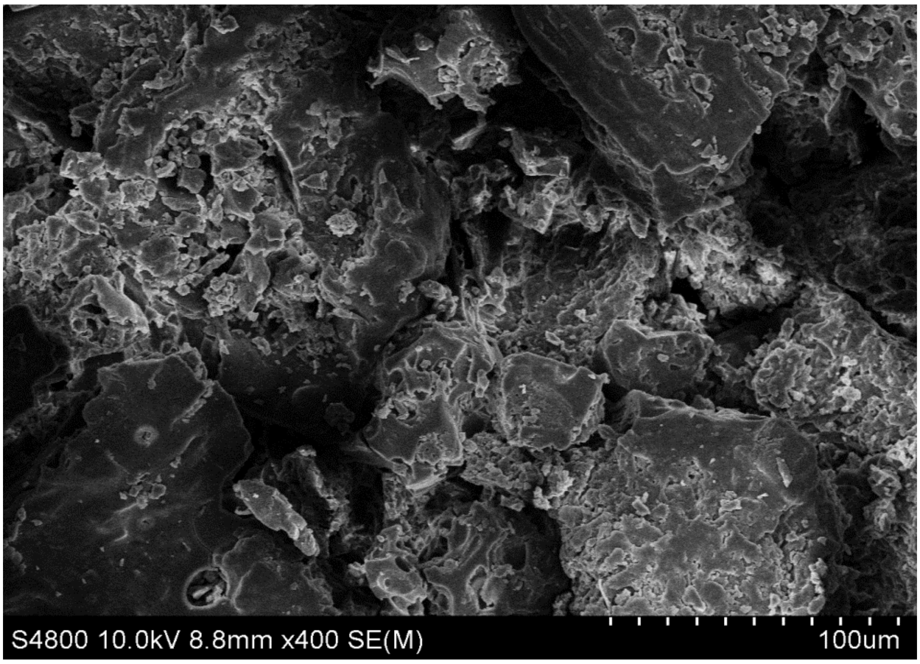


10 (a)

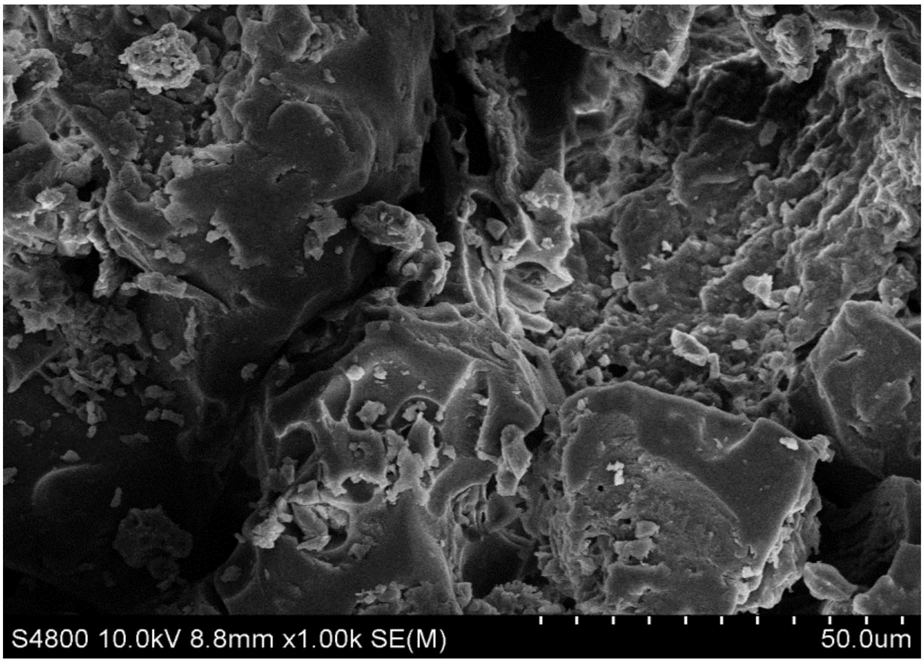


10 (b)

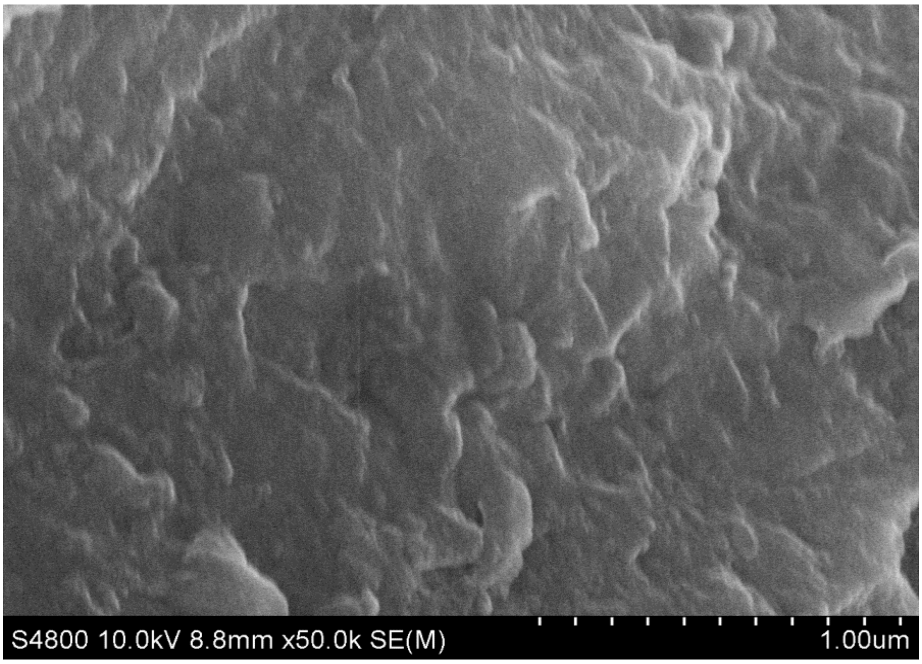
Figure 10 (a) and (b): SEM images of CATL-3



11 (a)



11 (b)



11 (c)

Figure 11 (a), (b) and (c): SEM images of Cd loaded CATL-3

4.2 FTIR analysis

Figure 12 shows the FTIR spectra of the biomaterial prior and after chemical modification to introduce amine groups on the surface of biomaterial. The spectra are complex due to various functional groups present on the surface of biomaterial. In FTIR spectrum a unique energy absorption band was shown by each specific chemical bond and it has been used as a useful tool to identify the functional group present on the surface of biomaterial (Sankararamakrishnan, 2006, Shriner, *et al.*, 1998, Silverstein, *et al.*, 1981).

In the spectrum of RTL, peaks are observed at 3382, 2924, 1646 and 1071 cm^{-1}. The strong band at 3382 cm^{-1} is due to OH stretching, 2924 cm^{-1} is due to aliphatic CH stretching in CH_3, CH_2 and CH group, 1646 cm^{-1} is due to C=O or C=C stretching and 1071cm^{-1} is due to C – O stretching.

The spectrum exhibits some significant changes in all of three modified biomaterials. The broad and strong band ranging from 3130 – 3666 cm^{-1} in CATL-1, 3118 – 3650 cm^{-1} in CATL-2 and 3045 – 3647 cm^{-1} in CATL-3 may be due to overlapping of OH and NH stretching. Peaks around 1650 cm^{-1} in CATL-1, 1640 cm^{-1} in CATL-2 and 1648 cm^{-1} in CATL-3 are in N – H bending range. Peaks at 1065 cm^{-1} in CATL-1, 1039 cm^{-1} in CATL-2 and 1032 cm^{-1} in CATL-3 are assigned to C – N stretching vibration. The spectra of aminated biomaterials have shown the presence of amino groups on their surface indicating the changes after modification.

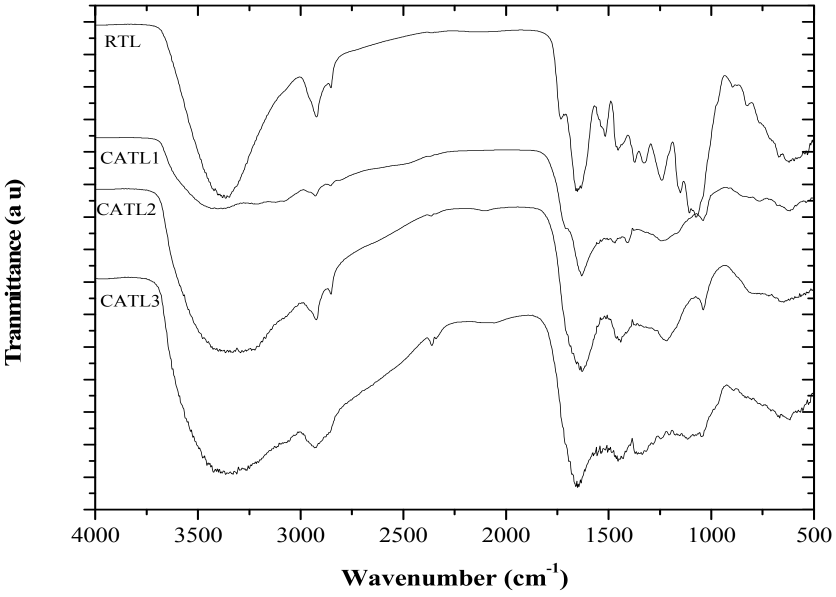


Figure 12: D- FTIR spectra of RTL, CATL-1, CATL-2 and CATL-3

Figure 13 and 14 shows the FTIR spectra of CATL-2 and CATL-3, before and after

adsorption of Cd (II), respectively. There is a significant decrease of transmittance in the peaks ranging from 3100 – 3600 cm^{-1} after cadmium adsorption, which indicates that N – H and O – H groups are involved in adsorption of Cd(II). There is also decrease in transmittance of peaks around 1640 and 1245 cm^{-1}. These peaks are closely related to the N – H bending and C – N stretching range, respectively. It confirmed that the cadmium adsorption is found to affect the bonds with N – atoms, which indicates the N – atoms of amine groups are mainly involved in cadmium adsorption (Thirumavalavan, *et al.*, 2010). In spectrum of CATL-2, the peak due to overlapping of N – H and O – H groups ranging from 3200 – 3640 cm^{-1}shifts towards lower range. Similarly the peak around 1640 cm^{-1} is also shifted to lower range, which also supported the involvement of amino groups for adsorption of cadmium

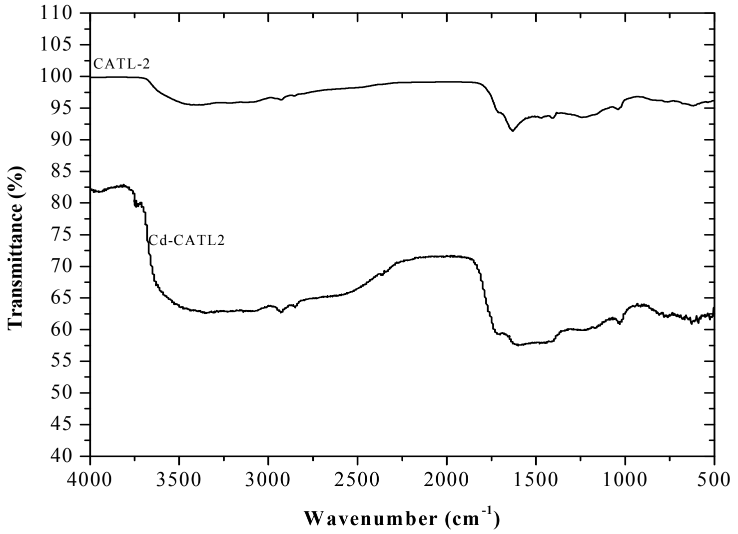


Figure 13: FTIR spectra of CATL-2 and Cd loaded CATL-2

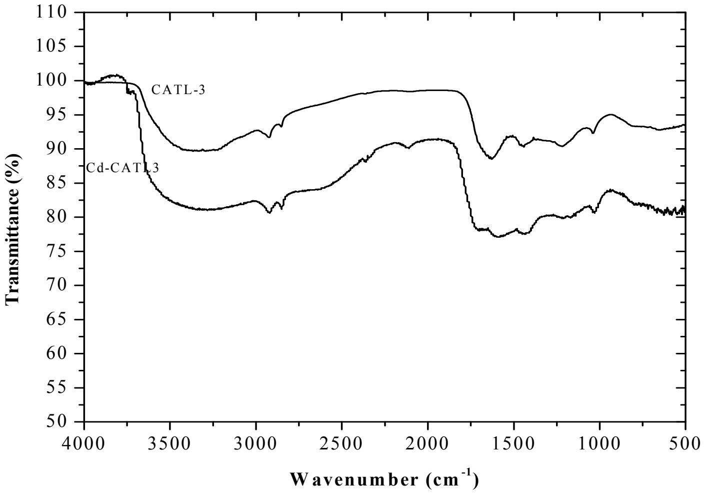


Figure 14: FTIR spectra of CATL-3 and Cd loaded CATL-3

4.3. Elemental analysis

The amount of carbon, nitrogen and sulphur in raw and aminated tea leaves are depicted in Table 1. The amount of nitrogen as well as sulphur are increased after amination as shown in the table which indicates the introduction of amino groups on the surface of biosorbent.

Table 1: % of carbon, nitrogen and sulphur in tealeaves before and after amination

Adsorbent	Carbon	Nitrogen	Sulphur
RTL	47.17	1.03	0.29
CATL-1	51.59	9.52	5.18
CATL-2	49.90	5.5	3.28
CATL-3	53.36	8.26	2.28

The major constituents present in the biosorbent are given in Table 2. As shown in the table lignin is the major constituent of the biosorbent.

Table 2: % of the major constituents of tealeaves before and after amination

Adsorbents	Lignin	Cellulose	Hemicellulose
RTL	28.70	22.33	11.37
CATL-1	77.74	3.97	4.93
CATL-2	50.62	4.42	3.39
CATL-3	62.75	5.24	3.71

The biosorbent was chemically analyzed to quantify the amount of acidic and basic functional sites on its surface, before and after amination. Boehm titration is used as a typical method to quantify acidic and basic functional sites on the surface of biosorbent. The method involves neutralization of surface acidic sites with a base, sodium hydroxide and surface basic sites with an acid, hydrochloric acid. The total acidic sites can be calculated from the amount of NaOH consumed by the adsorbent in neutralization reaction between the adsorbent and NaOH. Similarly, the basic sites can be calculated from the amount of HCl consumed by adsorbent in neutralization reaction between the adsorbent and HCl. The acidic functional sites on the surface of adsorbent before amination, were found to be 1.8 meq/g, which was slightly decreased to 1.2 meq/g and 0.9 meq/g after amination in CATL-2 and CATL-3, respectively. The basic functional sites were found to be 0.9 meq/g before amination, which was increased to 3.6 meq/g and 4.0 meq/g after amination.

4.4 XRD analysis

The amorphous nature of biosorbent is highly suitable for metal adsorption (Kurita, 1979). The XRD spectrum of waste tea leaves is shown in Figure 15. In XRD profile strongest reflection appears at 2Θ = 21°. This broad peak indicates the lesser crystallinity of biosorbent.

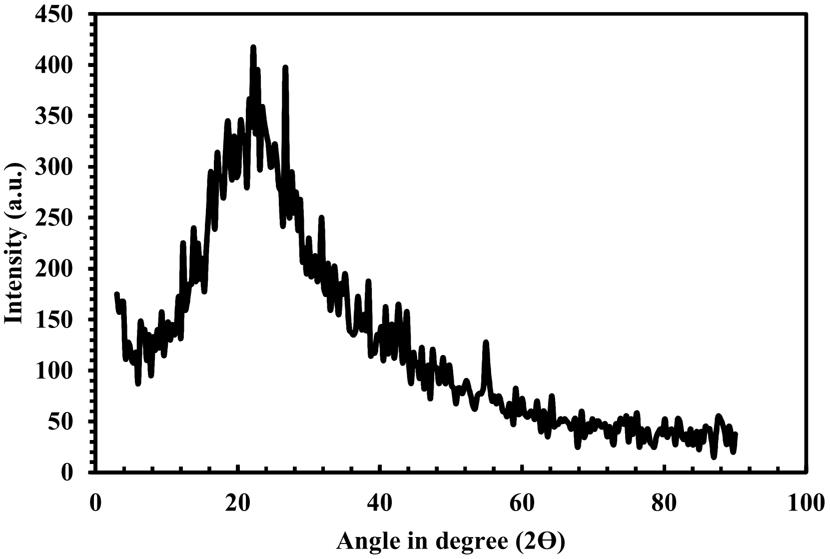


Figure 15: XRD spectrum of aminated tealeaves

4.5 Thermogravimetric analysis

The thermal stability and degradation behavior of waste tea leaves was evaluated by TGA under nitrogen atmosphere. The TGA and DTA curve is shown in Figure 16, in which the adsorbent degrades in two stages. The first stage begins at about 100°C with weight loss of 5-10%, which is due to loss of residual or physically adsorbed water molecules. The second stage degradation occurs with rapid weight loss at 230-560°C reaching a maximum value at 485°C.

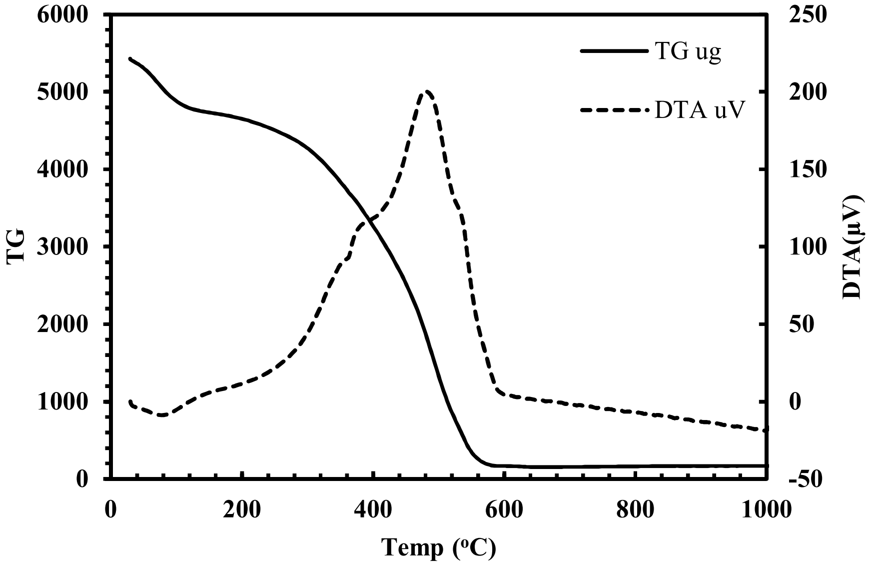


Figure 16: Thermal analysis of aminated tea leaves

4.6 Effect of pH

The variation in pH could change the characteristics and availability of metal ions in solution as well as the chemical status of the functional groups responsible for the biosorption. To study the effect of pH in the adsortption of metal ions, the experiments were carried out within the range of pH that was not influenced by the metal precipitation as their hydroxides. Figure 17 (a), (b), (c) and (d) illustrated the effect of pH in the adsorption of the metal ions onto the biosorbent in which the removal efficiency increased steadily with increasing pH of the solution (Homagai, *et al.*, 2011). At low pH range the removal efficiency was low. It is due to high concentration of protons with high mobility, in the solution which compete with metal ions in forming a bond with the active sites, the functional group on the surface of the biosorbent. The active sites after bonding with protons became saturated and they were inaccessible to other metal cations.

The increase in pH lowers the quantity of protons. Due to lower concentration of protons at high pH there was less competition between proton and metal cations. It increases the removal efficiency i.e. sorption capacity. At higher i.e. alkaline pH, however, other effects may arise that also alter the process, such as the predominant presence of hydrated species of heavy metals, changes in surface charge or the precipitation of the appropriate salt.

In the study of effect of pH in the adsorption of metal ions the optimum pH values were found to be 4, 5, 6 and 6 for Pb (II), Cu (II), Cd (II) and Zn (II), respectively. The percentage adsorption at optimum pH values were shown in Table 3. It was found that the CATL-3 has got the highest adsorption percentage at optimum pH of respective metal ions.

Table 3: **A% of metal ions on biomaterials at their optimum pH values**

Metal ions	Adsorbent	Optimum pH	% Adsoption
Pb(II)	CATL-1	4	90.69
	CATL-2		87.71
	CATL-3		90.69
Cu(II)	CATL-1	5	50.22
	CATL-2		91.90
	CATL-3		98.78
Cd(II)	CATL-1	6	41.13
	CATL-2		82.79
	CATL-3		97.40
Zn(II)	CATL-1	6	15.23
	CATL-2		42.57
	CATL-3		71.23

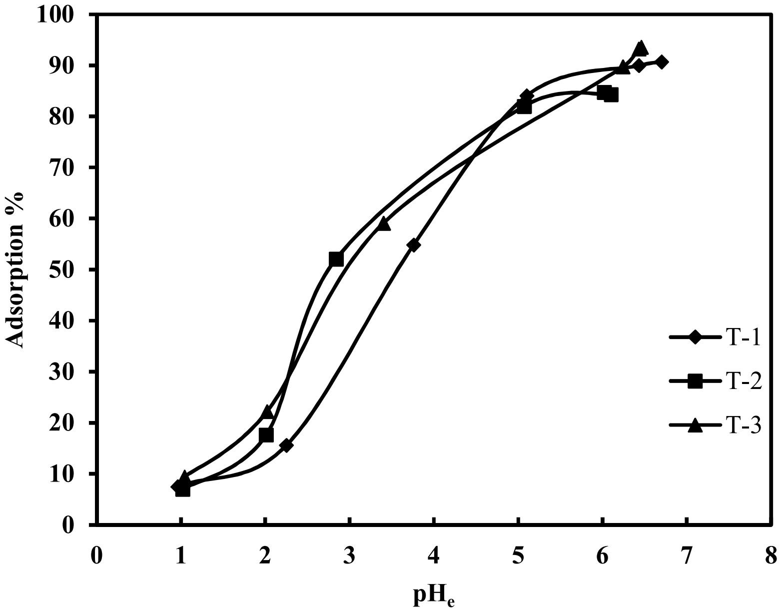


Figure 17 (a): Effect of pH on adsorption of Pb(II) onto CATL-1, CATL-2 and CATL-3

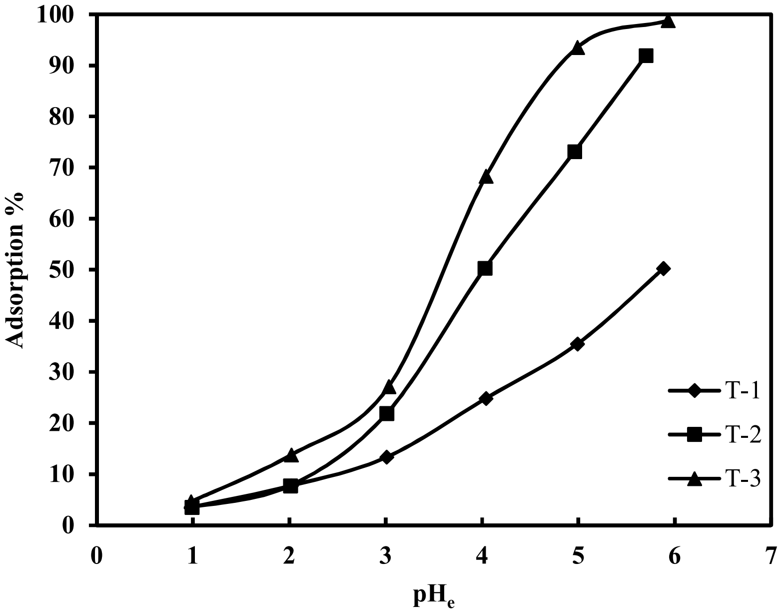


Figure 17 (b): Effect of pH onadsorption of Cu(II) onto CATL-1, CATL-2 and CATL-3

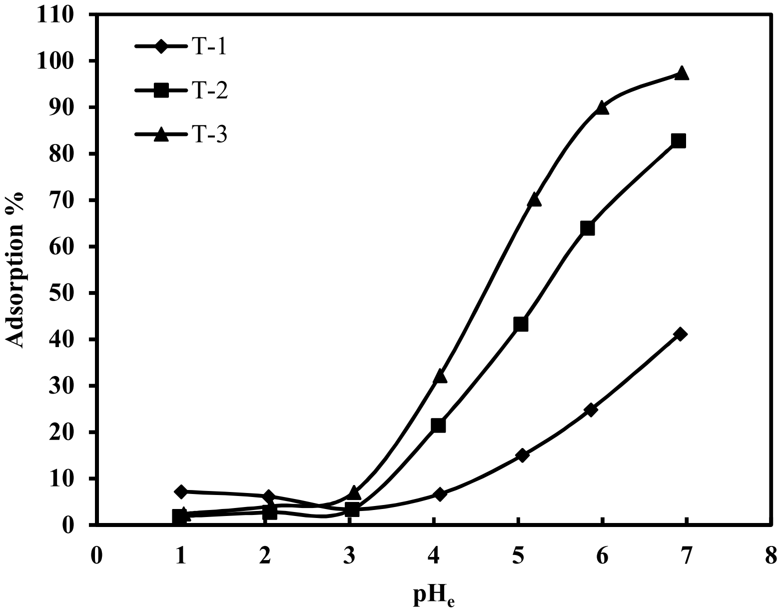


Figure 17 (c): Effect of pH on adsorption of Cd(II) onto CATL-1, CATL-2 and CATL-3

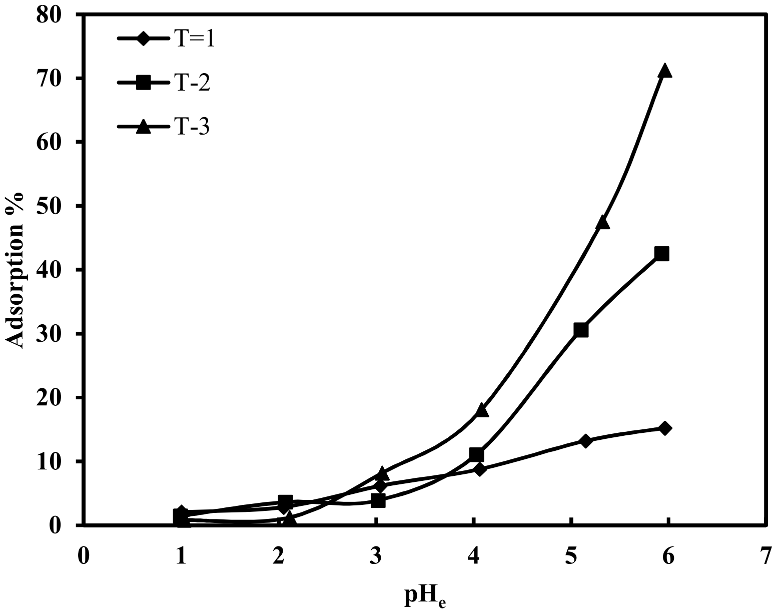


Figure 17 (d): Effect of pH on adsorption of Zn(II) onto CATL-1, CATL-2 and CATL-3

4.7 Zeta potential

The zeta potential i.e. pH_{pzc} of biomaterial is an important character that determines the nature of the surface of biosorbent. It is the pH at which surface of biomaterial has net electrical neutrality. The zeta potential of RTL in the solution of different pH values are shown in Figure 18. In the figure, it is indicated that zeta potentials of raw biosorbent are positive at pH < 5.9 and negative at pH > 5.9. It indicates that the surface of biosorbent becomes positive below pH 5.9, while it becomes negative above pH 5.9. After chemical modification, the pHpzc value shifts towards higher pH ranges. The pHpzc values for CATL – 1, CATL – 2 and CATL - 3 are above pH 9 as shown in Figure 18. The increase in pHpzc values after amination is due to protonation of amino groups introduced onto the surface of biomaterial. Hence increase in pHpzc values further confirms the successful amination onto the surface of biomaterial.

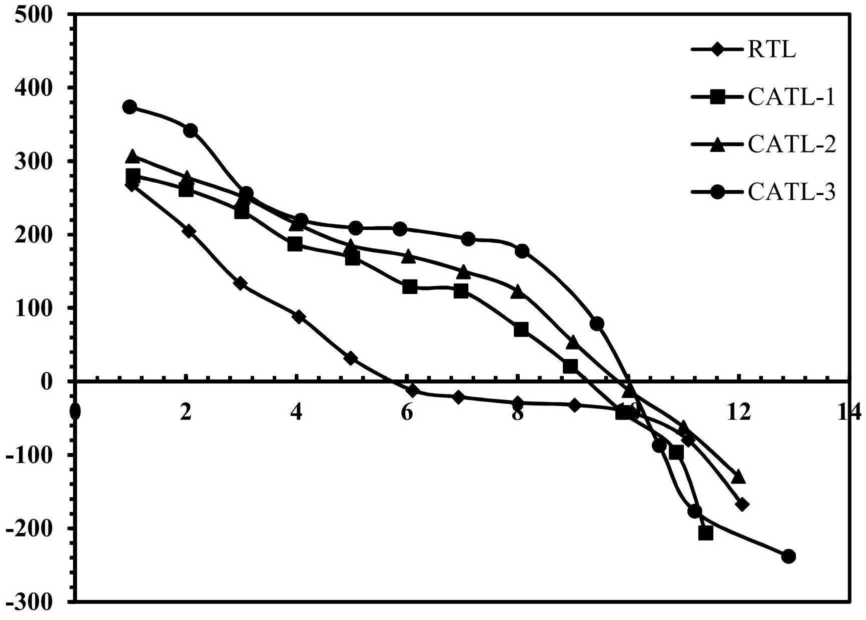


Figure 18: Zeta potentials of RTL, CATL-1, CATL-2 and CATL-3

4.8 Adsorption isotherm

Several mathematical relationships have been developed to describe the equilibrium distribution of solute between the solid and liquid phases which help in interpretation of adsorption data. When adsorption experiments are conducted at constant temperature (room temperature), these relationships can be applied and they are referred as adsorption isotherms. The isotherms are measured to determine the capacity of biosorbent to adsorb metal ions. The biosorbents are shaken with fixed volume of metal solution of varying concentration until equilibrium has been achieved. The relationship between the amount of metal ions adsorbed and the remaining metal ions in solution is described by an isotherm equation (Moussavi, 2010). Among the several models, three different types Langmuir isotherm, Fruendlich isotherm and BET (Brunaur – Emmett – Teller) isotherm are in common use (Wang & Qin, 2004) .

4.8.1 Langmuir isotherm

It is based on the assumption that points of valence exist on the surface of the adsorbent and that each of these sites are capable of adsorbing one molecule i.e. the adsorbed layer will be single molecule thick (monolayer). Furthermore, it is assumed that all the adsorption sites have equal affinity for the molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of the molecules at an adjacent site.

The Langmuir equation which has been extensively used for dilute solution can be expressed as in equation 5.

$$q_e = \frac{q_{max} \, b \, C_e}{1 + b \, C_e} \qquad (5)$$

where q_e is amount of metal ions adsorbed at equilibrium (mg/g), q_m is maximum sorption capacity (mg/g), C_e the concentration of solute at equilibrium (mg/L) and b is the equilibrium constant related to energy of sorption which quantitatively reflects the affinity between the sorbent and sorbate.

Taking the reciprocal of both sides gives equation 6

$$\frac{1}{q_e} = \frac{1 + bC_e}{q_m bC_e} \tag{6}$$

which on rearrangement gives equation 7

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \tag{7}$$

It is the linearised form of the Langmuir equation. If adsorption follows the Langmuir isotherm then plot of C_e/q_e versus C_e should be a straight line. The constants q_m and b can be determined from the slope and intercept of the plot.

4.8.2 Freundlich isotherm

One of the most widely used mathematical descriptions for adsorption process was developed by Freundlich (1926). This expression was based on the assumption that the adsorbent had a heterogeneous surface composed of different classes of adsorption sites, with adsorption on each class of site following the Langmuir isotherm. The Freundlich isotherm is expressed as

$$q_e = k\, C_e^{1/n} \tag{8}$$

where k and n are Freundlich constants denoting the relative adsorption capacity and the intensity of adsorption, respectively. C_e is equilibrium concentration in mg/L, q_e is amount of adsorbate adsorbed per unit weight of adsorbent in mg/g. The constant k is related to temperature and n is a characteristic constant for adsorption system under study. The Freundlich equation generates an exponential shaped theoretical equilibrium curve. The equation can be put in a useful form by taking the log of both sides.

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \tag{9}$$

It is the linearized form of Freundlich isotherm. A plot of log q_e versus log C_e should yield a straight line for adsorption data which follow the Freundlich isotherm model. The values k and n can be determined by the intercept and slop of the plot.

4.8.3 BET isotherm

Brunauer, Emmett and Teller in 1938 derived an adsorption isotherm and is based on the assumption that molecules could be adsorbed more than one layer thick on the surface of the adsorbent. Like the Langmuir equation this isotherm assumes that the adsorbent surface is composed of uniform localized sites and adsorption at one site does not affect adsorption at neighboring sites. It also assumes that the energy of adsorption holds the first monolayer but the condensation energy of the adsorbate is responsible for adsorption of successive layer. The equation is known as BET equation and given in equation 10.

$$q_e = \frac{A\,C_{xm}}{(C_s - C)[1 + (A-1)\frac{C}{C_s}]} \qquad (10)$$

where q_e amount of solute adsorbed (mg/g), X_m is amount of solute adsorbed in forming a complete monolayer (mg/g), C_s is saturation concentration of solute (mg/L), C is the concentration of solute at equilibrium and A is a constant to describe the energy of interaction between the solute and adsorbent surface.

The metal removal capacities by three aminated tealeaves with respect to different initial concentration of metal ions varying from 25 – 800 mg/L are shown in Figure 19-22. It indicates that the removal of metal ions decrease with increasing initial concentration of metal ions in solution which is due to the fixed number of adsorption sites on the surface of adsorbent. The removal of metal ions is also found to be dependent on the initial metal ions concentration in solution.

As the adsorption isotherms are important to describe the interaction of adsorbates with adsorbents, the isotherms are very useful for designing purposes and for practical adsorption operation the correlation coefficient of equilibrium data using an isotherm equation is essential.

In this study Langmuir isotherm, Freundlich isotherm and BET – isotherm models were adopted to analyze the experimental data. The data were found to be better fitted with the Langmuir model as shown in Figure 19-22. The Langmuir isotherm constants and their correlation coefficients (R^2) are given Table 4.

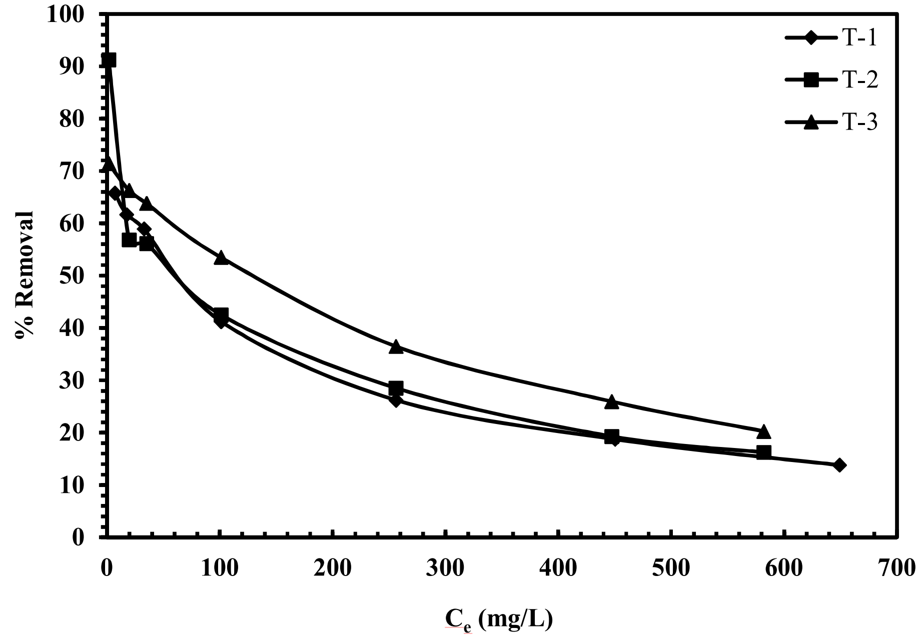


Figure 19 (a): % removal of Pb(II) by CATL-1, CATL-2 and CATL-3

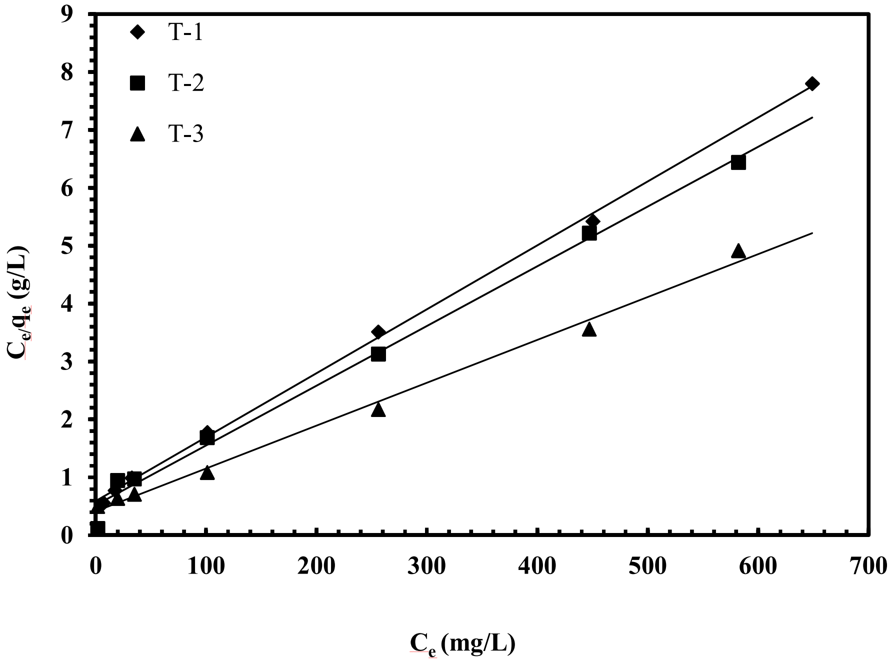


Figure 19 (b): Langmuir isotherm for adsorption of Pb(II) onto CATL-1, CATL-2 and CATL-3

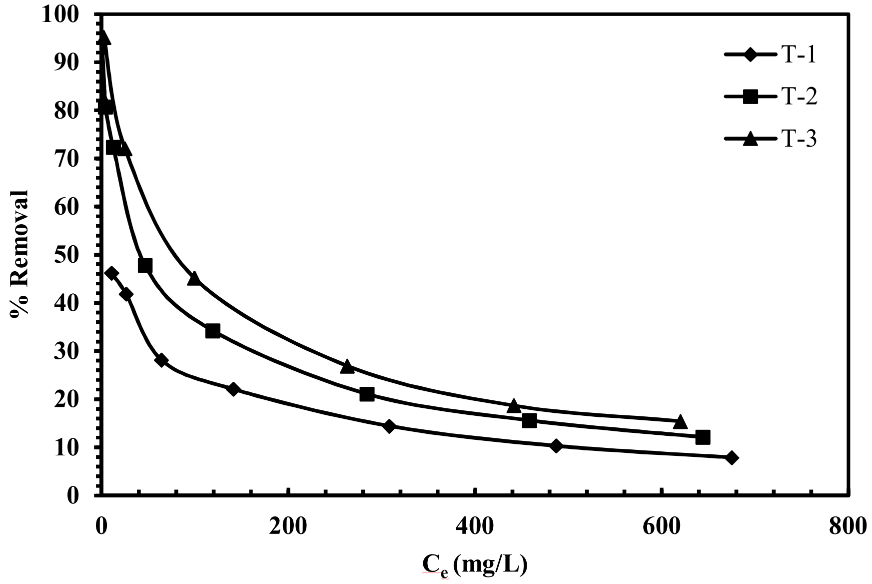


Figure 20 (a): % removal of Cu(II) by CATL-1, CATL-2 and CATL-3

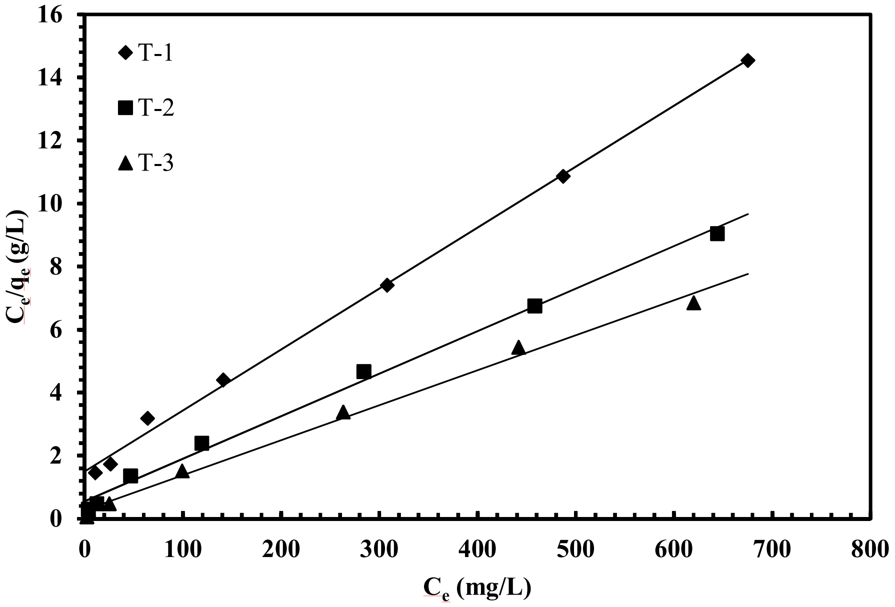


Figure 20 (b): Langmuir isotherm for adsorption of Cu(II) onto CATL-1, CATL-2 and CATL-3

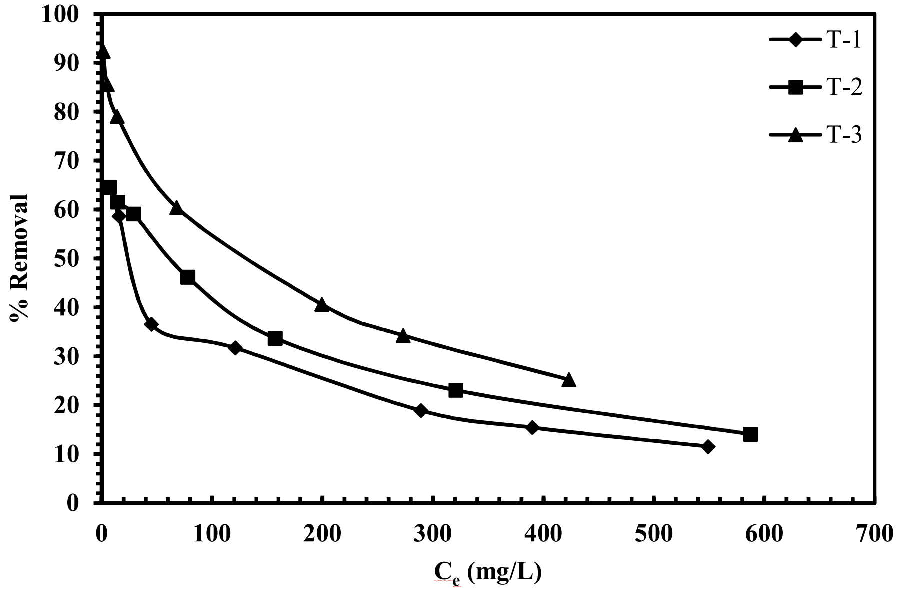


Figure 21 (a): % removal of Cd (II) by CATL-1, CATL-2 and CATL-3

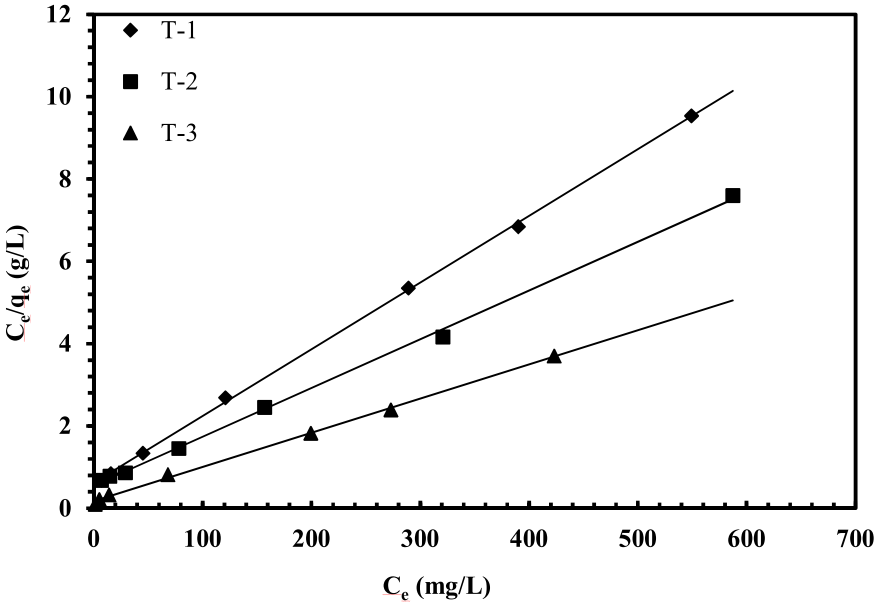


Figure 21 (b): Langmuir isotherm for adsorption of Cd(II) onto CATL-1, CATL-2 and CATL-3

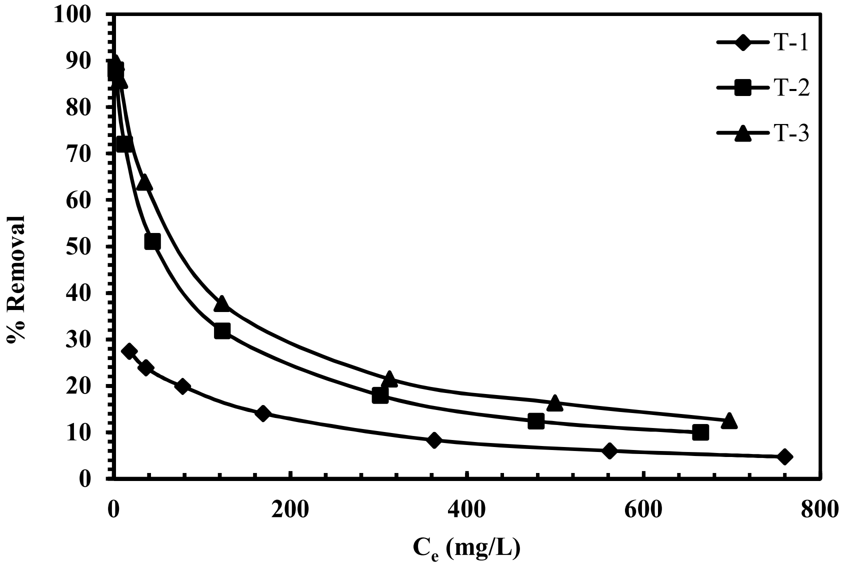


Figure 22 (a): % removal of Zn(II) by CATL-1, CATL-2 and CATL-3

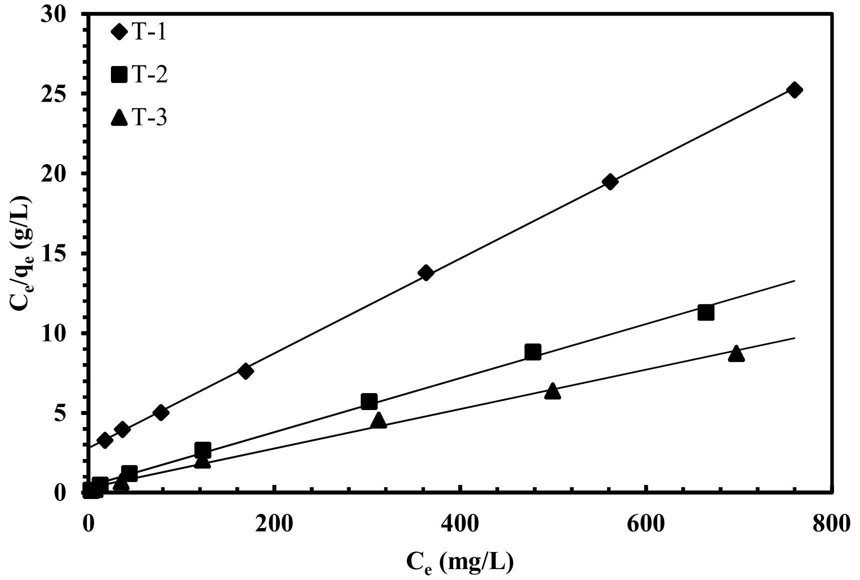


Figure 22 (b): Langmuir isotherm for adsorption of Zn(II) onto CATL-1, CATL-2 and CATL-3

Table 4: Langmuir adsorption isotherm model parameters and experimental q_{max} values of metal ions onto CATL-1, CATL-2 and CATL-3

Metal ions	Biosorbent	q_{max} (mg/g) (Experimental)	q_{max} (mg/g) (Langmuir)	b (L/mg)	R^2
Pb (II)	CATL – 1	83.20	90.90	0.02	0.99
	CATL – 2	90.40	97.08	0.02	0.99
	CATL – 3	120.80	135.13	0.02	0.99
Cu (II)	CATL – 1	46.40	51.81	0.01	0.99
	CATL – 2	71.20	74.07	0.02	0.99
	CATL – 3	90.40	90.09	0.04	0.99
Cd (II)	CATL – 1	57.50	61.72	0.03	0.99
	CATL – 2	7.30	84.74	0.02	0.99
	CATL – 3	114.30	120.48	0.05	0.99
Zn (II)	CATL – 1	30.08	33.67	0.01	0.99
	CATL – 2	56.00	58.13	0.02	0.99
	CATL – 3	79.76	81.30	0.04	0.99

The q_{max} values were calculated by fitting the Langmuir isotherm model to the experimental data. These values are considered very important as they give indication of the extent of binding sites which are available for metal ions. The maximum uptake values obtained are presented in Table 4.

According to Pearson's HSAB theory, the amine groups are soft bases and they have higher tendency to form stable complexes with heavy metals, which are considered as soft acids. The higher b values indicate the higher affinity of the biosorbent towards the metal ions. As given in the table, the affinity of biosorbents for Pb (II) is almost same, for Cu (II) and Zn (II) the affinity order is CATL – 3> CATL – 2> CATL – 1 and for Cd (II) ions the order is CATL – 3> CATL – 1> CATL – 2.

As shown in the table, lead showed higher adsorption onto all aminated biosorbents in comparison to other metals. The electronegativity for lead, copper, cadmium and zinc are 2.33, 1.90, 1.69 and 1.65 in Pauling scale, respectively. On the other hand, the hydrated radii (°A) for these metals are 4.01, 4.19, 4.26 and 4.30, respectively. The higher electronegativity and smaller hydrated radius of lead favors it's binding onto the aminated biosorbents.

A dimensionless constant called equilibrium parameter R_L, is the essential characteristics of Langmuir isotherm. It can be expressed as

$$R_L = \frac{1}{1 + bC_o} \qquad (11)$$

where b is the Langmuir constant and C_o is the initial metal ions concentration. The R_L values between 0 and 1 indicate more favorable adsorption. The R_L values evaluated for all metals (data not given) had shown that the values were found to be between 0 and 1. It further supports the Langmuir model for adsorption.

4.9 Effect of adsorption time: Kinetic modeling

According to McKay adsorption process involves four steps, of which one or more may control the rate at which the solute is adsorbed and the amount of solute that is adsorbed onto the adsorbent (Ho & McKay, 1999). These steps are

i. solute transfer from the solution to the boundary film bordering the adsorbent surface

ii. solute transfer from boundary film to the surface of the adsorbent

iii. solute transport from the adsorbent surface to the intraparticular active sites

iv. interaction of the solute molecules with the available sites on the internal surface

To investigate the potential rate controlling steps such as mass transport, chemical reaction process and mechanism of adsorption, three different types of kinetic models have been used to test the experimental data. These kinetic models under investigation are pseudo – first order model, pseudo – second order model and intraparticular diffusion model (Othman, 2011, Qiu, 2009, Rao & Khan, 2009).

4.9.1 Pseudo – first order model

The pseudo – first order rate expression of Lagergren is based on the solid capacity and is expressed as in equation 12

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{12}$$

where q_e and q_t (mg/g) are amount of metal ions adsorbed onto the surface of adsorbent at equilibrium and at time t, respectively. K_l is the rate constant (min^{-1}) of pseudo – first order adsorption model. After integration between boundary conditions (t = 0 – t and q_t = 0 – q_e) the above equation becomes

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{13}$$

4.9.2 Pseudo – second order model

The pseudo – second order model is based on the sorption capacity of the solid phase. It is expressed as in equation 14.

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{14}$$

where q_e and q_t (mg/g) are the adsorption capacity at equilibrium and at time t, respectively. K2 (g/mg-min) is the rate constant pseudo – second order adsorption. For the boundary conditions t = 0 – t and q_t = 0 – q_e, the equation 14 becomes

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \tag{15}$$

It is the integrated rate law for a pseudo – second order reaction. If pseudo – second order kinetic model is applicable to the experimental data, the plot of t/q_t versus 't' should give a linear relationship from which q_e and k_2 can be calculated from the slop and intercept of the plot. The pseudo – second order rate equation is based on the sorption capacity on the solid phase. It predicts the behavior over the whole range of studies and if the adsorption follows the pseudo – second order equation it is in agreement with chemisorptions mechanism being the rate controlling step.

4.9.3 Intraparticular diffusion model

The intraparticular diffusion model given by Weber and Morris is expressed as in equation 16.

$$q_t = \frac{k_w}{m} t^{1/2} \qquad (16)$$

where m is mass of adsorbent (g), q_t (mg/g) the amount of metal ions adsorbed at time t and k_w is initial rate of the intraparticular diffusion (mg/L-S).

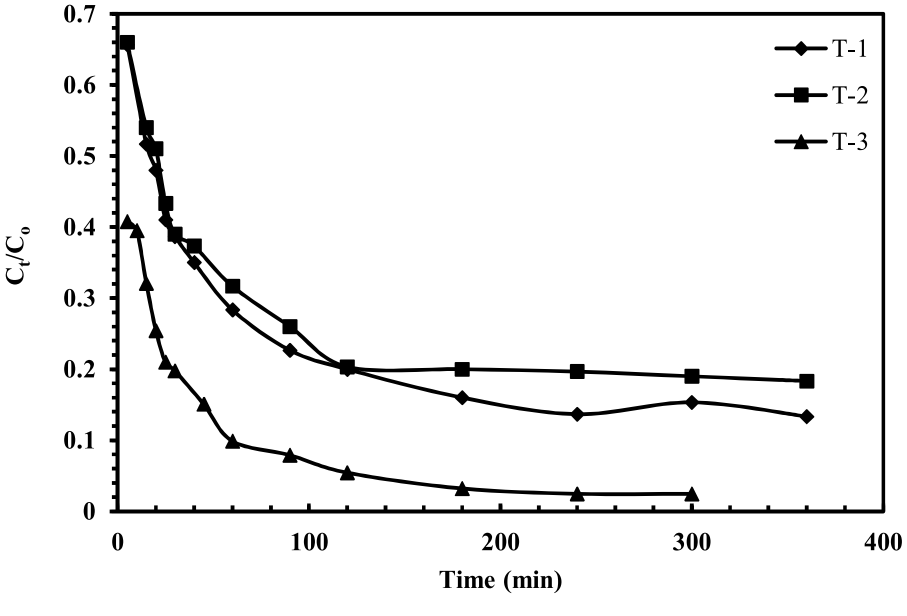


Figure 23 (a): Lead concentration- decay curves for CATL-1, CATL-2 and CATL-3

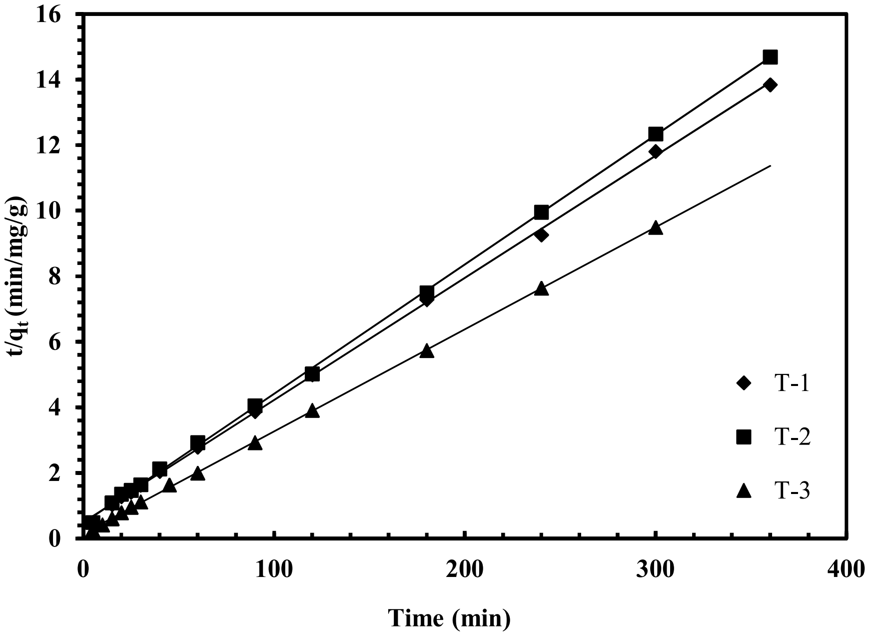


Figure 23 (b): Pseudo-second order adsorption kinetics of Pb(II) onto CATL-1, CATL-2 and CATL-3

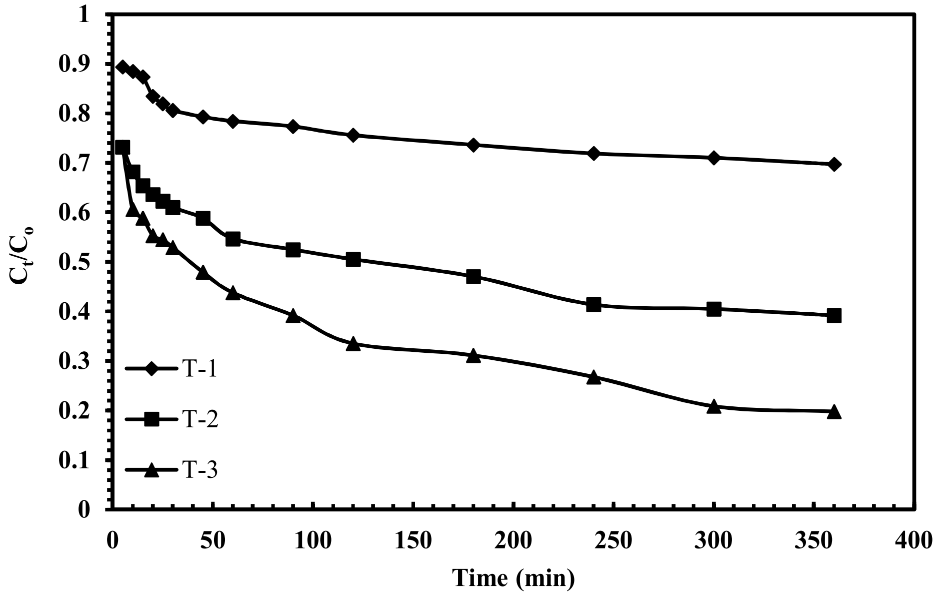


Figure 24 (a): Copper concentration- decay curves for CATL-1, CATL-2 and CATL-3

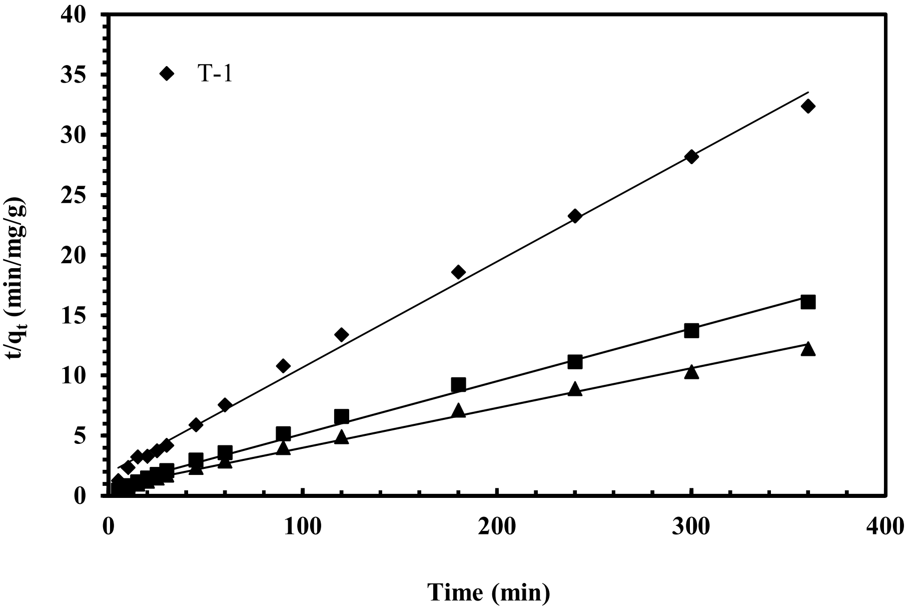


Figure 24 (b): Pseudo-second order adsorption kinetics of Cu(II) onto CATL-1, CATL-2 and CATL-3

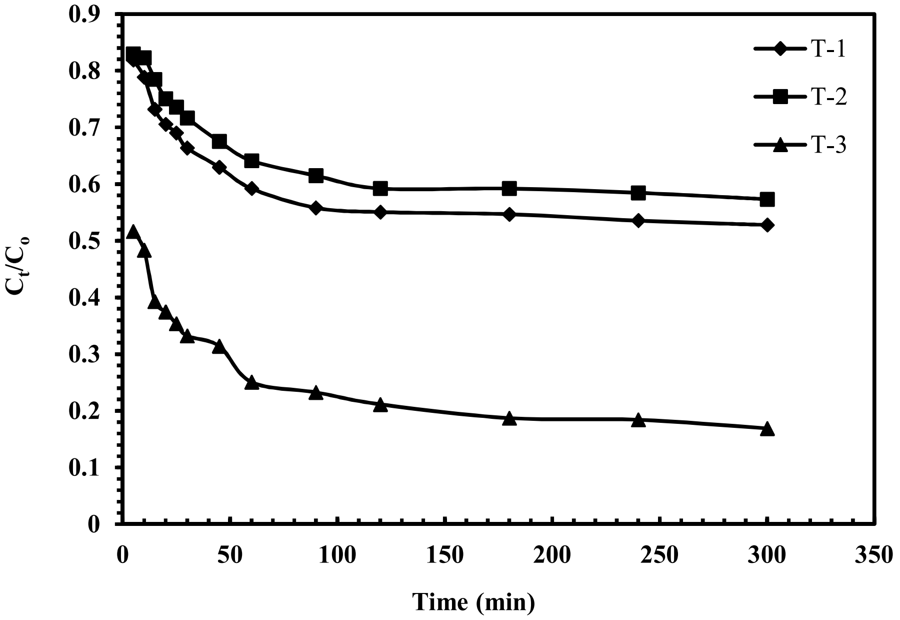


Figure 25 (a): Cadmium concentration- decay curves for CATL-1, CATL-2 and CATL-3

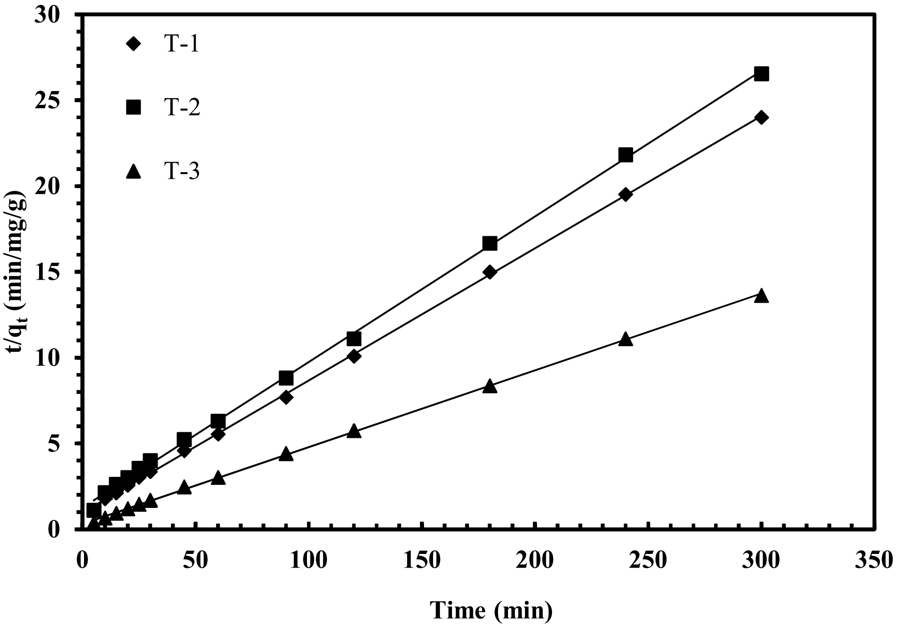


Figure 25 (b): Pseudo-second order adsorption kinetics of Cd(II) onto CATL-1, CATL-2 and CATL-3

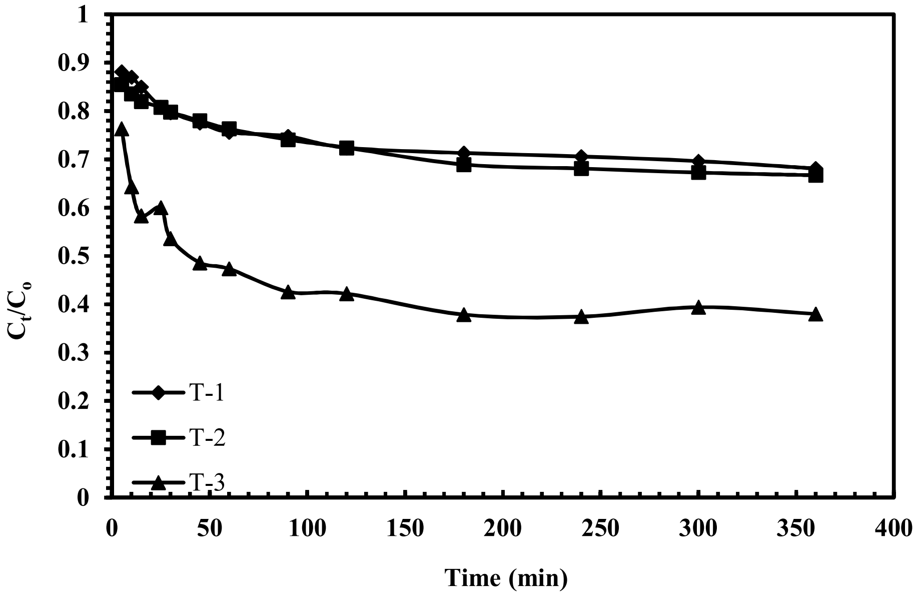


Figure 26 (a): Zinc concentration- decay curves for CATL-1, CATL-2 and CATL-3

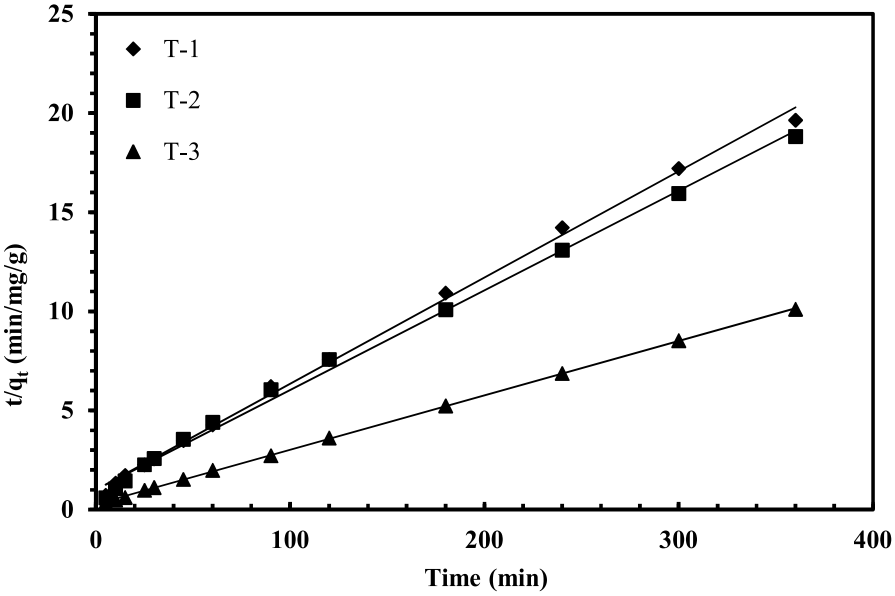


Figure 26 (b): Pseudo-second order adsorption kinetics of Zn(II) onto CATL-1, CATL-2 and CATL-3

The experimental data obtained from batch experiments for kinetics of adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) onto three aminated tealeaves were analyzed using three different types of kinetic models. They are pseudo – first order, pseudo – second order and intraparticular diffusion model. The data obtained were better fitted with pseudo – second order model with higher correlation coefficients. The model is based on the assumption that chemisorption, involving valency forces through sharing or exchange of electrons between the adsorbate and the adsorbent, is the rate limiting step. The R^2 values for pseudo – second order model calculated from linear plots and the parameters k_2 and q_t obtained from regression analysis are given in Table 5. For other models the correlation coefficient values were in lower range and especially the calculated q_e values were not in consistent with the experimental values, suggesting that the sorption was not pseudo – first order and intraparticular diffusion model.

The kinetic curves for the removal of metal ions from the solution were shown in Figure 23-26. The removal of metal ions was increased sharply at first stage and gradually slows down as the equilibrium was approached. Such behavior may be due to relatively less available adsorption sites on the surface of the biosorbent.

Table 5: Sorption kinetics of pseudo-second order for metal ions onto CATL-1, CATL-2 and CATL-3

Metal ions	Adsorbent	q_e(mg/g)	k_2 (g/mg/min)	R^2
Pb(II)	CATL – 1	26.80	2.82×10^{-3}	0.99
	CATL – 2	25.31	3.35×10^{-3}	0.99
	CATL – 3	32.05	6.47×10^{-3}	0.99
Cu(II)	CATL – 1	11.37	4.08×10^{-3}	0.99
	CATL – 2	22.88	2.43×10^{-3}	0.99
	CATL – 3	30.21	1.55×10^{-3}	0.99
Cd(II)	CATL – 1	12.98	6.15×10^{-3}	0.99
	CATL – 2	11. 77	5.76×10^{-3}	0.99
	CATL – 3	22.32	6.33×10^{-3}	0.99
Zn(II)	CATL – 1	18.65	2.90×10^{-3}	0.99
	CATL – 2	19.88	2.51×10^{-3}	0.99
	CATL – 3	36.36	2.77×10^{-3}	0.99

The experimental values for k_2 were given in Table 5. It is well known that higher the value of rate constant, faster is the rate of removal of metal ions from the solution. Hence the rate of removal of the metal ions by aminated tealeaves, found experimentally from k_2 values are in the following order: removal of Pb (II) by biosorbents is in the order – CATL-3 > CATL-2 > CATL-1, the order for removal of Cu (II) is – CATL-1 > CATL-2 > CATL-3, the order of removal of Cd(II) is – CATL-3 > CATL-1 > CATL-2 and the order for Zn (II) removal is CATL-1 > CATL-3 > CATL-2. From these results, it is clear that CATL-3 removes Pb (II) and Cd (II) faster than other biomaterials, while CATL-1 removes Cu (II) and Zn (II) faster than others.

The optimum removal times for Pb (II) by aminated biosorbents are around 120 - 150 min, that for Cu (II) are 130- 150 min, for Cd (II) are 90- 120 min, and for Zn (II) the values are 100- 150 min, respectively.

4.10 Thermodynamic studies

The thermodynamic parameters that must be considered to characterize the adsorption process are the standard Gibb's free energy (ΔG), the enthalpy of adsorption (ΔH) and the entropy (ΔS) changes due to transfer of one mole of solute from solution to solid- liquid interface. The standard free energy change (ΔG) was calculated from the following relation

$$\Delta G = -RT \ln K_C \tag{17}$$

where T(K) is the absolute temperature, $R(JK^{-1}mol^{-1})$ is gas constant and K_C is equilibrium constant. It can be calculated from the equation (18)

$$K_C = \frac{C_{ae}}{C_e} \tag{18}$$

where C_{ae} and C_e are the equilibrium concentration of metal ions (mg/L) on the sorbent and in solution, respectively.

The enthalpy change (ΔH) and entropy change (ΔS) were obtained from equation (19)

$$\ln K_C = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{19}$$

The plot of ln K_C as a function of 1/T yields a straight line. ΔH and ΔS were calculated from the slope and intercept of the plot, respectively. The thermodynamic parameters calculated by using above given relationships are given in Table 6.

Table 6: Thermodynamic parameters for adsorption of Cu(II) onto CATL-2 and CATL-3

Adsorbents	ΔG(J mol^{-1})	R^2	ΔH(J mol^{-1})	ΔS(J mol^{-1} K^{-1})
CATL-2	- 440.02	0.99	30961.34	105.01
CATL-3	- 2437.19	0.99	56169.38	196.71

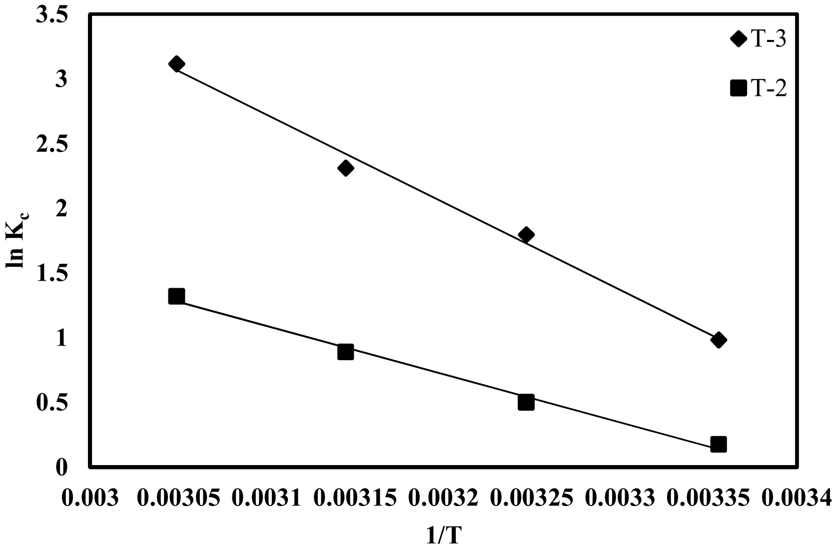


Figure 27: Thermodynamic parameters for adsorption of Cu(II) onto CATL-1, CATL-2 and CATL-3

4.11 Comparision of the adsorption capacities

The adsorption capacities of CATL-1, CATL-2 and CATL-3 were compared with other biosorbents given in literature. In the table 7, different biosorbents were given, which contain different types of functional groups on their surface. These functional groups have different metal binding capacity, due to which they have different capacities for metal adsorption. From the table, the biosorbents prepared from tea leaves have good metal binding capacity and they can be used as efficient biosorbents for removal of heavy metals.

Table 7: Comparison of adsorption capacities (mg/g) of different biosorbents for the removal of metal ions

Adsorbents	Pb(II)	Cu(II)	Cd(II)	Zn(II)	References
CATL-1	83.2	46.4	57.5	30.08	This study
CATL-2	90.4	71.2	73.00	56	This study
CATL-3	120.8	90.4	114.3	79.76	This study
Peanut husk	29.41				Li, *et al*. (2006a)
Redwood bark	68.18		27.6		Masri *et al*. (1974)
Alfalfa biomass	89.20				Tiemann, (2002)
Rastunsuo peat	20.03		5.05		TummavuoriAho, (1980 b)
Black gram husk	49.97		39.90	33.80	Saeed, (2005)
Nipah palmshoot		66.71			Wankasi, (2006)
Azolla filiculoides		62.00		48.00	Gangi, (2005)
Lemon peel				27.86	Marsal, (1996)
Spent tealeaves		90.00			Bajpai, (2010)
Orange peel		50.25			Ningchuan, (2008)

4.12 Desorption study

The biosorption process is cost effective, has high efficiency, requires minimum chemical modification and minimizes the toxic sludge production. One of its main advantages is regeneration of biosorbent with possibility of high metal recovery. The regeneration of biosorbent is crucially important to minimize the process cost. During the regeneration of the biosorbent the metal ions extracted from the liquid phase can be recovered, which is another great advantage of the process. The possibility of regeneration of the biosorbent and the recovery of metal ions can be explored by using desorption studies. The desorption study of lead adsorbed onto waste tealeaves was carried out by using batch experimental method. Nitric acid, hydrochloric acid and sodium hydroxide were used as desorbing agents. Among them good result was obtained with nitric acid as eluent.

Fig 28 (a) shows the adsorption capacity (mg/g) of the biosorbent for Pb (II) in six successive cycles. In the first cycle adsorption capacity of the biosorbent was found to be 41.8 mg/g, which was decreased to 35.1 mg/g in second cycle. In other successive cycles the adsorption capacity remains relatively constant indicating that solutes adsorbed onto micro-pores are relatively difficult for complete recovery.

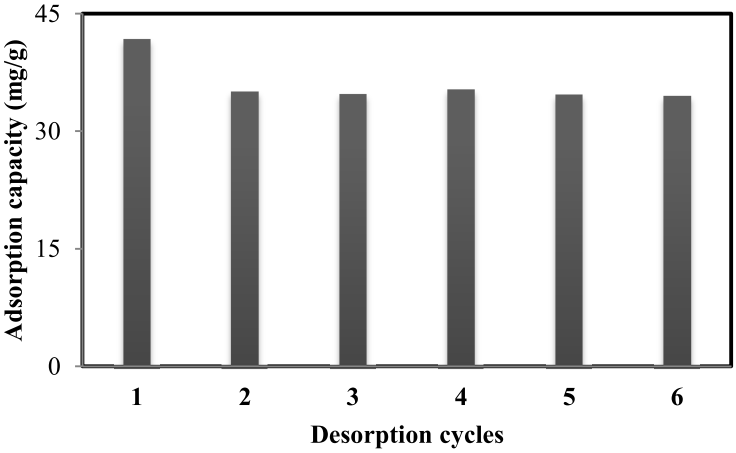


Figure 28(a): Reuse of the regenerated biosorbent for adsorption of lead

Figure 2 (b) shows the percentages desorption of the metal ions in six successive cycles. In all the cycles, above 90% metal ions were desorbed from the biosorbent. It indicates the chemical stability of the biosorbent and the biosorbent can be successfully regenerated by using 0.1 M solution of nitric acid.

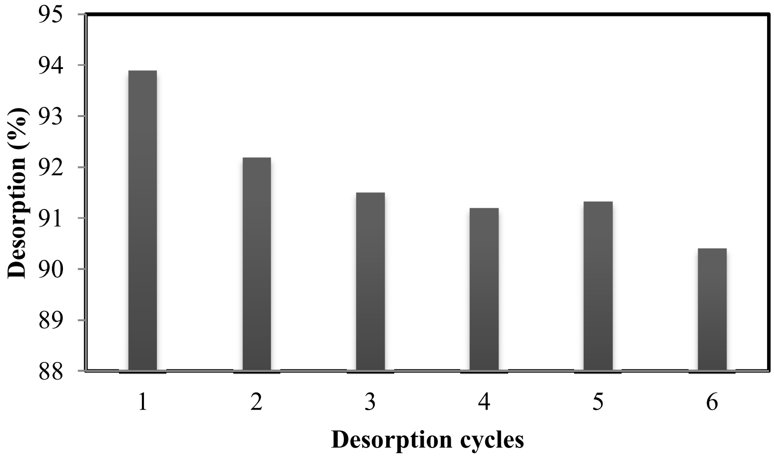
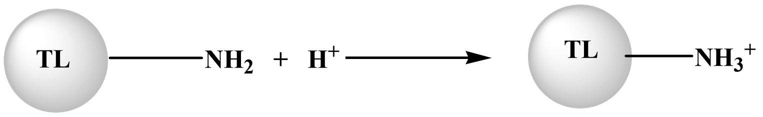


Figure 28(b): **Desorption percentage of lead from the reused biosorbent**

The adsorption desorption character was studied for lead ions onto the biosorbent. Acids and alkalies were used as desorbing agent. Among them Nitric acid showed more effective result.In all the adsorption desoption cycles above 90% of metal ions were desorbed. The adsorption capacity of biosorbent was found almost same for second to sixth cycles. Hence the metal loaded biosorbent was successfully regenerated by desorbtion with 0.1 M nitric acid.

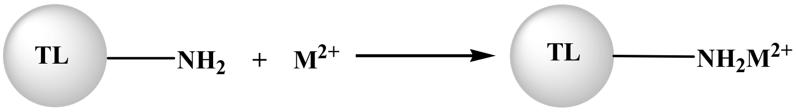
4.13 Plausible Mechanism

The mechanism involved during biosorption process may be one or combination of ion-exchange, complexation, electrostatic interaction and microprecipitation. One of the mechanism involved in the sorption of positively charged metal ions is the ion-exchange process between protons and the metal ions taken up from solution. The N-atom of amino group has greater tendency to donate lone pair of electrones for sharing with electropositive species like protons. This protonation reaction can be represented as in scheme 4 (a)



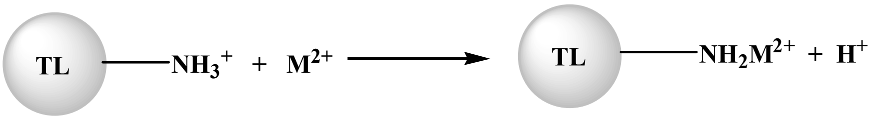
Scheme 4 (a)

When metal solution is added to the biosorbent then metal ions are also started to bind with amino group due to sharing of lone pair of electrones from N-atom, which is shown in scheme 4 (b)



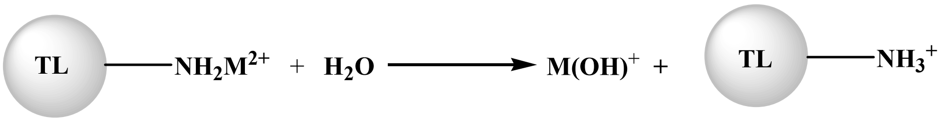
Scheme 4 (b)

The binding of a metal ion to N-atom is stronger than the binding of a proton to N-atom, because the force of electrostatic attraction between the lone pair of electrons from N-atom and divalent metal ion is stronger than that between lone pair of electrons and monovalent proton. This difference in binding force causes the compititive adsorption of metal ions and protons to the N-atom. It is considered as an ion-exchange mechanism and represented in scheme 4 (c)



Scheme 4 (c)

This amine metal complex then reacts with water and forms metal hydroxide as shown in scheme 4 (d). It is due to greater binding force of metal ions with -OH group from water than with N of amine group.



Scheme 4 (d)

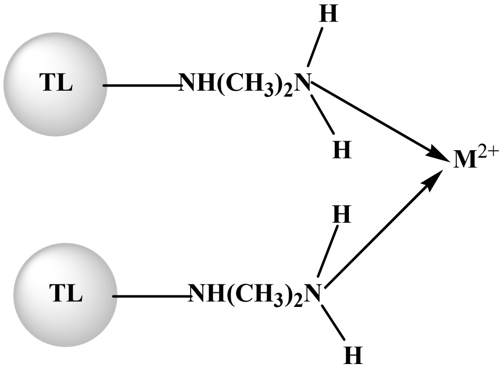
Scheme 4 (a), (b), (c) and (d): Ion-exchange mechanism

Another interaction of metal ions with polymers are mainly due to electrostatic forces and formation of coordinating bonds.

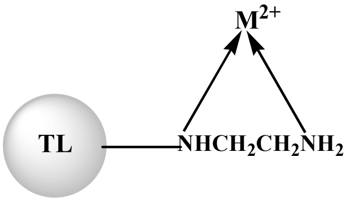
The combination of cations with molecules or anions containing free electron pair is termed coordination or complex formation. The coordination may be electrostatic or covalent in nature. The anions or molecules which forms coordination compounds are called ligands and heavy metal cations that is bound is designated as the central atom. If the ligand is composed of group of atoms then the atom that is responsible for basic or nucleophilic nature of the ligand is termed ligand atom. A base that contains more than one ligand atom i.e. multidentate ligand may form more than one coordination position in the complex. The complex formation with multidentate ligands is called chelation.

During chelation process metal ions are attracted from long range towards a polymer by electrostatic interaction. Once the metal ions are condenced on the polymer surface, they are fixed on the polymer sites which are various functional groups on the surface of the adsorbent. Such functional groups like amines, hydroxyl, carboxyl, amides etc. are called ligands. The polymers having functional groups with ability to form coordinate bond are chelating polymers. Among such ligands, the polymers with amines have been extensively studied. Figure shows the most accepted mechanism for such ligands and metal ion interaction.

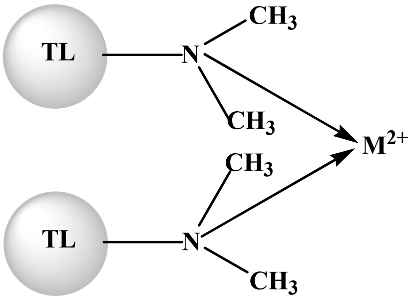
During the interaction of amino group and metal ions, the former group forms stable complexes using the free electron pair of N-atom. The availability of lone pair depends upon the pH of solution. Hence the stability of the complexes also strongly depends upon the pH of solution. At low pH, most of amine groups are protonated due to high mobility and affinity of protons. At low pH the affinity of metal ions is poor, which decreases the stability of metal - ligand complex. At higher pH the affinity of metal ions towards the ligands increases due to decreasing concentration of protons. Such increasing affinity also increases the stability of polymer - metal complexes. Besides the pH of solution, other variables that may affect the ligand - metal ion interactions are nature of functional group, ionic strength, nature and charge on metal ions, temperature and nature of counterions of the metal ions.



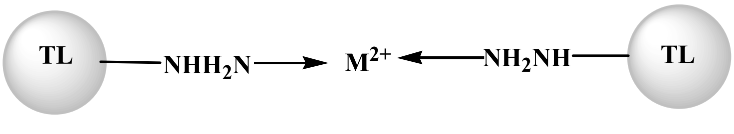
Scheme 5 (a): Intermolecular complexation between CATL-1 and metal ion



Scheme 5 (b): Intramolecular complexation between CATL-1 and metal ion



Scheme 5 (c): Complexation between CATL-2 and metal ion



Scheme 5 (d): Complexation between CATL-3 and metal ion

CHAPTER 5

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

In this study a new and cost effective biosorbent has been investigated by using waste tealeaves. It is abundant in nature and need proper disposal, which may be costly and may pollute the environment. Such waste material can be converted to useful and hopeful value added products. One of the possibilities could be their conversion into inexpensive adsorbent material, which can be used to remove toxic heavy metals from their aqueous solution.

Although, the agricultural wastes are effective adsorbents for heavy metals, they have low sorption capacity as well as poor physical stability. The waste tealeaves in raw form have adsorption capacity found to be below 20 mg/g. It is also practically soluble and leaches colour into the solution. To overcome these problems activation of raw biosorbent and its chemical modification is required.

From our literature survey, the adsorption capacity of biosorbent can be enhanced by introduction of amino groups on their surface. In this regard, a waste tealeaf was aminated by using three different reagents, ethylenediamine, dimethylamine and hydrazine monohydrate. The adsorbents were characterized by using SEM images, FTIR spectra, elemental analysis, XRD analysis, TG/DTA analysis. The biosorbents were used for removal of lead, copper, cadmium and zinc from their aqueous solution by using batch experiment.

In the study of pH, the adsorption capacities of all the biosorbents were found to be increased with increasing pH upto the optimum pH. The optimum pH for Pb(II), Cu(II), Cd(II) and Zn(II) were found to be 4, 5, 6 and 6, respectively.

In the study of effect of concentration of solutions, the removal of metal ions was increased with increasing concentration of metal ions, in initial stage. After optimum removal, the metal removal remains almost constant indicating the sorption of metal ions onto the available sites of adsorbent. It also indicates the monolayer sorption on the biosorbent. The data obtained were well fitted with Langmuir adsorption model with higher value of correlation coefficient.

In kinetic study, the adsorption process followed the pseudo-second order kinetic model with higher correlation coefficient value. The optimum contact time found for all of the biosorbents were within 120-150 min.

These experimental results revealed that the biosorbents, CATL-1, CATL-2 and CATL-3 can be used as efficient biosorbents for removal of lead, copper, cadmium and zinc from their aqueous solution. In addition these biosorbents are themselves environmental friendly and they also potentially eliminate toxicity due to heavy metals.

5.2 Recommendations

In this research, waste tea leaves is used as biosorbent for removal of toxic heavy metals. As this method uses locally available, organic waste material, the obvious advantage of the method is its lower cost. The biosorbent is environmental friendly. Similarly, this method is also technically feasible. So it is strongly recommended for the potential application of this bioadsorbent for treatment of industrial waste water.

By using the biosorption process, the metals can be recovered by eluting the adsorbed metal with a suitable reagent. Hence the use of low cost biosorbent contributes to the sustainability of the surrounding environment.

Undoubtedly, the biosorbent offers a lot of benefits for commercial use in future.

CHAPTER 6

6. Summary

Pollution of heavy metals is a great problem of developing countries. Several conventional techniques have been used to remove heavy metals from their aqueous solution. Each methods have their own defects, as well as these methods become costly for treatment of waste water. In such case synthetic ion exchange resins are effective for large volume operation. However, these resins are synthetic plastics materials and their disposal after exhaustive use by incineration pollutes the environment owing to generation of dioxane.

In this contest biosorbents have emerged as an attractive alternative for treatment of waste water. These biosorbents are cost effective as well as environmentally friendly. In this study, waste tea leaves are used to develop a low cost and efficient biosorbent. The adsorption capacity of the biosorbent was enhanced by introduction of amino groups on its surface. After introduction of amino groups, the biosorbent was found more effective for heavy metal removal. The efficiency of the biosorbent was determined by using batch experiment. Its adsoption capacity was measured as the function of solution pH, concentration of solution and contact time. The experimental data showed good sorption capacity for lead, copper, cadmium and zinc ions. So it can be potentially used for removal of heavy metals from waste water.

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