ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

Characterization and Thermal Modification of Local Bentonite for Removal of Zinc Ion from Aqueous Solution

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A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of
Master of Science

The undersigned have examined the thesis entitled ‘**Characterization and Thermal Modification of Local Bentonite for Removal of Zinc Ion from Aqueous Solution**’ presented by **Sishu Hailemariam**, a candidate for the degree of **Master of Science** and hereby certify that it is worthy of acceptance.

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I certify that research work titled “Characterization and Thermal Modification of Local Bentonite for Removal of Zinc Ion from Aqueous Solution” is my own work. The work has not been presented elsewhere for assessment. Where material has been used from other sources it has been properly acknowledged / referred.

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ABSTRACT

The natural bentonite has small specific surface area and cation exchange capacity. As a result, the focus of this research was directed towards the modification of the surface properties of bentonite to maximize its adsorption capacity. To achieve this aim, the research study was carried out by two stages; (1) Thermal modification of Ethiopian bentonite and (2) characterization, adsorption performance evaluation and kinetics study of the modified Ethiopian bentonite for removal of Zn(II). Characterization of both the raw and thermally modified bentonite clay for specific surface area and cation exchange capacity, surface functional groups, crystallinity and differential thermal analysis were studied using Methylene blue test, FTIR, XRD, DSC respectively. The surface area was increased from 147.1 m^2/g to 310.2 m^2/g as modification temperature increases from 300^oC to 500^oC. The results obtained from x-ray diffraction showed that the mineral is composed of montmorillonite and other impurities such as quartz, feldspar, muscovite, cristobalite and hematite. The thermal stability of the bentonite was studied using differential scanning calorimetry and from the result, it was confirmed that thermally stable up to 500 ℃. The effect of time, initial Zn(II) concentration and adsorbent dosage were experimentally studied using RSM. The results revealed that the amount of adsorption of Zn(II) increases with increasing contact time and adsorbent dosage and decreasing with increasing Zn(II) concentration. The optimum design parameters were recorded 75mg/l, 60min and1g and the percentage removal at those conditions was 99.54%. The results revealed that Langmuir isotherm and pseudo second-order kinetics provided better fits of the data. Therefore, the modified bentonite provides the large surface area and adsorption capacity and can be successfully employed for the removal of Zn(II) from wastewater.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
CEC	Cation exchange capacity
DF	Degre of freedom
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared radiation
PZC	Point of zero charge
RSM	Response surface methodology
SSA	Specific surface area
Std.Dev.	Standard deviation
WHO	World health organization
XRD	X-ray diffraction

CHAPTER 1 INTRODUCTION

1.1 Background

Massive human and industrial growth has changes the healthy condition of the environment towards a worse condition. The need to supply the basic needs for humans a massive development in the industrial sector as well as the modern agriculture sector has impacted on the world. These sectors have become sources of pollutants for nature. The pollutants coming from different sources as wastes are gaseous, liquid and solid form. These wastes have been released to the air, discharged to water or buried into landfill which causes further problems to the environment and living creatures.

Heavy metals are elements having a specific gravity greater than 5.0 (Srivastava and Majumder 2008). Heavy metals are typical and persistent environmental pollutants. Many toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution. Main industries containing heavy metals in discharged waters are mining, metal coating and battery production (Cheremisinoff 1995). Zn(II) is among the most common heavy metal in these wastewaters. Zn(II) being in the list of priority pollutants proposed by Environmental protection agency gives rise to serious poisoning cases (USEPA 2002). The main symptoms of zinc poisoning are dehydration, electrolyte imbalance, stomachache, nausea, dizziness and incoordination in muscles (Jain , Singhal and Sharma 2004). Therefore, the removal of excess heavy metal ions from wastewater is essential to protect human and environmental health.

Adsorption is the concentration of a substance at the surface or interface (Barrow 1996). The adsorption at a surface or interface is largely as a result of binding forces between atom, molecules, and ions of the adsorbate on the surface. The commercial adsorbents used today for the removal of heavy metals from solutions include a variety of clays, activated carbon, gels, alumina, silica, zeolites, and other residual materials (Puls and Bohn 1988). An ideal heavy metal adsorbent should have a very strong affinity for the target metal, binding it irreversibly under ambient conditions and simultaneously possessing ability to release the metal from the structure under different conditions such that the adsorbent can be regenerated for further cleanup.

Natural materials that are available in large quantities or certain waste products from industrial or agricultural operations, may have potential as inexpensive adsorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Cost is an important parameter for comparing the adsorbent materials. However, cost information is seldom reported, and the expense of individual adsorbents varies depending on the degree of processing required and local availability. In general, an adsorbent can be assumed as low cost if it requires little processing, abundant in nature, or a by-product or waste material from another industry.

Use of clays as adsorbents to remove contaminants has recently been paid increasing attention because they are readily available, cheap and environmental friendly. The wide usefulness of clays is a result of their high specific surface area, high chemical and mechanical stability and variety of surface and structural properties (Grimshaw 1972).

Bentonite is a clay consisting of smectite mineral of the montmorillonite group (Grimshaw 1972). Smectite group clays such as bentonite possess a net negative structural charge resulting from isomorphic substitution of cations in crystal lattice. This negative charge is neutralized by the adsorption of positively charged species, giving clay the ability to attract and hold cations such as toxic heavy metals. Generally, there are two types of bentonite which are sodium bentonite and calcium bentonite. Sodium bentonite is usually a high-swelling type, derived from volcanic ash that is deposited in marine environments. While calcium bentonite is a low-swelling type, which evolved from volcanic ash deposited in freshwater environments (Zhang, Sparks and Scrivner 1993). The usage of natural clay minerals such as bentonite and zeolite for water and wastewater treatment are increasing because of their abundance, low price, and adsorption capacity as well as ion exchange that is highly capable of adsorbing all kinds of pollutants for some organic and inorganic compounds, including heavy metals in waters. This outstanding capability is due to the presence of the mineral montmorillonite.

Bentonite has a variety of uses in industry; it is used as an emulsifying agent for asphaltic and resinous substances, as an adhesive agent in horticultural sprays and insecticides, in concrete mixtures, and as a plasticizer in ceramic bodies. It is also used in refining oils and fats, wastewater treatment, drilling mud, foundry sands, in some detergents and others (Zhang, Sparks and Scrivner 1993).

Bentonite as an adsorbent for the removal of Cd(II), Pb(II), Cu(II), Cr(III), Ni(II) and Zn(II) from aqueous solutions has already been reported in the literature (Blackman 1969). Apart from that, bentonite is a natural material that contains essential compounds such as aluminium, iron and clay materials which are useful for the treatment of wastewater. Moreover, bentonite is cheaper than chemicals and it fulfils the economic benefits of the operators as well as environmental concerns. However, coagulants that are commercialized in the market are mostly chemical-based, which are non- environmental friendly and may create adverse impacts on the surrounding environments. Bentonites, which contain high percentages of smectite, are greatly affected by thermal treatment. For example, physicochemical properties, such as strength, swelling, plasticity, cohesion, compressibility, particle size, cation-exchange capacity, pore structure, adsorptive properties, and catalytic activity as well as the chemical composition of the particles and the mineralogy can change considerably depending on thermal effects. The physicochemical properties of bentonite were examined at 300, 400 and 500℃.

Therefore, this study aims to investigate the adsorption capacity of thermally activated bentonite for zinc ion removal from aqueous solution to validate before application for wastewater treatment containing zinc.

1.2 Statement of the Problem

The conventional method for heavy metal removal includes chemical precipitation, membrane filtration, ion exchange, reverse osmosis, electro-dialysis, solvent extraction, evaporation, oxidation and activated carbon adsorption. Chemical precipitation is the most widely used for heavy metal removal from inorganic effluents based on pH adjustment in a basic solution. However, the disadvantages of chemical precipitation are the discharge of excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates and the long-term environmental impacts of sludge disposal.

Despite these methods being very costly, they contribute to most of the disposal problems and are even practicable for the treatment of water contaminated with heavy metals. The problems emerge during the conventional treatments which include high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary pollutants. Apart from this, it is crucial to look for an alternative treatment method to reduce the impact of conventional methods of removing heavy metal from polluted water sources. Recently, the adsorption process has gained interest as a more promising method for the long term as it is seen to be a more effective and economic approach for heavy metal removal by using low cost natural adsorbents. These problems can be overcome by using bentonite for water and wastewater treatment because of their abundance, low price, high adsorption capacity and ion exchange that adsorbs all kinds of pollutants for some organic and inorganic compounds, including heavy metals in waters by modifying the surface to enhance their adsorption performance.

Although huge amount bentonite resource available in our country, localities has indicated suitability for purification of water and making of household items, apart from minor and limited exceptions, these deposits have not been worked to provide material for use by local industries. Essentially almost all bentonite used within Ethiopia is imported, material coming from a range of countries (China, Italy, Egypt, UK, USA, India). For example, according to Ethiopian custom authority report in 2005 E.C, Ethiopia imports 169 tons of bentonite and which costs $49,158. The main use of this imported bentonite is in processing of edible oil. Other outlets are in drilling, metal casting and for filtering beer. Currently there are numerous small-scale edible oil producers who do not bleach their products, but forthcoming government regulations may make this mandatory. This should lead to an increase in demand for bleaching grade bentonite. Even though bentonite have multiple application little or no research haven done in our country on this mineral. Huge amount of money costed to import the product. Along with industrial development there is a huge amount of waste discharged to the environment. Unless this waste treated, it may cause irreversible environmental damage and complex social and economic problems. To track those and other problems, alternative treatment mechanism that could not generate secondary pollutants are the must conditions for sustainable development. In this regard, uses of bentonite is the one that enables to ensure environmental safety; due to their availability, low cost, environmentally friend and its capacity to adsorb all kinds of pollutants. These and other uses of bentonites and its applicability for treatment of heavy metals in general and zinc in particular triggers me to undertake this research.

1.3 Objectives

1.3.1 General Objective

The general objective of this study is to prepare high performing adsorbent via thermal modification from local bentonite clay for zinc ion removal from aqueous solution.

1.3.2 Specific Objectives

- To prepare thermally activated bentonite via thermal modification at 300, 400 and 500℃
- To characterize the physiochemical, surface and crystalline property of raw and activated bentonite
- To determine the specific surface area and cation exchange capacity
- To study the adsorption performance of activated bentonite for the removal of Zn ion from aqueous solution
- To examine the individual and interaction effect of contact time, initial concentration and adsorbent dosage Zn(II) adsorption performance of activated bentonite
- To determine the optimum adsorption condition using Box-Behnken response surface model
- To study the adsorption isotherm and kinetics

1.4 Scope of the Study

In this research, thermal modification, characterization and adsorption performance evaluation of local bentonite was performed for the zinc ion removal from aqueous solution. Batch studies was conducted using synthetic zinc nitrate solution. The influence of contact time, initial metal ion concentration and adsorbent dosage were studied to optimize the conditions for maximum zinc ion removal. The effect of temperature onto the surface modification of bentonite. The experimental data obtained were calculated and fitted using adsorption isotherm and kinetic models and the appropriate model was selected based the accurate fits of the experimental data. The adsorption experiments were carried out using synthetic solutions to validate the method before application to zinc ion removal from wastewater.

1.5 Significance of the Study

The significance of this study is to prove that thermally activated bentonite can act as an adsorbent for zinc ion removal from aqueous solution. From this study, the potential of thermally activated bentonite as an adsorbent to remove zinc ion from waste water can be utilized. Once the potential of bentonite in treatment of zinc containing solution proven, it can be used for wastewater treatment containing zinc. Due to high cost of conventional treatment methods of heavy metals removal; this study concerns to look back into the environment and searching the available, low cost and efficient method of heavy metal removal. It also contributes a lot for environmental pollution control since commercial adsorbents are costly and generate secondary pollutants. Localities are beneficial from this research output, keep them living in healthy environment. Industrialist also highly beneficial because they can reduce the cost for importing commercial adsorbent and reduction of sludge production which was a headache for disposal and treatment. Therefore, it has great role in reduction of foreign currency by import substitution of local resources. Generally, it has great significance in terms of showing directions of pollution prevention and resource utilization. In addition to this, the research can be used as an input for future studies to explore more about bentonite for other purpose and application.

CHAPTER 2 LITERATURE REVIEW

2.1 Heavy Metals

Heavy metals are abundantly present in nature and are also added to water by human activities such as battery production, electronics, paper and pulp industries, metal fabrication and mining activities, smelting, electrolyzing, drug manufacturing, paint preparation, alloy manufacturing, galvanizing, printing, dyeing, paper making, ceramics manufacturing and inorganic dyestuff preparation (Liu, et al. 2008) and (Sari, et a*l*. 2007).

The presence of potentially toxic heavy metals in the environment is of very much concern, primarily due to their non-biodegradability and persistence in the environment (Volesky 1999b). High concentrations of heavy metals in water supplies are undesirable and may have potentially adverse effects on the health of organisms, the suitability of water for various purposes, the longevity of water and sewer networks and the aesthetic of the environment (Demirbas 2008). High dosage of heavy metals may cause toxicity that is acute, chronic, synergistic or mutagenic or teratogenic (Burger and Gochfeld 2004). The presence of heavy metals at higher levels in surface and groundwater ecosystems also inhibits the growth of aqueous organisms and stops any beneficial use of the water bodies. These metal ions and their supplementary complexes could accumulate in the body of fishes and other aquatic organisms and finally could reach to the human body by bioaccumulation, bio-concentration and bio-magnification through the drink and food chains (Hong, et al. 2006).

2.2 Heavy Metals Sources, Toxicity and Environmental Fates

2.2.1 Sources of Heavy Metals

Heavy metals enter the environment through natural and anthropogenic activities. There are two sources of heavy metals.

Natural sources: In nature, excessive levels of trace metals may occur by geographical phenomena like volcanic eruptions, weathering of rocks, leaching into rivers, lakes and oceans due to action of water (Nriagu , et al. 2004).

Anthropogenic Sources: Large amounts of heavy metals are released while mining and uncontrolled smelting of large quantities of metal, ores in open fires. With the industrial revolution, metals were extracted from natural resources and processed in the industries from where heavy metals passed on into the atmosphere. Similarly traces of heavy metals get into the environment through discharge of waste from domestic, agricultural and auto exhausts (Nriagu , et al. 2004). Various industries produce and discharge wastes containing different heavy metals into the environment, such as mining and smelting of metalliferous ores, surface finishing industry, energy and fuel production, fertilizer and pesticide industry and application, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, metal surface treating, aerospace and atomic energy installation etc (Wang and Chen 2009).

Three kinds of heavy metals are of concern, including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides (such U, Th, Ra, Am, etc.) (USEPA 2002).

2.2.2 Forms and Fate of Heavy Metals in Aquatic Environment

Many hidden processes can change the physio-chemical forms or speciation of the heavy metals and can have a great influence on the stability of metals in aquatic environments. The processes involved are oxidation-reduction, adsorption or desorption, precipitation or dissolution and aggregation or disaggregation (Li, et al. 2009).

2.2.3 Toxicity of Heavy Metals

Metals that seep into ground waters will contaminate drinking water wells and harm the consumers of that water. Pollution from man-made sources can easily create local conditions of elevated metal presence, which could lead to disastrous effects on animals and humans (Mansour and Gad 2010). Actually, man’s exploitation of the world’s mineral resources and his technological activities tend to excavate, dislodge, and disperse chemicals and particularly metallic elements which have recently been brought into the environment in large quantities, concentrations at extreme rates (Jortner 2008).

Heavy metals in dosages higher than critical values can cause a series of health problems. The toxicity may damage or reduce mental and central nervous functions, lower energy levels and damage blood composition, lungs, kidneys, liver, and other vital organs (Lussier, Gentile and Walker 1985). Long-term exposure of toxic heavy metals may cause various cancers, Parkinson's disease, muscular dystrophy, multiple sclerosis and neurological degenerative processes (e.g., Alzheimer's disease) (ul Islam, et al. 2007). One can see that toxicity is affected by many factors (Oehme 1978). Heavy metals express their toxicity to human beings, which may result from the following mechanisms:

i) Heavy metals (divalent or higher) can easily form precipitates with anionic substances (CO_3^{-2}, SO_4^{-2}, and PO_4^{-3}). The precipitates (solids) may stay in the human body.

ii) Heavy metals can be adsorbed onto organic functional groups in various tissues of the human body, which may change their biological activities (e.g. enzymes). This may also force the essential metals to detach from enzymes and be replaced by harmful heavy metals (e.g. Cu versus Zn).

iii) Some heavy metals may cause redox reactions, forcing the basic elements (e.g., carbon) to change their chemistry. For example, hexavalent chromium CrO_4^{-2} can cause oxidation of carbon in tissues of the human body. The carbon may be oxidized, and thus its chemistry may be changed (Oehme 1978).

2.3 Zinc

In aqueous solutions zinc exists in the (+2) oxidation state (McBride 1995). Sorption of zinc by hydrous metal oxides, clay minerals and organic materials is common in aquatic systems (Jamali, et al. 2009) . In the presence of dissolved solids, zinc is transported in solution as hydrated cations or complex species. In the presence of suspended solids, sorption of zinc may occur (McBride 1995).

2.3.1 Sources of Zinc Pollution

The two major sources of zinc are domestic and industrial discharges.

2.3.1.1 Industrial Sources

Most of the zinc pollution is caused by industries. Zinc is released from industries such as: coal-burning power plants, iron and steel industries, manufacturing processes involving metals and atmospheric fallout (Denton, et al. 2001). Other sources are: Electroplating industries, pulp and paper industries, rubbers manufacture industries, pharmaceutical industries, textile mills, mining industries and automobile emission, etc. In Ethiopia iron and steel industries, galvanizing, electroplating, paper and textile mills are the most industrial sources of zinc.

2.3.1.2 Domestic Sources

Zinc occurs naturally in many foods. Some artifacts used in making our toilet contain zinc for example medicated shampoos with zinc to control dandruff. Residues of zinc from zinc-plated cold- water tanks leach into tap water and are flushed away when water is used (Denton, et al. 2001).

2.3.2 Harmful Effects of Zinc

Zinc is an essential trace element used for enzymatic reactions in humans and its extended and excessive ingestion may lead to several toxics such as carcinogenesis, mutagenesis and teratogenesis as a result of its bioaccumulation (Hooper, et al. 1980). Its toxicity can occur in both severe and chronic forms. Intake of zinc ranging from 100 to 150 mg/day interferes with copper metabolism and causes low copper status, reduced iron function, red blood cell microcytosis, and neutropenia, reduced immune function, and reduced levels of high-density lipoproteins (Hooper, et al. 1980). Ingesting 200–800 mg/day of zinc can cause abdominal cramp, nausea, vomiting, and loss of appetite, diarrhea, headaches etc). There are other reported effects including lethargy, anaemia, and dizziness (Hooper, et al. 1980).

2.3.3 Importance of Zinc

Zinc metal and zinc alloys are very resistant to corrosion. Due to its extensive usage in electroplating, metal plating, chemical manufacturing industries, etc. the demand of zinc has been increasing globally (Cousins 1996). Some important applications are specified below:

- In paint industry, zinc oxide used as a white pigment, zinc chromate used as a rust inhibitor.
- Zinc chloride used as an electrolyte in dry-cell batteries
- Depleted Zinc-64 is used widely in the nuclear industry
- Used as protective coatings for steel
- Casting industries
- Used as an alloying metal with copper to make brass
- Used as chemical compounds in rubber and paints

- Used as sheet zinc and for galvanizing iron
- Zinc oxide used in ointments for burns and skin protection, zinc pyrithione used in anti-dandruff shampoos
- Used in tablets
- Zinc chloride used in the manufacture of artificial silk and in printing and dyeing in textiles (Li, et al. 2009)**.**

Apart from industrial uses zinc plays a vital role in human metabolism. It is essential for plants, animals, and microorganisms and used by more than one hundred specific enzymes for their catalytic function (Cousins 1996). It helps in increase of immune system, wound healing, protein synthesis, normal taste and smell and is needed for DNA synthesis; and cell division (Cousins 1996). Zinc is stored in the brain, in specific synaptic vesicles by glutamatergic neurons and can modulate brain excitability (Bitanihirwe and Cunningham 2009). It plays a key role in synaptic plasticity and so in learning (Nakashima and Dyck 2009)**.**

2.4 Conventional Method of Zinc Treatment

According to the WHO standards the maximum contamination level of zinc is 5.0 mg/L (Mohan and Singh 2002). In Ethiopia, there have no ratified standard. But the draft standard specifies the maximum contamination level should be 5mg/L which is similar to WHO. The majority of the industries are discharging effluents containing zinc more than its permissible limit. Thus, the removal of zinc from the industrial wastewater before releasing it has turn out to be necessary. There are several convectional techniques available for the removal of zinc ions from wastewaters. These are: Chemical precipitation, ion -exchange, membrane filtration, electrochemical methods, biological and adsorption methods (Casqueira, Torem and Kohler 2006).

2.4.1 Chemical Precipitation

Chemical precipitation is an effective and widely used technique in industries because of its simplicity. chemical coagulation and precipitation by lime, H_2S and electro- Fenton process are used treat industry waste water containing Zn^{2+} (Chen, et al. 2009). The limitation of this process is high sludge production and chemical costs (Alvarez, Crespo and Mattiasson 2007).

2.4.2 Ion-Exchange

Ion exchange involves the reversible exchange of ions between a solution and a solid phase that are in direct contact**.** Ion-exchange processes have been extensively used for removal of heavy metals from wastewater due to their advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Alyüz and Veli 2009). Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Alyüz and Veli 2009). Formerly this process suffered from the limitation of high cost of ion exchange resins and higher operational costs. However, it is highly effective for trace metal removal depending on the chemical form of the given trace metals (Elshazly and Konsowa 2003).

2.4.3 Membrane Filtration

Membrane filtration technologies were generally used in removal of heavy metals as they are highly efficient, can be easily operated and space saving (Radjenovic, et al. 2008). The membrane processes commonly used for metal removal from the wastewater are ultrafiltration (micellar enhanced ultrafiltration), reverse osmosis and electro dialysis (Landaburu-Aguirre, et al. 2010). Reverse osmosis, the concentrated solution is subjected to high pressure (in excess of the osmotic pressure of the solution) as a result of which the solvent is forced out through a semi-permeable membrane to the dilute solution region. The three membranes most commonly used are cellulose acetate, aromatic polyamide and NS 100 (Landaburu-Aguirre, et al. 2010). Cellulose acetate is used in wastewater treatment. The factors that affect the membrane performance are membrane leakage, membrane fouling and concentration polarization. The reverse osmosis process is expensive i.e. both capital and operating costs are high (Radjenovic, et al. 2008).

In electro dialysis; instead of pressure an electric field is applied across a series of membranes which are inorganic in nature. Two types of membranes are placed alternatively in the electro dialysis cell. They are cation exchange membrane and anion exchange membrane. The cathode and anode are placed at the two ends of the cell. Raw wastewater is fed continuously into the concentrating compartments and treated wastewater withdrawn continuously from the alternate compartments (Garg, et al. 2008). Like reverse osmosis, fouling of membrane and concentration polarization are the common problems which affect the performance of electro dialysis unit. Availability of power at cheaper rates however, decides the economics of this method (Kitagawa, et al. 1977).

2.4.4 Electrochemical Methods

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state (Heidmann and Calmano 2010). Electrochemical wastewater technologies are rarely used as they involve relatively large capital investment and the expensive electricity supply. However, with the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades (Wang, Hung and Shammas 2007). Electro-coagulation using stainless steel electrodes for reduction of zinc from waste water originating from metal plating industry (Kabdas, et al. 2009).

2.4.5 Biological Methods

The use of biological process for wastewater treatment containing heavy metal ions is a recent development. Although the technique has been widely used in chemical and pharmaceutical industries in a commercial scale (Parameswari, Lakshmanan and Thilagavathi 2009). It is a very promising process in the removal of heavy metal contaminants (Murugesan, et al. 2009). The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive bio sorbents (Shankar, et al. 2007). Biosorption processes are particularly suitable to treat dilute heavy metal wastewater. In this process; algal, bacteria, fungi, yeast etc. are used as bio sorbents (Aminah and Babu 2009). Biosorption of zinc by sludge micro-organisms obtained from different steps of a conventional solid waste treatment plant (Artola and Rigola 1999). But, chemical precipitation can be used only to treat high concentration wastewater containing heavy metal ions and it is ineffective when metal ion concentration is low. And also, chemical precipitation produces large amount of sludge to be treated with great difficulties plant (Artola and Rigola 1999).

Ion exchange has been widely applied for the removal of heavy metal from wastewater. On the other hand, ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution (Alyüz and Veli 2009). And it is expensive, particularly when treating a large amount of wastewater containing heavy metal in low concentration, so they cannot be used at large scale solution (Alyüz and Veli 2009).

Membrane filtration technology can remove heavy metal ions with high efficiency, but it is having demerits such as high cost, process complexity, membrane fouling and low permeate flux which limited their use in heavy metal removal.

Electrochemical techniques for heavy metal removal are considered as the most rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge (Khelifa, Moulay and Naceur 2005). But, electrochemical technologies involving high initial capital investment and the expensive electricity supply, this restricts its development. The demerits of all the above process made to search for other process which can overcome all the difficulties in the above process. One of such kind is adsorption process.

2.4.6 Adsorption Methods

Adsorption is as an effective and economic method for heavy metal wastewater treatment among all the techniques (Dube , et al. 2000). The adsorption process offers flexibility in design and operation and will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process. In adsorption process a single or a group of ions or compounds get accumulated on the surface of another solid or liquid (Chih-Huang 2002). The substance on which the adsorption takes place is known as adsorbent and the substance which gets adsorbed is called adsorbate. Adsorption is classified into two types based on the extent of attraction between the adsorbent and adsorbate.

A) Physical adsorption

The Forces of attraction is weak van der Waals; Easily reversed by heating or decreasing the pressure; has low heat of adsorption (20-40kJ/mol); compound formation dose not takes place; adsorption can be monolayer or multi-layer and very effective at critical temperature of a given fluid (Ren, Wei and Zhang 2008).

B) Chemisorption

It is characterized by strong chemical bond; high heat of adsorption (40-400kJ/mol; formation of surface compounds; irreversible process because of strong electrostatic force of interaction and usually occurs at temperatures much higher than the critical temperature and leads to monolayer adsorption (Volesky 1999b).

Under favorable conditions, both the processes can occur concurrently or alternately. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and thereby, this process is exothermic in nature (Volesky 1999b).

Adsorption is a technology that appears more technically and economically feasible. The advantages of adsorption over other technologies are that no additional sludge is produced, additional reagents to overcome high alkalinity are not needed and the pH of discharged wastewater is unaffected (Urano and Tachikawa 1991). The adsorption process has many advantages such as:

- Low cost of adsorbent
- Easy availability of adsorbent
- Utilization of industrial, biological and domestic wastes as adsorbent
- Low operational cost
- Ease of operation compared to other processes
- Re-use of adsorbent after regeneration
- Capacity of removing heavy metal ions over a wide range of pH and to a much lower level
- Ability to remove complex form of metals that is generally not possible by other conventional method
- Environment friendly, cost effective and technically feasible alternative due to utilization of biomaterials (Vieira, et al. 2010b).

Adsorption studies were carried out using varieties of adsorbents such as: Activated carbon, low cost adsorbents for biomass, waste sludge, rice husk, sugarcane bagasse, lignite, bentonite etc. (Chih-Huang 2002). Due to the high cost of activated carbon limits its use in adsorption. Various low- cost adsorbent derived from various natural as well as anthropogenic sources have been implemented for treatment of waste water contaminated with heavy metals (Pradhan, Shyam and Kenneth 2005). The adsorbents mostly used are agricultural waste, industrial byproducts, natural materials or modified biopolymers (Peric, Trgo and Medvidovic 2004). The advantage and disadvantage of different adsorbent are listed in Table 2.1.

Table 2.1: Advantages and Disadvantages of adsorbents

Adsorbent	Advantage	Disadvantage
Activated Carbon	High surface a rea	High cost
Bio sorbents	High adsorption capacity	High market cost
Agricultural and industrial by-products	Available in abundance	Sorption properties depends on origin
Bentonite	High surface area, high cation exchange capacity and low cost	Need modification to enhance its adsorption performance
Zeolite	High ion exchange capacity and surface area	Complex sorption Mechanism

2.5 Bentonite

The basic structure of bentonite is made up of two silica tetrahedral sheets with an intermediate aluminium octahedral sheet (Vimonses, et al. 2009). Figure 2.1 shows the basic structure of bentonite. The charge between the octahedral and tetrahedral sheets is not balanced due to isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and generally Mg^{2+} for Al^{3+} in the octahedral sheet. The substitution by these ions of lower valence induces a permanent negative charge in the lattice structure. The negative charge is balanced by treating it with cations such as sodium, calcium or magnesium. These cations are exchangeable cations in the lattice structure due to loosen binding (Vimonses, et al. 2009). Depending on the exchangeable cations, commercial bentonites are known as Ca-bentonite or Na-bentonite (Babaki, Salem and Jafarizad 2008).

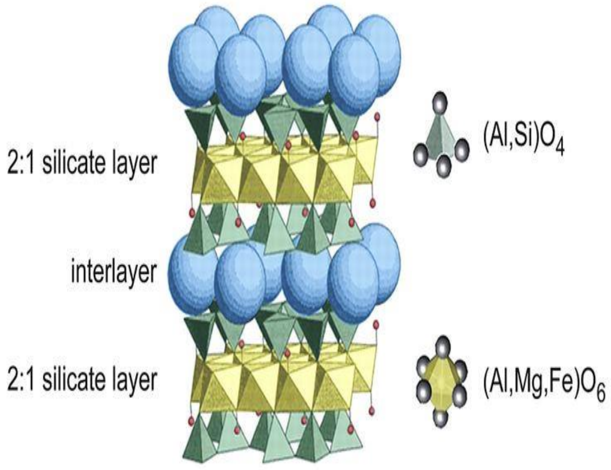


Figure 2.1: A Layer structure of bentonite

Bentonite is widely used in various industrial products and processes such as pharmaceuticals, cosmetics and drilling fluids to modify the rheology and control the stability of systems (Faur-Brasquet, et al. 2002). It is used as a plasticizer in ceramics, as an emulsifying agent in asphaltic substances, as thickener and extender for paints, as adhesive in concrete mixtures, horticultural sprays and insecticides, adsorbent in removal of dyes and heavy metals, and in bleaching earth in refining oils and fats (Pushpaletha, Rugmini and Lalithambika 2005).

The widespread use of bentonite can be attributed to its physical and chemical properties such as small particle size, high porosity, large surface area and high cation exchange capacity (Doulia, et al. 2009). The bentonite has excellent adsorption capacity and its adsorption ability is determined by the chemical nature and pore structure (Koyuncu 2008). In addition to, it is available in abundance in almost all parts of world (Khenifi , et al. 2007). Another reason for the wide use of bentonite is the ease of modification by using simple methods (Sanjay and Sugunan 2008). Recently a large reserve of bentonite has been found in Ethiopian Rift valley and its extension into the Afar depression in northeastern Ethiopia host extensive bentonite deposits. The wide spread silicic volcanism and lake environments produce the most favorable sites for the accumulation of acidic volcanic ash. The alteration of these ashes is the basis for the formation of bentonite.

Table 2.2: Explored bentonite resource deposit in Ethiopia

Area(province)	**Name of deposit**	**Easting**	**Northing**	**Resource in million tonnes**
Afar	Gewane Bentonite	40° 38' 05"E	10° 17' 50"N	126
Sidamo	Gidicho Bentonite	37° 56' 00"E	06° 24' 00"N	5
Afar	Warsissa Bentonite	40° 39' 00"E	11° 22' 20"N	10.5

Adapted from Geological Survey of Ethiopia

2.6 Modification of Clays Minerals

Modification can alter the clay structure to enlarge its surface area, therefore increasing the adsorption capacities (Dai and Huang, 1991). The term activation refers to chemical and physical treatments employed to enhance the adsorption capacities of clays (Christidis, Scott and Dunham 1997). There are various methods for modification of clay minerals such as, acid activation, treatment with cationic surfactant, clay rubber composite, thermal treatment, polymer addition, pillaring by different types of poly (hydroxo-metal) cations, intraparticle and interparticle polymerization, dehydroxylation and calcination, adsorption and ion exchange with inorganic and organic cations, binding of inorganic and organic anions (mainly at the edges) and grafting of organic compounds (P. Liu 2007).

2.7 Modification Methods of Clay Minerals

2.7.1 Intercalation with Bulky Poly-Oxy-Cations

Pillared clays are prepared by intercalating natural clays with bulky polyoxycations such as Al or Zr. Calcination at high temperatures results in transforming the intercalated polyoxycations into rigid oxide pillars producing pillared clays. Pillared clays have a highly porous structure. The use of pillared clays is limited due to lack of thermal stability of the clay (Carvalho, et al. 2003).

2.7.2 Modification by Polymer

The adsorption properties of clays can be enhanced by the incorporation of polymers in the interlayer spaces (Ding, et al. 2006). The polymer modified clays are generally formed by physical adsorption, chemical grafting or ion exchange with surfactants. Polyacrylamide is most widely used for preparing polymer modified clays (Chen, Peng and Su 2008). The physical adsorption enhances the physical and chemical properties of the clay, but does not affect the structure of the clay.

The drawback of this method is that the bond between the clay and the adsorbed molecules is not very strong (P. Liu 2007). The properties of polymer modified clays largely depend on the modification technique. The modification of clays by an ion exchange method using polymeric quaternary ammonium ions is less expensive than chemical grafting (Ding, et al. 2006). Synthesized polymer modified clay using oligomeric poly (styrene-co-acrylamide). These materials are widely used to form polymeric adsorbents, however the chemical bonding to polymers is difficult and expensive.

2.7.3 Modification by Cationic Surfactant

The cationic surfactants such as quaternary ammonium salts of the form $(CH_3)_3NR+$ (where R is an alkyl hydrocarbon) are commonly used for the formulation of organoclays (Paiva, Morales and Díaz 2008). The wide use of bentonite for the fabrication of organoclays is due to its high cation-exchange capacity, surface area, adsorption capacity and swelling capacity (Li and Bowman 1997).

The preparation of organoclays from cationic surfactants is a two-step process, which comprises cation-exchange and hydrophobic bonding. When the concentration of the cationic surfactants is low, only ion exchange takes place forming a monolayer. The formation of bilayer takes place when the concentration of the cationic surfactants increases as the Van der Waal interactions become prominent between the hydrocarbon tails (Li and Bowman 1997).These organic cations change the surface of the clay from hydrophilic to hydrophobic by replacing the exchange sites of clay with the alkyl hydrocarbons, resulting in increasing adsorption capacity for organic pollutants (Wang and Wang 2008).

Employed cationic surfactant dodecyl trimethyl ammonium bromide to modify bentonite by an ion exchange mechanism resulting in the increase in adsorption capacity of bentonite compared to natural bentonite. Though lipophilic surface of organo-bentonites makes them an excellent adsorbent for organic pollutants, they have a drawback as large amount of quaternary ammonium salts are required for the modification (Yue, et al. 2007). A large-scale production of organoclays is not practical due to the complexity of the process (Faur-Brasquet, et al. 2002) and the cost of modification of clays by surfactants is significantly high (Wang and Wang 2008).

2.7.4 Acid Activation

The clay formulated by treating it with inorganic acids at high temperatures is termed acid activated clays (Koyuncu 2008). The acid activation of the clays is normally done by treating it with HCl or H_2SO_4 and the cost of production of acid activated clays is low. The acid activation of the clays alters the physical properties such as, enhancing the surface area and average pore volume (Doulia, et al. 2009). It can also change the chemical properties such as cation exchange capacity and the surface acidity of the clays, thus, generating the desirable characteristics required for an effective adsorbent. Acid activation is a favorable method for increasing surface area as the decomposition of the crystalline structure can be controlled (Chaari, et al. 2008).

2.7.5 Thermal Activation

The thermal activation of clay is a physical treatment which involves calcination of clays at high temperatures (Al-Asheh, Banat and Abu-Aitah 2003). The change in structure and composition upon heating is different for different clays and largely depends on the particle size and the heating regime (Beragaya, Theng and Lagaly 2006). Furthermore, the clay minerals are generally calcined prior to their use in order to remove any impurities or moisture attached to the clay particles. The thermal activated clays are extensively used in textile, oil, tannery, electroplating and sugar industry to remove color, heavy metals and other impurities.

In the dehydration stage, the adsorbed hydrated water and impurities attached to the clay particles are removed. This results in the weight loss of the clay particles and increase in surface area, providing access to more sites for adsorption (Beragaya, Theng and Lagaly 2006). Further heating corresponds to the dehydroxylation. If heating is continued beyond dehydroxylation the clay structure and the surface functional groups are altered.

Breakdown of the bonds within the clay structure takes place; resulting in the collapse of structure and reduction in surface area (Beragaya, Theng and Lagaly 2006).

Thermal analysis of white calcium bentonite from Turkey was conducted in the temperature range between 100 and 1100 ^{0}C for 1 hour (Stojiljković, et al. 2015) and the following results were reported. Values V and A, which were 0.107 cm^3g^{-1} and 42 m^2g^{-1} in non-treated sample and reached maximum values of 0.149 cm^3g^{-1} and 89 m^2g^{-1} after thermal treatment at optimum temperature of 500 ^{0}C. A and V reach the maximum at 500 ^{0}C, which was achieved by irreversible dehydration without any changes in crystal structure and porosity bentonite reaches its maximum (Stojiljković, et al. 2015). In another literature, the value of specific surface area was increased with increasing temperature up to 500 °C and a rapid decrease above this temperature (Orolínová , et al. 2012).

The natural clay from southern Tunisia exhibited greater removal efficiency than those reported in the literature, confirming their beneficial use for the removal Cu(II) and Zn(II) from aqueous solutions (Sdiri , Higashi and Jamoussi 2014).

Cu(II) and Zn(II) adsorption from aqueous solutions using Cankırı natural bentonite was investigated and the effect of initial metal ion concentration, pH, clay dosage and agitation time were reported. The isotherm and kinetic models were developed and the following conclusion were reported. The second order reaction kinetic best describes the adsorption kinetics and the adsorption isotherm well described by both Langmuir and Freundlich models (Sevil and Bilge 2007).

To summarize, several hypotheses have been suggested to explain the changes in properties of montmorillonite when heated to temperatures from 300-500°C. These include permanently increased attractions owing to removal of adsorbed water, entry of exchangeable ions into the clay crystal structure, neutralizing the layer charge, polarization of clay surfaces and partial dihydroxylation to enhance the adsorption capacity of natural bentonite and also it can be used for removal of heavy metals.

Even though the above results were reported; the quality and composition of bentonite affects its properties and limit its application. The gap that this research addresses were: thermal modification of the local bentonite and studied its adsorption capacity. Since there is no published research work has been done on this local resource. Therefore, this study aims for characterization, modification and adsorption performance evaluation of local bentonite for heavy metals removal in general and zinc in particular and determine the optimum temperature that gives maximum surface area available for adsorption without structural loss of bentonite. Different isotherms and kinetic models also investigated and appropriate model were selected based on fitting the experimental data.

CHAPTER 3 MATERIALS AND METHODS

3.1 Raw Material

The raw bentonite used in this study was received from ministry of mines and biofuels organization which was delivered from Afar Region (Gewane area) in north eastern part of Ethiopia whose basic clay mineral is calcium-bentonite, was used for the adsorption experiments.

3.2 Instruments

Various instruments were used throughout the study of this research. The list of instruments and their functions are shown below in Table 3.1.

Table 3.1: List of instruments

Instruments	Maker and model	Function
Analytical balance	Sartorius	Weight Measurement
pH meter	JENWAY 3505	Measurement of pH
FTIR	Spectrum 65 FT-IR (PerkinElmer)	Analyze the functional groups present in the adsorbent
XRD	Miniflex 300/600 (Rigaka)	Measurement of crystallography of bentonite
AAS	novAA 400 p	Estimation of final metal ion concentration
DSC	DSC 8000 (PerkinElmer)	Differential thermal analysis
Ultra-pure water system (distiller)	Sartorius	Distilled water production
Muffle furnace		used for thermal activation of bentonite
Desiccator		To prevent moisture absorption

Jaw crusher, Attrition mill, mortar and pestle		Size reduction
Rotary sieve machine		Particle size distribution and separation
Magnetic stirrer		Mixing
Sonicator	SONOREX RK 106 S	Mixing by sound
Pycnometer	Duran	Bulk density measurement
PET bags		Air tighten sample holders
Beaker, volumetric flask, measuring cylinder		Used for solution and volume measurement
Centrifuge		Separation of solid from the solution using centrifugal force
Vacuum filter		Separation

3.3 Chemicals

All chemicals used were of analytical reagent grade and were bought from Neway plc. Zinc nitrate ($Zn(No_3)_2.6H_2O)$) was used as zinc source for preparation of stock solution. A 0.1M HCl and NaOH were used to adjust the solution pH. Methylene blue was used for determination of specific area and cation exchange capacity of the adsorbent. Analytical grade NaCl also used for bulk density measurement. Distilled water was used throughout the experimental studies.

3.4 Sample Preparation and Characterization

3.4.1 Size Reduction

Size reduction was performed to make ready for pretreatment. It was air-dried and size reduction was performed using hammer manually followed by jaw crusher to make ready the sample for pretreatment.

3.4.2 Pretreatment

The ground sample was purified by washing with distilled water several times to remove adhered impurities and soluble salts from the raw material. The solid suspension was stirred vigorously and centrifuged to filter out the liquid. The sample was washed three times and centrifuged. Then the solid was dried in an oven drier for 24 hours at 105ºC to vaporize the moisture adhered to it. Again, the purified sample was milled using hammer mill and mortar and pestle to obtain appropriate particle size. The ground powder sample was sieved using rotary shaker sieving machine and was allowed to pass through a 75μm sieve. The sample size of retain on 63μm and pass through 75μm sieve was taken for thermal activation.

3.4.3 Thermal Activation

The natural bentonite sample was thermally treated to enhance specific surface area and increase its adsorptive capacity. Thermal activation was performed in muffle furnace. The experimental procedures were used as follows.

The thermal activation was performed over a range of temperature at 300, 400 and 500ºC. For thermal activation 100g of bentonite was taken on a crucible. This given amount of bentonite was placed in the muffle furnace. Then the temperature of the muffle furnace was set to the desired temperature. The temperature was allowed to rise steadily to the desired temperature in 5min. After the desired temperature had been reached, the sample was maintained at the set temperature and was heated for predetermined time of 90 minute. When the heating was complete, the samples was taken out of the muffle furnace and cooled in the desiccator for 90 minutes. After that the sample was stored in air-tight plastic bottle in a desiccator for further use. Similar procedures were followed for all temperatures.

3.5 Physiochemical Characterization of the Adsorbent

3.5.1 Swell Index

Swelling index measurement is an index method that enables the evaluation of swelling properties of a clay mineral in reagent water for estimation of its usefulness for permeability or hydraulic conductivity reduction in geosynthetic clay liners. The swelling index also used for physical identification of bentonite types. The swelling index of bentonite was determined based on ASTM standard test method for swell index of clay mineral component of geosynthetic clay liners D 5890 – 95.

Experimental Procedure

The Experimental procedures followed during the determination of swell index were described here. The sample was ground by mortar and pestle or laboratory hammer mill as required and a particle size of passing through 75µm standard Sieve was taken for the test. A portion of ground sample was dried to constant weight at 105°C for 24 hours. A 2 g of dried and finely ground clay mineral was weighted onto a weighing paper. A clean 100mL graduated cylinder was filled with 90mL reagent water. A 0.1g increment of clay mineral with a volumetric spoon from weighing dish or paper was removed and carefully dusted over the entire surface of water in the graduated cylinder over a period of approximately 30 seconds. Do not use a funnel that may concentrate the clay mineral in a poorly hydrated agglomerate. The clay mineral was allowed to wet, hydrate and settle to the bottom of the graduated cylinder for a minimum period of 10 minute. Additional increments of the clay minerals powder were continued until the entire 2g sample had been added. After the final increment had settled, carefully any adhering particles from the sides of the cylinder into the water column was rinsed and raised the water volume to the 100mL mark. The temperature of the slurry was measured carefully by immersing the thermometer into the water, without disturbing the settled clay mineral and recorded. The glass stopper was placed on the cylinder and allowed to stand undisturbed for a minimum of 16 hours from the last incremental addition. After 2 hours, the hydrating clay mineral column for trapped air or water separation in the column was inspected. If present, gently tip the cylinder at a 45° angle and roll slowly to homogenize the settled clay mineral mass, allow the graduated cylinder with the hydrating clay mineral to remain undisturbed for a minimum of 16 hours before recording the volume of the hydrated clay mass and its temperature. After the minimum 16 hours hydration period from the last increment addition, the volume level in mL at the top of the settled clay mineral to the nearest 0.5 mL was recorded. The distinct change in appearance at the upper surface of the settled clay mineral was examined. Any low-density flocculated material (sometimes lighter in coloration to white) shall be ignored for this measurement. Finally, the observed volume of hydrated clay mineral and its temperature were recorded.

3.5.2 Bulk Density

Bulk density is the mass per volume ratio that includes the cavities in a porous material. Density determination is among the most often used gravimetric procedures in laboratories. Density can indicate a change in the composition of a material, or a defect in a product, such as a crack or a bubble in the voids. The bulk density of bentonite was measured according to ASTM method D2854- 83.

$$\rho_b = \frac{m}{V} \qquad (3.1)$$

Where, m is the mass of bulk sample in (g) and volume of bulk sample in(mL).

Experimental Procedure

A detail of experimental procedures was outlined here. Firstly, the pycnometer (Duran, 50 mL at 25 ◦C) was calibrated with distilled water, dried and weighted. Then the pycnometer was filled with 0.1 M NaCl solution and weighted to determine the specific gravity of NaCl. Then after an amount of clay between 7.3-15.2 g of bentonites was added to a container with approximately 40 mL of 0.1 M NaCl solution and sonicated for 5 min with a sonicator SONOREX RK 106 S which operated at a frequency of 20 kHz and a power output maintained at the maximum power of 600 W with a pulse on/off time of 5 sec. Afterwards the sample was shaken minimum overnight and poured into the pycnometer, filled up with 0.1 M NaCl solution and weighted. Three repetitions were made and the average of the results was taken as the bulk density of the sample.

3.5.3 Moisture Content

The aim is to determine the moisture content of clay with a view to increase the active site and hence improve the adsorptive capacity. The moisture content of the sample was determined based on ASTM D 2216 standard test method of fluid loss of clay.

Experimental Procedure

The experimental Procedures followed during determination of the moisture content were described as follows. The Petri dish was cleaned, dried and weighted. Then 3.6967g of bentonite sample was measured and put on Petri dish and allowed to dry in an oven for

24hr at a temperature of 105C◦. After cooling in a desiccator, the mass loss was measured. The moisture content of the sample was determined as follows.

$$\%X = \frac{W_1 - W_2}{W_1} \text{ x}100 \qquad (3.2)$$

Where, X is moisture content, w_1 is sample weight before drying and w_2 is sample weight after drying

3.5.4 Point of Zero Charge

The zero point of charge is a fundamental description of a mineral surface and is more or less the point where the total concentration of surface anionic sites is equal to the total concentration of surface cationic sites and most (but not all) of the sites are as the neutral hydroxide. At pH values above the PZC, the surface has a net negative or anionic charge, and the surface would participate in cation attraction, and cation exchange reactions. At pH values below the PZC, the surface has a net positive charge, and the surface will attract anions, and participate in anion exchange reactions.

Experimental Procedure

The experimental procedure followed for determination of point of zero charge were outlined as follows. A 5mg portion of bentonite was added to 5 mL of distilled water having a pH between 7.50 and 11.50. The initial pH of the solution was adjusted with 0.1m HCl or NaOH. After each addition of 5 mg of solid bentonite, the pH was measured with a JENWAY 3505 pH meter. The suspension was continuously stirred and purged by nitrogen gas. When equilibration was achieved (equilibration time 15 min), a new amount of bentonite was added. This procedure was continued until further bentonite additions did not change the pH of the solution. This pH value had been obtained to be a good approximation of the PZC of oxide and clay surfaces (Avena and De Pauli 1998).

3.5.5 pH

The aim was to determine pH of clay to know its level of acidity or alkalinity of the clay sample. In the determination of pH of the sample, distilled water of neutral pH was used and detail of its experimental work outlined here. A 100ml of distilled water was measured in a 200ml beaker. A mass of 2g of bentonite powder was measured and added to the beaker containing 100ml distilled water. The mixture was stirred vigorously and the pH of the clay suspension was measured using pH meter in every one minute until the pH becomes constant.

3.5.6 Specific Surface Area

3.5.6.1 Methylene Blue Test

Methylene blue is a cationic dye that has been used to identify redox reactions for a wide range of applications in the fields of chemistry and biology. In the field of clay chemistry, the adsorption of methylene blue to the edges, external surfaces and accessible interlayer regions of clay minerals dispersed in an aqueous solution is often used to measure cation exchange capacity and specific surface area of clay minerals (Yukselen and Kaya 2008). The spot method was used for determination of specific surface area and cation exchange capacity. The method is very commonly used in engineering practice (Verhoef 1992).

Preparation of Methylene Blue Solutions and Test Procedure

Methylene blue tests was performed based on (AFNOR 1993) standard. Methylene blue solution was made by dissolving methylene blue powder in distilled water. It was prepared by mixing to dissolve 10g of methylene blue in 1 L of distilled water in a beaker at room temperature, for one hour. Bentonite solution was prepared by mixing 7.5 g of bentonite sample passing sieve 420µm in 50 ml distilled water in a beaker with a mixer running at 700 rpm for 5 min (Çokça 1991).

Experimental Procedure

The mixture made by adding increasing amounts of methylene blue solution to bentonite solution was pipetted and dropped onto standard filter paper. A 5 ml of methylene blue solution was mixed with bentonite solution. From this moment on, mixer speed must be adjusted to 400 rpm to remain at this speed until the end of the test. At the end of one minute, an amount of mixture was taken using a glass pipette and dropped onto filter paper. The filter paper should be placed on a beaker or other appropriate support so that the wetted surface does not touch any solid or liquid. Generally, at the stage of placing the first drop on the filter paper, a dark blue spot surrounded by a colorless moist halo was observed (this means that the test is negative). A 5 ml of methylene solution was added each time to the bentonite solution until a halo of light blue dye surrounds the dark blue spot on the filter paper. At that point, no more methylene blue solution was added and the mixture was inspected for 5 min in total, checking at each 1 min intervals to determine the permanence of the light blue halo. At the end of the test, the light blue halo around the dark blue spot was surrounded by a zone of clear water (meaning that the test was positive). That indicates there was excessive amount of methylene blue that was no longer adsorbed by clay mineral and was remains in suspension. At that point, no more methylene blue was added and the suspension was checked at 1 min intervals to determine the stability of the light blue halo. If the light blue ring that surrounds the spots dropped in intervals of 1 min disappears, then the methylene solution amount to be added should be reduced to 2 ml by following the same procedure.

The specific surface area and cation exchange capacity of both raw and activated bentonite was calculated as follows.

$$\mathrm{SSA} = \frac{\mathrm{m_{MB}\, A_v\, A_{MB}}}{\mathrm{M_{MB}\, m_s}} \qquad (3.3)$$

$$\mathrm{CEC} = \frac{\mathrm{V_{MB} N_{MB}}}{\mathrm{m_s}} *100 \qquad (3.4)$$

Where m_{MB} is the mass of the adsorbed methylene blue at the point of complete replacement, m_s is the mass of the clay specimen, $M_{MB}$is the molecular weight of methylene blue dye which is 319.87g/mol, Av is Avogadro's number (6.02 $*10^{23}$/mol), A_{MB} is the area covered by one methylene blue molecule which is 130$Å^2$ (1Å= 0.1nm=10^{-10} m), V_{MB} is the volume of methylene blue injected and N_{MB} is the normality of the methylene blue (meq/100g).

3.5.7 XRD

X-ray diffraction is powerful nondestructive technique for characterizing crystalline materials. The crystallography of both raw and activated bentonite was studied using Miniflex 300/600 (Rigaka) x-ray diffraction instrument. Each mineral type is defined by a characteristic crystal structure, which will give a unique X-ray diffraction pattern, allowing rapid identification of minerals present within a rock or soil sample. The XRD data can be analyzed to determine the proportion of different minerals present.

The diffraction was described by Bragg's law: $n\lambda=2d\sin\theta$. The intensity of the scattered x-ray is proportional to the number of electrons that the x-ray is scattered from.

where n is an integer, λ is the wavelength of the X-rays, d is the interplanar spacing generating the diffraction, and θ is the diffraction angle.

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the compound because each compound has a set of unique d-spacings. Typically, this was achieved by comparison of d-spacings with standard reference patterns.

3.5.8 FTIR

The functional groups of bentonites were characterized using spectrum 65 FT-IR (Perkin Elmer) machine. Fourier transform infrared spectroscopy is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular fingerprint. The functional groups of the raw and activated bentonite were analyzed by Fourier transform infrared (FTIR) spectroscopy.

The spectra data was collected in the IR wavelength of 400 to 4000 cm^{-1}. Samples was prepared by the standard KBr pellets method. Solid samples were milled together with potassium bromide to form a very fine powder which was then uniaxially compressed into a thin pellet which can be further analyzed.

3.5.9 DSC

The thermal stability of bentonite sample was analyzed using DSC 8000 (PerkinElmer) differential scanning calorimetry. A differential calorimeter measures the heat of sample relative to a reference. DSC is the most often used thermal analysis method, primarily because of its speed, simplicity, and availability (Skoog , Holler and Crouch 2011).

Experimental Procedure

A mass of 0.05mg of sample was measured and put into the sample holder which made from aluminum. The temperature and heating rate was set to 50-550 ◦C, 40 ◦C /min respectively. Then after, nitrogen gas was purged continuously at 20ml/min for about 30 minutes. Finally, the print out raw data was analyzed.

3.6 Zinc Adsorption Experiment

Adsorption of Zn^{2+} onto thermally activated bentonite was carried out in a batch process. Stock solution of Zn^{2+} was prepared by dissolving 1g of analytical reagent grade of $Zn(NO_3)_2.6H_2O$ in one liters of distilled water to achieve concentration of 1000 mg/l. Other samples for all experiments was prepared by diluting the stock solution to the pre-determined concentration. Known amount of activated bentonite (0.5,1 and 1.5g) was placed in a conical flask containing zinc solution of known concentration (50,75 and 100mg/l) and pH 4.5. The resulting mixture was mixed continuously using hot plate magnetic stirrer for a given time period (30, 60 and 90 minute), 275 rpm stirring speed and 25°C temperature was applied in the stirrer. Afterward, samples were taken out and the bentonite was separated by filtration using filter paper or centrifuge. The filtrate was analyzed for zinc ion concentration by novAA 400p atomic absorption spectrophotometer. The effects of several factors such as initial metal ion concentration, adsorbent dosage and contact time on zinc removal percentage were studied. The initial pH of the solution was adjusted with 0.1M HCl and NaOH. The percentage removal of zinc ion from the solution was calculated by the following equation.

$$\%\text{Removal} = \frac{C_o - C_t}{C_o} * 100 \qquad (3.5)$$

Where C_0 (mg/l) is the initial zinc ion concentration and C_t (mg/l) is the final zinc ion concentration in the solution.

3.7 Design of Experiments

3.7.1 Response Surface Design

Box-Behnken is a kind of response surface method; often used to study the influence of the test factors and response value, with accurate determination of the relationship between influence factors and the response values (Nie, et al. 2013). The effect of adsorption parameters: initial metal ion concentration, adsorbent dosage and contact time were studied using Box-Behnken design response surface method and the optimum design conditions and model was developed. Design Expert 6.0.8 portable software was used as the fitting system to seek the optimal value.

Table 3.2: Box-Behnken Design experimental levels

Levels	**Factors**		
	Time(min)	Concentration (mg/L)	Dosage (g)
-1	30	50	0.5
0	60	75	1
1	90	100	1.5

Table 3.3: Box-Behnken Design total number of experiments

	Factors		
No.	Time (min)	Concentration (mg/L)	Dosage(g)
1	30	50	1
2	90	50	1
3	30	100	1
4	90	100	1
5	30	75	0.5
6	90	75	0.5
7	30	75	1.5
8	90	75	1.5
9	60	50	0.5
10	60	100	0.5
11	60	50	1.5
12	60	100	1.5
13	60	75	1
14	60	75	1
15	60	75	1
16	60	75	1
17	60	75	1

3.7.2 Isotherm Models

The mechanism of adsorption could be determined by evaluating the equilibrium or adsorption data obtained from the experiments. An equilibrium relationship between the amounts of zinc adsorbed on the surface of an adsorbent could be established through adsorption isotherms (Bulut, Özacar and Şengil 2008). In this study both Langmuir and Freundlich isotherm models were examined to fit the experimental data.

3.7.2.1 Langmuir Isotherm Model

The basic assumption of Langmuir model is that the formation of monolayer takes place on the surface of the adsorbent indicating that only one metal ion could be adsorbed on one adsorption site and the intermolecular forces decrease with the distance. It is also assumed that the adsorbent surface is homogeneous in character and possess identical and energetically equivalent adsorption sites. The Langmuir model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (3.6)$$

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad (3.7)$$

where C_e is the equilibrium concentration of Zn^{2+} (mg/l), q_e is the amount of Zn^{2+}adsorbed per unit of adsorbent (mg/g), q_m is the maximum monolayer coverage capacity (mg/g) and K_L is the Langmuir constant for energy of adsorption (L/mg), V is the volume of the adsorbate (mL), m is the mass of the adsorbent. The values of q_m and K_L will be obtained from the slopes ($\frac{1}{q_m}$) and intercept ($\frac{1}{K_L q_m}$) of the linear plot of C_e/q_e versus C_e.

A dimensionless constant, commonly known as the separation factor (R_L) or equilibrium parameter defined by (Torab-Mostaedi, et al. 2013) can be represented as:

$$R_L = \frac{1}{1+K_L C_o} \qquad (3.8)$$

where K_L (L/mg) refers to the Langmuir constant and C_o is to denote the adsorbate initial concentration (mg/L). In a deeper explanation, R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), irreversible ($R_L = 0$).

3.7.2.2 Freundlich Isotherm Model

This empirical model can be applicable for multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Febrianto, et al. 2009). It is demonstrating that the ratio of the metals to adsorbate onto a given mass of adsorbent to the solute was not a constant at different solution concentrations (Torab-Mostaedi, et al. 2013). In this point of view, the amount of adsorbate which adsorbed in the adsorbent is the summation of adsorption on all sites, with the stronger binding sites being occupied first, until the adsorption energies are exponentially decreased upon the completion of adsorption process (Gorgievski, et al. 2013).

The slope ranges between 0-1 and which is a measure of the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value below unity implies chemisorption process where 1/n above one is an indicative of cooperative adsorption (Buasri, et al. 2012). The general Freundlich equation is Eqn 3.9 and could be linearized into Eqn 3.10.

$$q_e = K_F C_e^{1/n} \qquad (3.9)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (3.10)$$

Where q_e is the amount of metal ion adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration (mg/L), K_F and n are Freundlich equilibrium constants which are obtained from linear plot of $\ln q_e$ versus $\ln C_e$. where 1/n is a heterogeneity parameter, the smaller 1/n, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when 1/n = 1. If n lies between one and ten, that indicates a favorable sorption process.

3.7.3 Kinetic Models

The study of adsorption kinetics in wastewater is important as it afford important insight into the reaction pathways and mechanism of the reaction. Further, it is important to predict the time at which the adsorbate is removed from aqueous solution in order to design a proper sorption treatment plant. Numerous kinetic models have been proposed to explain the mechanism of a solute sorption from aqueous solution onto an adsorbent:

3.7.3.1 Pseudo First Order Model

It is one of the most extensively used sorption rate equations for sorption of a solute from a liquid solution. Lagergren equation is given by the following equation (Ho and McKay 1999a).

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (3.11)$$

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

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (3.12)$$

The values of k_1 and q_e are calculated from the slope and intercept of plots of ln (q_e - q_t) versus t respectively.

3.7.3.2 Pseudo Second Order Model

The pseudo second-order equation can be written as (Ho and McKay 1999a)

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (3.13)$$

Where k_2 is the rate constant in g/mg.min, k_2 and q_e can be obtained from the intercept and slope by applying the conditions of q_t =0 at t = 0 and q_t = q_t at t = t.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k_2} \qquad (3.14)$$

The value ofq_e and k_2 are obtained from the linear plot of $\frac{t}{q_t}$ versus t.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Physiochemical Characteristics of the Adsorbent

The physiochemical properties of the adsorbent before and after thermal treatment were determined using the specified methods and procedures described in the methodology part and the values are presented in Table 4.1.

Table 4.1: Physiochemical characteristics of the adsorbent

Physical properties of raw bentonite		Average Values
Specific gravity		2.41
Moisture content (%)		9.83
Swell index (ml/2g)		14.2
Chemical properties		
Before thermal treatment		After thermal treatment
pH	8.2	6.2
PZC	6.56	4.77

The specific gravity of pure montmorillonite mineral was reported to vary between 2-2.7; decreasing with increasing water content (Cheremisinoff 1995). The result was complementary with other findings. The pH of natural calcium bentonite is alkaline in nature because of the exchangeable cation and presence of excess hydroxyl groups in the structure of montmorillonite. Since calcium bentonite is non-swelling types of bentonite and the swelling index much smaller than sodium bentonite. The swelling index of Ca-bentonite varies in the range of 10-15ml/2g while Na-bentonite more than 25ml/2g since it absorbs more water. After calcination, the pH as well as PZC decreases since more OH^- were removed due to thermal treatment and the pH become acidic. Figure 4.1 shows the graphical description of both the raw and activated bentonite PZC. From the Figure 4.1 , more or less the point where the total concentration of surface anionic sites is equal to the total concentration of surface cationic sites were determined before and after activation. The PZC of raw is larger than the calcined one because it contains more hydroxyl groups. The pH and stirring speed were taken as constant and referred from literature. The fact that in acidic environment (pH<4), the sorption of metal ions was suppressed by the excessive presence of H^+ which compete for available reactive sites. when pH>6, precipitation of Zn(II) with OH^-predominates and percentage removal of Zn(II) decreases (Sdiri , Higashi and Jamoussi 2014).The pH decreases during mass titration due to protonation of the oxide surfaces in aqueous environment.

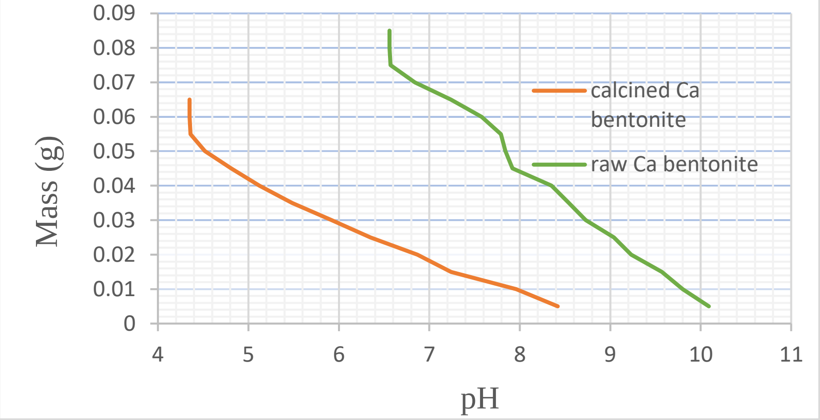


Figure 4.1: PZC of raw and calcined Ca-bentonite

4.2 Characterization results of the Adsorbent

4.2.1 Specific Surface Area and Cation Exchange Capacity

The specific surface area and cation exchange capacity of the sample were determined using ASTM C837-99 methylene blue test method. The specific area and cation exchange capacity of the raw sample were 147.1 m^2/g and 18.78 meq/100g respectively. The specific surface area and cation exchange capacity of the activated bentonite at different temperature are summarized in Table 4.2.

Table 4.2: Specific surface area and cation exchange capacity

Activation temperature (℃)	SSA (m^2/g)	CEC (meq/100g)
300	196.06	25.04
400	261.3	33.40
500	310.2	39.65

From the result in Table 4.2, thermal treatment significantly increases both specific surface area and cation exchange capacity of raw bentonite due the removal of impurities such as carbonates, water, hydroxyl groups and other organic substances. Due to thermal modification, any of the impurities mentioned above removed from the surface of bentonites and surface area available for adsorption significantly increases. The same is true for CEC, removal of impurities from the surface allow the bentonite to have free of surface charges that are available for cation exchange. Therefore, the adsorption capacity as well as removal efficiency were improved significantly. From the result in Table 4.2, the sample with largest specific surface area was selected for further analysis. In this case bentonite with SSA of $310.2 m^2/g$ was selected for adsorption of Zn(II).

4.2.2 XRD Analysis

The crystallography and composition of both raw and activated bentonite was studied using MiniFlex 300/600 (Rigaka) x-ray diffraction instrument equipped with CuKa radiation (40 kv,40mA). The characterization of the clay samples by XRD aimed to verify the existence of associated minerals and clay minerals. The results are shown below in Figure 4.2. The patterns showed the presence of diffraction peaks corresponding to angles (19.69, 26.67, 35 and 61.32º), confirming the presence of montmorillonite in the samples. The data also showed the presence of impurities such as Muscovite (17.82º), Cristobalite (22.12º), Hematite (24.26 and 55.15º), Feldspar (28.01º) and quartz (21.03 and 26.67º) in bentonite clay evaluated. Similar results were reported (De Oliveira, et al. 2016). The crystalline structure of the bentonite was preserved after the heating, what is observable from the Figure 4.2 below. Also, it could be confirmed from Figure 4.4 of differential scanning calorimetry curve, the sample did not undergo phase changes and thermally stable up to 500 º C. Therefore, the crystallinity of bentonite was preserved and no significant difference on its crystalline structure except the quartz peak at 47º appeared and other quartz peaks enlargement were indicated after thermal treatment due to partial conversion of Si^{4+} to SiO_2 and removal of impurities (Orolínová , et al. 2012). Montmorillonite (Mo), Muscovite (Mu), Quartz (Q), Cristobalite (C), Hematite (H) and Feldspar (F) are name of minerals designated in the Figure 4.2.

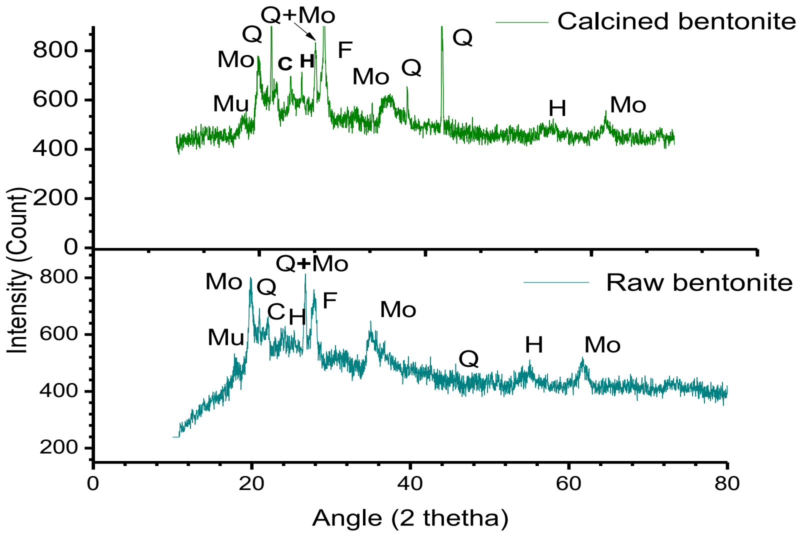


Figure 4.2: X-ray diffractogram of raw and calcined bentonite

4.2.3 FTIR Analysis

The functional groups of bentonites were characterized using spectrum 65 FT-IR (Perkin Elmer) machine. IR spectroscopy has significantly contributed to the understanding of the structure, bonding and reactivity of clay minerals. The examination for the IR spectra in the range 4000 - 400 cm^{-1} provides information on fundamental vibrational modes of the constituent units of these materials. OH, stretching and bending vibrations occur in the spectral region of 3750-3500 and 950-600 cm^{-1} respectively. Water in montmorillonite gave a broad band at about 3420-3450 cm^{-1} corresponding with the H_2O stretching vibrations. The bands corresponding with the Al-Al-OH and Al-Mg-OH bending vibrations from 950- 900 and 850-750 cm^{-1}, respectively. Si-O and Al-O stretching modes are found in the 1200-700 cm^{-1} range, while Si-O and Al-O bending modes dominate in the 600-400 cm^{-1} region (Orolínová , et al. 2012). Figure 4.3 shows the infrared spectrum of the bentonite samples. The IR spectrum of the natural bentonite did not show significant difference in comparison with the samples heated from 300- 500 °C (Orolínová , et al. 2012). The absorption band at the position about 3620 cm^{-1} is due to the stretching vibrations of structural OH groups of montmorillonites. The broad band at about 3435 and 1635 cm^{-1} corresponding with the H_2O stretching and bending vibrations respectively. A complex band at 1041 cm^{-1} is related with the stretching vibrations of Si-O groups, while the bands at 571 and 493 cm^{-1} are due to the Al-O-Si and Si-O-Si bending vibrations, respectively. The band at the position 692 cm^{-1} was assigned to the couple Al-O and Si-O out-of-plane vibrations. The band at 791 cm^{-1} was assigned to bending vibration of Al-

Mg-OH. The band at 2332.6cm^{-1} was assigned to the aliphatic C-H stretching vibration (Tomic´, Antic´ Mladenovic´ and Babic 2011). From Figure 4.3, one can observe that, the bands 3620, 3435 and 1635 cm^{-1} were reduced in size after thermal treatment due to the removal of OH^{-} groups and water. And also, the absorption band of 2332 cm^{-1} was disappeared, because the aliphatic compounds burnt out during thermal treatment that is why no absorption band was observed. Other visible changes were observed at 571 and 493 cm^{-1} bands due to conversion of Al-O-Si and Si-O-Si into oxides (Orolínová , et al. 2012).

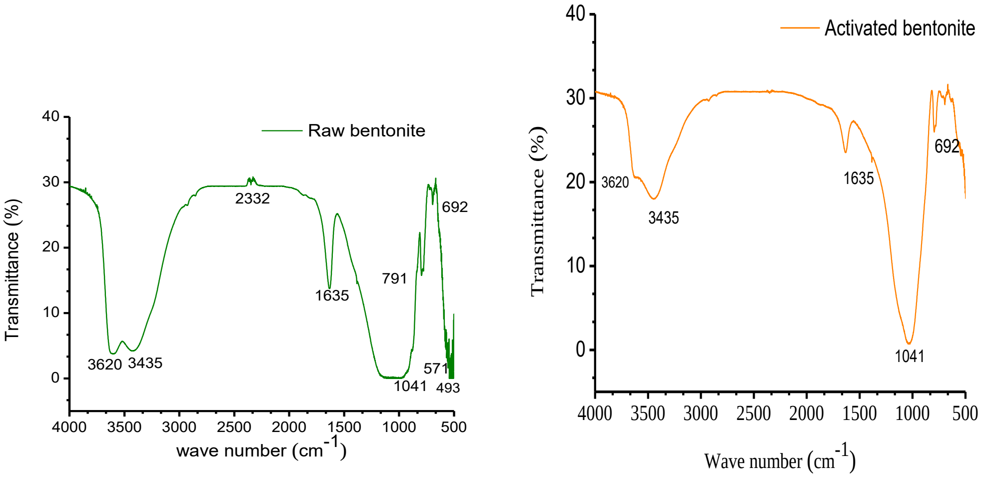


Figure 4.3: The IR spectra of raw and activated bentonite

4.2.4 DSC Analysis

The Differential thermal analysis of bentonite sample was studied using DSC 8000 (PerkinElmer) differential scanning calorimetry. Endothermic maximums between 100 and 200°C is related to water loss from the pores of bentonite, which is dehydration. From 300 to 500°C , there is a slight loss in mass due to partial loss of structural water (OH^{-}), that indicates excess heat required to remove structural water from the sample. Figure 4.4 shows differential scanning calorimetry curves of bentonite sample. Endothermic maximums between 600 and 750°C are related to dehydroxylation, and exothermic maximums between 950 and 1050°C are related to break of the crystal structure of 2:1 layers (Stojiljković, et al. 2015).

From DSC result, it can be concluded that the specific surface area as well as cation exchange capacity was enhanced without the structural loss of bentonite clay in the temperature region of 300-500℃. The differential scanning above 500℃ was not done because of operational limitation and referred from literature as indicated above. Since the sample holder is made of aluminum and doesn’t resist beyond this temperature.

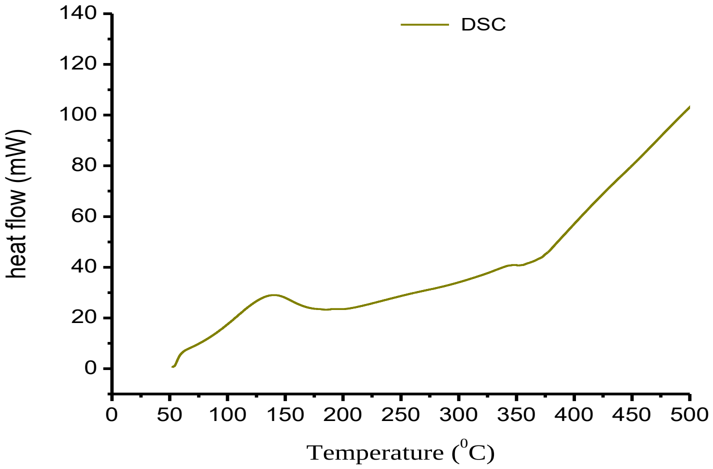


Figure 4.4: DSC curve of bentonite

4.3 Adsorption of Zn(II) onto Bentonite

Batch adsorption experiments were performed by contacting specified adsorbent dosage (0.5, 1 and 1.5g) of the calcinated bentonite powder with 50 ml of zinc aqueous solution of different initial concentrations (50, 75 and 100mg/L) at adjusted solution pH 4.5. The experiments were performed stirring with hot plate magnetic stirrer for a period of 30, 60 and 90 minutes using 250 ml Erlenmeyer flasks at room temperature (25°C). Continuous mixing was provided during the experimental period with a constant agitation speed of 275 rpm for better mass transfer with high interfacial area of contact. The residual zinc concentration was determined by novAA 400p atomic absorption spectrometry at 213.9nm maximum wavelength. The effect of different parameters on adsorption of zinc were investigated.

4.3.1 Effect of Time and Initial Concentration onto Adsorptive Capacity

From an economical point of view, the contact time required to reach equilibrium is an important parameter in waste water treatment. Adsorption of zinc was measured at given contact time 30, 60 and 90 minutes for different initial zinc concentrations 50,75 and 100 mg/L. As it is shown in

Figure 4.5, the plot reveals that the curves are a saturation type and the chemical equilibrium is attained rapidly. In fact, one can notice that there are two distinct phases, the first one is very short and adsorption is rapid due to the attachment of metal ions to the surface of adsorbent and the second is relatively slowing progressively and reached a maximum value at about 60 min. This phenomenon could be attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The equilibrium was reached within 120 min.

The two -stage sorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature (Yang, Wang and Lei 2010). The amount of Zn(II) adsorbed at equilibrium increased from 2.4949, 3.7449 and 4.4393mg/g as the initial con centration was increased from 50,75 and 100mg/L respectively. This is a result of the increase in the driving force and the concentration gradient, as an increase in the initial metal concentrations, because the resistance to the metal uptake decreased as the mass transfer driving force increased. The graphical description shown in Figure 4.5 below at condition of pH = 4.5, adsorbent dosage = 1g, stirring speed = 275rpm and temperature = 25℃.

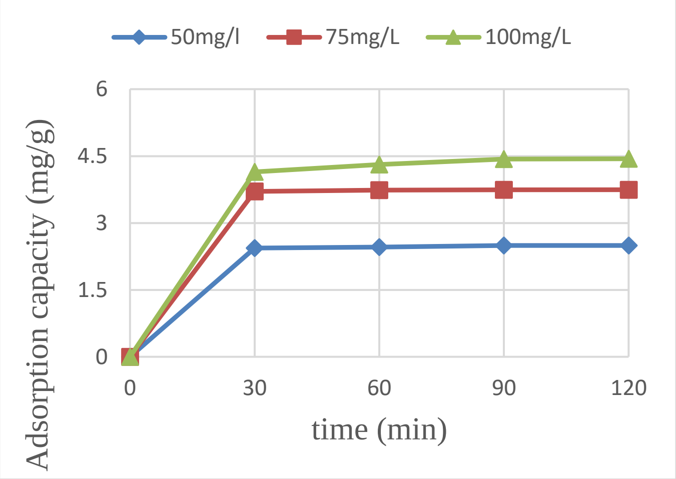


Figure 4.5: Effect of time and initial Zn(II) concentration onto adsorption capacity

4.3.2 Effect of Adsorbent Dosage onto Percentage Removal of Zn(II)

The results of the experiments with varying bentonite dosage were presented in Figure 4.6. It was found that as the amount of bentonite increased from 0.5 g to 1.5 g. The percentage removal of Zn (II)increased from 88.55 to 99.99, 87.57 to 99.86 and 81.78 to 97.93 % for initial concentration of 50, 75 and 100mg/L respectively. From those results, it was found that the optimum dosage of bentonite for Zn (II) is 1g from design of experiment. Other works had reported similar results for adsorption of metal ions (Kaya and Hakan Oren 2005). The residual concentration of zinc metal decreases as the dosage of bentonite increases. This may be due to those higher amounts of bentonite means availability of a larger surface area or a larger number adsorption sites which results higher capacity for adsorption (Kanti Sen and Gomez 2011).Those phenomena are described in Figure 4.6 below at specified conditions of pH = 4.5, time = 60min, stirring speed = 275rpm and temperature = 25℃.

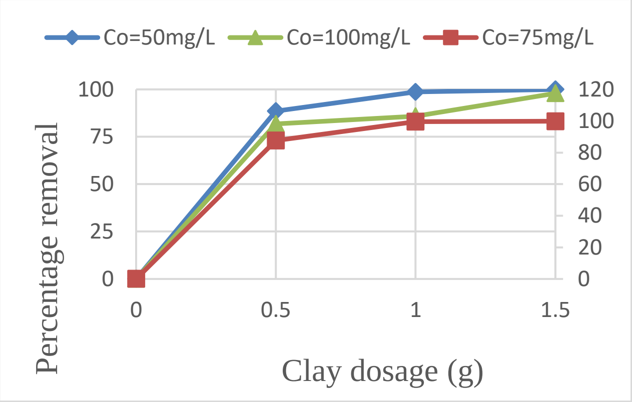


Figure 4.6: Effect of adsorbent dosage onto percentage removal of Zn(II)

4.3.3 Effect of Initial Zinc Ion Concentration

Figure 4.7, Indicates the effect of initial concentration of Zn(II) ions on the percentage removal of zinc. It was found that as the initial concentration of Zn (II) increases from 50 mg/L to 100 mg /L, the percent removal of Zn (II) decreases from 88.55 to 81.78%. This means the residual concentration in the solution increases from 5.725 to 18.22mg/L. From Figure 4.7, it was evident that at high concentration, the available sites for adsorption become fewer. This behavior of surface, prevent the metal ions from passing deeply inside the bentonite and the adsorption occurs on the surface only (Al-Asheh, Banat and Abu-

Aitah 2003). The effect of initial zinc ion concentration onto percentage removal at conditions of pH=4.5, time=60min, stirring speed =275rpm, temperature =25℃ and clay dosage= 0.5g.

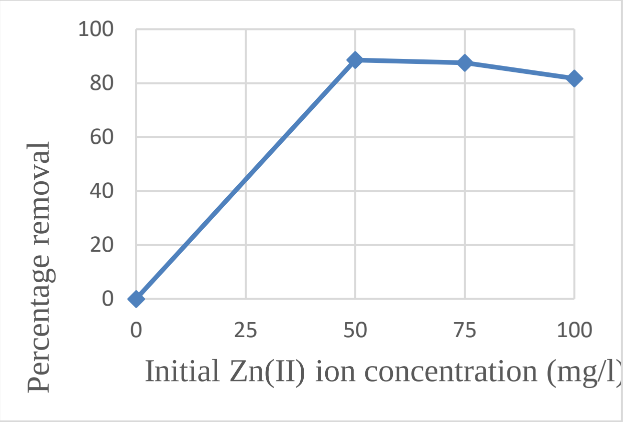


Figure 4.7: Effect of initial concentration onto percentage removal of Zn(II)

4.3.4 Effect of Contact Time

The effect of contact time onto percentage removal of zinc ions was studied. From

Figure 4.8, as the contact time between zinc ions and bentonite increased, the percentage removal increased and almost complete removal was observed after 60 mins for 50 and 75 mg/L of initial concentration of zinc ions. It was also seen that the rate of adsorption was very rapid in the first 30 minutes, then it was nearly become in equilibrium which can be explained that the available adsorption sites available were sufficient in the beginning. As the process goes on, the adsorption sites became saturated gradually. The uptake rate was controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles, so that the adsorption become much slower (AL-Anber 2010). This can be explained graphically at specified conditions of pH = 4.5, stirring speed = 275 rpm, clay dosage = 1g and temperature = 25℃.

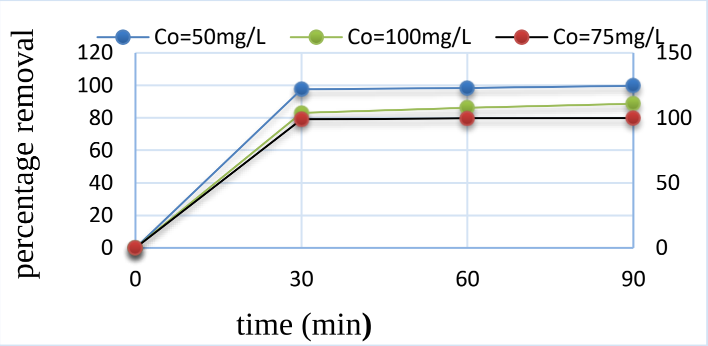


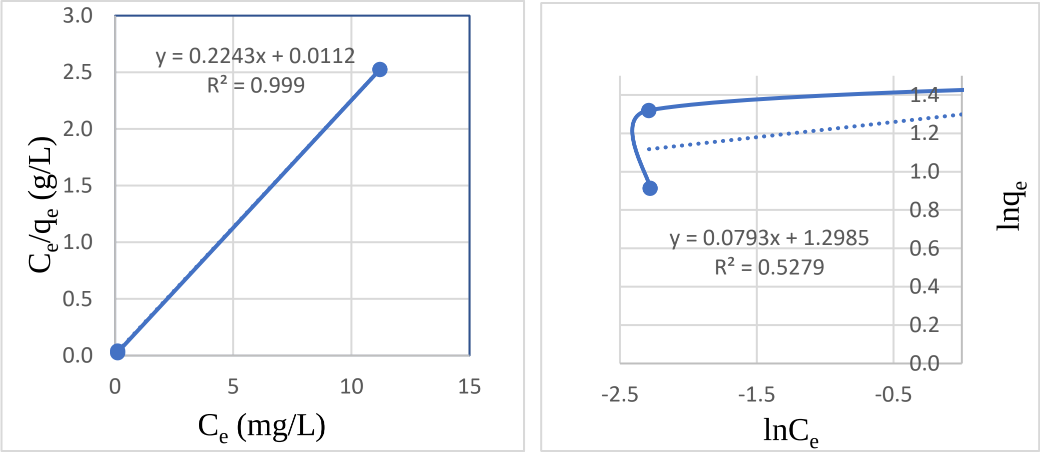
Figure 4.8: Effect of contact time onto percentage removal of Zn(II)

4.4 Adsorption Isotherm

The equilibrium data for the adsorption are commonly known as adsorption isotherms. It is essential to know them so as for comparing the effectiveness of different adsorbent materials under different operational conditions and to design and optimize an adsorption system. Adsorption equilibrium was studied and the experimental data were examined to which model the data better fits. In this study, both Langmuir and Freundlich isotherms models were used. The values of various constants of the two models were calculated and presented in Table 4.3. By comparing the correlation coefficients, it was observed that Langmuir isotherm gives a good model for the adsorption system, which is based on monolayer sorption onto the surface of finite number of identical sorption sites. Figure 4.9a, also confirms that Langmuir model better fits the experimental data than Freundlich model. The maximum adsorption capacity of zinc from Langmuir isotherm was found to be 4.4583 mg/g and all the R_L values are for 50-100mg/L are 0.0005-0.001which are within the favorable adsorption range ($0<R_L<1$).

Table 4.3: Langmuir and Freundlich models' constants

Isotherm	Parameters
Langmuir	
q_m (mg/g)	4.4583
K_L (L/mg)	20.0269
R^2	0.999
R_L	0.0005-0.001
Freundlich	
K_F ($mg^{1-1/n}$)	1.083
n	12.61
R^2	0.5279



a) b)

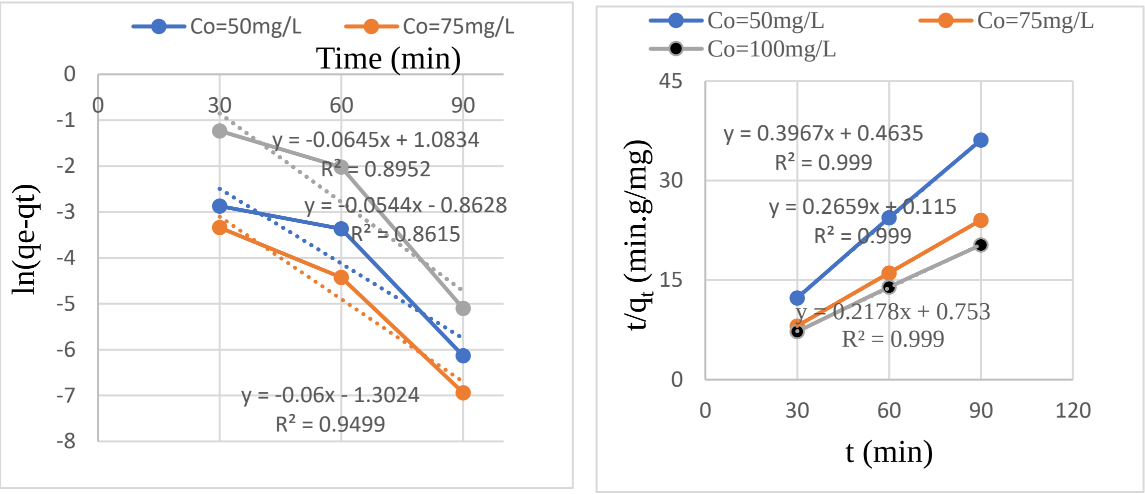
Figure 4.9: Fitting lines of (a) Langmuir and (b) Freundlich isotherms

4.5 Adsorption Kinetics

The kinetics of adsorption was studied for a contact time of 30, 60, 90 and 120min. The experimental data was fitted to the pseudo first and second order kinetic model in Figure 4.10. The R^2 value indicates that the experimental results show better fit to pseudo-second order model. Parameters for both pseudo first and second order kinetic models were determined from linear plot of experimental data and summarized in Table 4.4.

Table 4.4: Values of pseudo-first and second order kinetic model constants

Pseudo first order kinetic					**Pseudo second order kinetic**		
C_o (mg/L)	q_e, exp (mg/g)	q_{e1}, cal (mg/g)	K_1 (min^{-1})	R^2	q_{e2}, cal (mg/g)	K_2 (g/mg min)	R^2
50	2.4949	0.422	0.0544	0.862	2.521	0.3395	0.999
75	3.7449	0.272	0.06	0.95	3.761	0.615	0.999
100	4.4393	2.955	0.0645	0.895	4.5913	0.2893	0.999



a) b)

Figure 4.10: Fitting lines of (a) Pseudo first and (b) second order kinetic models

4.6 Statistical Design Experiment

Box-Behnken method was used to study the influence of the test factors and response value. The Box-Behnken design optimization process involves main steps: (i) conducting designed experiments; (ii) proposing the statistical model using regression analysis technique; (iii) Using diagnostic plots to checking the adequacy of the obtained model and experimental results; (iv) predict the experiment response at a certain factor and level combination and consequently checking model using a confirmation test (Ray, Lalman and Biswas 2009).

4.6.1 Model Selection and Adequacy Checking

To estimate the regression coefficient, a multiple regression analysis was performed on the experimental data. Linear, interactive, quadratic and cubic models were fitted to the experimental data to obtain the regression equations. To decide about the adequacy of models among the various models to represent, two different common tests namely sequential model sum of squares and model summary statistics were carried out (Ray, Lalman and Biswas 2009) . According to Table 4.5 and Table 4.6, Cubic model was found to be aliased. Sequential model sum of squares indicate that the p-value was lower than 0.01 for quadratic model only. Model summary statistics showed that the excluding cubic model which was aliased, quadratic model was found to have maximum adjusted R-squared and the predicted R-squared values. Therefore, quadratic model was chosen for further analysis.

Therefore, after performing experiments according to Box-Behnken design in Table 4.7, second-order polynomial (as the model of the experimental design) function of the adsorption capacity with interaction factors terms was obtained in equation 4.2.

Model equation in terms of coded factors:

$$\mathrm{Logit(Removal\ (\%))} = \mathrm{Ln}[(\mathrm{Removal\ (\%)} - 81.779)/(99.90 - \mathrm{Removal\ (\%)})]$$

$$= +3.89 + 1.34A - 2.03B + 2.98C + 0.64A^2 - 3.71B^2 - 2.37C^2 + 0.90\ AC + 2.98BC \qquad (4.2)$$

where Logit(Removal (%)) is predicted percent removal (%), and A, B and C are the coded variables corresponding to the time, initial Zn(II) concentration and adsorbent dosage, respectively.

ANOVA is a common statistical method that assays the significance and the adequacy of the total variation in a set of data into component parts associated with specific sources of variation for the target of trial hypotheses on the factors of the model (Mourabet, et al. 2012). Also, this technique was used to test the statistical significance of the proposed quadratic model. To measure how well the suggested model fits the experimental data, the statistical parameters of F-value, R^2, p-value, and lack of fit were evaluated (Chowdhury, Chakraborty and Saha 2013). The ANOVA result is reported in Table 4.7. From data in Table 4.7, it can be fined that the model was highly significant at 95% of confidence level for uptake of Zn(II) using modified bentonite due to its p-value is lower than 0.0001. Thus, the model can be used to predict the percentage removal with Eqn 4.1 . As a general rule, values of p-value less than 0.05 indicates the significant of the source of variation. The p-value of the lack of fit term is 0.078 and it implies that the lack of fit is not significant relative to the pure error. The model has to be transformed into other function to minimize the errors (Zhang, et al. 2015). In this case Logit transform function was choosen

Table 4.5: Model summary statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	Precision	
Linear	3.11	0.4841	0.3651	0.0495	232.02	
2FI	2.95	0.6429	0.4287	-0.2970	316.58	
Quadratic	0.42	0.9950	0.9885	0.9210	19.28	Suggested
Cubic	0.076	0.9999	0.9996			Aliased

Table 4.6: Sequential model sum of squares

Source	Sum of Squares	DF	Mean Square	F Value	P value	
Mean	30.17	1	30.17			
Linear	118.17	3	39.39	4.07	0.0305	
2FI	38.76	3	12.92	1.48	0.2781	
Quadratic	85.93	3	28.64	163.58	< 0.0001	Suggested
Cubic	1.20	3	0.40	69.48	0.0007	Aliased

Table 4.7: ANOVA for response surface reduced quadratic model

Source	Sum of squares	DF	Mean square	F Value	p value	
Model	242.81	8	30.35	189.26	< 0.0001	significant
A	14.28	1	14.28	89.04	< 0.0001	
B	33.05	1	33.05	206.10	< 0.0001	
C	70.84	1	70.84	441.77	< 0.0001	
A^2	1.72	1	1.72	10.70	0.0113	
B^2	57.82	1	57.82	360.55	< 0.0001	
C^2	23.60	1	23.60	147.16	< 0.0001	
AC	3.25	1	3.25	20.28	0.0020	
BC	35.45	1	35.45	221.09	< 0.0001	
Residual	1.28	8	0.16			
Lack of Fit	1.26	4	0.31	2.59	0.078	not significant
Pure Error	0.023	4	5.770E-003			
Cor total	244.09	16				

Table 4.8: Correlation coefficients

Standard Deviation	0.40	R^2	0.9947
Mean	1.33	Adj R^2	0.9895
Coefficient of variation	30.06	Pred R^2	0.9496
Precision	12.29	Adequacy Precision	60.208

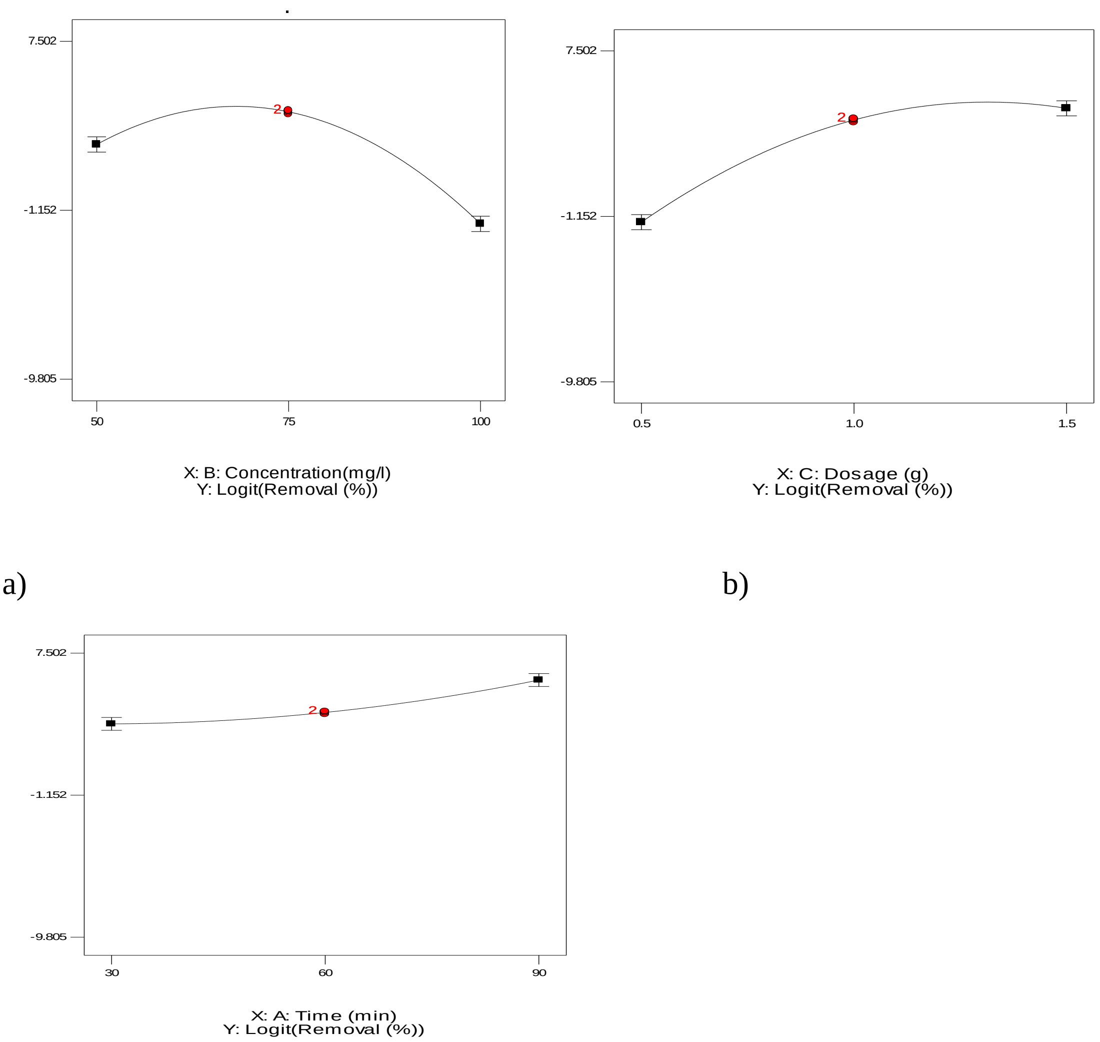
Therefore, the model was transformed into Logit function for the sake of error minimization. The quality of the regression equation was further expressed by the correlation coefficients: R^2, adj R^2 and pred R^2 which represents, the experimental, adjusted and model predicted values respectively. Adj R^2 is a modified R^2 that has been adjusted for the number of terms in the model and the proximity of these values indicates that unnecessary variables have not been included. From Table 4.8 correlation coefficients R^2, Adj R^2 and pred R^2 values were 0.9947, 0.9895 and 0.9496, respectively. The obtained result shows little difference between the values of Adj R^2 and pred R^2 (0.0399) indicates that there is a good correlation between the model and the experimental data. As a general rule, the difference higher than 0.2 in the values of R^2, adj R^2 and pred R^2 indicate the objection with the experimental data and the fitted model (Mourabet, et al. 2012).

Based on the ANOVA Table 4.7, the P-values were utilized as a tool to introduce the significant or non-significant variables. Each variation source with p-value less than 0.05 would be a significant one. Accordingly, the effects of A, B, C, A^2, B^2, C^2, AC and BC were significant, while AB was the non-significant variable. It implies that the initial Zn(II) concentration, adsorbent dosage, and time interaction have a significant effects on the adsorption capacity. As it can be find from Table 4.7, the effects of initial concentration, time and adsorbent dosage were highly significant ($p < 0.0001$). In conclusion, a suitable model for Zn^{2+} adsorption was provided by the regression equation Eqn 4.2.

4.6.2 Effect of Adsorption Process Variables

4.6.2.1 Effects Individual Factors onto Percentage Removal of Zn(II)

The effect of each individual factor was studied and shown in Figure 4.11 below. From Figure 4.11a, one can see that adsorption efficiency increase to a certain level and remain stable as concentration increases. Since the adsorption sites were saturated. In Figure 4.11 b, percentage removal increases with increasing adsorbent dosage due to the availability of unsaturated sites for adsorption. In similar manner from Figure 4.11c, percentage removal increases as contact time increases because having sufficient time allows enough time for the adsorbate to get adsorbed onto the adsorbent surface. Similar findings were reported (Sevil and Bilge 2007).



a)

b)

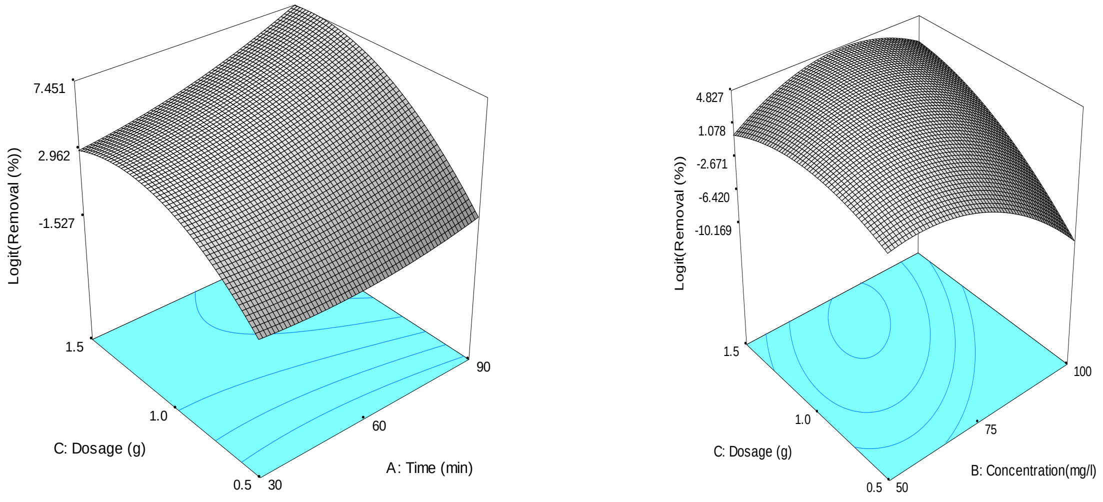
c)

Figure 4.11: Effects of individual factors

4.6.2.2 Effects Interaction Factors onto Percentage Removal of Zn(II)

The graphical representations were drawn according to the regression analysis and used to demonstrate the relationship between the percentage removal and factors. These plots are useful for investigating the main and interaction effects of the variables. Figure 4.12a and b shows the adsorbent interaction with concentration and contact time respectively. From Figure 4.12a, it can be seen that percentage removal increases as time increases and reach maximum at 1.5g adsorbent dosage and 90minute. Interaction is highly significant at high adsorbent dosage and contact time due to the presence of unsaturated sites and having sufficient contact time enables adsorbate molecules easily adsorbed.

Figure 4.12b, shows the combined effect of the initial concentration and adsorbent dosage on the percentage removal of Zn(II). When the adsorbent dosage is constant, the percentage removal increases to a certain level with an increase of initial zinc ion concentration. Mass transfer driving force would increase logically with an increase of the initial zinc ion concentration. However, increasing initial concentration enhances the probability of the collision between the adsorbate molecules and the adsorbent adsorbing sites (Sepehr, et al. 2014). And also, a decrease in percentage removal as concentration increases and become stable due to saturation of adsorption sites. In the same manner, when the initial zinc ion concentration is constant, the percentage removal would decrease gradually with decreasing adsorbent dosage. The resulted percentage removal decrement can be mainly due saturation of adsorbent sites during the adsorption and therefore, excess amounts of adsorbent would be required for the uptake of zinc ions (Sepehr, et al. 2014). The maximum percentage removal was observed at adsorbent dosage of 1gram and initial zinc ion concentration of 75mg/L.



a) b)

Figure 4.12: Effect of the interaction factors

4.6.3 Optimum Design Conditions

Model validation or the experimental confirmation is the final step in the optimization process using response surface model. The model developed from experimental data is confirmed as follows using optimization by point prediction at 95%CI in Table 4.9 below.

Table 4.9: Optimized response value

	Prediction	SE Mean	95% CI low	95% CI high	SE Pred	95% PI low	95% PI high
Logit (Removal (%))	3.890	0.18	3.48	4.30	0.44	2.88	4.90

From Table 4.9, the optimum design conditions are concentration=75mg/L, time=60min and adsorbent dosage =1g. At this optimum design conditions the percentage of zinc ion removal was 99.54%.

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The results of this study indicate that bentonite can be successfully used for the Zn^{2+} ion removal from aqueous solutions. Natural clays present a major advantage of giving low cost recovery processes making them suitable for use in water purification and wastewater treatment. Taking into account the results, I have considered it of great interest to assess the ability of locally available bentonite for the adsorption of metal ions from aqueous solutions in the batch technique and optimization of conditions for its adsorption. The empirical values are evaluated according to the Langmuir and Freundlich isotherms that are generally used to describe the adsorption processes. It is stated that the Langmuir isotherm model fit very well the experimental data. It is also determined that the adsorption is fast in the first 30minute and become slower time periods. Maximum removal efficiencies were succeeded within 60 min. Optimum design conditions were determined after optimization by point prediction and optimum zinc adsorption achieved at contact times 60min, initial zinc ion concentration of 75mg/L and adsorbent dosage 1g. Zinc(II) adsorption from aqueous solutions using Ethiopian bentonite is well described with the second order reaction kinetic and q_e, calculated and q_e, experimental values are quite close to each other whereas in the first order kinetic the difference between these values are greater. Furthermore, the correlation coefficients are higher in the second order reaction kinetic. As a result of this study, it can be concluded that Ethiopian bentonite, can be used for elimination of heavy metal pollution from wastewater since it is a low-cost, abundant and locally available adsorbent.

5.2 Recommendation

Thermal modification was performed to improve the adsorptive capacity of bentonite without structural loss of the adsorbent. Thus, thermal modification confirms that improved uptake of zinc ions from aqueous solution in batch studies. Zn(II) ions can be further investigated under continuous flow conditions for real wastewater. The following recommendation can be made for the future study:

- A combination of modification method: acid treatment followed by thermal treatment can be used to improve the surface properties of the adsorbent that maximizes its adsorptive capacity.
- Adsorption of different heavy metals can be conducted and compared to check the adsorbent preference to certain metals.
- Other factors which are not addressed by this study such as temperature, shaking speed and pH that had been taken as constant can be considered and thermodynamics study can be conducted.
- Adsorption performance evaluation of the adsorbent onto real wastewater could be conducted.
- The multiple application of this adsorbent other than waste treatment can be assessed, evaluated, analyzed and tested.
- A pilot-scale column with the developed adsorbent can be conducted for real wastewater.

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APPENDICES

Appendix A: Calculations and experimental data

Table 1.1: The Experimental response value results

No.	Factors			Final concentration (mg/L)	Response: Removal (%) =(C_o-Ct)/C_o *100
	A: Time (min)	B: Concentration (mg/L)	C: Dosage(g)		
1	30	50	1	1.235	97.53
2	90	50	1	0.1458	99.71
3	30	100	1	17.0412	82.96
4	90	100	1	11.3351	88.67
5	30	75	0.5	10.9275	85.43
6	90	75	0.5	7.7145	89.71
7	30	75	1.5	0.8753	98.83
8	90	75	1.5	0.0825	99.89
9	60	50	0.5	5.726	88.55
10	60	100	0.5	18.2201	81.78
11	60	50	1.5	0.0057	88.55
12	60	100	1.5	2.0723	97.93
13	60	75	1	0.3752	99.49
14	60	75	1	0.3414	99.55
15	60	75	1	0.3517	99.53
16	60	75	1	0.3402	99.55
17	60	75	1	0.3317	99.56

Table 1.2: Diagnostics case statistics

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t
1	1.89	1.40	0.49	0.750	2.364	1.676	4.873 *
2	4.55	4.31	0.24	0.750	1.131	0.384	1.159
3	-2.66	-2.43	-0.24	0.750	-1.131	0.384	-1.159
4	-0.49	6.212E-003	-0.49	0.750	-2.364	1.676	-4.873 *
5	-1.38	-1.25	-0.13	0.750	-0.610	0.112	-0.580
6	-0.25	-0.38	0.13	0.750	0.623	0.116	0.593
7	2.77	2.90	-0.13	0.750	-0.623	0.116	-0.593
8	7.50	7.37	0.13	0.750	0.610	0.112	0.580
9	-0.52	-0.15	-0.37	0.750	-1.754	0.923	-2.169
10	-9.80	-10.17	0.36	0.750	1.741	0.910	2.141

11	-0.52	-0.15	-0.36	0.750	-1.741	0.910	-2.141
12	2.10	1.74	0.37	0.750	1.754	0.923	2.169
13	3.77	3.89	-0.12	0.200	-0.331	0.003	-0.309
14	3.93	3.89	0.038	0.200	0.101	0.000	0.093
15	3.87	3.89	-0.019	0.200	-0.051	0.000	-0.047
16	3.93	3.89	0.038	0.200	0.101	0.000	0.093
17	3.96	3.89	0.067	0.200	0.180	0.001	0.167

Table 1.3: Adsorption equilibrium study

Time (min)	C_o=50mg/L		C_o=75mg/L		C_o=100mg/L	
	C_t	q_t	C_t	q_t	C_t	q_t
30	1.235	2.4383	0.8102	3.7095	17.0412	4.1479
60	0.7904	2.4605	0.3414	3.7329	13.8632	4.3068
90	0.1458	2.4927	0.1209	3.7440	11.3351	4.4332
120	0.1024	2.4949	0.1015	3.7449	11.2134	4.4393

Table 1.4: Bulk density determination

Run	m_{pc} (g) (1)	m_s (g) (2)	$m_{pc} + m_{sol}$ (g) (3)	$m_s + m_{pc} + m'_{sol}$ (g) (4)	m_{sol} (g)	m'_{sol} (g)
					(3) –(1)	(4)- (2)- (1)
1	28.197	8	77.8501	82.5392	49.6531	46.3422
2	28.197	8	77.8033	82.5241	49.6063	46.3271
3	28.197	8	77.8023	82.4923	49.6053	46.2953

Mass of pycnometer (m_{pc}) =28.197g

Mass of sample (m_{s}) =8g

V_s =volume of the solid

m_{sol} = mass of solution filled in empty pycnometer

Note: m_{sol} was used to denote the mass of solution filled in empty pycnometer, m'_{sol} for the mass of the solution in pycnometer together with sample and V'_{sol} is for solution volume in the pycnometer together with the sample.

$\rho sol = m_{sol}/V_{sol}$ (1)

$V'sol = m'_{sol} / \rho sol$ (2)

$Vs = V - V'sol$ (3)

$\rho s = m_s / V_s$ (4)

Where V = V_{sol} = volume of pycnometer=50ml and V'sol =volume of solution filled in pycnometer with the sample.

Table 1.5: Calculated bulk density results

run	ρsol(kg/m3)	V'sol (ml)	Vs (ml)	ρs (kg/m3)	Average ρs (kg/m3)
1	993.062	46.666	3.334	2,399.52	2,406.06
2	992.126	46.695	3.305	2,420.57	
3	992.106	46.664	3.336	2,398.08	

Table 1.6: Specific surface area and cation exchange capacity

No.	Item	Activation temperature (℃)	Number of increments (N)	Injected volume (V_I)	Total volume injected
1	Raw	-----------	9	5ml	45ml
2	Activated	300	12	5ml	60ml
3	Activated	400	16	5ml	80ml
4	Activated	500	19	5ml	95ml

Specific surface area and cation exchange capacity

I) $SSA = \frac{m_{MB}}{M_{MB}} A_v \, A_{MB} \frac{1}{m_s}$ (1) II) $CEC = 100 \frac{V_{MB}}{m_s} N_{MB}$ (2)

Where m_{MB} is the mass of the adsorbed methylene blue at the point of complete replacement, m_s is the mass of the clay specimen, M_{MB} is the molecular weight of methylene blue dye which is 319.87g/mol, Av is Avogadro’s number ($6.02 * 10^{23}$/mol), A_{MB} is the area covered by one methylene blue molecule which is 130Å² ($1A°= 0.1nm=10^{-10}$ m), V_{MB} is the volume of methylene blue injected and N_{MB} is the normality of the methylene blue (meq/100g).

$n = \frac{m}{M} = \frac{10g}{319.87g/mol} = 3.13 * 10^{-2}mol$

$C = \frac{n}{V} = \frac{3.13*10^{-2}\text{mol}}{1\text{L}} = 3.13 * 10^{-2}$mol/L, $N_{MB} = Z*C = 3.13 *10^{-2}$ eq/L

Where Z is valence of methylene blue which is equal to 1equi/mol

To calculate m_{MB} adsorbed at the point of complete replacement, first calculate mole of methylene blue adsorbed from methylene blue solution and injected volume.

1) Raw bentonite

$C = \frac{n}{V_{MB}}$, $n = C* V_{MB} = 0.0313\text{mol/L}*0.045\text{L} = 1.41*10^{-3}$ mol

Then $m_{MB} = n*M = 1.41*10^{-3}\text{mol}*319.87\text{g/mol} = 0.451$ g

2) Activated at 300 ℃

$C = \frac{n}{V_{MB}}$, $n = C* V_{MB} = 0.0313\text{mol/L}*0.125\text{L} = 1.878*10^{-3}$ mol

Then $m_{MB} = n*M = 1.878*10^{-3}\text{mol}*319.87\text{g/mol} = 0.601$ g

3) Activated at 400 ℃

$C = \frac{n}{V_{MB}}$, $n = C* V_{MB} = 0.0313\text{mol/L}*0.08\text{L} = 2.504*10^{-3}$ mol

Then $m_{MB} = n*M = 2.504*10^{-3}\text{mol}*319.87\text{g/mol} = 0.801$ g

4) Activated at 500 ℃

$C = \frac{n}{V_{MB}}$, $n = C* V_{MB} = 0.0313\text{mol/L}*0.095\text{L} = 2.974*10^{-3}$ mol

Then $m_{MB} = n*M = 2.974*10^{-3}\text{mol}*319.87\text{g/mol} = 0.951$g

Specific surface area and cation exchange capacity

A) $\text{SSA} = \frac{\text{m}_{\text{MB}}}{\text{M}_{\text{MB}}} \text{A}_{\text{v}}\ \text{A}_{\text{MB}} \frac{1}{\text{m}_{\text{s}}}$

B) $\text{CEC} = 100 \frac{V_{MB}}{m_s} N_{MB}$

i) Raw

$\text{SSA} = \frac{m_{MB}}{M_{MB}} A_v\ A_{MB} \frac{1}{m_s} = \frac{0.451\text{g}}{319.87\text{g/mol}} *6.02 *10^{23}/\text{mol}*1.3*10^{-18}\text{m}^2*\frac{1}{7.5g} = 147.1\text{m}^2/\text{g}$

$\text{CEC} = 100 \frac{V_{MB}}{m_s} N_{MB} = 100*\frac{0.045L}{7.5g} *3.13*10^{-2}\ \text{eq/L} = 2.84 *10^{-2}\ \text{eq/g} = 0.01878\text{eq/g} = 18.78$ meq/g

ii) Activated at 300 ℃

$\text{SSA} = \frac{m_{MB}}{M_{MB}} A_v\ A_{MB} \frac{1}{m_s} = \frac{0.601}{319.87\text{g/mol}} *6.02 *10^{23}/\text{mol}*1.3*10^{-18}\text{m}^2*\frac{1}{7.5g} = 196.06\text{m}^2/\text{g}$

CEC = $100\,\frac{V_{MB}}{m_s}\,N_{MB}$ = $100*\frac{0.06L}{7.5g}$ $*3.13*10^{-2}$ eq/L = 0.02504 eq/g= 25.04 meq/g

iii) Activated at 400 ℃

SSA = $\frac{m_{MB}}{M_{MB}}\,A_v\,A_{MB}\,\frac{1}{m_s}$ = $\frac{0.801\text{g}}{319.87\text{g/mol}}$ $*6.02*10^{23}$/mol$*1.3*10^{-18}$m$^2*\frac{1}{7.5g}$ = 261.3m^2/g

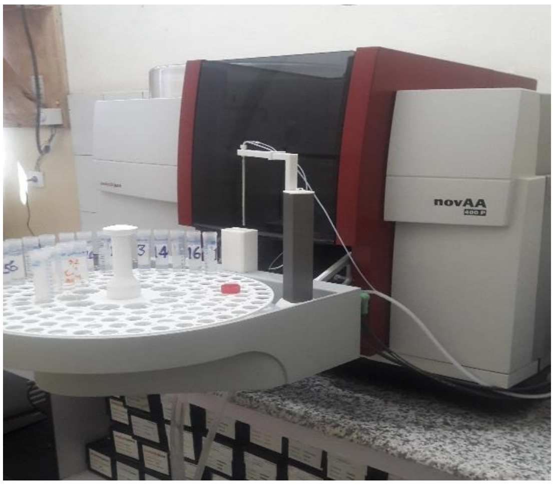
CEC = $100\,\frac{V_{MB}}{m_s}\,N_{MB}$= $100*\frac{0.08\text{L}}{7.5\text{g}}$ $*3.13*10^{-2}$ eq/L= 0.0334eq/g= 33.4 meq/g

iv) Activated at 500 ℃

SSA = $\frac{m_{MB}}{M_{MB}}\,A_v\,A_{MB}\,\frac{1}{m_s}$ = $\frac{0.951\text{g}}{319.87\text{g/mol}}$ $*6.02*10^{23}$/mol$*1.3*10^{-18}$m$^2*\frac{1}{7.5g}$ = 310.2m^2/g

CEC = $100\,\frac{V_{MB}}{m_s}\,N_{MB}$= $100*\frac{0.095\text{L}}{7.5\text{g}}$ $*3.13*10^{-2}$ eq/L= 0.03965eq/g= 39.65 meq/g

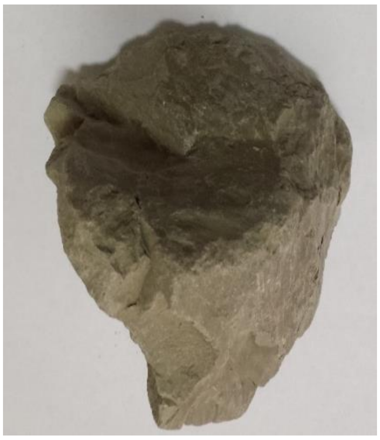
Appendix B: Main equipment photos



novAA 4000p atomic absorption spectroscopy 65 FT-IR (Perkin Elmer)

DSC 8000 (PerkinElmer) SONOREX RK 106 S

Appendix C: Photos of main experimental activities



Raw bentonite pretreated bentonite Swelling index test

Bulk density measurement

PZC test

Adsorption experiment

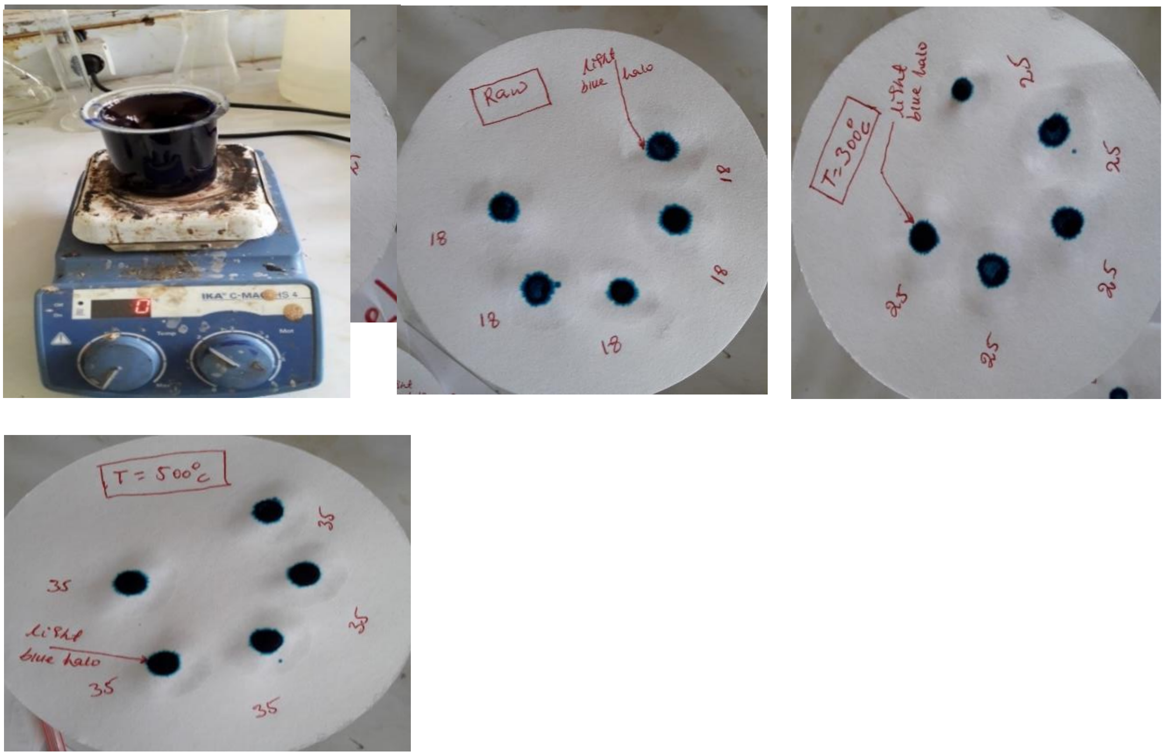
Result

Raw

Activated at 300℃

Activated at 400 ℃

Activated at 500℃



Methylene blue test of the raw and activated bentonite at different temperature