Investigation of Adsorption Capacity of Ledi's Afar Region Natural Bentonite for Removal of Pb (II), Cd (II) and Cu (II) From Aqueous Solution

By:

Sanyi Gudina Gutema

A Thesis Submitted to

The department of chemistry

School of natural science

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in chemistry

Office of Graduate Studies

Adama Science and Technology University

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September, 2017

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Advisor: Tegene Desalegn (PhD)

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Approval of Board of Examiners

We, the undersigned, members of the Board of Examiners of the final open defense by Sanyi Gudina have read and evaluated his thesis entitled" Determination of adsorption capacity of natural bentonite for removal of heavy metals (Pb (II), Cd (II) and Cu (II)" and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of master's.

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To: chemistry department

Subject: Thesis Submission

This is to certify that the thesis/dissertation entitled “Investigation of Adsorption Capacity of Ledi Afar Region Natural Bentonite for Removal of (Pb (II), Cd (II) and Cu (II)) From Aqueous Solution” submitted in partial fulfillment of the requirements for the degree of Master’s in science, the Graduate program of the department of chemistry, and has been carried out by Sanyi Gudina Id. No GSS/0222/05, under my/our supervision. Therefore, I recommend that the student has fulfilled the requirements and hence hereby he can submit the thesis to the department.

_____	_____	_____
Name of major Advisor	Signature	Date

DECLARATION

I hereby declare that this MSc Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

Name: Sanyi Gudina

Signature:_____

This MSc Thesis has been submitted for examination with my approval as thesis advisor

Name: _____

Signature:_____

Date of submission_____

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ACRONYMS

AAS	Atomic absorption spectroscopy
LOI	Loss on ignition
Rpm	rate per minute

ABSTRACT

Bentonite clay in its natural form, obtained from Afar region, near Ledi river, was utilized as a low-cost adsorbent for removal Cu^{2+}, $Cd^{2+}$and Pb^{2+} ions from aqueous solution. This clay material was characterized with X-ray diffraction and elemental analysis (complete silicate analysis). Batch adsorption experiments were carried out as a function of initial concentration of metal ions, amount of adsorbent, pH and contact time with natural bentonite. The maximum removal efficiency obtained for each parameter were: from effect of dose, for Pb^{2+} (% removal=99.9%),for Cu^{2+}(% removal =99.99%), for Cd^{2+}(% removal=99.95%),from effect of contact time, for Pb^{2+} (% removal=99.78%), for Cu^{2+} (% removal=99.46%), for Cd (% removal=99.95%), from effect of pH, for Pb^{2+} (% removal= 100%),for Cu^{2+} (% removal=99.66%), for Cd^{2+}(% removal=99.06%), from effect of initial concentration, for Pb^{2+} (% removal=100%), for Cu^{2+} (% removal=82.08%), for Cd^{2+} (% removal =99.9%).The result obtained revealed, it was found that the removal of ions depends on initial concentration, amount of adsorbent, pH of solution and contact time. In treatment with clay, the removal of Cu (II), Cd (II) and Pb (II) ions from aqueous solution generally was very efficient for the three heavy metal ions. Except copper in acidic solution, the percent removal for all parameters were performed more than 95% was achieved by natural Bentonite. Therefore, natural Bentonite obtained from Afar region near Ledi River is an important adsorbent of heavy metal from aqueous solutions. The data obtained from adsorption experiment are fitted better with the Langmuir isotherm compared to the Freundlich model. The value of separation factor, (R_L =0.322) from Langmuir equation gives an indication of favorable adsorption.

Key words: Natural Bentonite, Adsorption, heavy metal, adsorbent

CHAPTER ONE

1. INTRODUCTION

1.1. Back ground of the study.

Next to oxygen, water is the most important substance for human existence and it is essential for everything on our planet to grow and prosper [1]. Freshwater rivers, lakes and ground water are used to irrigate crops, to provide drinking water and to act as a sanitation system. Although we as humans recognize this fact, we disregard it by polluting our rivers, lakes, and oceans. Most of our water resources are gradually becoming contaminated due to the addition of foreign materials from the surroundings [2]. These include organic matter of plant and animal origin, land surface washing and industrial and sewage effluents. Rapid urbanization and industrialization with improper environmental planning often lead to discharge of industrial and sewage effluents into rivers. In addition to the process of desertification, pollution is also reducing the volume of safe fishing, irrigation and drinking water. The problem of water pollution due to toxic metals has begun to cause concern now in the world [3].

Heavy metals have been immoderately released into the environment due to rapid industrial development and cause a major problem worldwide. The pollution of heavy metal ions can arise from many sources but most commonly arises from metal plating, mining activities, pesticides, battery production, tanneries and photographic industries, etc. [4]. Heavy metal ions are reported priority pollutants, due to their mobility in natural water ecosystems and toxicity [5]. Heavy metal ions are stable and persistent environmental contaminants since they cannot be degraded and destroyed [6]. These problems initiate the researcher to conduct this research.

Traditional technologies for the removal of heavy metals from water and waste water include precipitation, ion exchange, adsorption, coagulation, electrolysis, extraction membrane separation and reverse osmosis [7]. These methods differ in their effectiveness and cost. Chemical precipitation, reverse osmosis and other methods (ultrafiltration, electrochemical deposition etc.) become inefficient when contaminants are present in trace concentration and do not seem to be economically feasible for such industries because of their relative high costs [8]. Therefore, there is a need to look into alternatives to investigate a low-cost method which is effective and

economic. For high strength and low volumes of wastewater, heavy metal removal by adsorption technique is good proposition. Adsorption is one of the alternatives for such cases and is an effective purification and separation technique used in industry especially in water and wastewater treatments [9]. It is the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. Adsorption has advantages over other methods. The design is simple, and it is sludge-free and can involve low investment in terms of both the initial costs and land. Cost is an important parameter for comparing the adsorbent materials [10].

Various substances, such as activated carbon, natural and synthetic zeolites, aluminosilicate (clay minerals) and ion exchange resins have been used as adsorbents for the removal of heavy metals from water and wastewater [11]. Clay has typical properties (large surface area, high cation exchange capacity, chemical and mechanical stability and a layered structure) that predispose them to be good adsorbents. Bentonite belongs to the group of clay minerals. Bentonite is clay consisting essentially of smectite mineral of the montmorillonite group [12]. Montmorillonite, kaolinite, and illite are widely used in adsorption because of their high specific surface area, chemical and mechanical stability, a variety of surface and structural properties, and low cost [13].

Adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed by natural clay [14]. Adsorption isotherm is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent (e.g., natural bentonite) and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations [15]. The three well known isotherms are: a) Freundlich, b) Langmuir, and c) BET adsorption isotherm [16]. Then, the main objective of this paper was to investigate adsorption capacity of natural bentonite for removal of heavy metal from aqueous solution.

1.2. Statement of the problem

Natural and artificial/man made factors are responsible for the pollution of water in any of the countries in the world. Human waste is often disposed of in nearby surface water bodies in which people use water for convenience. This contributes to the contamination of water sources [17].

Heavy metals from waste water can accumulate and persist in soils at an environmentally hazardous level [18]. This constitutes serious health and environmental concerns because of phytotoxicity of these metals to the plants and the potentially health implications to humans and animals consuming such vegetables [19].

Trace metals may enter the human body via consumption of contaminated drinking water or ingestion of soil or crops grown on contaminated land [20]. Metals such as lead, mercury, cadmium and copper are cumulative poisons, cause environmental hazards and are reported to be exceptionally toxic [21]. These metals are a major source of oxidative stress in the cell and play an important role in the etiology of diverse human pathologies such as carcinogenesis [22]. Exposure to heavy metal toxicity leads to brain damage, mental retardation, cerebral palsy, lung cancer, gastrointestinal abnormalities, and dermatitis, and death of the unborn fetus [23].

A number of studies are already available which deal with elimination of heavy metal ions using various kinds of adsorbents. However, there is little or no report on the removal of heavy metal using natural Bentonite from afar region, Ethiopia. This work attempts to focus on determination of adsorption capacity of natural Bentonite obtained from Afar regional state for the removal of Pb (II), Cd (II) and Cu (II) using natural bentonite and compare the results with the present study.

1.3. Objective of the Study

1.4. General Objective.

The main objective of research was:

To investigate adsorption capacity of natural Bentonite for removal of heavy metals from the aqueous solution

1.5. Specific Objectives

The specific objectives of this study were:

1. To investigate the adsorption capacity of natural bentonite clay for removal of Pb (II), Cd (II) and Cu (II) from the aqueous solution;

2. To characterize natural bentonite with X-ray diffraction and chemical analysis.

3. To determine the effect of adsorbent dosage, contact time, initial concentration of heavy metal ions and pH on the adsorption capacity of the used adsorbents and

4. To study the applicability of parameter isotherm models and kinetic equations for determination of the adsorption mechanisms and characteristic parameters.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Water resource

Water is important because it is needed for life to exist. Water is the main component of the human body. Many uses of water include agricultural, industrial, household, recreational and environmental activities. Only 2.5% of water on the Earth is fresh water, and over two thirds of this is frozen in glaciers and polar ice caps.

Water demand already exceeds supply in many parts of the world, and many more areas are expected to experience this imbalance in the near future. It is estimated that 70% of world-wide water use is for irrigation in agriculture [24].

Climate change will have significant impacts on water resources around the world because of the close connections between the climate and hydrologic cycle. Due to the expanding human population competition for water is growing such that many of the worlds' major aquifers are becoming depleted [25]. Many pollutants threaten water supplies, but the most widespread, especially in underdeveloped countries, is the discharge of raw sewage into natural waters.

A toxic substance also is a chemical pollutant that is not a naturally occurring substance in water body. The greatest contributors to this toxic pollution are herbicides, pesticides and industrial compounds [26].

Metals, acid mine drainage, acid rain caused by industrial or volcanic discharges, acid pollution of lakes by runoff from acid soils, carbon dioxide discharges and runoff, volcanic or mineral, chemical waste industrial byproducts silt in storm water runoff from cleared land are the major source of water pollution [27].

2.2. Heavy metals in natural water

The discharge of heavy metal wastes into receiving waters may result in numerous physical, chemical, and biological responses. These can be separated into two broad categories: (i) effects of the environment on the metal, and (ii) effects of the metal on the environment. The first category emphasizes that conditions in receiving waters may lead to a change in the speciation

and toxicity of metals. Such conditions include differential input of anthropogenic and geochemical material, quality of industrial effluents, and concentration of chelators and suspended solids [28]. Biological responses under the second category are often equally diverse [29].

Depending on environmental conditions, there may be a change in density, diversity, community structure, and species composition of populations. The nature and extent of change depends largely on the concentration of heavy metal species in the water and sediment [30]. Hence, physicochemical processes within effluents and natural waters have a major, albeit indirect, effect on biological responses.

2.3. Toxicity of heavy metals

The term ‘‘heavy metal’’ refers to any chemical metal and metalloid element that has a relatively high density ranging from 3.5 to 7 g/cm^3 [31]. In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products.

Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and so forth [32].

The heavy metals are among the most common pollutants found in wastewater. These metals pose a toxicity threat to human beings and animals even at low concentration. Lead is extremely toxic and shows toxicity to the nervous system, kidneys and reproductive system. Exposure to lead causes irreversible brain damage and encephalopathic symptoms [33]. Cadmium is used widely in electroplating industries, solders, batteries, television sets, ceramics, photography, insecticides, electronics, metal finishing industries and metallurgical activities. It can be introduced into the environment by metal ore refining, cadmium containing pigments, alloys and electronic compounds, cadmium containing phosphate fertilizers, detergents and refined petroleum products. Rechargeable batteries with nickel–cadmium compounds are also sources of cadmium [34]. Cadmium exposure causes renal dysfunction, bone degeneration, liver and blood damage. It has been reported that there is sufficient evidence for the carcinogenicity of cadmium.

Copper, as an essential trace element, is required by biological systems for the activation of some enzymes during photosynthesis but at higher concentrations it shows harmful effects on the human body. High level exposure of copper dust causes nose, eyes and mouth irritation and may cause nausea and diarrhea. Continuous exposure may lead to kidney damage and even death. Copper is also toxic to a variety of aquatic organisms even at very low concentrations.

2.4. Heavy metals Contamination.

Heavy metal ions existing in wastewater streams of various industries such as electroplating, mining operations, battery manufacturing and tannery fabrication are posing environmental disposal problems due to their non-degradable and persistence nature. Leaking of these toxic heavy metals to the soil contaminates ground water and surface water leading to adverse effects on the health of human and animals in addition to marine life [35]. Treatment of large volumes of wastewater containing low concentrations of heavy metals pollutants is becoming increasingly important as the discharge regulations become more stringent [36]. The harmful heavy metals ions associated with various industrial activities include Ni(II), Cr(III), Co(II), Cd(II), Pb(II), Mn(II), Cu(II), Zn(II), Fe (III), Hg(II) and Ag(I).

2.4.1. Heavy metals contamination in Ethiopia.

Agricultural soils normally contain low background levels of heavy metals. Contamination from industrial activities or byproducts can increase the natural levels of heavy metals in soil, creating a health hazard to people, livestock and plants. Fertilizers and other soil amendments also add small amounts of heavy metals to the soil, which can build up over time with repeated applications [37]. The actual toxicity of a heavy metal will be affected by soil texture, organic matter, and pH. The health effects of exposure to heavy metals depend on the amount and duration of exposure, i.e. the volume of contaminated soil or food consumed over time [38]. The final disposal of industrial sludge in Ethiopia has become a critical issue due to public concern and the limited availability of land. The most effective strategy is to reduce the quantity of sludge produced by various industrial processes. If this reduction is not feasible, then the reuse of sludge should be considered [39]. One of the biggest industries, Textile and dyeing, are now viewed as a major environmental threat in the industrial area of Ethiopia and they contribute huge amounts of sludge in wastewater treatment processes [40]. Although characteristics of sludge depend on the

wastewater treatment process and sludge stabilization methods, it contains substantial amounts of toxic heavy metals [41, 42]. Another recent investigation reported that elevated levels of heavy metals in vegetables are found from the areas having long term uses of treated or untreated wastewater [43]. Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in different body parts [44, 45]. Excessive accumulation of heavy metals in agricultural soils through wastewater irrigation may not only result in soil contamination, but also affect food quality and safety [46]. Some research also confirmed that heavy metals such as Cd, Pb, Cu, Zn and Ni have carcinogenic or toxic effects on human beings and environment [47, 48].The management of sludge is becoming increasingly difficult due to the presence of heavy metals [49]. It is now established that application of sludge into land can increase soil water holding capacity, decrease soil bulk density, increase soil aeration and root penetrability and stimulate soil microorganism activity [50]. In addition, land utilization of sludge could represent a step forward to more sustainable farming practices and municipal waste management. Achieving this purpose it is pivotal to know the heavy metal content in textile sludge as without investigating toxic substances it is not feasible to use sludge as a soil conditioner or fertilizer in agricultural land.

One study found that manganese and iron levels in the Akaki River exceeded limits set by the Ethiopia Environmental Protection Agency. This study also found measurable amounts of cadmium, chromium, copper, zinc, manganese, iron, and nickel in soil and vegetables irrigated by the Akaki River, with all vegetables having chromium levels that exceeded the maximum limit [51]. Another study found that vegetables irrigated by the Akaki River had levels of cadmium and lead that exceeded the maximum limit [52].

2.5. Removal techniques.

Various technologies have been applied for the treatment of heavy metals contaminated waste streams over the past few decades. These technologies include chemical precipitation, ion exchange, membrane filtration, carbon adsorption, co-precipitation/adsorption and reverse osmosis. Each technology has its merits and limitations in application [53]. In this regard, tremendous efforts have been made to apply various biomass and natural materials as low cost adsorbents for heavy metal removal from wastewater, which recently reviewed by Gupta et al [54].Among all, ion exchange method and its associated electrochemical applications have been

successfully used in many industries for the removal of heavy metals from waste streams of various characteristics [55]. This was prompted by its heavy metal removal effectiveness especially when large volumes of waste water containing trace quantities are treated in addition to its simplicity and suitability for operation under a wide range of variable reaction conditions. Most of ion exchange processes use selective chelating/ ion exchange resins possessing anion functional groups having affinity towards heavy metal ions [56].

Precipitation processes

In industry, by far the most widely used process for removal of heavy metals from solution is that of chemical precipitation; approximately 75% of the electroplating facilities employ precipitation treatment [57],using either hydroxide, carbonate, or sulfide treatment, or some combination of these treatments to treat their waste waters. The most commonly used precipitation technique is hydroxide treatment due to its relative simplicity, low cost of precipitant (lime), and ease of automatic pH control. The solubility of the various metal hydroxides is minimized for pH in the range of 8.0 to 11.0.

Coagulation

Coagulation/flocculation has been known capable of removing heavy metals from solution. Coagulation refers to the charge neutralization of the particles. Flocculation involves slow mixing to promote the agglomeration of the destabilized particles. Environmental protection Agency [58] investigated the use of lime softening and coagulation (using ferric sulfate or alum) removal of such heavy metals as Pb, Cd, Cr, etc. While lime softening achieved removals of greater than 98% in the pH range of 8.5-11.3 for cadmium, cadmium removals by ferric sulfate and alum coagulation were lower than that of lime softening and were shown to depend on pH. Cadmium removals increased with increasing pH. Ferric sulfate coagulation of a river water containing 0.3mg/L Cd showed removal to increase from 20% at pH 7.2 to above 90% at pH $\geq$ 8.

Flotation

Foam flotation depends on the use of a surfactant that causes a non-surface active material to become surface active forming a product that is removed by bubbling a gas through the bulk solution to form foam. The use of foam flotation techniques for removal of heavy metals has been well studied. With dilute wastewaters containing heavy metals in the parts per billion or parts per million ranges, foam flotation offers several distinct advantages: simplicity flexibility and

effectiveness of operation, Limited space requirements due to rapid reactions, Production of small, concentrated volumes of sludge, Moderate costs comparable to that of lime precipitation, Low cost in terms of labor, energy, and chemicals.

Adsorption

Due to the historical development and use of activated carbon in water and wastewater treatment, most of the applications and research effort on activated carbon have been oriented towards organics removal [59]. Research efforts on inorganics removal by activated carbon, specifically metallic ions, have been markedly limited. Huang [60] provides an excellent review of inorganics removal by activated carbon by considering such factors as surface properties (and their measurement) and adsorption characteristics of cationic and anionic species onto activated carbon surfaces. Important physical-chemical properties affecting inorganic electrolyte adsorption include: specific surface area, pore structure, electrophoretic properties, and surface acidity. The adsorptive capacity of metal cations increases with increasing pH of the Sorption system, but not in a linear relationship [61]

2.5.1. Removal of heavy metals using natural bentonite.

There are several methods to remove dye and heavy metals from waste water such as ion-exchange, ultra-filtration, electro dialysis, reverse osmosis, precipitation and coagulation and adsorption processes [62]. Adsorption is an effective separation process due to its low operating cost and low energy consumption. Activated carbon is widely used as an adsorbent for removal a variety of pollutant species from waste water, particularly metal ions, organic compounds and dyes due to its large surface area, suitable pore size distribution and presence of surface functional groups [63].

Despite the higher maximum adsorption capacity of activated carbon, this adsorbent has some problems, such as its reusability and higher production costs [64]. Thus, using adsorbents that have high efficiency in removing contaminants, in addition to having some benefits, such as inexpensiveness, availability, reusability and easy modification, can play important role in this field [65].Therefore, natural bentonite collected from Ethiopia, Afar region, near Ledi river was used as adsorbent in this study.

2.6. Natural Bentonite

Bentonite is clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite [66]. Other smectite group minerals include hectorite, saponite, beidelite and nontronite. Smectites are clay minerals, i.e. they consist of individual crystallites the majority of which are <2μm in largest dimension. Smectite crystallites themselves are three layer clay minerals [67].

Depending on the nature of their genesis, bentonites contain a variety of accessory minerals in addition to montmorillonite. These minerals may include quartz, feldspar, calcite and gypsum. The presence of these minerals can impact the industrial value of a deposit, reducing or increasing its value depending on the application [68]. Bentonite presents strong colloidal properties and its volume increases several times when coming into contact with water, creating a gelatinous and viscous fluid. The special properties of bentonite (hydration, swelling, water absorption, viscosity, thixotropy) make it a valuable material for a wide range of uses and applications and also Since bentonite is widely present in nature, low-cost, and has a high specific surface area and high exchange capacity, it is considered a great potential adsorbent for the treatment of heavy metal ions such as Pb^{2+}, Fe^{2+}, Zn^{2+} and Cr^{3+} [69] in aqueous solutions. Surface complexation contributes mainly to the adsorption of Pb^{2+} on bentonite, and it is dominated by outer-sphere surface complexation and ion exchange with cations on interlayer surfaces at low pH [70].

2.7. Adsorption isotherms

An adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. There are several isotherm equations available for analyzing experimental sorption equilibrium parameters, the most common being the Langmuir and Freundlich models [71].

2.7.1. Langmuir isotherm.

Langmuir isotherm based on the assumption that all the adsorption sites are energetically identical (monolayer adsorption) and adsorption occurs on a structurally homogeneous adsorbent. In its formulation, binding to the surface is primarily by physical forces and implicit in its derivation is the assumption that all adsorption sites have equal affinities for adsorbate molecules and that the

presences of adsorbed molecules at one site do not affect the adsorption of molecules at an adjacent site [72, 73]. The linear form of Langmuir isotherm is

$$\frac{ce}{qe} = \frac{ce}{Qe} + \frac{1}{bQe} \qquad 1$$

Where qe is the amount of metal ions adsorbed per unit mass of adsorbent (mg/L), Ce the equilibrium concentration of the adsorbate(mg/L), Qe and b represent maximum adsorbate capacity and energy adsorption respectively. Langmuir parameters, Qe and b are determined from the slope and intercept of the linear plot Ce/qe versus Ce respectively.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless separation factor or equilibrium parameter, R_L which is defined as

$$R_{L=\frac{1}{1+bc_o}} \qquad 2$$

Where, C_o is the initial concentration of the adsorbate in the solution, b the Langmuir's adsorption constant(L/mg).The value of R_L indicates the type of the isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L =0) [74].

2.7.2. Freundlich isotherm

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules, and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centers of the adsorbent. The well-known expression for the Freundlich model is given as [75].

$$Logqe = logkf + \frac{1}{n} logce \qquad 3$$

Where qe is the amount of adsorbate adsorbed at equilibrium (mg/L), Kf is the Freundlich constant, 1/n is the heterogeneity factor which is related to the capacity and intensity of the adsorption, and Ce is the equilibrium concentration (mg/L). The values of Kf and 1/n can be obtained from the slope and intercept of the plot of logqe against logCe. The value of 1/n

indicates the type of isotherm to be irreversible (1/n=0), favorable (0<1/n<1), unfavorable (1/n>1) [76].

The equilibrium adsorption capacity, q_e (mg/L) can be calculated using the mass balance equation given [77].

$$q_e = \frac{V(c_o - c_e)}{m} \quad (4)$$

Where C_0 and Ce are the amounts of initial and retained heavy metal ion concentrations in the solutions at time t (mg/L), respectively, V is the volume of the solution (L) and m is the weight of the adsorbent (g). The amount of adsorbate adsorbed, q_t (mg/L) at any time can be calculated by

$$q_e = \frac{V(c_o - c_t)}{m} \quad (5)$$

Where C_t is concentration of adsorbate (mg/L) at any time.

The percentage removal of adsorbate can be calculated using the following relationship [78].

$$\%\, removal\ of\ metal\ ions = \frac{(c_o - c_e)}{c_o}\ x100\% \quad (6)$$

Where C_o and C_e are initial and final equilibrium concentration of adsorbate(mg/L). The applicability of two adsorption isotherm (Langmuir and Freundlich) can be compared by evaluating the multiple regression correlation coefficients; R^2.In regression the R^2 coefficient of determination is a statistical measure of how well the regression line approximates the real data point. R^2 is a number between zero and one that would give some information about the best fit of a model. If the value of R^2 close zero suggests the poor model. If the value of R^2 is 1 indicates that the regression line perfectly fits the data. If the value of R^2 obtained outside the range 0 to 1, it is used to measure the agreement between observed and modeled value [79]

2.8. Kinetic studies

Several kinetic models have been applied to examine the controlling mechanism of heavy metal ions adsorption from aqueous solution. It describes the rate of uptake of the adsorbate molecule

onto adsorbent, which determines the residence time required for design adsorption systems. In this study pseudo-first-order and pseudo-second order were applied.

2.8.1. Pseudo first order kinetics

Lagergren's first order rate equation is the earliest known to describe the adsorption rate based on adsorption capacity. The linear form of Lagergren's first order rate equation is as follows [80]

$$\ln(q_e - q_t) = lnq_e - K_1 t \qquad 7$$

where qe is the amount of metal ions adsorbed onto the adsorbent at equilibrium (mg/g), qt is the amount of metal ions adsorbed onto the adsorbent at any time t (mg/L), and K_1 (1/min) is the rate constant of the pseudo-first-order adsorption which can be calculated from the slope of the linear plot of ln(qe-qt) Vs t (slope= K_1, qe = exp intercept)

2.8.2. Pseudo second order kinetics

The mathematical form of the pseudo-second order equation was first proposed by Blanchard [81] to describe the kinetics of heavy metal removal by natural zeolites. At present it is the most commonly used mathematical expression applied to description and correlation of the kinetic data monitored in the solid/solution sorption systems [82]. The application of pseudo-second-order equation includes the systems containing various kinds of sorbates (heavy metals in cationic and anionic forms, organic dyes, phenols, etc.) and sorbents (inorganic minerals, activated carbons, raw biomass, etc.) An extraordinary high efficiency of Pseudo-second-order equation in correlating very broad spectrum of kinetic data originating from diverse systems suggests that this equation cannot represent just one kinetic model.

The good applicability of this equation is usually associated with the situation when the rate of direct adsorption/desorption process (seen as a kind of chemical reaction further referred to as "surface reaction") controls the overall sorption kinetics chemical reaction further referred to as "surface reaction") controls the overall sorption kinetics [83]. This is obviously caused by the fact that each known theoretical ground of pseudo-second-order equation is based on fundamental theories of surface reactions. The linearized form of the pseudo-second-order model as given by Ho [84] is

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{1}{qe} t \qquad 8$$

Where K_2 (g/mg1/min) is the rate constant of the pseudo-second-order adsorption, qe is the amount of metal ions adsorbed on the adsorbent at equilibrium qe (mg/L), and qt is the amount of metal ions adsorbed on the adsorbent at any time, t (mg/L). K_2 (g/mg1/min) can be calculated from the slope and intercept of the plot of t/qt against t.

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Instruments and Apparatus

Instrument used in this study include: Beam balance, different of volumetric flask, pH meter, hot air oven, magnetic stirrer, measuring cylinder, funnel, what man No 1 filter paper, mortar and pestle, beakers, aluminum foil, conical flask, muffle furnace and Varian AAS

3.2. Chemicals and Reagents

Chemicals used in this research were: Natural bentonite (adsorbent), nitrate salts of Cd, Pb and Cu ($Cd(NO_3)_2.4H_2O$,$Cu(NO_3)_2.3H_2O$ and $Pb(NO_3)_2$) distilled water, concentrated hydrochloric acid (HCl), sodium hydroxide (NaOH)

3.3. Preparation of the adsorbent material

Natural bentonite collected from Ledi River, Afar region Ethiopia was used as an adsorbent. The natural bentonite was dried at 120 ^{0}C for 4 hour in order to remove water and other volatile matter, and then grounded, sieved to mesh size 300mesh (refere, Heba H. El-Maghrabi, 2014, Vol.4, No.19)

3.4. Characterization of the adsorbent material.

The natural bentonite was characterized by chemical analysis (complete silicate analysis) and X-ray diffraction.

3.5. Preparation of the adsorptive compounds

Analytical grade metal salts $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)_2$, and $Cu(NO_3).3H_2O$ were used without further purification. All experiments employed distilled water. Stock solutions (1000 mg/L) of Cd(II), Pb(II), and Cu(II) were prepared in 1 L of distilled water using 2.1032 g, 1.615 g and 3.798 g of metal salts respectively. The stock solutions were diluted as required to obtain standard solutions containing 30 mg/L, 60 mg/L, 100 mg/L and 140 mg/L by using dilution law formula

$$C_iV_i = C_fV_f$$

Where, C_i = initial concentration, C_f = final concentration

V_i = initial volume, V_f = final volume

3.6. Adsorption method.

Adsorption measurements were made by a batch technique at room temperature. The batch mode was selected because of its simplicity and reliability. Batch adsorption experiments were carried out by allowing an accurately weighed amount of adsorbents to reach equilibrium with Cd (II), Pb (II) and Cu (II) solutions of various initial concentrations at 298K. Known weights of adsorbents were added to 150 mL conical flasks, each containing 120 mL of solution. The bottles were shaken in a temperature controlled magnetic stirrer at a constant speed of 300rpm. At the end of the equilibrium period, the contents of the bottles were filtered and the supernatant was subsequently analyzed for residual concentration of Cd (II), Pb (II), and Cu (II) with an atomic absorption spectrophotometer (AAS) operating with an air acetylene flame. The amount of heavy metal ions in the solid phase qe(mg/L) was calculated by equation (4) given in literature.

where C_0 and C_e are the amounts of initial and retained heavy metal ion concentrations in the solutions at time t (mg/L), respectively, V is the volume of the solution (L) and m is the weight of the adsorbent (g). Kinetic studies were performed following a similar procedure with three adsorbents at 298 K, pH of the solutions was not adjusted, and the initial concentration was set as 100 mg/L for Cd (II), Pb (II) and Cu (II). The uptake of the adsorbate at time t, q_t(mg/L) was calculated by the equation(5) written in the literature section.

where C_t is the concentration of the adsorbate (mg/L) in the solution at time t.

The removal efficiency was determined by computing the percentage sorption using the formulae in Eq. (6)

3.7. Experimental set up and effects of various parameters on adsorption efficiency of natural bentonite.

3.7.1. Effect of Initial concentration of ions.

The effect of initial concentration of Pb(II), Cd(II) and Cu(II) ions on the extent of adsorption of Pb (II), Cd (II) and Cu (II) ions on natural bentonite was studied by taking 120 mL of the diluted stock solutions of Pb, Cd and Cu ions containing 30 mg/L,60 mg/L, 100 mg/L and 140 mg/L using 0.8 gram bentonite at the same time. After stirring the mixture of bentonite and each

solution of the metal ions for 15min, the samples were filtered by whatman1 filter paper. Concentration of Pb (II), Cd (II) and Cu (II) ions free from suspended was estimated by using Varian AAS instrument with model 20 Plus. All other parameters were kept constant. Amount adsorbed and percent removal of Pb(II), Cd (II) and Cu(II) ions were then calculated and the plot of percent removal of Pb(II), Cd(II) and Cu (II) ions versus initial concentrations of Pb (II), Cd(II) and Cu(II) ions was plotted.

3.7.2. Effect of Contact time.

The effect of contact time was studied by taking 120 mL of Pb(II), Cd(II) and Cu(II) ions solution with initial concentration of 60 mg/L using 0.8 gram of natural bentonite. The adsorption studies of Pb (II), Cd(II) and Cu(II) ions on natural bentonite was carried out at different time interval 2hr, 6hr, 16hr and 32hr with 30min agitation time. All parameters are held constant. Finally, the amount adsorbed and percent removal of Pb (II), Cd (II) and Cu (II) ions versus contact time were plotted for the three metals ions under consideration.

3.7.3. Effect of pH

The effect of pH was studied at the pH values of 1.5, 4, 6.5 and 8.5 at the interval of each time using 120 mL Pb (II), Cd (II) and Cu (II) ions solution with 100 mg/L and treating it with 0.8 gram of natural bentonite at room temperature. The adjustment of pH of the solution was made by adding 0.1M HCl and 0.1NaOH solution using a pH meter. After shaking the sample for 20min, the Pb (II), Cd (II) and Cu (II) ions solutions were separated from the adsorbent by filtering with what man No1 filter paper.

The concentration of Pb (II), Cd (II) and Cu (II) ions free from suspended natural bentonite was analyzed by Varian AAS instrument with model 20 plus. All other parameters were held constant. Finally, the amount adsorbed and percent removals of Pb (II), Cd (II) and Cu (II) ions were calculated and the plot of percent removal of Pb (II), Cd (II) and Cu (II) ions versus pH was plotted.

3.7.4. Effect of dosage of bentonite.

The effect of amount of natural bentonite added to the Pb^{2+}, Cd^{2+} and Cu^{2+} ions solution was studied by taking 120 mL Pb^{2+}, Cd^{2+} and Cu^{2+} ions with initial concentration 100 mg/L solution

treated with 1 g, 1.5 g, 2 g and 2.5 g of natural bentonite. The sample was shaken for 20min.After stirring the sample was separated from the suspended natural bentonite by what man No 1 filter paper. The separated sample was analyzed by Varian AAS with model 20 plus. Finally, the amount adsorbed and percent removal were calculated and plot of percent removal of Pb^{2+}, Cd^{2+} and Cu^{2+} ions versus dosage was plotted.

3.8. Data analysis and Interpretation

All data Obtained from the above laboratory experiments were analyzed through the origin 6, Microsoft excel and origin 8 software were used to perform graphs and calculate R^2 values.

CHAPTER FOUR

4. RESULT AND DISCUSSION

4.1. X-ray diffraction

The information concerning the crystalline phases was determined by comparing the characteristics d-spacing (^{0}A) and the relative intensity I/I_0 with the data obtained. The x-ray diffraction pattern for the clay material in fig.1 reveals the presence of the following minerals: Montmorillonite, as indicated by its basal reflections near 14.46 ^{0}A, 4.24 ^{0}A and 3.85 ^{0}A and it is the main constituent of this clay material. Kaolinite: as indicated by its two basal reflections near 7.17 ^{0}A and 3.56 ^{0}A. Quartz: considerable amounts of quartz were detected at 3.33 ^{0}A.

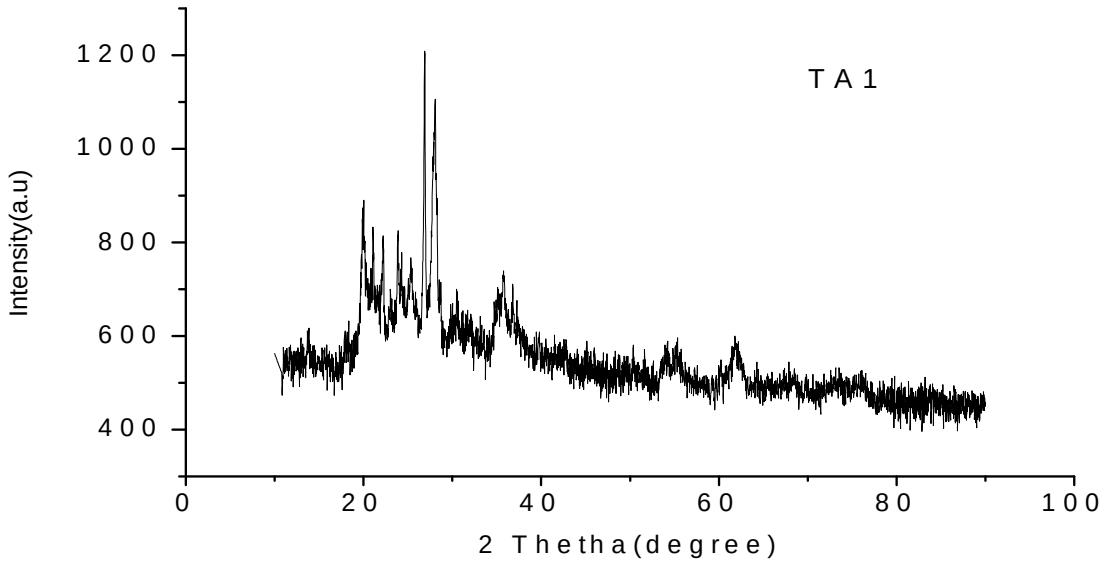

Figure 1: X-ray diffraction pattern for Natural bentonite clay.

4.2. Chemical analysis

Chemical analysis was carried out to evaluate total silica, alumina, iron and alkali metals by complete silicate analysis. The result is presented in Table1

Table 1 Chemical composition of natural bentonite after heated in muffle furnace for 4hr

Material	Chemical composition[%]											
Natural bentonite	CaO	Al_2O_3	Fe_2O_3	SiO_2	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	H_2O	LOI
	4.28	13.93	7.72	61.2	2.44	2.76	0.84	0.61	0.15	0.06	0.40	6.0

4.3. Effect of different parameters

4.3.1. Effect of adsorbent dosage

In the experimental studies, the optimum adsorbent dosage for heavy metal ions removal was investigated with an initial adsorbate concentration, 100 mg/L, volume 120 mL at 298K. The effect of the adsorbent (natural bentonite) dosages on the adsorption of heavy metal ions is shown in Figure 2. Adsorbent dosages were varied in the range of 1 g, 1.5 g, 2 g and 2.5 g for all the three adsorbate. It can be concluded from Figure 2 that the removal of heavy metal ions increases with the increase in adsorbent dosages. The increase in adsorption efficiency with the adsorbent dosage may be attributed to a higher surface area and the availability of more adsorption sites, as reported by other authors [56, 57]. As can be seen in Figure 2, the adsorbed amount increases with adsorbent concentration but this increase does not show a linear trend. It can be indicated from the results that the optimum, natural bentonite dosage was 2.5 g. For dosage of natural bentonite more than 2.5 g, no significant changes were observed in heavy metal ions removal efficiencies.

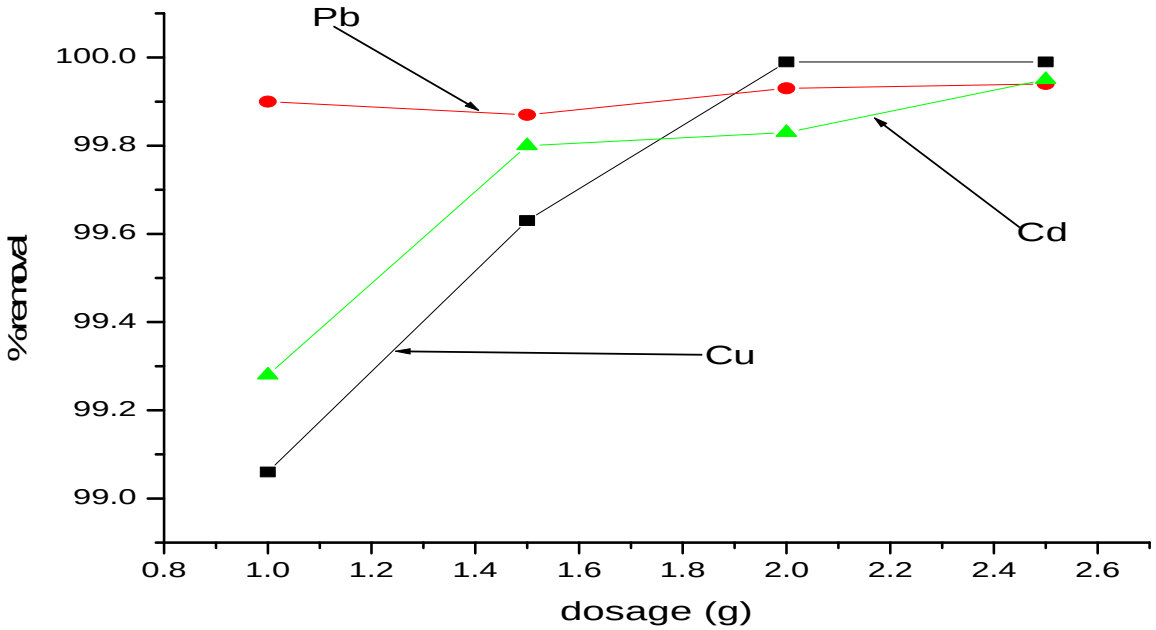

Figure 2: plote of % removal versus adsorbent dosage

4.3.2. Effect of contact time

Effect of contact time was studied using natural bentonite dosage of 0.8 g was added to 120 mL of 60 mg/L of Pb(II),Cd(II) and Cu(II) solution. Experiments were conducted at a temperature of 298K for 2hr, 6hr, 16hr and 32hr to test the effect of contact time on the adsorption process. The results (Figure 3) indicates that the adsorption of Pb(II) onto natural bentonite was gradually increases until the equilibrium was reached. Adsorption of Cu^{2+} decreases for the first 6hr, but rapidly increases for the left hr. Adsorption of Cd(II) on the given adsorbent gradually increases from the beginning until the equilibrium was reached.

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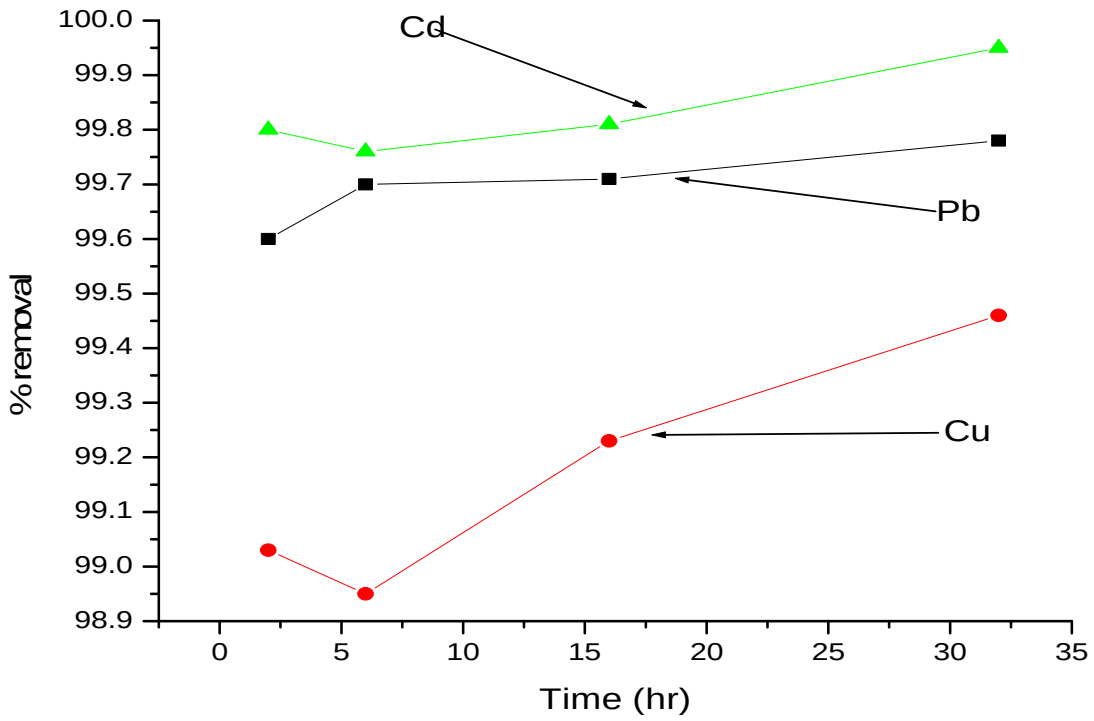

Figure 3 : plot of % removal of Pb^{2+}, Cd^{2+} and Cu^{2+} versus time

4.3.3. Effect of initial concentration.

Figures 3 present the plot of heavy metal ions removal versus initial concentration for natural bentonite adsorbent at 298K,volume of the solution 120 mL and 0.8 gram, at initial concentrations between 30 mg/L, 60 mg/L, 100 mg/L and 140 mg/L, concentrations for Cu (II), Pb (II) and Cd (II). Removal efficiency of Cu (II) dramatically decreases as the initial concentration increases. This may be adsorption based on hydration ability and charge density of the ions. The effect of initial concentration of the metal ions was not exhibit this much change for Pb^{2+} and $^{2+}$ ions with increasing of initial concentration. Results showed that the removal efficiencies of heavy metal ions by natural adsorbents decreased as the initial concentration increased for the three metal ions. It is noted that described procedure of removal of heavy metal ions is the most efficient in processes containing lower pollution concentrations.

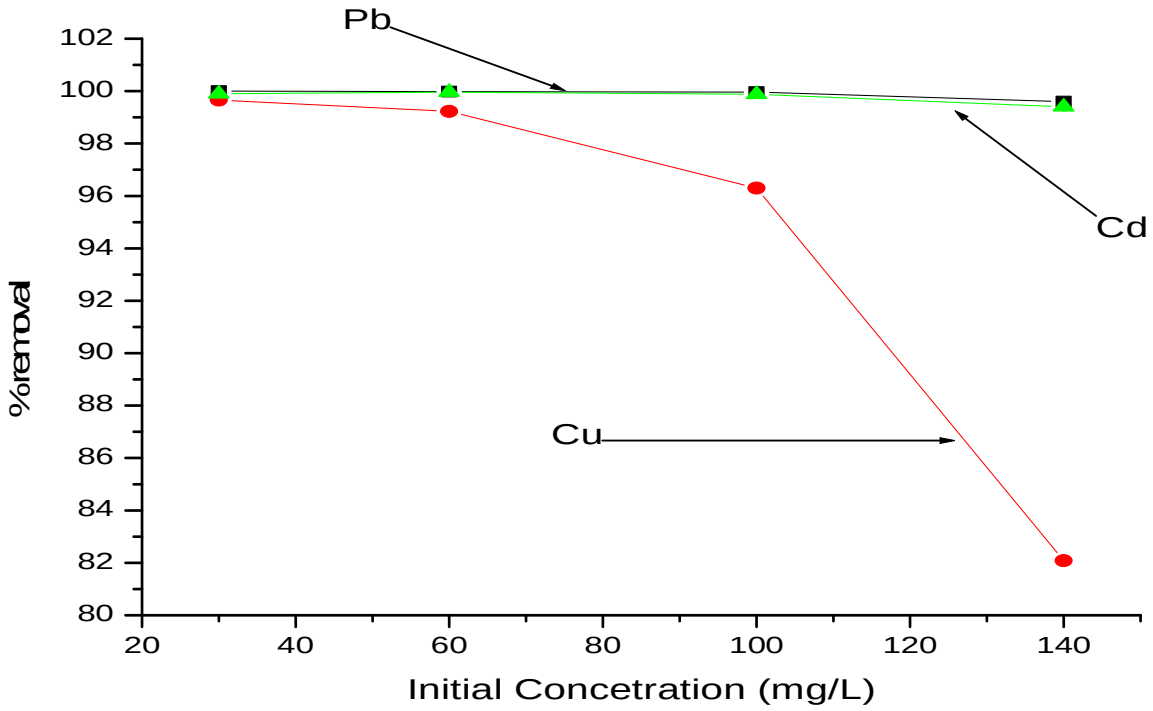

Figure 4 : plot of % removal versus initial concentration

4.3.4. Effect of pH of the adsorptive solution.

The pH of the aqueous solution is an important variable which controls the adsorption of the metal at the clay water interfaces. Hence, the influence of pH on the adsorption was investigated in the pH range of 1.5–8.5 using clay amount of 0.8 gm and metals concentration of 100 mg/L. As the acidity of the medium decreased from 1.5 to 8.5, the percent removal of Pb (II), Cd (II) and Cu (II) ions increases as indicated in (Fig. 5) [64]. With further increase in the PH of solution, the adsorption % is constant. Clays are known to possess a negative surface charge in solution as pH changes, surface charge also changes, and the sorption of charged species is affected (attraction between the positively charged metal ion and the negatively charged clay surface). It is conceivable that at low pH values, for removal of Pb (II) whereas it is conceivable at high pH value for removal of cadmium and copper ions. As the pH increases and the balance between H_3O+ and OH^- are more equal, more of the positively charged metal ions in solution are adsorbed to extent limit on the negative clay surface and thus the percentage removal of the metal ions

increases. On the other hand, (i.e. directed to basicity) precipitation of metal hydroxides may also occur as the pH in solution increases, which will lead to a corresponding decrease in the amount of metal ions adsorbed onto the clay. Thus it can be concluded that the change of pH of solution from weak acid to neutral has no significant effect on the removal Pb^{2+} whereas it has significant change on the removal of Cd^{2+} and Cu^{2+}.

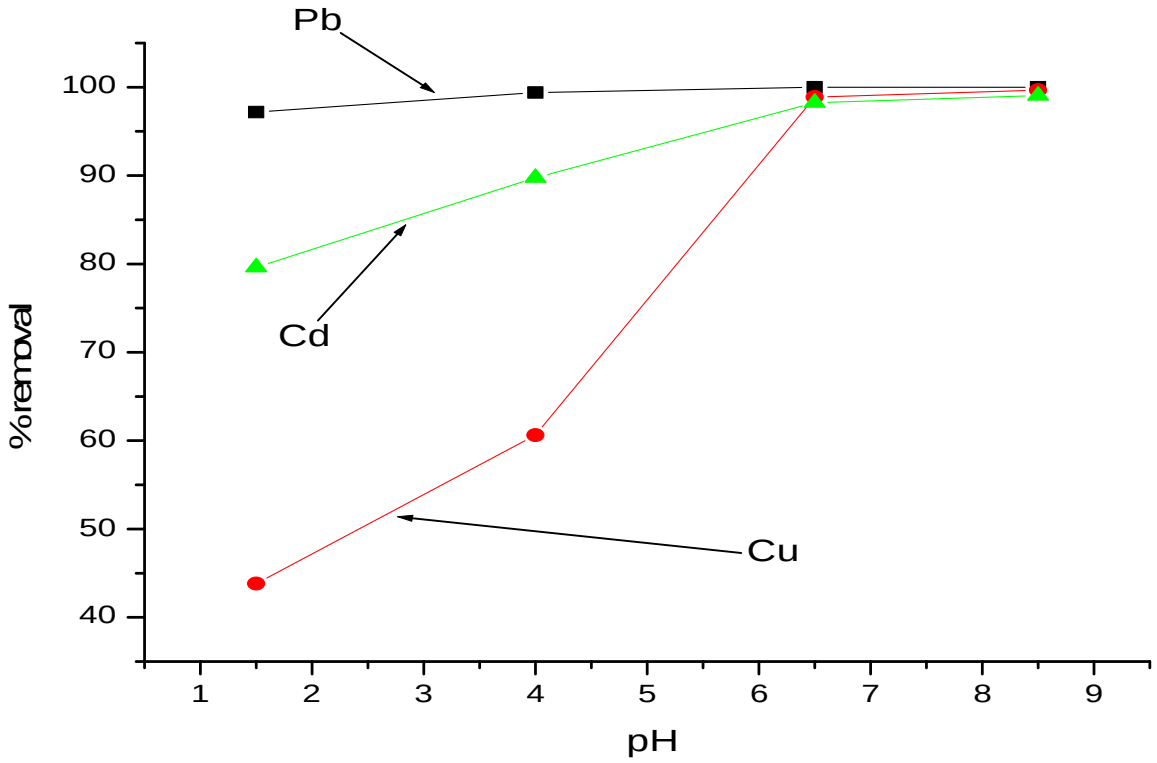

Figure 5 : plot of % removal of heavy metal ions versus pH

4.4. Adsorption isotherms

The adsorption isotherms for Pb(II), Cd(II) and Cu(II) removal were studied using initial concentration of metal ions between 30 mg/L, 60 mg/L, 100 mg/L and 140 mg/l, room temperature (25 ± 1^0C) an using adsorbent mass of 0.8 g.Both Langmuir and Freundlich isotherm were used to study the adsorption process. But the data obtained were more fitted to the Langmuir isotherm than Freundlich. The data were collected in Table 2 and indicated in figures 6 by the plot of ce/qe versus Ce .The Langmuir isotherm can describe the experimental data quite

well as one can see from the figure and the correlation coefficients (R^2) are greater than 0.95. This can be implied that the adsorption of heavy metal ion is the monolayer behavior.

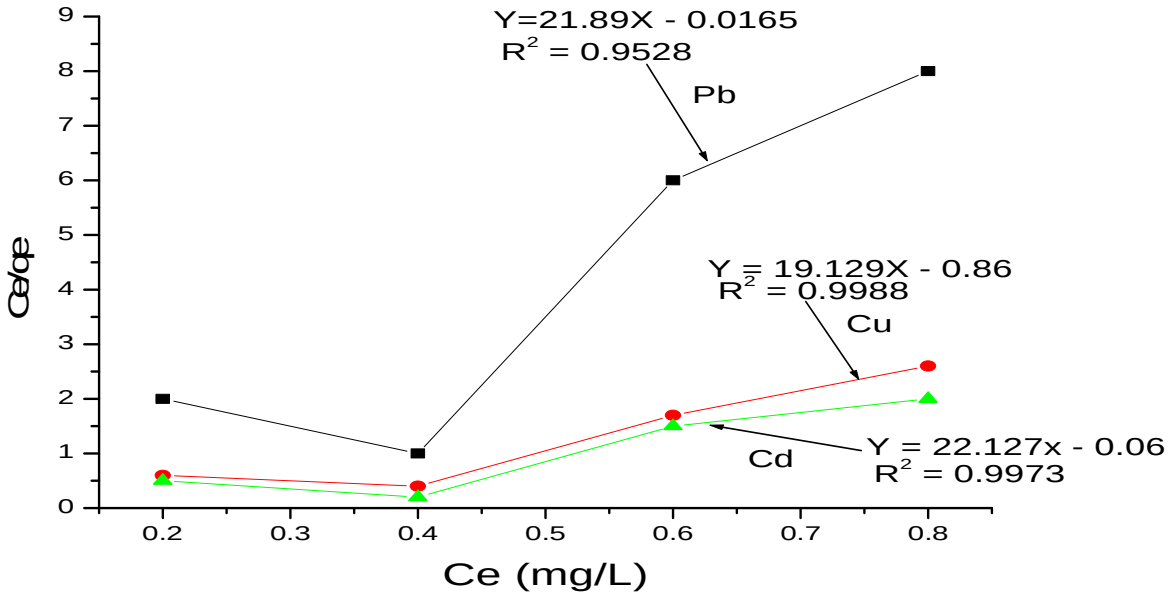

Figure 6 : plot of Langmuir adsorption isotherm for Pb^{2+}, Cu^{2+} and Cd^{2+} on natural bentonite.

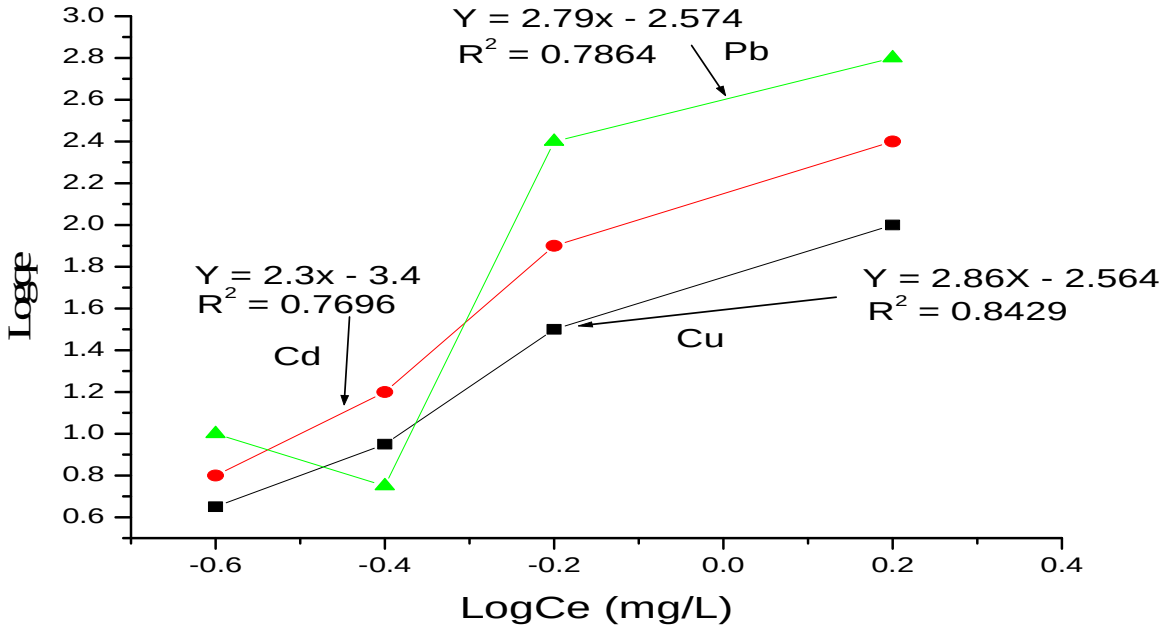

Figure 7 : Freundlich adsorption isotherm for Pb^{2+}, Cu^{2+} and Cd^{2+}on natural bentonite

Table 2 results of the Langmuir and Freundlich adsorption isotherm studies at room temperature for adsorption of heavy metals on natural bentonite.

	Freundlich			Langmuir	
Ions	Kf	N	R^2	R_L	R^2
Pb	1.18	0.558	0.786	0.322	0.953
Cu	11.87	6.66	0.843	0.045	0.9988
Cd	13.8	3.448	0.7696	0.019	0.9975

Table 3 comparison of adsorption capacity of natural bentonite for removal of heavy metals from aqueous solution with other similar work

Material used	Metal ions	Removal %	Parameter	Reference
Bentonite	Cu	100	pH	S.pare.I.P.B 2012
	Pb	90		
	Cd	90	Dosage	Naseem Z.S.T.K.J, 2006
	Cd	100	Initial concentration	O.Yavuz, R.G.F.A,I. 2006
	Pb	100		
	Pb	70	Time	V.J.Inglezakis M.A., 2005
	Pb	40		
	Cu	12	Time	AtichatW.Y.S.B., 2012
	Cd	40		
Magadiite	Cd	97		Soon.Y.J.and Jung-minlee, 1998
	Cu	78	Time	
Xanthiumpensytvanicum	Pb	77		Jabber S.2013
	Cd	25	Dosage	
	Cu	76		
Natural bentonite	Pb	100		Present work
	Cu	99.6	pH	
	Cd	99.06		
	Pb	99.78		
	Cu	99.46	Time	
	Cd	99.95		
	Pb	100		
	Cu	99.6	Initial concentration	
	Cd	99.9		
	Pb	99.94		
	Cu	99.99	Dosage	
	Cd	99.95		

4.5. Kinetic studies

The results of the kinetics experiments of adsorption of Pb^{2+}, Cd^{2+} and Cu^{2+} with natural bentonite clay are shown in figure 8 and 9. The rapid adsorption observed during the first 2hr is probably due to the abundant availability of active sites on the natural bentonite clay surface. The adsorption of three metals reached equilibrium within 32 hr. Therefore 32 hr was suitable soaking

time for the study of the adsorption isotherm of all three metals. The maximum adsorption was observed on Cd^{2+} with 60 mg/L while Cu^{2+} had the lowest adsorption on natural bentonite clay. The kinetic data were then analyzed by applying pseud of first-order and pseudo-second-order models to gain a better understanding of the adsorption dynamic behavior.

4.5.1. Pseudo- first- order kinetics model.

The Lagergren's kinetics equation describes the adsorption of liquid –solid systems based on solid capacity. To distinguish kinetic equations based on the concentration of solution and adsorption of a solid, Lagergren's first order rate equation was used [65].The plot of $Log(q_e-q_t)$ versus t described in the literature section gives the following curve (Fig 8) at initial concentration 30 mg/L, 60 mg/L, 100 mg/L and 140 mg/L, adsorbent dosage 0.8 g/120 mL, contact time 2hr, 6hr, 16hr and 32hr, agitation speed 300rpm,pH=6.5, performed room temperature. As the value of R^2 indicates, Pseudo-first-order was not appropriate to describe the data obtained.

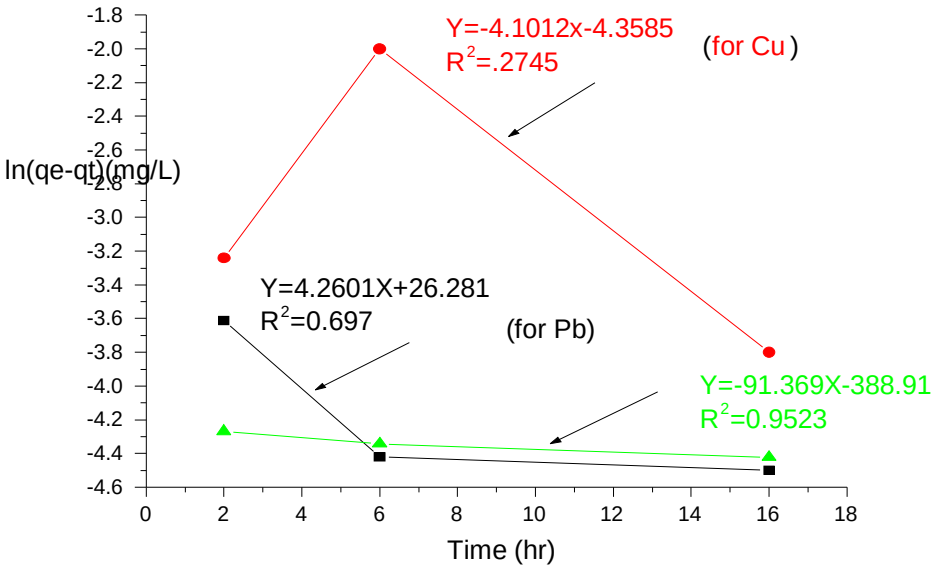

Figure 8 : pseudo-first-order kinetics adsorption for Cd^{2+}, Cu^{2+} and Pb^{2+} on natural bentonite.

4.5.2. Pseudo-second-order kinetic model

The pseudo-second-order describes the adsorption capability of solids. The plot of t/q_t versus t could be plotted using the equation (8) given in literature with initial concentration 60 mg/L , adsorbent dosage 0.8 g/120 mL of solution, contact time =2hr, 6hr,16hr and 32hr, stirring time=30min,stirring speed=300rpm.

The values of q_{e2} and K_2 were determined from the slope and intercept of the plot, respectively and the values obtained as such are presented in table 3.The experimental data were analyzed and predicted values from both models are compared based on the respective values of R^2. The relative high value of R^2 value indicates that the model successfully describes the kinetics of adsorption of an adsorbate on adsorbent surface.

As the values of R^2 collected in table 3 indicates pseudo-second-order kinetics model could be more favorable than that of pseudo-first-order kinetics model to describe adsorption of Pb^{2+}, Cd^{2+} and Cu^{2+} by natural bentonite. This further suggests that the adsorption process is of a chemisorption type that would possibly involve exchange or sharing of electrons between the adsorbent and adsorbate .As it is observed from the figure below the graphs and values R^2 were exactly the same and linear for adsorption of Pb^{2+}, Cd^{2+}, and Cu^{2+} by natural bentonite. The plot of t/qt versus t is shown in figure 13.

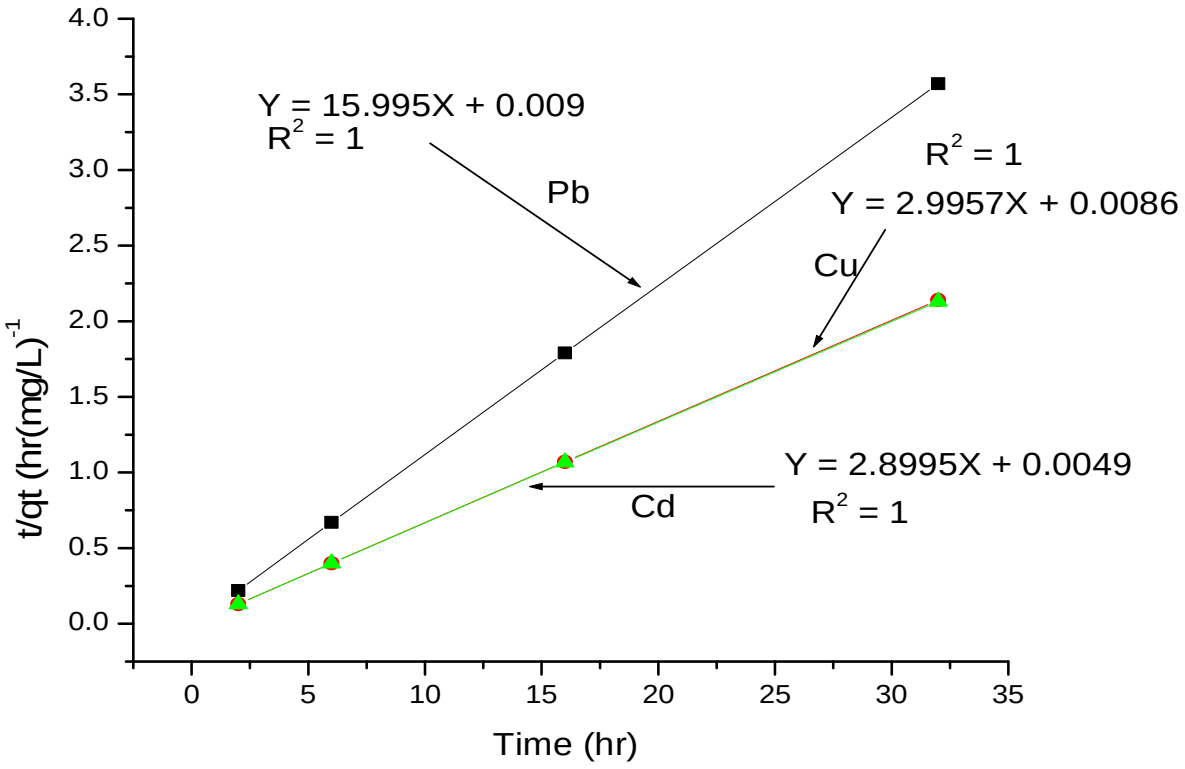

Figure 9 : Plot of pseudo-second-order for adsorption of Pb^{2+}, Cd^{2+} and Cu^{2+} on natural bentonite.

Table 4: Show the kinetic adsorption of pseudo-first-order and pseudo-second-order rate constant for adsorption of Pb^{2+}, Cd^{2+} and Cu^{2+} on natural bentonite.

Ions	Pseudo-first-order			Pseudo-second-order		
Ions	R^2	Qe(mg/L)	$K_1(hr^{-1})$	R^2	Qe(mg/L)	$K_2(hr^{-1})$
Pb	0.697	0.039	0.2	1	9.09	0.606
Cu	0.2745	0.398	0.18	1	8.96	1.25
Cd	0.9525	0.014	0.0185	1	8.968	12.5

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

1. Conclusions

Due to the environment concern of heavy metal contained in the waste water discharged to the public sewage, the removal of these metals from waste water becomes an important issue for environmental study. The experiment was carried out under optimum, dosage = 2.5 g, pH = 6.5 for Pb, pH = 8.5 for Cu and Cd, contact time, t =32hr for Pb, Cu and Cd. The clay material has been characterized by x-ray diffraction analyses to investigate the crystalline structure and complete silicate analysis to determine content of different oxides. High removal efficiency of the adsorbent used was achieved in nearly neutral and basic media, which was for Pb (at PH=6.5, % removal=100%), for Cu (at pH = 8.5, % removal = 99.66%), for Cd (at pH = 8.5, % removal = 99.06%)

For the kinetic study, the pseudo-second-order model can describe the adsorption kinetic for metal adsorption onto the natural Bentonite quite well which was confirmed from value of (R^2 = 1) while the adsorption isotherm corresponds to that of Langmuir equation, (R^2 = 0.956, R^2 = 0.987 and R^2 = 0.998, for Pb, Cu and Cd respectively). This suggests that the adsorption of heavy metal onto natural Bentonite is monolayer mechanism. Natural bentonite clays should be a promising material to adsorb the heavy metal from aqueous solution. The removal percentage is high as compared to other recent similar work.

2. Recommendations

1. Since the study dealt with only lead, copper and cadmium, it is therefore, recommended that further study be carried out for other heavy metals and investigate removal ability of the material used as adsorbent in this study.

2. As this is the study on the removal of heavy metal from aqueous solution using natural bentonite, it is important if further work be focused on activating natural bentonite in order to increase removal efficiency of the clay material.

3. As it is stated in literature part of this study, bentonite clays are found abundantly near other rivers of Afar region, therefore, further study should targeted to investigate adsorption capacity of that natural bentonite in removal of heavy metals.

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APPENDIX

Appendix 1: Effect of time on the removal of Cd^{2+}, Cu^{2+} and Pb^{2+} from aqueous solution by natural bentonite.

Ions	Time(hr)	C_o(mg/L)	Ct(mg/L)	q_t(gm/L)	q_e(gm/L)	ln(qe-qt)	% removal
Pb	2	60	0.4	8.94	-	-3.611	99.6
	6	60	0.3	8.955	-	-4.42	99.7
	16	60	0.29	8.9565	-	-4.5	99.71
	32	60	0.22	8.967	8.967	-	99.78
Cu	2	60	0.58	8.913	-	-3.24	99.03
	6	60	0.63	8.9055	-	-2	98.95
	16	60	0.46	8.931	-	-3.8	99.23
	32	60	0.32	8.952	8.852	-	99.23
Cd	2	60	0.12	8.982	-	-4.268	99.8
	6	60	0.14	8.979	-	-4.342	99.76
	16	60	0.11	8.9835	-	-4.422	99.81
	32	60	0.03	8.995	8.995	-	99.95

Appendix 2: Values for Langmuir and Freundlich adsorption isotherm plot

Ions	C_o(mg/L)	Ce(mg/L)	qe(mg/L)	Ce/qe	logCe(gm/L)	logqe(gm/L)
Pb	30	0	4.5	0	-	0.65
	60	0.03	8.99	0.0033	-1.5	0.95
	100	0.04	14.99	0.0026	-1.39	1.17
	140	0.19	20.97	0.009	-0.72	1.32
Cu	30	0.29	4.45	0.065	-0.53	0.648
	60	0.46	8.93	0.05	-0.337	0.95
	100	3.7	14.44	0.25	0.568	1.15
	140	17.92	18.3	0.979	1.25	1.26
Cd	30	0.02	4.49	0.0044	-1.69	0.65
	60	0.02	8.99	0.0022	-1.69	0.95
	100	0.12	14.98	0.008	-0.92	1.17
	140	0.82	20.877	0.039	-0.086	1.319

Appendix 3: shows the kinetic adsorption of pseudo-first-order and pseudo-second-order.

Ions	Co(mg/L)	Pseudo-first-order			Pseudo-second-order		
		q_{1ecal}(mg/L)	K_1(hr^{-1})	R^2	q_{2ecal}(mg/L)	K_1(hr^{-1})	R^2
Pb	30	0.014	0.115	0.795	4.48	6	1
	60	0.013	0.0133	0.803	9	3.08	0.999
	100	1.555	0.81	0.805	15.15	1.09	0.999
	140	0.013	0.0135	0.806	21.73	0.529	0.999
Cu	30	0.199	0.799	0.8902	4.444	5.076	0.999
	60	0.194	0.799	0.8902	8.89	1.78	1
	100	0.046	0.079	0.8902	14.92	10.64	1
	140	0.047	0.078	0.888	20.83	4.6	1
Cd	30	0.02	0.0322	0.574	4.478	0.64	1
	60	0.025	0.316	0.730	8.894	12.5	1
	100	0.02	0.322	0.631	15.15	1.08	1
	140	0.02	0.324	0.459	21.09	1.41	1

Appendix 4: Effect of Pb^{2+}, Cu^{2+} and Cd^{2+} ions initial concentration on adsorption of the metal ions on natural bentonite. Adsorbent dosage=0.8gram, contact time=20min, agitation speed=300rpm

Metal ions	Initial conc. C_o(mg/L)	Final conc. Ce(mg/L)	Amount of metal ions adsorbed, qt (mg/L)	% removal
Pb	30	0	4.5	100
	60	0.03	8.9955	99.98
	100	0.04	14.994	99.96
	140	0.19	20.9715	99.8
Cu	30	0.29	4.4565	99.66
	60	0.46	8.931	99.23
	100	3.7	14.445	96.3
	140	17.92	18.312	82.08
Cd	30	0.02	4.497	99.9
	60	0.02	8.997	99.96
	100	0.12	14.982	99.88
	140	0.82	20.877	99.4

Appendix 5: Effect of pH on adsorption of metal ions on natural bentonite.

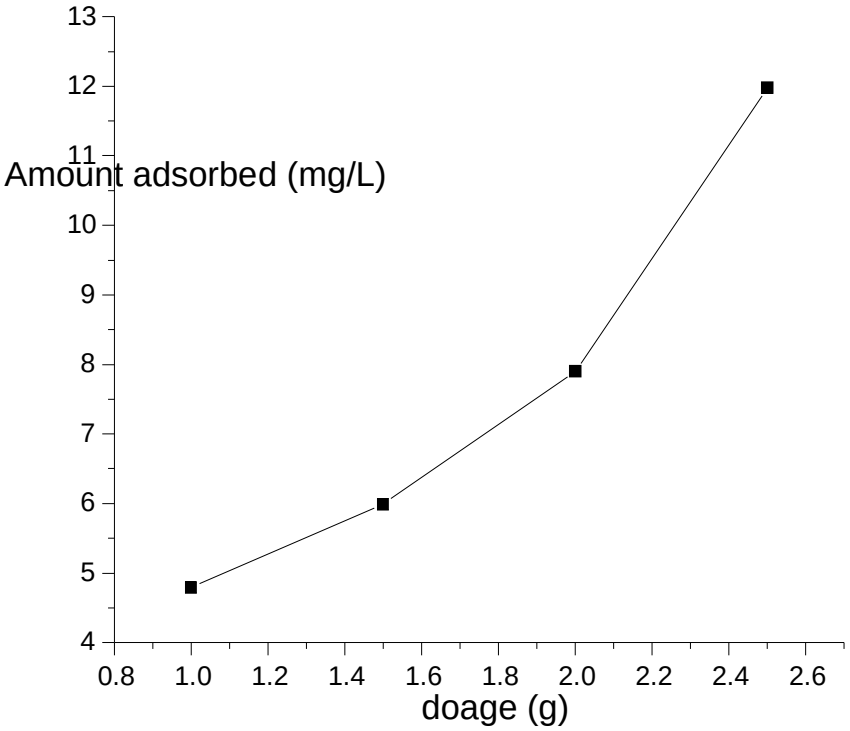
Adsorbent dosage=0.8gram, contact time=20min, agitation speed=300rpm

Metal ions	pH	Final Conce. Ce (mg/L)	Amount of metal ions adsorbed, qt (mg/L)	% removal
Pb	1.5	1.14	14.829	97.18
	4	0.3	14.955	99.4
	6.5	0	15	100
	8.5	0	15	100
Cu	1.5	56.17	6.57	43.83
	4	39.38	9.09	60.62
	6.5	1.11	14.83	98.89
	8.5	0.34	14.94	99.66
Cd	1.5	12.22	13.167	79.63
	4	6.14	14.07	89.766
	6.5	1.05	14.84	98.76
	8.5	0.56	14.916	99.06

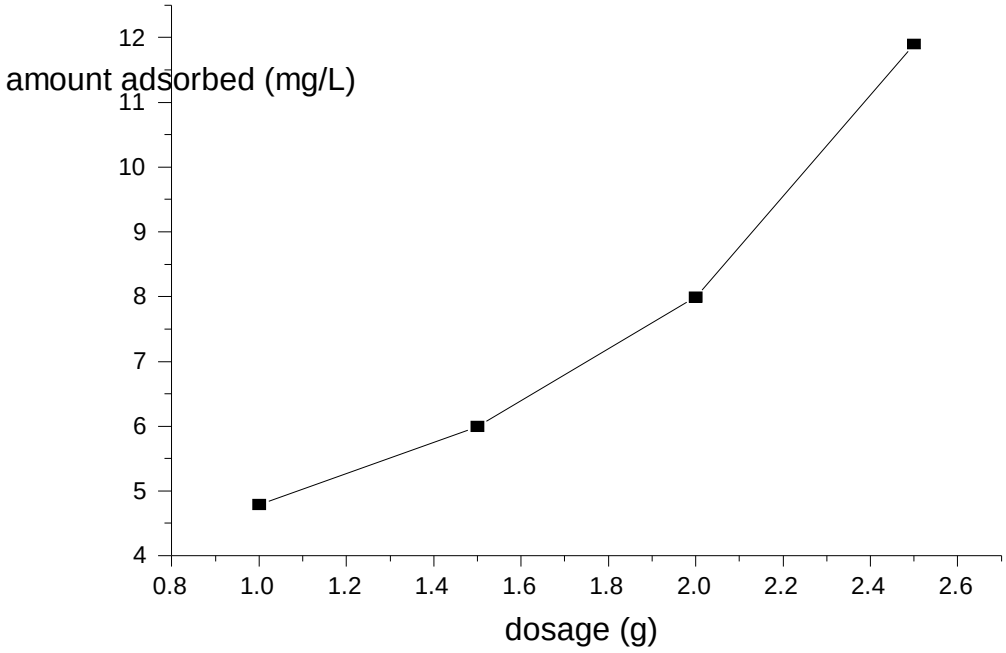
Appendix 6: Effect of adsorbent dosage on adsorption of metal ions on natural bentonit

Contact time=20min, agitation speed=300rpm

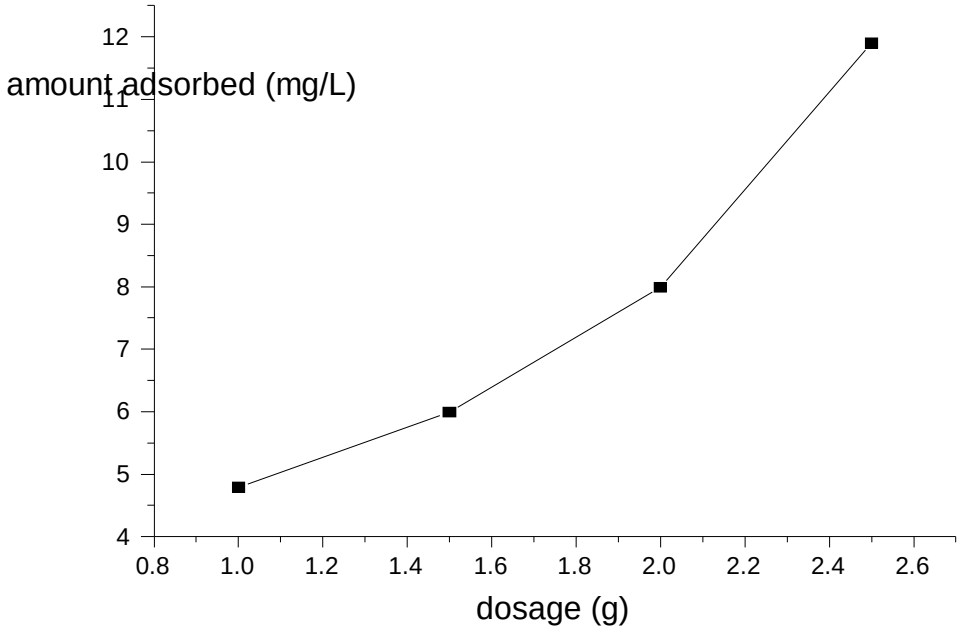
Metal ions	Adsorbent dosage(g)	Final conc. Ce(mg/L)	Amount of adsorbate adsorbed qe(mg/L)	% removal
	1	0.1	8.985	99.45
Pb	1.5	0.13	8.98	99.87
	2	0.06	8.989	99.93
	2.5	0.06	8.99	99.99
	1	0.28	8.958	99.06
Cu	1.5	0.11	8.98	99.63
	2	0.07	8.989	99.99
	2.5	0.07	8.989	99.99
	1	0.43	8.93	99.82
Cd	1.5	0.12	8.98	99.8
	2	0.1	8.985	99.83
	2.5	0.03	8.99	99.95



Appendix 7: Amount of Pb^{2+} adsorbed on natural Bentonite versus dosage



Appendix 8: Amount of Cu^{2+} adsorbed on natural bentonite versus dosage



Appendix 9: Amount of Cd^{2+} adsorbed by natural Bentonite versus dosage