REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION USING NATURAL BENTONITE FROM LEDI AREA, AFAR REGION, ETHIOPIA

By:

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A THESIS SUBMITTED TO DEPARTMENT OF CHEMISTRYSCHOOL OF NATURAL SCIENCE

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This is to certify that the thesis entitled ''REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION USING NATURAL BENTONITE FROM LEDI AREA, AFAR REGION, ETHIOPIA 'submitted in partial fulfillment of the requirements for the degree of Master's in Chemistry, the Graduate program of the department of Chemistry and has been carried out by Tibebu Abdisa Id.No GSS/0230/05, under my 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: Tibebu Abdisa

Signature: _____

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

Name: _____

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Date of submission _____

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LIST OF ABREVATION

RPM	revolution per minuet
XRD	x- ray diffraction
AAS	atomic absorption spectroscopy
WHO	world health organization
ASTM	American standard Testing method
LOI	loss on ignition

ABSTRACT

In this study natural bentonite obtained from Ledi area, Affar regional state was investigated as adsorbent for removal of Cr (VI) from aqueous solution since. It was readily available, reusable and cost effective. 100g of bentonite weighted, dried in oven at 120 ^{0}c for 4 hours, cooled, crushed and ground. It was characterized by XRD and AAS for complete silicate analysis. The study was employed with 250µm particle size and by varying working parameters such as pH (1, 3, 5), adsorbent dose (1g, 2 g, 3 g, 4 g), initial concentration (20 (mg/L), 40 (mg/L), 60 (mg/L), 80 (mg/L), 90 (mg/L), 120 (mg/L), 150 (mg/L), 180 (mg/L)and contact time (30 min, 60 min, 90 min , 150 min, 180 min) have been studied at room temperature. Adsorbent efficiency was Optimum at pH = 3, dose 1g, initial concentration 60 (mg/L) and contact time 120min were obtained. To determine adsorption effiecy Ledi area bentonite real sample was adjusted at optimized working parameters. The mechanism and characteristics of parameters adsorption were analyzed by six different isotherm models. Temkin adsorption isotherm fit experimental data. From Langmuir model it was identified that adsorption was favorable, from freundlich model adsorption was normal and from D- R isotherm adsorption is physical. The maximum adsorption was found to be 1.94 (mg/g) and kinetic adsorption process was studied by pseudo first, pseudo second, intra-particle diffusion and Elovich equations. The result showed pseudo first order fit experimental result and it reveals as adsorption is physical. The result of thermodynamic parameter shows that adsorption is feasible since ΔG^0 is negative. The concentration of chromium discharged to Mojo River from Hora tannery was 305.6 (mg/L). The efficiency of bentonite to remove Cr (VI) from real sample was examined at optimized condition 0.049 mg/L. It was identified that adsorption efficiency of Ledi area bentonite is low.

Key words; Natural bentonite, Cr(VI), Adsorption isotherm, Adsorption, kinetics, Thermodynamic parameter, leather industry effluent.

1. INTRODUCTION

As everybody knows, water is an essential for life of human, plants and animals. But in recent years, it was polluted by heavy metals like chromium (Cr), lead (Pb), mercury (Hg) discharged from several industries such as tanneries, plating facilities, and mining operations (Tamene Fite and Seyoum Leta, 2015). Water pollution by chromium has become considerable concern as this metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation. Leather industry effluents are considered to be major source of water pollution and tannery wastewater has environmental concern because of its high concentration of chromium ion. More than 95% leather industry use chrome for tanning and the tanning requires huge amount of chromium powder and Liquor (Hossain MA *et al*, 2009). The heavy metal chromium is a carcinogenic, tasteless and odorless chemical that is associated with industrial waste from metal plating operations and other manufacturing concerns. Wastewater containing a significant quantity of chromium from tannery industry is discharged as effluent and enters into air, soil and water in the form of two oxidation state as Cr (III) and Cr (VI. The presence of chromium even in trace amount in sea or in river water can have toxic influence on aquatic life. Cr (III) less toxic than Cr (VI) and is essential for human body, their compounds are widely used as mordant, in textile dying, tanning of leather and in paint pigments. The environmental consequence of long term exposure to such oxidation state is uncertain, but chromium seems enzymatic sulphur uptake of cells affecting lung, liver and kidney (Addis Mokonnin, 2006). The maximum concentration of Cr (VI) should not exceeded (0.05 - 50µg/L) in drinking water as it was recommended by *(WHO, 2017)*

Removal of heavy metals such as cadmium, lead, nickel, chromium, iron, zinc and copper from aqueous solution is necessary because of the frequent appearance of these metals in waste streams from many industries (Heba H, 2014).Those heavy metals in the waste streams can be readily absorbed by marine animals and directly enter the human food chains, thus

presenting a high health risk to consumers (Mukesh and Londra, 2013). For these reasons, researchers have used several methods to remove heavy metals, such as ion exchange, ultra filtration, reverse osmosis, electro dialysis, chemical precipitation, evaporation, solvent extraction, membrane processes coagulation, flocculation, biological treatment and chemical oxidation (Vaiopoulou and Gikes P, 2012). However, all these techniques have their inherent advantages and limitations in application. For instance limitation of reverse osmosis is expansiveness, in ion exchange corrosion could become a significant limiting factor, chemical precipitation the need for chemical matters, ultra filtration high demand for energy (Jiang G and Tang J, 2012). In the last few years, adsorption has been shown to be an alternative technique for removing dissolved metal ions from liquid wastes due to its simple design and easy operation, proper efficiency and low cost (Akpomie *et al*, 2015). Previously different adsorbents have been used to remove Cr, including both organic and inorganic materials, such as activated carbon and modified Bentonite (M A Mohammed *et al*, 2012) , (Moraldi *et al*, 2015), Rice bran (Sing B and Dash SK, 2009),cocked waste tea (S,Dhanaky Mar *et al*, 2007), potato peels

(M ,Abdullah and A ,Devil,2009), pre-boiled sun flower (M, Jain *et al*, 2009), saw dust (M,Dakiky et al, 2002),) (granular activated carbon and powder activated carbon (Elsay Mokennin et al, 201), oak saw dust (Argum S,E and Dursun S, 20075).

Despite of their maximum adsorption capacity some adsorbent like powder activated carbon (49.6 mg/g) has problem of reusability and higher production cost (Moraldi *et al*, 2015).

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. Adsorbent, like bentonite is readily available, inexpensive materials and offer a cost-effective alternative to conventional treatment (Akpomie et al, 2015). Even though bentonite is readily available, its adsorption

Efficiency depends on swelling capacity Na- bentonite and Ca-bentonite. (MesfinTessema, 2012).

Acid modified natural bentonite referred as acid activation because it increases the specific surface area and number of active sites of the solids and this increases the adsorptive power of the activated clay mineral but need chemical matter (Moraldi et al, 2015). Comparison between adsorption of Cu (II) and Pb (II) onto natural and modified bentonite revealed that the adsorption on Na-bentonite is better and is affected by increasing pH with maximum adsorption in the range of 3.5 - 6 (A.Taufik, 2011). This study deals with naturally available bentonite obtained from Ledi area, Affar regional state, Ethiopia were investigated as an adsorbent for the removal of Cr (VI) from aqueous solutions under different isotherm model, kinetics models, thermodynamic and equilibrium condition has been investigated in detail.

1.1 Statement of problem.

Chromium has been considered as top 16^{th} toxic pollutant, teratogenic and carcinogenic characteristic to human health. Therefore it is very important work on removal of chromium from aqueous solution using natural Bentonite. In Ethiopia, due to increasing number of industries which could be source of effluents containing chromium, the problem of contamination of water is unavoidable. Even though different reports are available on chromium removal using different natural adsorbent; removal of chromium from aqueous solution using natural bentonite has not been yet studied in Ethiopia. This study is meant to provide information on the efficiency Ledi area, Affar region bentonite towards removal of chromium from aqueous solution by adsorption method.

1.2 Objectives of study

1.2.1 General objectives

The general objective of the study is to investigate the removal of chromium from aqueous solution Ledi area natural bentonite.

1.2.2 Specific objectives

This study has the following specific objectives;

- ✓ To investigate the effect of pH, concentration, contact time and dose of adsorbent towards chromium removal from aqueous solution.
- ✓ To find optimum condition for chromium removal using natural bentonite of Ledi Afar, from aqueous solution.
- ✓ To characterize Ledi area natural bentonite.

1.3 Significance of study

It is very important to know the level of chromium in water around different industries especially leather industry since high level of chromium can cause carcinogenic and teratogenic characteristics on human health. The study will also provide information regarding the removal efficiency of ledi area, Affar bentonite from aqueous solution.

1.4 Scope of the study

The study was limited to adsorption of chromium (VI) from aqueous solution on bentonite using different adsorption methods. The characterization of adsorbent was limited to XRD and AAS.

2. LITERATURE REVIEW

2.1. Source of waste water pollution

There are many source of water pollution, but the two general categories are direct and indirect sources. The direct contaminant source includes; metal plating industries, mining activities, battery manufacture, tanneries, petroleum refining, paint manufacture, pigment manufacture, printing and photographic industries (Gunatilake S.K, 2015). Other direct sources are wood processing industry where a chromate copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide.

The indirect source includes contaminant that enters to the water supply from soil ground stream system (fertilizer, pesticides and from atmosphere via of rain water. Atmospheric contaminant is the indirect human practice contaminant such as gaseous emission from automobiles and factories.

2.2. Method of waste water treatment

2.2.1. Physical methods

Physical separation techniques are primarily applicable to particulate forms of metals, discrete particles or metal bearing particles. Physical separation consists of mechanical screening, hydrodynamic classification, gravity concentration, flotation, magnetic separation, electrostatic separation, and attrition scrubbing. The efficiency of physical separation depends on various soil characteristics such as particle size distribution, particulate shape, clay content, moisture content, heterogeneity of soil matrix, density between soil matrix and metal

contaminants, magnetic properties, and hydrophobic properties of particle surface. (Gunatilake S.K, 2015)

2.2.3. Chemical methods

In addition to physical and biological processes, a wide range of chemical processes are involved in the removal of contaminants. The most important chemical removal process is adsorption, which results in short-term retention or long-term immobilization of several classes of contaminants. Sorption is a broadly defined term for the transfer of ions (molecules with positive or negative charges) from the solution phase (water) to the solid phase (soil). Sorption actually describes a group of processes, which includes adsorption and precipitation reactions. Adsorption refers to the attachment of ions to soil particles, by either cation exchange or chemisorptions. Cation exchange involves the physical attachment of cations(positively charged ions) to the surfaces of clay and organic matter particles in the soil. This much weaker attachment than chemical bonding, therefore the cations are not permanently immobilized in the soil. The capacity of soils for retention of cations, expressed as cation exchange capacity (CEC), generally increases with increasing clay and organic matter content. Chemisorptions represent a stronger and more permanent form of bonding than cation exchange. A number of metals and organic compounds can be immobilized in the soil via chemisorptions with clays, iron (Fe) and aluminum (Al) oxides, and organic matter (Gunatilake S.K, 2015).

2.2.2. Biological methods

Biological removal of heavy metals in wastewater involves the use of biological techniques for the elimination of pollutants from wastewater. In this processes microorganisms play a role of settling solids in the solution. Activated sludge, trickling filters, stabilization ponds are widely used for treating wastewater. Activated sludge is the most common option uses

microorganisms in the treatment process to break down organic material with aeration and agitation, and then allows solids to settle out. Trickling filters which consist beds of coarse media (often stones or plastic) 3-10 ft. Wastewater is sprayed into the air (aeration), and then allowed to trickle through the media and microorganisms break down organic materials in the wastewater. Trickling filters drain at the bottom and the wastewater is collected and then undergoes sedimentation. Stabilization ponds or lagoons are slow, cheap, and relatively inefficient, biological method that can be used for various types of wastewater. They rely on the interaction of sunlight, algae, microorganisms, and oxygen (Gunatilake S.K, 2015).

2.4. Toxicity of heavy metals

Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritized as major contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies Imply that through natural processes such as biomagnifications, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics. These metals can either be detected in their elemental state, which implies that they are not subject to further biodegradative processes or bound in various salt complexes. In either instance, metal ions cannot be mineralized. Apart from environmental issues, Technological aspects of metal recovery from industrial waters must also be considered (Watson P et al, 2002).The heavy metals which hazardous to humans include Copper, Zinc, Nickel, Lead, Mercury, Cadmium, Arsenic, and Chromium. Such metals are found naturally in the soil in trace Amounts, which pose few problems.

2.5. Chemistry of Chromium

The properties of Cr are highly dependent on the molecular structure of the Cr compound, particularly on the oxidation state (or oxidation number) of the Cr. Cr is an element that exists

primarily in two different oxidation states, hexavalent and trivalent. These oxidation states are symbolized as Cr (VI) and Cr (III), respectively. Except for the rarely, naturally-found, elemental Cr with an oxidation number of zero, Cr(0), other oxidation states of Cr are unstable and therefore, are not found in the natural environment. The oxidation state of the Cr has a significant effect on the transport and fate of Cr and on the type and cost of treatment required to reduce Cr concentrations less than regulatory health based standards.

Cr (VI) is far more mobile than Cr (III) and more difficult to remove from water. *It can act as an oxidant directly on the skin surface or it can be absorbed through the skin, especially if the skin surface is damaged. Interestingly enough, irritation of the skin a most frequently reported human health effect from exposure to Cr (VI) (Huffer and Taeger T,2004) taking the form of skin ulceration (dermatosis) and allergic sensitization (dermatitis). Indeed, dermatosis was the first observed health effect associated with chromium (VI) exposure, although improved industrial hygiene practices have greatly reduced its incidence. Allergic contact dermatitis is the most prominent reaction from the interaction of chromium with skin.* The most common Cr (VI) forms are chromate (CrO_4^{2-}), Dichromate ($Cr_2O_7^{2-}$) and hydrogen chromate ($HCrO_4^-$).

2.6. Methods of removing chromium from waste water

Continuous discharge of industrial, domestic and agricultural wastes in rivers and Lakes causes deposit of pollutants in sediments. Such pollutants contain chromium, which endanger public health after being incorporated in food chain. Excessive amounts chromium ions can toxify organism through their inorganic salts or via organic compounds from which the metal can become easily detached or introduced into the cell.

Several methods have been used for the treatment and removal of chromium ions. The commonly used procedures include chemical precipitation, lime, coagulation, ion exchange, reverse osmosis, Adsorption, and solvent extraction (Ahaly N and Ramacha, T,V,2003).

2.6.1. Chemical precipitation

Chemical precipitation is the most widely used for heavy metal removal from inorganic effluent. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Equation (Baraket M,A et al 2011).

$$M^{2+} + 2(OH)^{-} \longrightarrow M(OH)_{(2)}$$

Precipitation of Cr (III) occurs as $Cr(OH)_3(s)$, $FeCr_2O_4(s)$, or $Fe_xCr_y(OH)_3(s)$ (Rahula, A et al, 2004). As pH increases, OH^- concentration increases and more Cr precipitate. Organics can complex with dissolved Cr, making removal by precipitation or adsorption difficult. The precipitation of Cr(III) is useful for increasing Cr(VI) to Cr(III) reaction rates, by Le Chatelier's Principle. In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge (Jufter K and schimidar H, 2000). Other drawbacks are its excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Bose P et al, 2002).

2.6.2. Ion exchange

Ion exchange is a reversible chemical reaction method used successfully in the industry for the removal of heavy metals from effluent. It is physical process in which an ion with a high affinity for the resin material of the ion exchange column replaces an ion with a lower affinity that was previously bound to the column resin. As water flows through, dissolved Cr (VI) ions bind to the resin and displace the previously bound ions (usually Cl^- or OH^- ions). The resins used for Cr sequestration are typically either a naturally occurring inorganic zeolite or a synthetic weak base or strong base anion exchanger resin. Once the resins have accumulated Cr on enough exchange sites that breakthrough surpasses a threshold value, they must be regenerated. Ion exchange resins are capable of reducing Cr (VI) concentrations to less than

the detection limit. Resins are typically most effective at low pH values, because Cr (VI) will be present as $HCrO_4^-$ and $Cr_2O_7^{2-}$, not as CrO_4^{2-}. The ratio of ion exchange sites to Cr ions sequestered is then 1/1. When CrO_4^{2-} is present, two ion exchange sites are used to sequester each Cr ion. Competition by other anions (namely $SO_4^{2-,}$ nitrate (NO_3^-), and $Cl^{-)}$ is not a problem in most applications, since Cr has a higher affinity for all polymeric anion exchangers. The disadvantage of this method is highly sensitive to the pH of the solution and corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced (Babel,S et al, 2006).

2.6.3. Electro dialysis

Electro dialysis (ED) a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics (Chen G, H, 2004). In the electro dialysis process, ionic components of a solution are separated through the use of semi permeable ion-selective membranes. This process may be operated in either a continuous or a batch mode. Problems associated with the Electro dialysis process for wastewater renovation include chemical precipitation of Salts with low solubility on the membrane surface.

2.6.4. Ultra filtration

Ultra filtration technologies can be used in a variety of ways in wastewater treatment and water reuse systems. Ultra filtration can reduce the amount of treatment chemicals, has smaller space requirements, and reduce labor requirements. On the contrary in this method uses more electricity, may need pre-treatment, and requires replacement of membranes (Gunatilake S.K, 2015).

2.6.5. Coagulation–Flocculation

Coagulation–flocculation can be employed to treat wastewater laden with heavy metals. Principally, the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation (Shammas N. K, 2004).In spite of its advantages; coagulation–flocculation has limitations such as high operational cost due to chemical consumption. To overcome such problems, electro-coagulation may be a better alternative than the conventional coagulation, as it can remove the smallest colloidal particles and produce just a small amount of sludge (Mukesh and Londra, 2013).

2.6.6. Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a Solid or liquid (adsorbent), forming a molecular or atomic film (adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. Adsorption is an operative in most physical, biological, and chemical systems and widely used in industry. At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed (Mukesh and Londra, 2013).

Adsorption processes for Cr can also be used in treatment strategies. However, Cr (III) is the primary form of Cr that is retained by sorption. The kinetics of Cr(III) sorption is rapid in clays, sands, and soil containing Fe and manganese oxides Cr(III) behaves like a positively charged ion (such as Cr^{3+}) when adsorbing onto surfaces. As pH increases, surfaces are deprotonated, by increasing the attraction between Cr (III) and the surface. Sorption is therefore enhanced as pH increases.

The process of adsorption has an advantage over the other methods due to its cost-effectiveness and sludge free clean operation (Gubta,V and K,Juhas, 2009) . Adsorbents that are commercially available like commercially activated carbon are very effective but expensive (Etim U, T et al, 2012). Therefore, the natural adsorbents have gained much

attention for the adsorption of various pollutants from an aqueous medium (Abdurahamn Ali Alaz, 2015). Bentonite clay has been considered as a potential adsorbent for the removal of pollutants from waste water.

2.7. Property and application of bentonite

2.7.1. Property of bentonite

Bentonite is clay consists of smectite minerals like montmorrolonite, quartz, illite, kaolinite etc. It has exchangeable Na, Ca, or Mg cations, and exhibits far greater ion-exchange worldwide capacity than any other mineral except for zeolite. Na-bentonite has high swelling capacity and Ca- bentonite has a relatively low swelling capacity (MesfineTessma, 2012).Substitutions of silicon by cations produce an excess of negative charges in the lattice, which is balanced by cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) in the interlayer space. These cations are exchangeable due to their loose binding and, together with broken bonds (approximately 20% of exchange capacity) give montmorillonite (Zontan *et al*, 2005).

The basic unit of montmorillonite crystals is an extended layer composed of an octahedral alumina sheet between two tetrahedral silica sheets (Bailey, 1980a). The stacks layers produce the montmorillonite crystals. Isomorphic substitutions in the octahedral sheet (few tetrahedral substitutions are observed in montmorillonite) create an excess of negative structural charge that is delocalized in the lattice. Cations located between two consecutive layers contribute to compensate the structural charge and to keep the layers bound. These cations can easily be exchanged, since they are retained by electrostatic attractions. The surface area associated with the basal surfaces of the extended unit is known as the interlayer surface when it corresponds to consecutive layers or as the external surface when it corresponds to the external basal surfaces of a crystal. The external and interlayer surface area represents approximately 95% of the total surface area of montmorillonite. On the other hand, the periodic structure of the montmorillonite crystals is interrupted at the edges, where the broken

bonds compensate their charge by the specific adsorption of protons and water molecules (WHO, 2005)

Quartz is the most relevant accessory mineral in bentonite. Its structure is a tridimensional framework of silicate tetrahedral arranged sharing corners. In contrast with montmorillonite and kaolinite, quartz surface area is defined only as an external surface having broken bonds, which compensate charge by adsorption of protons or water molecules found in all the crystal phases.

The kaolinite layers are formed only by a tetrahedral sheet of silica and an octahedral sheet of alumina, which contain almost no isomorphic substitutions. Hydroxyls of the octahedral sheet bind to oxygens of the tetrahedral sheet of the consecutive layer in the kaolinite crystal. The surface area of the kaolinite is thus reduced to external surface area and to edge surface area which similar to montmorillonite.

2.7.2. Application of bentonite

The presences of different minerals in bentoniteincreaseits demand industrially. 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 (MesfinTessema, 20120).

Bentonite used as coagulant and adsorbent to treat the waste water. Raw, acid activated and basic activated Bentonite is used to remove macronutrients particularly NH^{+4}, K^{+}, PO_4^{-3}, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) plant Sewage Plant (Moraldi et al. (2015),

3. MATERIALS AND METHODS

3.1. Description of study area

Ledi Bentonite sediments were found in Afar Regional State at $11^0$9'30" N and$40^0$41'E. The area was located at 20 km from Addis Abeba road to south of Desse junction and 500 m from Led River. The lacustrine clays underlying the plain are exposed in river gullies and outliers. In ledi area 4 bentonite occurrence were identified, Horizontally bedded grey clay with a greasy luster ,The grey green to brownish salty to sandy clay with indistinct horizontal bedding. The south of Ledi River on the northern bank of Ledi River grey –green bentonitic clay which is compact and massive containing minor salt and silt is exposed. In this area the betonite outcrop is without an overburden and has 8.5 thicknesses. 5-6km west of the gewane-mile highway grayish to brownish bentonite clay is exposed in the huana River valley. It has an average thickness of 7.5 m. In this area the reserve was estimated to be 1784000m^3 with an overburden of 1200000m (MesfinTessema, 2012)

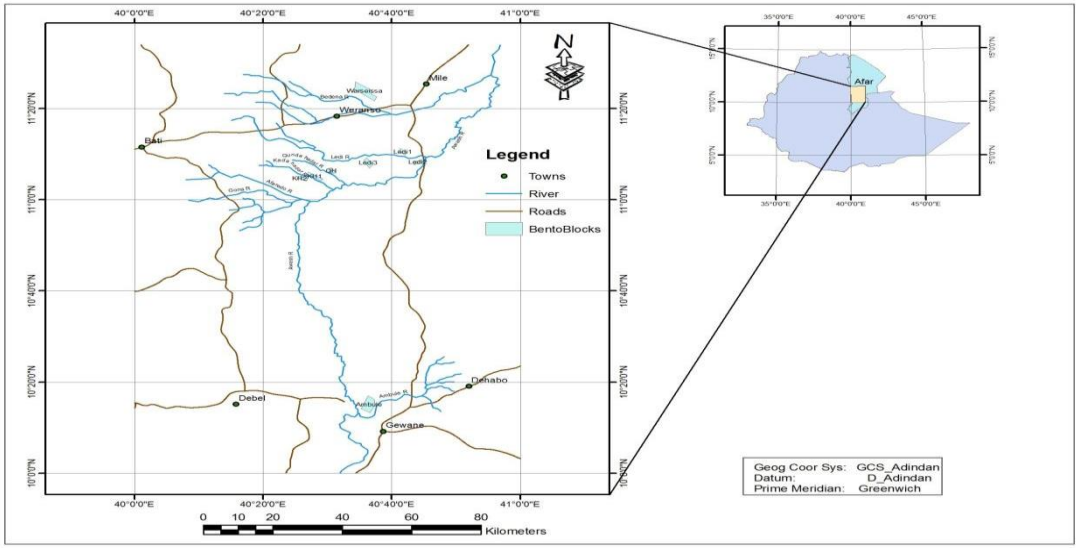

Figure1. Bentonite occurrence map of Afar area (Tibebu M et.al, 1983)

3.2. Material and apparatus

3.2.1. Chemicals

Hydrochloric acid, HCl (37 %, Riedel-deHaën, Germany), potassium hydroxide, KOH (90 %, BDH, England), potassium dichromate ($K_2Cr_2O_7$ 99.9 %, FINKEM, England), Double ionized water for all preparation and purification and standard buffer solution. All chemicals used in this study were analytical reagent grade and were used without further purification.

3.3. Sampling and Sample collection area

Bentonite was taken from Ledi area,Affar Region, Ethiopia and kept in ASTU laboratory and effluent discharged to Mojo river was taken from Hora tannery of Mojo, eastern shoa zone, Oromia Regional, Ethipia. Clean polyethylene bottles were used to carry the effluent taken from Hora tannery to ASTU PG laboratory.

3.3.1. Preparation of stock solution

The standard stock solution of chromium (1000 mg/L) was prepared by dissolving 2.828 g of 99.9 % analytical grade $K_2Cr_2O_7$ in 1000 mL of distilled water. All the required solutions were prepared with analytical reagents and double-distilled water. Standard solutions of chromium with different concentrations were prepared from the stock solution by appropriate dilutions.20 (mg/L), 40 (mg/L), 60 (mg/L), (80 mg/L and 100 (mg/L) of chromium standard solution were prepared by diluting 20 mL, 40mL, 60mL, 80mL and 100mL of 1000 ppm chromium stock solution with distilled water in 1000 mL volumetric flask (PYREX,UK) up to the mark respectively. The pH of aqueous solution was adjusted to p H (1, 3, and 5) by addition of 0.1 M HCl or 0.1M NaOH solution.

3.4. Preparation and characterization of adsorbent material

3.4.1. Preparation of adsorbent material

Natural bentonite used in this study was taken from Ledi Affar regional state, Ethiopia. 100g of bentonite weighted by electronic balance (OHAUS,Swizerland) and dried in oven at 120 ^{0}c for 4 hours (Hebab H, 2014). After it was cooled, crushed, ground by mortar and sieved to mesh size ‹ 250µm using an ASTM standard seiver in ASTU civil engineering laboratory.

3.4.2. Characterization of Adsorbent

3.4.2, 1. Characterization by XDR

The bentonite material was characterized chemically by x-ray diffraction XRD (Bruker D8 Advance Diffractometry) and performed to analyze its chemical constituent Addis Abeba University Chemistry Department. 2 gram of powdered bentonite clay sample was packed with standard sample holder and analyzed by using continues scanning XRD instrument with Cu k alpha radiation at (λ1= 1.54059nm andλ2=1.5444nm) source operating at voltage 40kv in range 2θ from 10 ^{0} -90 ^{0} in step of 0.02 at rate 0.12 per second.

3.4.2.2. Characterization by elemental analysis

0.1 gram of bentonite was added to 1.5 gram of $LiBO_2$ and the mixture was heated in blast furnace for 45min at 950 ^{0}c. After it was cooled over night the mixture was stirred with magnetic stirrer, washed and transferred to round bottom flask by adding lanthanum chloride at Ethiopian geological survey The solution was used for AAS (Varian, model spectra 20 AA plus) to determine metals like Ca, K, Al, K, Mn, Fe, Na, and etc. The amount of silica was determined by tacking 0.1 gram bentonite, 3mL of HCl and 2mL of boric acid directly red by

AAS and the amount of TiO_2 and P_2O_5 was determined by Uv-Vis spectroscopy (DR 5000, Hatch, USA). .

3.5. Determination of concentration of chromium by Atomic absorption spectroscopy.

Flame atomic absorption used to determine concentration of chromium before and after addition of bentonite. The instrument was calibrated between 30mg/L -100mg/L at optimized parameters wave length359.5 nm, slight width 0.2nm, current 5mA.

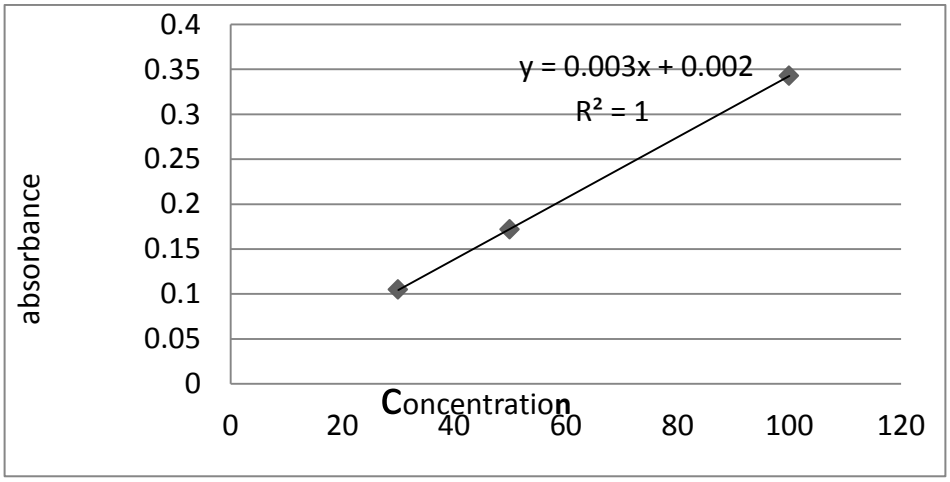

Figure 2. Calibration of standard solution

3.6. Determination of adsorption efficiency

Adsorption measurement was made by batch techniques' at room temperature because of its simplicity and reliability. The batch adsorption studies were carried out at desired pH value, contact time and adsorbent dose. The pH of solution was monitored by adding 0.1 M of HCl and 0.1M NaOH as per required value using pH meter (pH -016). The required amount of bentonite was added to 150ml of potassium dichromate solution in beaker and it was shaked

with orbital shaker (SOL.UK) for desired time with 120 rpm at 24±1 ^{0}c. The time required for reaching equilibrium condition was estimated by drawing graph at regular interval of time and the concentration of chromium was determined after filtration through what man No1 filter paper. The amount of chromium adsorbed on bentonite was known after comparing concentration of chromium before and after treatment. The amount of chromium per unit mass of bentonite was evaluated by the following mass balance equation.

$$qe = (co - ce) \times \frac{v}{m} \text{ ---------- (1)}$$

Where co = initiation concentration of chromium solution in mg/L, v = volume of chromium solution in liters,ce = concentration of chromium solution at equilibrium (mg/L), qe= amount of chromium adsorbed on bentonite (mg/g).

The percentage removal of chromium (VI) was evaluated as follows.

$$\% \text{ removal of Cr (VI)} = \left(\frac{co-ce}{co}\right)\boldsymbol{x100}\Big) \text{..... (2)}$$

3.7. Effect of adsorption parameters

The effect of pH (1 - 5) was determined by taking 100(mg/L) of standard solution with 2g of bentonite by shaking (Orbital shaker) for 15min. The effect of concentration was determined by adding 2g of bentonite into 20 (mg/L) – 80 (mg/L) at pH= 3 for 45 min at room temperature. The effect of bentonite dose (1g - 4g) was determined at optimized pH = 3 and optimized concentration 60(mg/L) for 90min at room temperature. The effect of contact time on adsorption was studied by varying time from (30 min – 180 min) at the optimized pH =3, concentration 60(mg/L) and bentonite dose 1g at room temperature. The adsorption isotherm study were carried out with concentration Cr (VI) from 60mg/L, at pH =3, contact time 120 min and 1 g of bentonite dose. Analysis of Cr (VI) sample was carried out in doublet to reduce reproducibility in experimental result

3.8. Adsorption method

3.8.1. Adsorption isotherm

Six different isothermal models (Langmuir, Freundlich, Hassley, Durbinin- Raduskeive (D-R), Temkin and independent site oriented model) were used to identify the type of models fit for experimental data.

The first isotherm applied was Langmuir because it gave information whether adsorption is favorable or not. His assumption is based on the of monolayer coverage with fixed number of well defined sites and all adsorption sites are equally favorable. Based up on his assumption Langmuir represents the following equation.

$$\mathbf{qe} = \frac{\mathbf{qmaxbce}}{\mathbf{1+bce}} \quad \text{---------- (3)}$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation into linear form

$$\frac{\mathbf{Ce}}{\mathbf{qe}} = \frac{\mathbf{1}}{\mathbf{b\ q\ max}} + \frac{\mathbf{ce}}{\mathbf{qmax}} \text{---------- (4)}$$

Were qe = amount Cr adsorbed on bentonite at equilibrium (mg/L),ce = concentration of chromium solution at equilibrium (mg/L), q max = maximum adsorption capacity (mg/g),b = adsorption equilibrium constant (L/mg).The plot of $\frac{ce}{qe}$vsce is drawn and its linearity is observed by calculating correlation coefficient (R^2). Essential future of Langmuir isotherm may expressed in terms of dimensionless parameters $R_{L,}$ which is known as separation factors (Dad A.O, et al, 2012)

$$\mathbf{RL} = \frac{\mathbf{1}}{\mathbf{(1+(1+bc0))}} \text{---------- (5)}$$

The value of R_L indicates the type of adsorption isotherm. If the value of $R_{L\,=}$ 0, adsorption is irreversible, if the value of R_L = 1, linear and if the value of R_L > 1, unfavorable and itis favorable if 0< R_L <1 (Akpomie et al, 2015)

Freundlich isotherm is empirical expression based on adsorption onto heterogeneous adsorbent system. Its equation is given as;

$qe = kfce^{1/n}$……..(6)

Were kf = Freundlich constant, n = Freundlich coefficient, the constant Kf is an approximate indicator of adsorption capacity and 1/n is a function of the strength of adsorption in the adsorption process (H,Egli et al, 2002). If 1/n = 1 then the partition between the two phases are independent of the concentration, If 1/n <1 normal adsorption and 1/n > 1 indicates cooperative adsorption (Dad A, O et al, 2012)

The 3rd adsorption isotherm applied to express the adsorption model was D-R isotherm because it gave information whether adsorption is physical or chemical depend on the value of mean free energy adsorption (E). It is called physical adsorption if the value of E is less than 8 kj/mol and chemical if the value of E between 8 kj/ mol and 16 kj /mol (InduSherma and Dinesh Goya, 2009).It was generally applied for Gaussian energy distribution onto a heterogeneous surface and the model often successfully fitted for high solute activities with an intermediate range of concentrations data well (Dad A, O et al, 2012).

$\ln qe = \ln qs - \beta\epsilon^2$……... (7)

$\epsilon = RT \ln(1 + 1/ce)$ ……(8)

$\mathbf{E} = \frac{\mathbf{1}}{\sqrt{\mathbf{2\beta}}}$……(9)

Where, ϵ = Polanyi potential, qe = amount of adsorbate in the adsorbent at equilibrium (mg/g), qs = theoretical isotherm saturation capacity (mg/g); β= constant for adsorption energy

The Durbin in - Raduskevich isotherm can be linearized by drawing lnqe vs ϵ^2 and its linearity observed from correlation coefficient (R^2).

The other adsorption isotherm model applied for the experimental data was Hassley's isotherm. According to Hassleys multilayer adsorption is formed and adsorbent is heterogeneous in nature. Generally its equation has been expressed as;

$$qe = \frac{\exp(\ln kH - \ln ce)}{nH} \quad \text{..... (10)}$$

When equation (10) is linearized it can be written as;

$$\ln qe = \frac{\ln kH}{nH} - \frac{\ln ce}{nH} \quad \text{..... (11)}$$

The plot of $\ln qe$ vs. ln Ce was drawn and its linearity observed from correlation coefficient (R^2).

Temkin isotherm model was applied for experimental data because it state why adsorbent–adsorbate interacts by ignoring the extremely low and large value of concentrations. The model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly. It is good fit for an arrangement which is not tightly packed structure with the same orientation (Indu Sherma and Dinesh Goya, 2009). Temkin equation is given by the following

$$qe = \frac{RT\ln(ATce)}{b} \quad \text{.....(12)}$$

Temkin adsorption parameter were determined by transforming the temkin equation into linear form

$$qe = \frac{RT\ln AT}{bT} + \frac{RT\ln ce}{bT} \quad \text{..... (13)}$$

When $\frac{RT}{bT}$ represents by B the equation is becomes;

$$\mathbf{qe = BlnAT + Blnce} \quad \text{.....(14)}$$

The constants were determined from the slope and intercept. The plot of qevslnCe was drawn and its linearity was determined from correlation coefficient (R^2).

Where qe = amount of Cr adsorbed in (mg/g), R= universal gas constant, T= temperature, AT= Temkin isotherm equilibrium binding isotherm (L/g), B = constant related to heat of adsorption, b = Temkin isotherm constant

Furthermore, in order to obtain more comprehensive information about the nature of the binding sites on the adsorbent and to analyze the results of the equilibrium

isotherm, the scat chard plot analysis also called independent site oriented model was applied to the experimental data. The scat chard equation is given by*:*

$$\mathbf{qe/ce = qmaxb - qeb} \text{……………………………….. } \textit{(15)}$$

Constants qmax (mg/g) and b (L/mg) are the scat chard isotherm parameters. The shape of the scat chard plot provides useful information about the interactions between metal ions and the adsorbent. If a straight line is obtained from the plot of qe/Ce vs qe, then only one type of binding site adsorbent is available (homogeneous nature), but if a deviation from linearity, it implies that the surface of the adsorbent has more than one type of binding sites (heterogeneous in nature) (Akpomie et al, 2015).

3.8.2. Adsorption kinetics

In order to understand mechanism of adsorption and potential of rate controlling step, numbers of kinetics models have been used to determine experimental data of Cr (VI) adsorption (Chem.G,H. 2004).

The first kinetic model applied for experimental data was pseudo first because it has been widely used to predict metal adsorption kinetics of solid/liquid system. Its equation is expressed as;

$$\frac{dqe}{dt} = k1(qe - qt) \text{……………………………………………… (16)}$$

After integration and at initial condition qt = 0 at t = 0 the becomes

$$\ln(qe - qt) = \ln qe - k1t \text{………………………………………….(17)}$$

Where qe = amount of Cr (VI) adsorbed at equilibrium (mg/g), qt = concentration of Cr (VI) solution at instant time (mg/g), k1= rate constant for pseudo first order. The plot of $\ln(qe - qt)$ vs. t was drawn for its linearity and the value of r^2 is determined.

Pseudo- second order kinetics was the other type of adsorption kinetics that has been successfully applied to metal ions and organic substance. It state that the slowest step is

chemical adsorption (AldiwinH,Ibe et al, 2017).The linearzed form of its equation is expressed as;

$$\frac{dq}{dt} = k2\,(qe - qt)^2 \quad \text{..... (18)}$$

After integrating equation for boundary condition the equation becomes

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{t}{qe} \quad \text{..... (19)}$$

Were k_2 = second order rate (g/mg min) and $h = k_2 qe^2$is initial adsorption rate.The plot of t/qt vs. t was drawn and its linearity was observed by considering r^2 value

The 3rd type kinetic model applied for experimental data was Elovich model because it provides types of adsorption. It is applicable for chemo adsorption kinetics and cover wide range of slow adsorption rate (M Braket et al, 2014). It has been formulated as follows.

$$\frac{dq}{dt} = \alpha e^{-\beta qt} \quad \text{..... (20)}$$

After integration with boundary condition

$$qt = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln(t)}{\beta} \quad \text{.....21)}$$

Where α = initial adsorption rate (mg/g min), β = the desorption constant related to extent of surface coverage and activation energy for chemo adsorption (mg/g). The plot of qtvslnt is drawn and its linearity was compared using R^2 value.

The diffusion mechanism was determined by the intra-particle diffusion (Dad A, O et al,2012) explored by using Weber and Morris equation due to the fact that metal ions can transported from the aqueous phase to the surface of the adsorbent and can diffuse into the interior of the particles of porous. The intera particle diffusion equation is given as:

$$qt = kit^{\frac{1}{2}} + c \quad \text{.....(22)}$$

Where qt =amount of Cr (VI) adsorbed at time t (mg/g), ki = inter particle diffusion rate constant (mg/g.$min^{1/2}$) and C intercept. The value of ki and c are obtained from plot of qtvs t

½ at different time interval and room temperature. If plot of qt vs $t^{1/2}$ is linear and pass through the origin, intra-particle diffusion is the sole rate determining step (Akpomie et al, 2015).The magnitude of the intercept c measure thickness of adsorbed layer and the greater value of c the greater boundary layer effect (Dad A, O et al, 2012).

3.8.3. Thermodynamic study for adsorption

In order to determine the thermodynamics feasibility, the Gibbs free energy (ΔG^0) is fundamental criteria to determine the spontaneity of process. It has been evaluated by the following equation

$\mathrm{lnkc} = \mathrm{qe}/\mathrm{ce}$……(23)

$\Delta G° = -\mathrm{RTlnkc}$…… (24)

3.11. Quality control and assurance

Special precautions were taken during the collection of samples, the sample container was thoroughly washed and well-rinsed with de ionized water routinely, dried, and stored in clean area to prevent contamination. Then, the collected sample was preserved by in refrigerator from the time of collection until analysis in laboratory

3.12. Data analysis

All data generated from the above experiments were analyzed using the Microsoft word excel, Microsoft window program and origin soft ware 8. Linear regression values were computed as required.

4. RESULTS AND DISCUTION

4.1. Characterization of adsorbent

4.1.1. Characterization by using XRD

The XRD spectrum of Ledi area, Afar Regional State shows that bentonite contains smectite groups like kaolite , illite, montimorollonite, quartz when compared with the result reported on bentonite characterization in terms of intensity vs 2θ by (S.Deka, 2016). The occurrence Montimorollonite at 2θ =37 and 2θ=22, quatz 2θ = 27 and 20 due to different intensity observed at their 2θ, kaolite 2θ=69 and illite at 2θ = 39 when compared with literature.

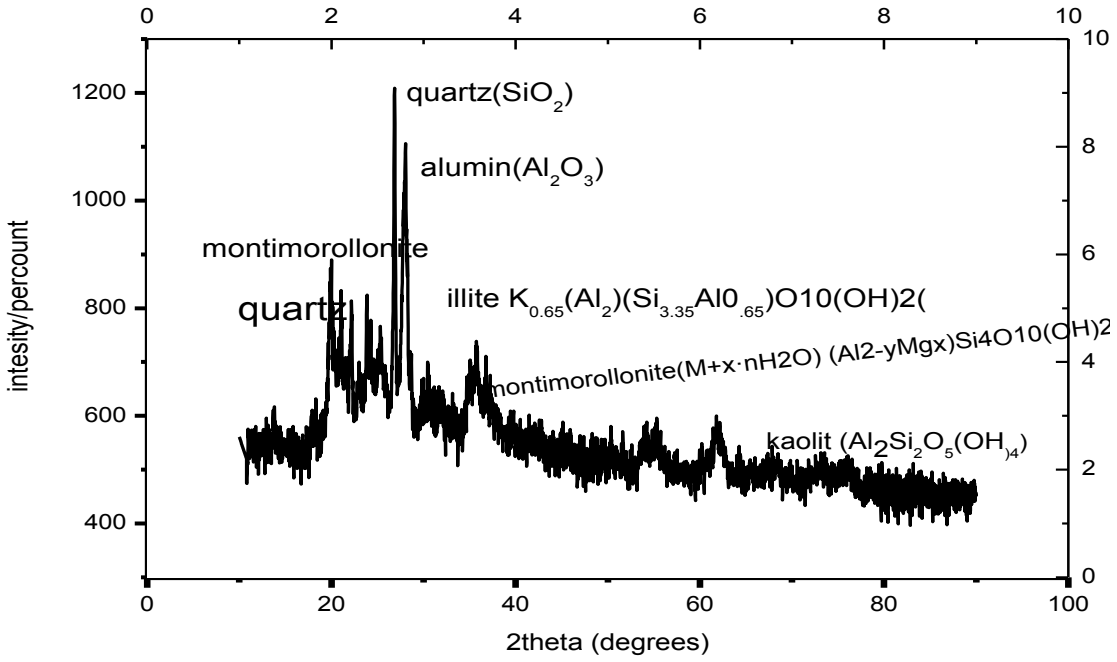

Figure 3. XRD spectrum of Lediarea ,Afarbentonite

4.1.2. Characterization by silicate analysis

The chemical analysis of bentonite having 200μm size was analyzed by $LiBO_2$ fusion, HF attach, gravimetric, colorimetric and AAS analytical methods Table1.

Table1. Silicate analysis of Ledi area natural bentonite

Oxides	Percentage
SiO_2	61.2
Al_2O_3	13.93
Fe_2O_3	7.72
CaO	4.28
MgO	2.44
Na_2O	2.27
K_2O	0.83
MnO	0.06
P_2O_5	0.15
TiO_2	0.61
H_2O	0.4
LOI	6.01

Previously major and minor oxide composition of Ledi area bentonite was reported by (MesfinTessema, 2012) i.e. SiO_2 54.2 % Al_2O_3 %, 12.65 %, Fe_2O_3 %, 7.75 % , TiO_2 1.35 %, CaO 4.15 %, Na_2O 1.85 %, , K_2O 1.35 %, MnO 0.1%. Both results reveal that ledi area bentonite is Ca- bentonite.

4.2. Effect of parameters on adsorption process

Various parameters for effective removal of Cr (VI) from aqueous solution as adsorbent were studied.

4.2.1 Effect of pH

PH of solution plays important role in adsorption process since the adsorbent surface acquire positive or negative in response to charge in pH (Chen G.H, 2004). The effect of pH on adsorption of Cr (VI) ions was investigated by varying the pH from 1-5 at different times. The effect on uptake adsorption of Cr (VI) is shown (Figure 6) and amount of Cr (VI) adsorbed on bentonite is 4.02 mg/g at pH 3 and very small amount of Cr(VI) adsorbed at pH 1.The minimum adsorption at pH 1 is due to high concentration and high mobility of H^+ which is preferably adsorbed itself on bentonite rather than Cr (VI) ions and exist as $H_2Cr_2O_7$. From various chromium forms stated in literature $HCrO_4^{-1}$ is adsorbed prefentially at pH 3 on Ledi area bentonite. Similar observation has been reported for removal of Cr (VI) on low cost adsorbent by (Gubta V and K Juhas, 2009).

Table 2. Effect of pH adsorption of Cr (VI) on Ledi area bentonite with 2g of bentonite

pH	**C_0**	**Ce_1**	**Ce_2**	**Average ce(mg/L)**	**qe_1**	**qe_2**	**Average of qe (mg/g)**
1	114.4	113.5	113.2	113.35	0.075	0.105	0.09
3		72	60.8	66.4	4.85	3.18	4.02
5		76.6	57.2	66.9	283	4.29	3.56

4.2.2. Effect of initial concentration on adsorption of Cr (VI)

The adsorption of Cr (VI) ions on bentonite as function of initial concentration was studied in range of 20 mg/L – 80 mg/L by keeping all parameters constant. It is clear that adsorption efficiency increased when metal ions concentration decreased. At low concentration the ratio of number of ions to number of available sites is small, so adsorption is independent of initial concentration. As concentration increase the situation changes due to the competition for the adsorption sites and the extent of adsorption comes down and but the amount of adsorbed per unit mass of adsorbent increase. But the result represented in (Figure7) shows the amount of Cr (VI) adsorbed on bentonite was increased from 20 mg/L – 60 mg/L and decreased at 80

mg/L. This may be explained as, excess number of Cr (VI) ions comes to bind on bentonite surface but bentonite surface became saturated. It also explained as adsorption of Cr (VI) on Ledi area bentonite was physical adsorption. Physical adsorption has lower energy barrier of metal ions to overcome their adsorption and promotes easy desorption of metal ions from adsorbent (Akpomie et al, 2015).Similar observation has been reported for Cr (VI) removal using activated carbon by (M, A Mohammed et al, 2012).

Table 3. Effect of initial concentration adsorption of Cr (VI) on Ledi area bentonite

Initial concentration	Ce_1	Ce_2	Average of ce in (mg/L)	qe_1	qe_2	Average ofqe in (mg/g)
17.5	15	15.52	15.26	0.187	0.148	0.1675
37.47	35.67	34.79	35.23	0.135	0.201	0.168
60.44	35.7	36.5	36.1	1.856	1.956	1.8258
81.94	69	68.67	68.83	1.02	0.99	0.953

4.2.3. Effect of dosage

The amount of bentonite was varied from 1 g to 4 g with initial metal concentration 60 mg/L at pH= 3 and shaking time 90 min with 120 rpm. It is known that when adsorbent dose increase the amount of chromium adsorbed also increase due to increasing adsorbent surface area and availability of more adsorption sites. But the result represented in (Figure 8) shows that increasing bentonite dose decrease amount of Cr (VI) adsorbed on Ledi area bentonite. This may be due to instauration of bentonite active sites during the adsorption process on rate of adsorption of Cr (VI) (Moraldi *et al*, 2015). This may also be due to decrease total surface area of adsorbent and an increase in diffusion path length caused by aggregate of bentonite particle (Akpomie, 2015). Maximum adsorption was observed with bentonite dose 1 g

Table 4. Effect of Ledi area bentonite dosage on adsorption of Cr (VI)

Dose	**c_0**	**ce_1**	**ce_2**	**Average of ce in (mg/L)**	**qe_1**	**qe_2**	**Average of qe in (mg/g)**
1g	60.44	47.3	49.24	49.27	1.97	1.68	1.8255
2g		56.01	56.8	56.42	0.27	0.33	0.3
3g		55.8	57.8	56.44	0.23	0.168	0.2
4g		60.3	60.43	60.365	0.00525	0.00005	0.0026

4.2.4. Effect of Contact time

The influence of contact time on adsorption of metal ions was investigated within the time range of 30 min to 180 min at 24±1 ^{0}c. It was shown in (Figure 9) that the adsorption efficiency of Cr (VI) ions increased with increasing contact time up to 120 min and later, it would remain constant. For instance, during 120 min, the amount of Cr (VI) adsorbed reached 1.94 mg/g. Therefore, the optimum contact time was fixed at 120 min for the further experiment. The decrease adsorption between (120 min – 150 min) may be due to adsorption and desorption takes place simultaneously on adsorbent surface. The results indicated that equilibrium was reached slowly similar to the results reported by (M. Barkat et al. (2014).

Table 5. Effect of contact time adsorption of Cr (VI) on Ledi area bentonite with 1g of dose

Time	*Initialco.*	*Ce_1*	*ce_2*	*Average of ce in (mg/L)*	*qe_1*	*qe_2*	*Average of qe in (mg/g)*
30min	*60.44*	*60.2*	*60.28*	*60.24*	*0.036*	*0.024*	*0.03*
60min		*59.2*	*59.8*	*59.5*	*0.186*	*0.094*	*0.14*
90min		*58*	*59.01*	*58.506*	*0.366*	*0.214*	*1.94*
120min		*47.2*	*47.813*	*47.506*	*1.986*	*1.894*	*1.94*

150min		*54.49*	*55.04*	*54.89*	*0.89*	*0.77*	*0.83*
180min		*55*	*54.01*	*54.507*	*0.816*	*0.964*	*089*

4.3. Adsorption equilibrium Isotherm studies

Temkin isotherm model fit to the experimental data well and it was obtained from graph of qe vs.ln Ce plotted. Its linearity was determined from correlation coefficient (R^2). As it was observed from (Table3)T emkin adsorption isotherm parameters A_T ($1.6x10^{-2)}$, B (-7.64) and R^2 is 0.986 which is strong correlation coefficient. From this point of view adsorption of chromium on bentonite not packed with similar structural arrangement.

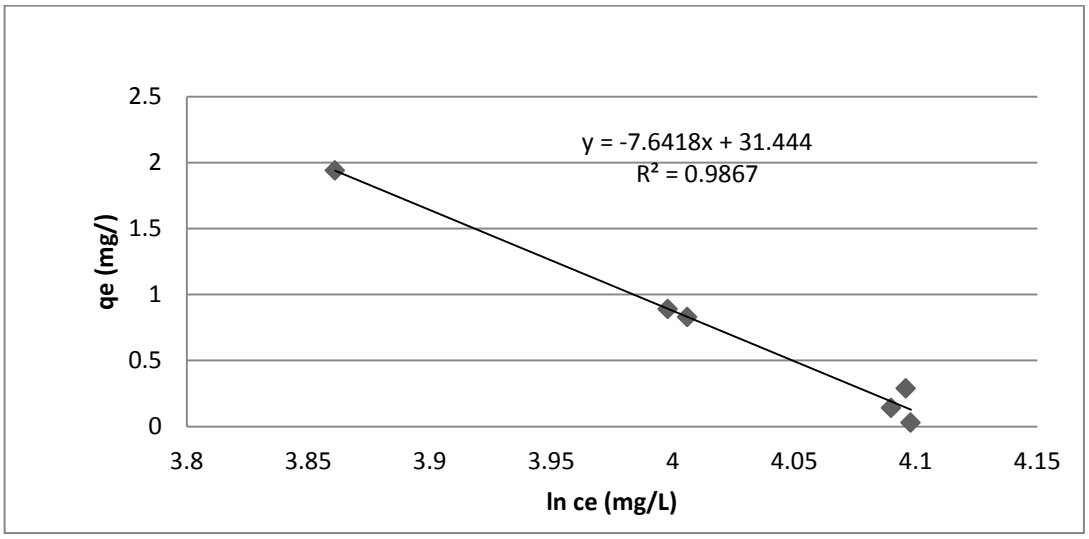

Figure 4.Temkin isotherm model of adsorption of Cr (VI) on Ledi area bentonite

From the (Figure11) it observed that the binding site of bentonite is not purely homogeneous since r^2 is 0.979.So more than one binding site is available since it deviate from linearity.

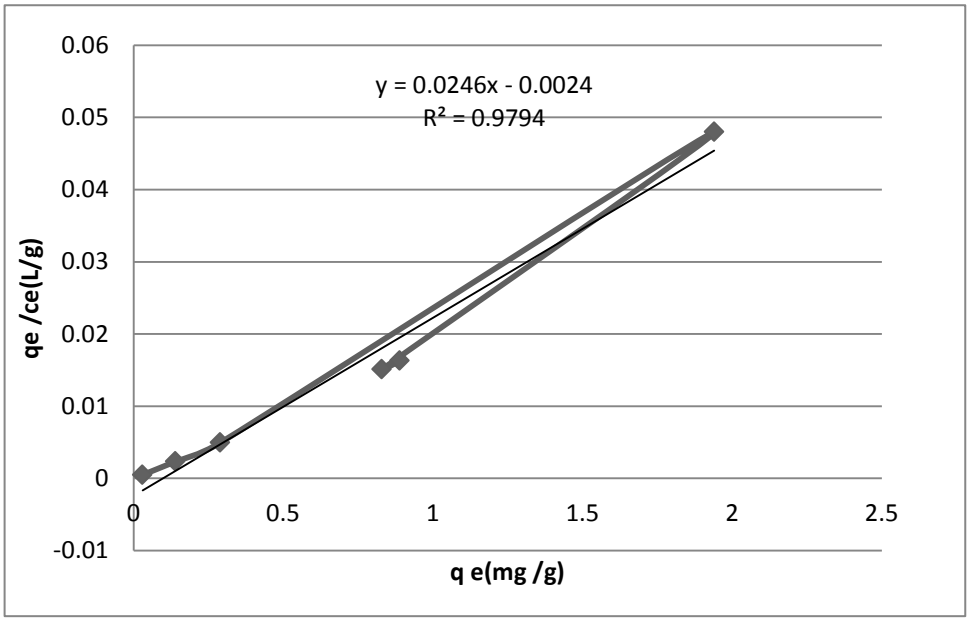

Figure 5.Independent site model isotherm adsorption of Cr (VI) on Ledi area bentonite

Langmuir isotherm second isotherm identified to confirm favorability of adsorption process using separation factor R_L calculated in (Table 3).The RL value lies between 0 and 1which confirm that the adsorption process of chromium (VI) is favorable on bentonite. As it was observed from (Figure3) below the graph of ce /qe vs ce was drawn and the correlation coefficient (R^2) and Langmuir constant parameters were calculated. The value of R^2 is 0.326 which indicate that Langmuir isotherm model does fail to describe the experimental finding.

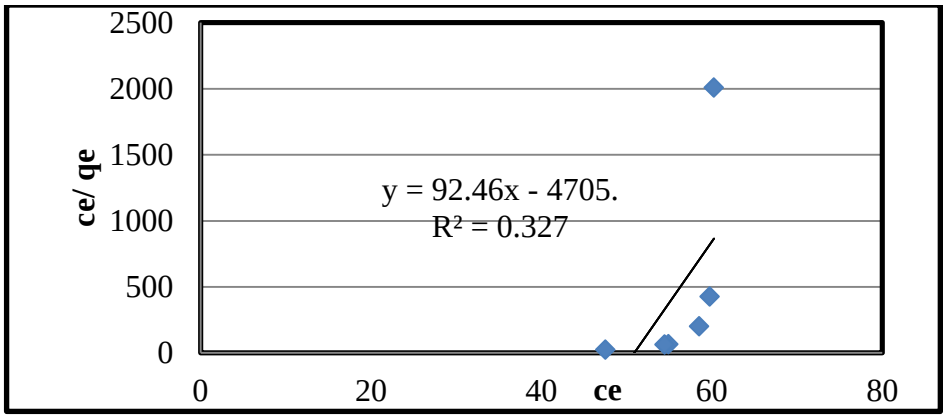

Figure 6. Langmuir isotherm model of adsorption of Cr (VI) on Ledi area bentonite

The other type of isotherm determined is Freundlich isotherm model by plotting graph of log qe vs log Ce. Its adsorption parameters kf ($10^{24.07}$), 1/n (-14.2) and R^2 (0.562) was calculated. As stated in literature review the value of 1/n < 1, so adsorption chromium on Ledi area Afar bentonite is normal (Dad A,O et al, 2012).

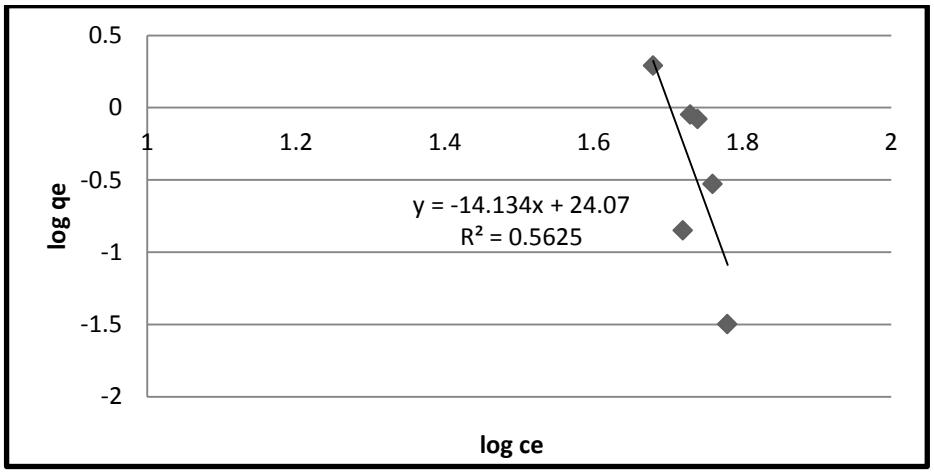

Figure 7.Freundlich isotherm model of adsorption of Cr (VI) on Ledi area bentonite

The graph of lnqe vs RT $(1+1/ce)^2$ was plotted as shown in (Figure 14) to determined whether Durbinin-Radushkevich isotherm fit the experimental value or not. The D-R isotherm parameters qs (1.5 $x10^{-3}$ mol/g), E (0.417 J/mol), Kad (0.002 $(mol/g)^2$) and R^2 (0.748). Even though D-R adsorption isotherm can fit the experimental data but it is less compared to Temkin adsorption isotherm. The value of mean free energy adsorption (E) calculated in (Table 3) is 0.417 kJ/mol and adsorption is physical since it is less than 8kJ/mol as stated in literature.

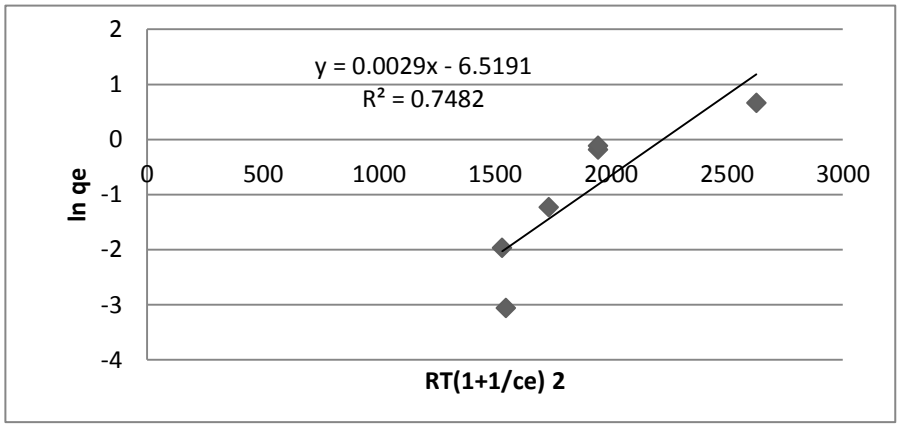

Figure 8. (D-R) isotherm model adsorption of Cr (VI) on Ledi area bentonite

The isotherm determined by plotting the graph of ln qe vs. ln Ce is Hassley isotherm. Its linearity observed from correlation coefficient (R^2). The value of Hassley parameters $1/n_H$ (12.72), (k_H $2x10^{-2}$), and R^2 (0.73) which is less fit than Temkin isotherm.

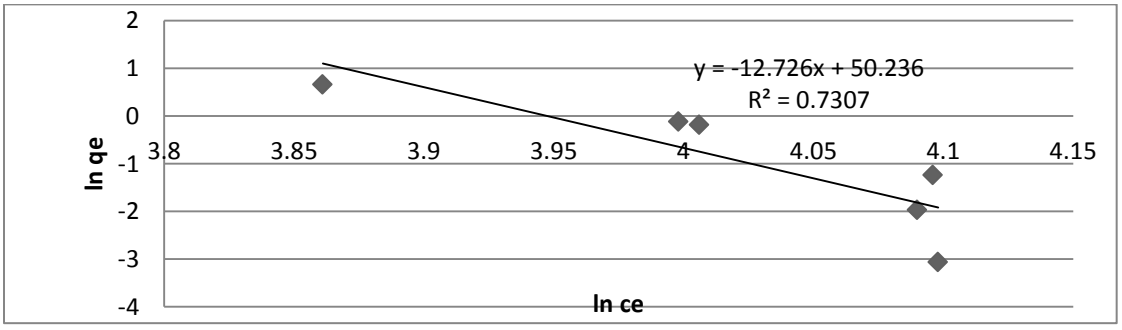

Figure 9. Hassley isotherm adsorption of Cr (VI) on Ledi area bentonite

Table 6. Adsorption isotherm parameters

Isotherm	Parameters	Unit with value
Langmuir	Qmax	0.0108 mg/g
	R_L	0.815
	R^2	0.326
	B	-0.02
Freundlich	N	-0.07
	Kf	$10^{24.07}$
	R^2	0.562
D-R	E	0.417kj/mol
	K_{ad}	0.002 $(mol/g)^2$
	Qs	$1.5x10^{-3}$ mol/g
	R^2	0.748
Hasley	nH	-0.078
	KH	2×10^{-2}
	R^2	0.73
Temkin	B	-7.64 KJ/mol
	A_T	1.6×10^{-2} L/g
	R^2	0.986

4.4. Adsorption Kinetics

Various sorption kinetics models have been used to describe the removal of metals from solution, whereas most often used are pseudo-first order, pseudo-second order, intra- particle and Elovich equations. For evaluating the adsorption kinetics of Cr (VI) ions, pseudo-first order, pseudo-second order, intra-particle and Elovich kinetics models were used to find which adsorption kinetics fit of the experimental data.

The fist sorption kinetics determined is pseudo first since it predicts metal adsorption kinetics of solid/liquid system and it states the rate determining step is physical adsorption (Indu Sharma and Dinesh Goy, 2009). To determine whether adsorption kinetics is physical adsorption or not the graph of $\ln(qe - qt)$ vs t was plotted as stated in equation (17) and the value of R^2 is determined for its linearity. The value of R^2 (0.962) and k1 ($0.004 min^{-1}$) as observed in (Table 4). From correlation coefficient point of view pseudo first order kinetic equation is the best fit the experimental data and the adsorption process is physical.

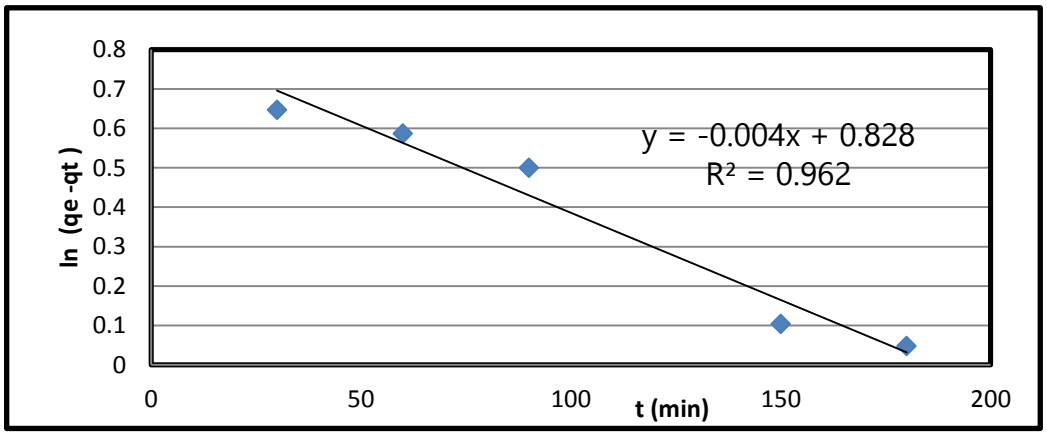

Figure 10. Fist order kinetics adsorption of Cr (VI) on Ledi area bentonite

Pseudo- second order kinetics has been successfully applied to metal ions, organic substance and dyes. It indicates that the slowest step is chemical adsorption (InduSherma and Dinash

Goya, 2009).To determine whether adsorption mechanism is determined by pseudo second order or not the graph of t/qt vs. t was drawn as stated in equation (19) and its linearity was observed by considering R^2 value. The value of K_2 (0.026 mg/gmin) and R^2 (0.629) as it shown in (Table 4) and (Figure17).Pseudo second is order less fit to experimental data.

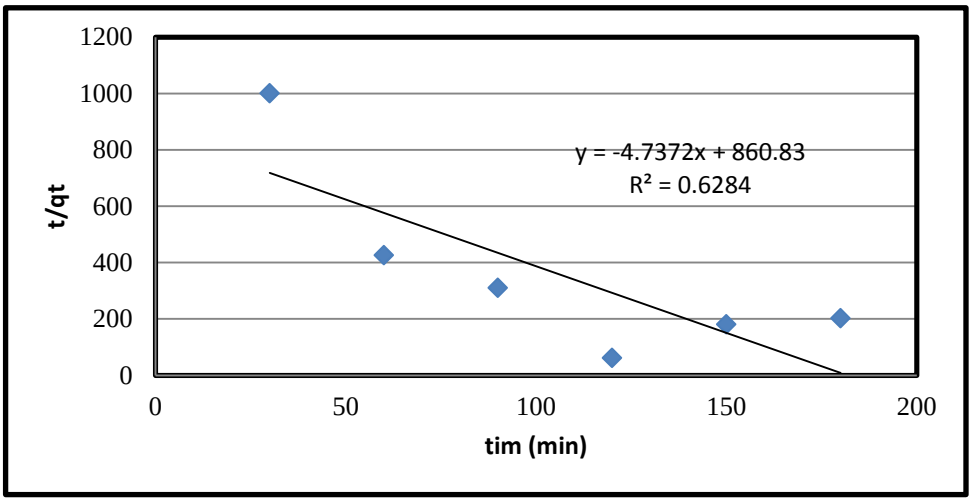

Figure 11. Second order kinetics adsorption of Cr (VI) on Ledi area bentonite

In order to understand about adsorption mechanism and to determine whether intera-particle diffusion is rate limiting step or kinetic experimental result were fitted to the Weber particle diffusion the graph of qt vs $t^{1/2}$ was drawn. A plot of qtvs $t^{1/2}$ describes in equation (22) was drawn and as shown in (Figure18). The value of ki (0.152), c (-0.819) and R^2 (0.399). From (Figure18) the plot of inter particle diffusion of Cr (VI) on bentonite with initial concentration of 60 mg/L, pH 3, adsorbent dose 1g at 24±1 ^{0}c with different contact time. It was shown that linear plot do not pass through the origin, this indicate that although intra-particle diffusion was involved in adsorption process it was not the sole rate determining step. This also confirm that adsorption of Cr (VI) on bentonite was multistep process which involve adsorption on external surface and diffusion into the interior once (Dad A, O *et al*, 2012).

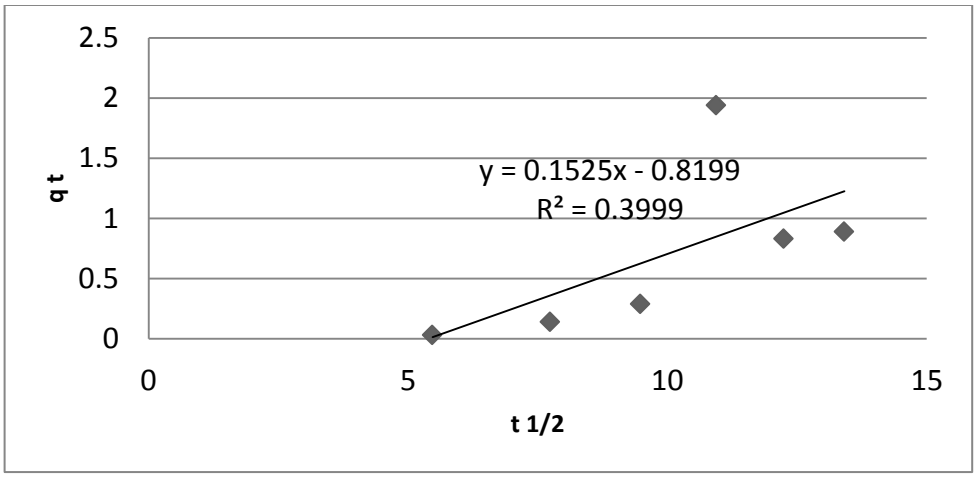

Figure 12. Intra- particle diffusion adsorption of Cr (VI) on Ledi area bentonite

The Elovich model is generally applicable to chemo adsorption kinetics. It has been applied satisfactorily to some chemo adsorption process and cover wide range of slow adsorption rate (M Baraket *et al*, 2014). To determine whether adsorption is favorable by Elovich model or not the graph of $q_t$vs lnt was plotted and its linearity was observed from correlation coefficient. From value of Elovich parameters (Table4) and (Figure 19) it was observed that as Elovich model is less fit to experimental data.

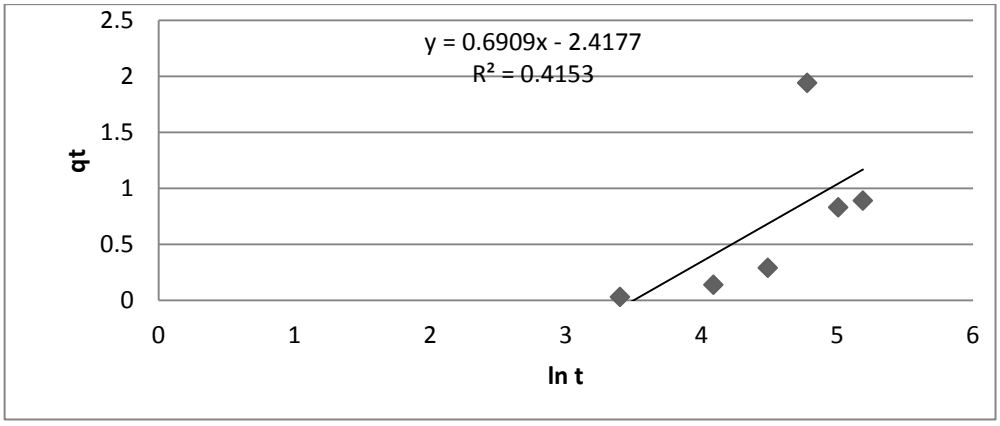

Figure 13. Elovich kinetic model adsorption of Cr (VI) on Ledi Natural bentonite

Table 7. Kinetics adsorption parameters

Pseudo first order	**K1**	**R^2**	
	0.04 min^{-1}	0.962	
Pseudo sec. order	K2	R^2	
	0.026(mg/gmin)	0.629	
Elovich equation	A	B	R^2
	0.02 mg/gmin	1.45 g/mg	0.415
Intra-particle diffusion	K_i	C_0	R^2
	0.152	0.819 mg/g	0.399

4.5. Comparison of chromium adsorption with various adsorbents

The adsorptive capacities of the adsorbents used in this work have been compared with those of others reported in the literature and the values of adsorption capacity as presented in (Table 5). The experimental data of the present investigation were compared with reported values. Results of the investigation revealed that the adsorbents have higher adsorption capacity than rice bran, oak saw dust and activated carbon (merk). The difference in adsorption capacity of bentonite in this report to those previously reported could be due to the type of bentonite from which bentonite was obtained and the difference in experimental conditions for the study of adsorption of Cr (VI).

Table 8. Adsorption capacity of different adsorbents towards removal of Cr (VI)

Adsorbents	**adsorption capacity (mg/L)**	**reference**
Rice bran	0.067	Sing B and Dash SK, 2009
Cocked waste tea	30.39	S,Dhanaky Mar et al, 2007
Pre boiled sun flower stem	4.9	M,Jain et al, 2009
Potato peels	8.012	M,Abdullah and A, Devil, 2009
Saw dust	20.7	M, Dakiky et al, 2015
Oak saw dust	1.72	Argum M, E and Dursun S, 2007
Activated carbon (merk)	0.09	M,A Mohamed et al,2012
Activated bentonite	4.22	Morald et al, 2015
Powder activated carbon,	49.6	Morald ET al, 2015
Na bentonite,	26.2	M, Baraket ET al, 2014
Ledi area, Affar Region, Ethiopia bentonite	1.94	present study

Preliminary test was done to identify the effectiveness of adsorbents toward the removal of chromium from real sample at the optimized condition. Knowing the effectiveness Ledi bentonite need further analysis, due to constraint of time and budget it was limited to the following characterization. Adsorption experiments on this real sample was done at optimized condition and amount of chromium adsorbed was 0.049mg/g (milligram of chromium adsorbed on gram of bentonite).

Table 9. Physico-chemical properties of Hora tannery

Color	Bluewish
pH	5.3
Conductivity	14,130µs/cm
Odour	un pleasant
Cr concentration after (1:5)dilution	3 05.6mg/L

4.6. Thermodynamic Study

In order to describe the thermodynamic behavior of removal of Cr (VI) ions on natural bentonite the thermodynamic parameters like the change in free energy was calculated from general equation (23) and (24). From the value of thermodynamic

parameters given in Table 2, ΔG is negative indicating that the adsorption of metal ion on natural bentonite is spontaneous.

Table 10. Thermodynamics parameters

ΔG	**Kc**
-39.5 kJ/mol	1.6×10^{-2} L/g

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Adsorption efficiencies of bentonite toward the removal of Cr (VI) in aqueous solution and tannery waste effluent were investigated by 250 µm particle size. The effect of concentration 20 mg/L , 30 mg/ L, 40 mg/L, 60 mg/L and 80 mg/L was determined 2g dose. Effect of dose of bentonite was determined using 1 g, 2 g, 3 g and 4 g. Effect of contact time was determined using 30 min – 180 min and pH (1 – 5) was determined. The adsorption of Cr (VI) was found to be dependent on the pH of the system, the best results being obtained at pH 3. The optimized working parameters are pH3, contact time120 min, concentration 60 (mg/L and adsorbate dose 1g at room temperature with 120 rpm. The adsorption equilibrium data obtained for removal of Cr (VI) ion onto the adsorbent studied showed best fit to the Temkin isotherm and from this model point of view it was identified the orientation with tightly packed structure is not observed. The adsorption kinetic data fitted pseudo first order well and it reveals that adsorption of chromium on bentonite was physical. Thermodynamic study predicted that the adsorption is feasible, spontaneous at room temperature.

As it was observed from silicate analysis of (Table1) calcium oxide is the dominant when compared magnesium oxide and sodium oxide. It was stated in literature that Ca-bentonite has low swelling capacity than Na bentonite; this leads Ledi area bentonite to have less adsorption capacity.

5.2. Recommendation

The study revealed that the removal efficiency of Chromium using natural bentonite is low. We recommend other researchers to do modification on to natural bentonite to improve the efficiency.

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ANNEX

Annex1; Ledi area Afar natural bentonite