ADSORPTION OF VANADIUM IONS FROM AQUEOUS SOLUTION USING DAGARA CLAY.

BY

FADELE ANUOLUWA BOLUWATIFE

PSC1609469

DEPARTMENT OF CHEMISTRY

FACULTY OF PHYSICAL SCIENCE

UNIVERSITY OF BENIN, BENIN CITY.

2021

CERTIFICATION

This is to certify that this project was carried out by **FADELE ANUOLUWA BOLUWATIFE** of the department of chemistry, Faculty of physical s Sciences, University of Benin, Benin city, Nigeria.

…….. ……..

FADELE ANUOLUWA BOLUWATIFE DATE

…,..... …. ……...

Dr. E.E.I. IRABOR DATE

PROJECT SUPERVISOR

…….. ……

PROF IYASELE DATE

H O D OF DEPARTMENT

DEDICATION

These study is dedicated to God Almight for his grace, faithfulness, and tender mercy for always been there for me.

Also to my everloving Mummy and Pops.

ACKNOWLEDGEMENT

I want to express my deepest appreciation to God Almight for his grace, sustenance, faithfulness, protection, provision for always been there for me.

I wish to express my gratitude to my supervisor Dr. E.E.I Irabor for his enthusiasm, patience and advise towards the success of this project.

I want appreciate my parent for their support financially, morally and prayer towards the success of my academic and this project.

TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

This study was aimed to examine suitability of Dangara middle layer clay as an adsorbent for the removal of vanadium ions. variable parameter such as adsorbent dosage, initial concentration, contact time, pH and temperature were at moderate level such that they can affect the removal of vanadium ions. For pH, it was observed that the % removal was increases with an increasing in pH. The optimum % removal was obtained from 79.39 at pH 9, and the lower % removal was obtained at 70.50 from pH 3. For adsorbent dosage it was discover % removal increases with an increasing in adsorbent dosage, the optimum % removal was obtained 82.15 at 1g and the lower % removal was obtained from 69.28 at 0.2g. for initial concentration there an increases in percentage removal with an increasing in initial concentration the optimum percentage removal was obtained at 86.91 at 50g and lower percentage removal was obtained from 81.56 at 10g. for contact time it was discover there is increases in percentage removal with an increasing in contact time, the optimum percentage removal was obtained from 80.52 at 50mins And the lower percentage removal was obtained at 76.07 at 10mins also there is an increases in percentage removal with an increasing in temperature, optimum percentage removal was obtained at $80^{O}C$ (81.07) and lower percentage at $40^{O}C$ (78.67). The efficiency determination (r2) fitted for both langmuir and freundlich. For Langmuir isotherm it was discover that the efficiency determination (r2) obtained was 0.999 and efficiency determination for freundlich was 0.995

Maximum adsorption capacity calculated for Langmuir was 0.345mg/g why the freundlich constant obtained was o.457. The Langmuir model was found to better described the adsorption behavior. Overall, the clay is not considered competent enough as an adsorbent for the removal of vanadium ions from aqueous solution because of low adsorption capacity calculated to be 0.345mg/g. Modification of the surface of the clay could improve its adsorption capacity.

CHAPTER ONE

1.0 INTRODUCTION

Heavy metals are group of metals and metalloids that have relatively high density and are toxic even at ppb levels Examples include Pb, As, Hg, Cd, Zn, Ag, Cu, Fe, Cr, Ni, Pd, and Pt. Heavy metals are defined as metallic elements that have a relatively high density compared to water With the assumption that heaviness and toxicity are inter-related, heavy metals also include metalloids, such as arsenic, that are able to induce toxicity at low level of exposure (Fergusson JE (eds.) 1990)

These metals are released into the environment by both natural and anthropogenic sources such as industrial discharge, automobiles exhaust, and mining. Unlike organic pollutants, heavy metals are non biodegradable and have tendency to accumulate in living beings. In fact, most of them are known to be potential carcinogens. Various adverse health hazards are known due to long term and continuous exposure to heavy metals. Since they are non degradable and tend to bio-accumulate, suitable methods need to be established for their efficient removal from the environment. Natural phenomena such as weathering and volcanic eruptions have also been reported to significantly contribute to heavy metal pollution Industrial sources include metal processing in refineries, coal burning in power plants, petroleum combustion, nuclear power stations and high tension lines, plastics, textiles, microelectronics, wood preservation and paper Nriagu JO (1989). Environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operation Some heavy metals are either essential nutrients (typically iron, cobalt, zinc and vanadium), or relatively harmless (such as ruthenium, silver, and indium), but can be toxic in larger amounts or certain forms lie vanadium can be used in the treatment of heart disease lower blood sugar when they are taken in small amount but when was taken in large amount

damages the kidney. Other heavy metals, such as cadmium, mercury, and lead, are highly poisonous. Potential sources of heavy metal poisoning include mining, tailings, industrial waste, agricultural runoff, occupational exposure, paints and treated timber(Baird and Cann, 2012).

Clay minerals are naturally hydrous aluminium phyllosilicates composed of variable amount of iron magnesium, alkali and alkaline earth metal that contain large percentage of water trapped within the silicate sheet. (Grim *et al*., 1953). Clay minerals are important constituents of soils, and have been useful to Humans in agriculture and manufacturing. They are Very common in soils, in fine-grained sedimentary rocks, metamorphic slate and phyllite as well as In ultrafine-grained form. Clay are used in the drilling mud Bentonite and other clays are used in the drilling of oil and water wells. The clays are turned into mud, which seals the walls of the boreholes, lubricates the drill head and removes drill cuttings. Filtering: Clays are used to decolorize, filter, And purify animal, mineral, and vegetable oils And greases due to their high absorbing properties it is also used in Environmental Sealants: Bentonite Is used to establish low permeability Liners in landfills, sewage lagoons, Water retention ponds, golf course Ponds, and hazardous waste sites. Paints: Finely ground clays are used in the Paint industry to disperse pigment evenly Throughout the paint. Without clays, it Would be extremely difficult to evenly mix The paint base and color pigment.

Vanadium, V, is a transition metal and is among the 20 most abundant Elements in the Earth's crust, in the same concentration range as lead and Copper. Its main application in human society is within the steel industry in Alloys ,Vanadium is a transition metal that widely exists in earth crust with a global average concentration of 150mg kg^{-1} (Byerrum *et al*.,1974). In low quality Vanadium can be used in treatment of low blood sugar, diabetes heart disease high cholesterol and tuberculosis, but when it is taken in large amount it damage the kidney. The anthropogenic input to the environment is dominated by burning of Fossil

fuels. The steel industry generates by-products that due to their alkalinity And physical properties are suitable as soil amendments, road fill materials and Cement. In Sweden, these materials are naturally high in vanadium.

1.2 STATEMENT OF PROBLEMS

Since the Human body always contains traces of vanadium, there are ethical and practical Issues with investigating the impact of vanadium deficiency in humans. Thus Vanadium essentiality to humans has still not been confirmed. However, excessive vanadium concentrations may be carcinogenic (Beyersmann and Hartwig, 2008). Historical there are cases of accidental Releases of vanadium to the environment. One of the most recent was a spillage Of the bauxite residue “red mud” in Ajka, Hungary, in 2010. In addition to Alkalinity and sodium concentrations, the red mud also contained 900 mg kg^{-1}Vanadium (Ruyters *et al*., 2011). In the 1980s, basic slag containing 3%. Vanadium was inappropriately applied as a soil amendment in Lillpite in Northern Sweden. The amendment resulted in contamination of hay, which Caused the death of 23 cattle due to acute vanadium toxicity (Frank *et al*., 1996). Knowledge of vanadium behaviour in soils is poor compared with that of Heavy metals such as copper, lead and zinc, and many countries lack threshold Values for vanadium in soils and waters. The median value of total vanadium Concentration in European topsoils is 60 mg kg^{-1}, but some soils may have up To 500mg V kg^{-1}. In comparison, most toxicity-based values for unacceptable Risks range from 90 to 500mg V kg^{-1}For those member states of the European Union that have established limit values for vanadium in soils (Carlon, 2007).

1.2 SCOPE OFWORK

The scope of this study is to adsorb vanadium on Dangara clay, the parameter adsorption process such adsorbent dosage, effect of initial concentration, effect of contact time, effect of

pH and temperature were an instrumental key in the removal of vanadium from aqueous solution, the adsorption data were calculated and fitted using adsorption isotherm.

1.3 AIM

- The aim of this Research is to determine the Adsorption of Vanadium ion from aqueous solution using Dangara middle layer clay, obtained from Kwali area, Abuja.

1.4 OBJECTIVE

- The overall objective of this research Is to investigate the removal of Vanadium From aqueous solution by Adsorption solution using Dangara middle layer clay as an adsorbent. The specific objectives are to determine ;
- The overall objective of this research is to investigate the removal of Cadmium ion from aqueous solution by adsorption using Dangara middle layer clay as an adsorbent. The specific objectives are to determine;
- Effect of adsorbent dosage
- Effect of initial concentration
- Effect of contact time
- Effect of pH
- Effect of temperature

1.5 LITERATURE REVIEW

CLAY

Clay is a type of fine-grained natural soil material containing clay minerals (Olive *et al*., 1989). Clays develop plasticity when wet, due to a molecular film of water surrounding the

clay particles, but become hard, brittle and non–plastic upon drying or firing (Guggenheim and Martin, 1995; Science Learning Hub, 2010; Breuer, 2012). Most pure clay minerals are white or light-coloured, but natural clays show a variety of colours from impurities, such as a reddish or brownish colour from small amounts of iron oxide (Klein and Hurlbut, 1993; Nesse, 2000).

Clay is the oldest known ceramic material. Prehistoric humans discovered the useful properties of clay and used it for making pottery. Some of the earliest pottery shards have been dated to around 14,000 BC (Scarre, 2005), and clay tablets were the first known writing medium (Ebert, 2011). Clay is used in many modern industrial processes, such as paper making, cement production, and chemical filtering. Between one-half and two-thirds of the world's population live or work in buildings made with clay, often baked into brick, as an essential part of its load-bearing structure.

Clay is a very common substance. Shale, formed largely from clay, is the most common sedimentary rock (Boggs, 2006). Although many naturally occurring deposits include both silts and clay, clays are distinguished from other fine-grained soils by differences in size and mineralogy. Silts, which are fine-grained soils that do not include clay minerals, tend to have larger particle sizes than clays. Mixtures of sand, silt and less than 40% clay are called loam. Soils high in *swelling clays*, which are clay minerals that readily expand in volume when they absorb water, are a major challenge in civil engineering (Olive *et al*., 1989).

ORIGIN AND MODE OF CLAY

Clay minerals most commonly form by prolonged chemical weathering of silicate-bearing rocks. They can also form locally from hydrothermal activity (Foley, 1999). Chemical weathering takes place largely by *acid hydrolysis* due to low concentrations of carbonic acid,

dissolved in rainwater or released by plant roots. The acid breaks bonds between aluminium and oxygen, releasing other metal ions and silica (as a gel of orthosilicic acid) (Leeder, 2011).

The clay minerals formed depend on the composition of the source rock and the climate. Acid weathering of feldspar-rich rock, such as granite, in warm climates tends to produce kaolin. Weathering of the same kind of rock under alkaline conditions produces illite. Smectite forms by weathering of igneous rock under alkaline conditions, while gibbsite forms by intense weathering of other clay minerals (Leeder, 2011). There are two types of clay deposits: primary and secondary. Primary clays form as residual deposits in soil and remain at the site of formation. Secondary clays are clays that have been transported from their original location by water erosion and deposited in a new sedimentary deposit (Murray, 2002). Secondary clay deposits are typically associated with very low energy depositional environments such as large lakes and marine basins (Foley, 1999).

PHYSICAL AND CHEMICAL PROPERTIES OF CLAY

The defining mechanical property of clay is its plasticity when wet and its ability to harden when dried or fired. Clays show a broad range of water content within which they are highly plastic, from a minimum water content (called the plasticity limit) where the clay is just moist enough to mould, to a maximum water content (called the liquid limit) where the moulded clay is just dry enough to hold its shape (Moreno-Maroto and Alonso-AzcAarate, 2018).The plastic limit of kaolinite clay ranges from about 36% to 40% and its liquid limit ranges from about 58% to 72% (White, 1949). High-quality clay is also tough, as measured by the amount of mechanical work required to roll a sample of clay flat. Its toughness reflects a high degree of internal cohesion (Moreno-Maroto and Alonso-AzcAarate, 2018).

Clay has a high content of clay minerals that give it its plasticity. Clay minerals are hydrous aluminium phyllosilicate minerals, composed of aluminium and silicon ions bonded into tiny, thin plates by interconnecting oxygen and hydroxyl ions. These plates are tough but flexible, and in moist clay, they adhere to each other. The resulting aggregates give clay the cohesion that makes it plastic (Bergaya and Lagaly, 2006). In kaolinite clay, the bonding between plates is provided by a film of water molecules that hydrogen bond the plates together. The bonds are weak enough to allow the plates to slip past each other when the clay is being moulded, but strong enough to hold the plates in place and allow the moulded clay to retain its shape after it is moulded. When the clay is dried, most of the water molecules are removed, and the plates hydrogen bond directly to each other, so that the dried clay is rigid but still fragile. If the clay is moistened again, it will once more become plastic. When the clay is fired to the earthenware stage, a dehydration reaction removes additional water from the clay, causing clay plates to irreversibly adhere to each other via stronger covalent bonding, which strengthens the material. The clay mineral, kaolin, is transformed into a non-clay material, metakaolin, which remains rigid and hard if moistened again. Further firing through the stoneware and porcelain stages further recrystallizes the metakaolin into yet stronger minerals such as mullite (Breuer, 2012).

The tiny size and plate form of clay particles gives clay minerals a high surface area. In some clay minerals, the plates carry a negative electrical charge that is balanced by a surrounding layer of positive ions (cations), such as sodium, potassium, or calcium. If the clay is mixed with a solution containing other cations, these can swap places with the cations in the layer around the clay particles, which gives clays a high capacity for ion exchange (Bergaya and Lagaly, 2006). The chemistry of clay minerals, including their capacity to retain nutrient cations such as potassium and ammonium, is important to soil fertility (Hodges, 2010). Clay is a common component of sedimentary rock. Shale is formed largely from clay and is the

most common of sedimentary rocks (Boggs, 2006). However, most clay deposits are impure. Many naturally occurring deposits include both silts and clay. Clays are distinguished from other fine-grained soils by differences in size and mineralogy. Silts, which are fine-grained soils that do not include clay minerals, tend to have larger particle sizes than clays. There is, however, some overlap in particle size and other physical properties. The distinction between silt and clay varies by discipline. Geologists and soil scientists usually consider the separation to occur at a particle size of 2 μm (clays being finer than silts), sedimentologists often use 4–5 μm, and colloid chemists use 1 μm (Guggenheim and Martin, 1995). Geotechnical engineers distinguish between silts and clays based on the plasticity properties of the soil, as measured by the soils' Atterberg limits. ISO 14688 grades clay particles as being smaller than 2 μm and silt particles as being larger. Mixtures of sand, silt and less than 40% clay are called loam.

Some clay minerals (such as smectite) are described as swelling clay minerals, because they have a great capacity to take up water, and they increase greatly in volume when they do so. When dried, they shrink back to their original volume. This produces distinctive textures, such as mudcracks or "popcorn" texture, in clay deposits. Soils containing swelling clay minerals (such as bentonite) pose a considerable challenge for civil engineering, because swelling clay can break foundations of buildings and ruin road beds (Olive *et al*., 1989).

HISTORICAL AND MODERN USES

Clays are used for making pottery, both utilitarian and decorative, and construction products, such as bricks, walls, and floor tiles. Different types of clay, when used with different minerals and firing conditions, are used to produce earthenware, stoneware, and porcelain. Prehistoric humans discovered the useful properties of clay. Some of the earliest pottery

shards recovered are from central Honshu, Japan. They are associated with the Jōmon culture, and recovered deposits have been dated to around 14,000 BC (Scarre, 2005). Cooking pots, art objects, dishware, smoking pipes, and even musical instruments such as the ocarina can all be shaped from clay before being fired.

Clay tablets were the first known writing medium (Ebert, 2011). Scribes wrote by inscribing them with cuneiform script using a blunt reed called a stylus. Purpose-made clay balls were used as sling ammunition (Forouzan *et al*., 2012). Clay is used in many industrial processes, such as paper making, cement production, and chemical filtering (Nesse, 2000). Bentonite clay is widely used as a mold binder in the manufacture of sand castings (Boylu, 2011; Eisenhour and Brown, 2009).

Clay, being relatively impermeable to water, is also used where natural seals are needed, such as in the cores of dams, or as a barrier in landfills against toxic seepage (lining the landfill, preferably in combination with geotextiles) (Kockar *et al*., 2005). Studies in the early 21st century have investigated clay's absorption capacities in various applications, such as the removal of heavy metals from waste water and air purification (Garcia *et al*., 2002; Churchman *et al*., 2006).

Medical Uses

Traditional uses of clay as medicine goes back to prehistoric times. An example is Armenian bole, which is used to soothe an upset stomach. Some animals such as parrots and pigs ingest clay for similar reasons (Diamond, 1999). Kaolin clay and attapulgite have been used as anti-diarrheal medicines (Dadu *et al*., 2015).

As a building material

Clay as the defining ingredient of loam is one of the oldest building materials on Earth, among other ancient, naturally-occurring geologic materials such as stone and organic

materials like wood (Grim, 2016). Between one-half and two-thirds of the world's population, in both traditional societies as well as developed countries, still live or work in buildings made with clay, often baked into brick, as an essential part of its load-bearing structure. Also a primary ingredient in many natural building techniques, clay is used to create adobe, cob, cordwood, and rammed earth structures and building elements such as wattle and daub, clay plaster, clay render case, clay floors and clay paints and ceramic building material. Clay was used as a mortar in brick chimneys and stone walls where protected from water.

The forecasted mass of clay minerals to be discharged into the tailings of ore processing makes up millions of tons. Worryingly, when macro- and micro-components are found in non-hazardous concentrations, fewer efforts are put into the environmental management of the tailings, though technogenic sediments offer prospects for reuse and valorization beyond their traditional disposal. Saponite is a demonstrative example of the tailings constituent that is often left unfairly mistreated. Electrochemical separation helps to obtain modified saponite-containing products with high smectite-group minerals concentrations, lower mineral particles size, more compact structure, and greater surface area. These characteristics open possibilities for the manufacture of high-quality ceramics and heavy-metal sorbents from saponite-containing products (Chanturiya *et al*., 2018). Furthermore, tail grinding occurs during the preparation of the raw material for ceramics; this waste reprocessing is of high importance for the use of clay pulp as a neutralizing agent, as fine particles are required for the reaction. Experiments on the Histosol deacidification with the alkaline clay slurry demonstrated that neutralization with the average pH level of 7.1 is reached at 30% of the pulp added and an experimental site with perennial grasses proved the efficacy of the technique (Pashkevich and Alekseenko, 2020).

Heavy Metals

Heavy metals are generally defined as metals with relatively high densities, atomic weights, or atomic numbers. The criteria used, and whether metalloids are included, vary depending on the author and context (Pourret and Olivier, 2018). In metallurgy, for example, a heavy metal may be defined on the basis of density, whereas in physics the distinguishing criterion might be atomic number, while a chemist would likely be more concerned with chemical behaviour. More specific definitions have been published, but none of these have been widely accepted. The definitions surveyed in this article encompass up to 96 out of the 118 known chemical elements; only mercury, lead and bismuth meet all of them. Despite this lack of agreement, the term (plural or singular) is widely used in science. A density of more than 5 g/cm^3 is sometimes quoted as a commonly used criterion and is used in the body of this article.

The earliest known metals—common metals such as iron, copper, and tin, and precious metals such as silver, gold, and platinum—are heavy metals. From 1809 onward, light metals, such as magnesium, aluminium, and titanium, were discovered, as well as less well-known heavy metals including gallium, thallium, and hafnium.

Some heavy metals are either essential nutrients (typically iron, cobalt, and zinc), or relatively harmless (such as ruthenium, silver, and indium), but can be toxic in larger amounts or certain forms. Other heavy metals, such as cadmium, mercury, and lead, are highly poisonous. Potential sources of heavy metal poisoning include mining, tailings, industrial waste, agricultural runoff, occupational exposure, paints and treated timber.

Physical and chemical characterisations of heavy metals need to be treated with caution, as the metals involved are not always consistently defined. As well as being relatively dense, heavy metals tend to be less reactive than lighter metals and have far fewer soluble sulfides and hydroxides. While it is relatively easy to distinguish a heavy metal

such as tungsten from a lighter metal such as sodium, a few heavy metals, such as zinc, mercury, and lead, have some of the characteristics of lighter metals, and, lighter metals such as beryllium, scandium, and titanium, have some of the characteristics of heavier metals.

Heavy metals are relatively scarce in the Earth's crust but are present in many aspects of modern life. They are used in, for example, golf clubs, cars, antiseptics, self-cleaning ovens, plastics, solar panels, mobile phones, and particle accelerators.

OCCURRENCE OF HEAVY METAL IN NATURE

Heavy metals up to the vicinity of iron (in the periodic table) are largely made via stellar nucleosynthesis. In this process, lighter elements from hydrogen to silicon undergo successive fusion reactions inside stars, releasing light and heat and forming heavier elements with higher atomic numbers (Cox, 1997).

Heavier heavy metals are not usually formed this way since fusion reactions involving such nuclei would consume rather than release energy (Cox, 1997). Rather, they are largely synthesised (from elements with a lower atomic number) by neutron capture, with the two main modes of this repetitive capture being the s-process and the r-process. In the s-process ("s" stands for "slow"), singular captures are separated by years or decades, allowing the less stable nuclei to beta decay (Podosek, 2011), while in the r-process ("rapid"), captures happen faster than nuclei can decay. Therefore, the s-process takes a more or less clear path: for example, stable cadmium-110 nuclei are successively bombarded by free neutrons inside a star until they form cadmium-115 nuclei which are unstable and decay to form indium-115 (which is nearly stable, with a half-life 30000 times the age of the universe). These nuclei capture neutrons and form indium-116, which is unstable, and decays to form tin-116, and so on (Cox, 1997; Padmanabhan, 2001). In contrast, there is no such path in the r-process. The

s-process stops at bismuth due to the short half-lives of the next two elements, polonium and astatine, which decay to bismuth or lead. The r-process is so fast it can skip this zone of instability and go on to create heavier elements such as thorium and uranium (Hofmann, 2002).

Heavy metals condense in planets as a result of stellar evolution and destruction processes. Stars lose much of their mass when it is ejected late in their lifetimes, and sometimes thereafter as a result of a neutron star merger (Hadhazy, 2016), thereby increasing the abundance of elements heavier than helium in the interstellar medium. When gravitational attraction causes this matter to coalesce and collapse, new stars and planets are formed (Cox, 1997).

The Earth's crust is made of approximately 5% of heavy metals by weight, with iron comprising 95% of this quantity. Light metals (~20%) and nonmetals (~75%) make up the other 95% of the crust (Lide, 2004). Despite their overall scarcity, heavy metals can become concentrated in economically extractable quantities as a result of mountain building, erosion, or other geological processes (Berry and Mason, 1959).

Heavy metals are found primarily as lithophiles (rock-loving) or chalcophiles (ore-loving). Lithophile heavy metals are mainly f-block elements and the more reactive of the d-block elements. They have a strong affinity for oxygen and mostly exist as relatively low density silicate minerals (Hartmann, 2005). Chalcophile heavy metals are mainly the less reactive d-block elements, and period 4–6 p-block metals and metalloids. They are usually found in (insoluble) sulfide minerals. Being denser than the lithophiles, hence sinking lower into the crust at the time of its solidification, the chalcophiles tend to be less abundant than the lithophiles (Yousif, 2007).

In contrast, gold is a siderophile, or iron-loving element. It does not readily form compounds with either oxygen or sulfur (Berry and Mason, 1959). At the time of the Earth's formation, and as the most noble (inert) of metals, gold sank into the core due to its tendency to form high-density metallic alloys. Consequently, it is a relatively rare metal (Yousif, 2007). Some other (less) noble heavy metals—molybdenum, rhenium, the platinum group metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum), germanium, and tin—can be counted as siderophiles but only in terms of their primary occurrence in the Earth (core, mantle and crust), rather the crust. These metals otherwise occur in the crust, in small quantities, chiefly as chalcophiles (less so in their native form) (Wiberg, 2001).

Concentrations of heavy metals below the crust are generally higher, with most being found in the largely iron-silicon-nickel core. Platinum, for example, comprises approximately 1 part per billion of the crust whereas its concentration in the core is thought to be nearly 6,000 times higher (Emsley, 2011; Litasov and Shatskiy, 2016). Recent speculation suggests that uranium (and thorium) in the core may generate a substantial amount of the heat that drives plate tectonics and (ultimately) sustains the Earth's magnetic field (Sanders, 2003; Preuss, 2011).

The winning of heavy metals from their ores is a complex function of ore type, the chemical properties of the metals involved, and the economics of various extraction methods. Different countries and refineries may use different processes, including those that differ from the brief outlines listed here.

Broadly speaking, and with some exceptions, lithophile heavy metals can be extracted from their ores by electrical or chemical treatments, while chalcophile heavy metals are obtained by roasting their sulphide ores to yield the corresponding oxides, and then heating these to obtain the raw metals (MacKay *et al*., 2002), Radium occurs in quantities too small to be economically mined and is instead obtained from spent nuclear fuels (Emsley, 2011; Keller *et*

al., 2012). The chalcophile platinum group metals (PGM) mainly occur in small (mixed) quantities with other chalcophile ores. The ores involved need to be smelted, roasted, and then leached with sulfuric acid to produce a residue of PGM. This is chemically refined to obtain the individual metals in their pure forms (Chen and Huang, 2006; Crundwell *et al*., 2011). Compared to other metals, PGM are expensive due to their scarcity (Crundwell *et al*., 2011),and high production costs.

Gold, a siderophile, is most commonly recovered by dissolving the ores in which it is found in a cyanide solution (McLemore, 2008). The gold forms a dicyanoaurate(I), for example: 2 Au + H_2O +½ O_2 + 4 KCN → 2 $K[Au(CN)_2]$ + 2 KOH. Zinc is added to the mix and, being more reactive than gold, displaces the gold: 2 $K[Au(CN)_2]$ + Zn → $K_2[Zn(CN)_4]$ + 2 Au. The gold precipitates out of solution as a sludge, and is filtered off and melted (Wiberg, 2001).

THE ANTHROPOGENIC SOURCE OF HEAVY METAL

Humans are exposed to toxic heavy metals in the environment through different routes including ingestion, inhalation, and dermal absorption. People are more exposed to toxic metals in developing countries . Generally, people have no awareness and knowledge about exposure to heavy metals and its consequences for human health, especially in the developing countries [102]. People may be exposed to heavy metals in the work place and in the environment. Human exposure to toxic chemicals in the work place is called occupational exposure while exposure to such chemicals in the general environment is called nonoccupational or environmental exposure. Workers are exposed to heavy metals in mining and industrial operations where they may inhale dust and particulate matter-containing metal particles. People extracting gold through the amalgamation process are exposed to Hg vapors. It has been reported that welders with occupational prolonged exposure to welding fumes had significantly higher levels of the heavy metals Cr, Ni, Cd, and Pb in blood than the control

and showed increased oxidative stress. Cigarette smoking is also a principal source of human exposure to Cd and other toxic heavy metals present in the tobacco leaves.

Ingestion of heavy metals through food and drinking water is a major exposure source for the general human population. Industrialization, urbanization, and the rapid economic development around the globe have led to intensification in industrial and agricultural activities. Such activities may cause contamination of water, air, and soils with toxic heavy metals. Growing human foods in heavy metal-contaminated media lead to bioaccumulation of these elements in the human food chains from where these elements ultimately reach the human body.

HUMAN EXPLOSURE & HEALTH HAZARDS ASSOCIATED WITH HEAVY METAl

Humans are exposed to toxic heavy metals in the environment through different routes including ingestion, inhalation, and dermal absorption. People are more exposed to toxic metals in developing countries . Generally, people have no awareness and knowledge about exposure to heavy metals and its consequences for human health, especially in the developing countries . People may be exposed to heavy metals in the work place and in the environment. Human exposure to toxic chemicals in the work place is called occupational exposure while exposure to such chemicals in the general environment is called nonoccupational or environmental exposure. Workers are exposed to heavy metals in mining and industrial operations where they may inhale dust and particulate matter-containing metal particles. People extracting gold through the amalgamation process are exposed to Hg vapors. It has been reported that welders with occupational prolonged exposure to welding fumes had

significantly higher levels of the heavy metals Cr, Ni, Cd, and Pb in blood than the control and showed increased oxidative stress. Cigarette smoking is also a principal source of human exposure to Cd and other toxic heavy metals present in the tobacco leaves.Ingestion of heavy metals through food and drinking water is a major exposure source for the general human population. Industrialization, urbanization, and the rapid economic development around the globe have led to intensification in industrial and agricultural activities. Such activities may cause contamination of water, air, and soils with toxic heavy metals. Growing human foods in heavy metal-contaminated media lead to bioaccumulation of these elements in the human food chains from where these elements ultimately reach the human body.

Heavy metal toxicity can have several health effects in the body. Heavy metals can damage andalter the functioning of organs such as the brain, kidney, lungs, liver, and blood. Heavy metal toxicity can either be acute or chronic effects. Long-term exposure of the body to heavy metal can progressively lead to muscular, physical and neurological degenerative processes that are similar to diseases such as Parkinson's disease, multiple sclerosis, muscular dystrophy and Alzheimer's disease. Also, chronic long-term exposure of some heavy metals may cause cancer. The various health effects of some heavy metals will be highlighted below.

Behaviour of heavy metal in the environment.

Heavy metals are well-known environmental pollutants due to their toxicity, persistence in the environment, and bioaccumulative nature. Their natural sources include weathering of metal-bearing rocks and volcanic eruptions, while anthropogenic sources include mining and various industrial and agricultural activities Environmental pollution is one of the major challenges in the modern human society H. Ali and E. Khan., 2017. Toxicity refers to the property of a chemical to affect survival, growth, and reproduction of an organism. Certain

heavy metals have been reported to be carcinogenic, mutagenic, and/or teratogenic to different species depending on dose and duration of exposure. Heavy metals affect both wildlife and human health. Some species are more sensitive to heavy metals than others. The mechanisms by which heavy metals affect different organs, tissues, and systems in different organisms are very complex, and so far some of them are not fully explored. Exposure of the bivalve *Anodonta anatina* to Cd has been found to affect carbonic anhydrase (CA) in its tissues, an enzyme playing a role in osmoregulation and Ca metabolism H. T. T. Ngo, S. Gerstmann, and H. Frank., 2011.

Vanadium

Vanadium is a chemical element with the symbol **V** and atomic number 23. It is a hard, silvery-grey, malleable transition metal. The elemental metal is rarely found in nature, but once isolated artificially, the formation of an oxide layer (passivation) somewhat stabilizes the free metal against further oxidation.

Andrés Manuel del Río discovered compounds of vanadium in 1801 in Mexico by analyzing a new lead-bearing mineral he called "brown lead". Though he initially presumed its qualities were due to the presence of a new element, he was later erroneously convinced by French chemist Hippolyte Victor Collet-Descotils that the element was just chromium. Then in 1830, Nils Gabriel Sefström generated chlorides of vanadium, thus proving there was a new element, and named it "vanadium" after the Scandinavian goddess of beauty and fertility, Vanadís (Freyja). The name was based on the wide range of colors found in vanadium compounds. Del Rio's lead mineral was ultimately named vanadinite for its vanadium content. In 1867 Henry Enfield Roscoe obtained the pure element.

Vanadium occurs naturally in about 65 minerals and in fossil fuel deposits. It is produced in China and Russia from steel smelter slag. Other countries produce it either from magnetite directly, flue dust of heavy oil, or as a byproduct of uranium mining. It is mainly used to produce specialty steel alloys such as high-speed tool steels, and some aluminium alloys. The most important industrial vanadium compound, vanadium pentoxide, is used as a catalyst for the production of sulfuric acid. The vanadium redox battery for energy storage may be an important application in the future.

Large amounts of vanadium ions are found in a few organisms, possibly as a toxin. The oxide and some other salts of vanadium have moderate toxicity. Particularly in the ocean, vanadium is used by some life forms as an active center of enzymes, such as the vanadium bromoperoxidase of some ocean algae.

Vanadium was discovered in 1801 by the Spanish mineralogist Andrés Manuel del Río. Del Río extracted the element from a sample of Mexican "brown lead" ore, later named vanadinite. He found that its salts exhibit a wide variety of colors, and as a result he named the element *panchromium* (Greek: παγχρώμιο "all colors"). Later, Del Río renamed the element *erythronium* (Greek: ερυθρός "red") because most of the salts turned red upon heating. In 1805, French chemist Hippolyte Victor Collet-Descotils, backed by del Río's friend Baron Alexander von Humboldt, incorrectly declared that del Río's new element was an impure sample of chromium. Del Río accepted Collet-Descotils' statement and retracted his claim (Cintas and Pedro, 2004).

In 1831 Swedish chemist Nils Gabriel Sefström rediscovered the element in a new oxide he found while working with iron ores. Later that year, Friedrich Wöhler confirmed del Río's earlier work (Sefstrom, 1831). Sefström chose a name beginning with V, which had not yet been assigned to any element. He called the element *vanadium* after Old Norse *Vanadís* (another name for the Norse Vanr goddess Freyja, whose attributes include

beauty and fertility), because of the many beautifully colored chemical compounds it produces (Sefstrom, 1831). In 1831, the geologist George William Featherstonhaugh suggested that vanadium should be renamed "*rionium*" after del Río, but this suggestion was not followed (Featherstonhaugh and George, 1831).

The vanadium redox battery, a type of flow battery, is an electrochemical cell consisting of aqueous vanadium ions in different oxidation states (Joerissen et al., 2004). Batteries of the type were first proposed in the 1930s and developed commercially from the 1980s onwards. Cells use +5 and +2 formal oxidization state ions. Vanadium redox batteries are used commercially for grid energy storage.

Vanadate can be used for protecting steel against rust and corrosion by conversion coating (Guan and Buchheit, 2004). Vanadium foil is used in cladding titanium to steel because it is compatible with both iron and titanium (Lositskii *et al*., 1966). The moderate thermal neutron-capture cross-section and the short half-life of the isotopes produced by neutron capture makes vanadium a suitable material for the inner structure of a fusion reactor (Matsui *et al*., 1996).

Lithium vanadium oxide has been proposed for use as a high energy density anode for lithium ion batteries, at 745 Wh/L when paired with a lithium cobalt oxide cathode (Kariatsumari and Koji, 2008).Vanadium phosphates have been proposed as the cathode in the lithium vanadium phosphate battery, another type of lithium-ion battery (Saidi *et al*., 2003).

Adsorption

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface (Brownfields and Land Revitilization Technology Support Center, 2009). This

process creates a film of the *adsorbate* on the surface of the *adsorbent*. This process differs from absorption, in which a fluid (the *absorbate*) is dissolved by or permeates a liquid or solid (the *absorbent*) Adsorption is a *surface phenomenon*, while absorption involves the whole volume of the material, although adsorption does often precede absorption (Atkins *et al*., 2018). The term *sorption* encompasses both processes, while *desorption* is the reverse of it.

Adsorption is present in many natural, physical, biological and chemical systems and is widely used in industrial applications such as heterogeneous catalysts (Czelej *et al*., 2016; Czelej *et al*., 2016), activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increasing storage capacity of carbide-derived carbons and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Pharmaceutical industry applications, which use adsorption as a means to prolong neurological exposure to specific drugs or parts thereof, are lesser known.

The word "adsorption" was coined in 1881 by German physicist Heinrich Kayser (1853–1940) (Kayser and Heinrich, 1881).

Physiosorption

The fundamental interacting force of physisorption is Van der Waals. Even though the interaction energy is very weak (~10–100 meV), physisorption plays an important role in nature. For instance, the van der Waals attraction between surfaces and foot-hairs of geckos provides the remarkable ability to climb up vertical walls (Autumn *et al*., 2000).

Van der Waals forces originate from the interactions between induced, permanent or transient electric dipoles.

In comparison with chemisorption, in which the electronic structure of bonding atoms or molecules is changed and covalent or ionic bonds form, physisorption does not result in changes to the chemical bonding structure. In practice, the categorisation of a particular adsorption as physisorption or chemisorption depends principally on the binding energy of the adsorbate to the substrate, with physisorption being far weaker on a per-atom basis than any type of connection involving a chemical bond.

Chemisorption

Chemisorption is a kind of adsorption which involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the adsorbant surface. Examples include macroscopic phenomena that can be very obvious, like corrosion, and subtler effects associated with heterogeneous catalysis, where the catalyst and reactants are in different phases. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds (Oura *et al*., 2003).

In contrast with chemisorption is physisorption, which leaves the chemical species of the adsorbate and surface intact. It is conventionally accepted that the energetic threshold separating the binding energy of "physisorption" from that of "chemisorption" is about 0.5 eV per adsorbed species.

Due to specificity, the nature of chemisorption can greatly differ, depending on the chemical identity and the surface structural properties. The bond between the adsorbate and adsorbent in chemisorption is either ionic or covalent.

Freundlich Isotherm

The **Freundlich equation** or **Freundlich adsorption isotherm**, an adsorption isotherm, is an empirical relationship between the quantity of a gas adsorbed into a solid surface and the gas pressure. The same relationship is also applicable for the concentration of a solute adsorbed onto the surface of a solid and the concentration of the solute in the liquid phase. In 1909, Herbert Freundlich gave an expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with gas pressure (Freundlich *et al*., 1909).This equation is known as Freundlich adsorption isotherm or Freundlich adsorption equation. As this relationship is entirely empirical, in the case where adsorption behavior can be properly fit by isotherms with a theoretical basis, it is usually appropriate to use such isotherms instead (see for example the Langmuir and BET adsorption theories). The Freundlich equation is also derived (non-empirically) by attributing the change in the equilibrium constant of the binding process to the heterogeneity of the surface and the variation in the heat of adsorption (Adamson, 1997).

Formula: $Lnq_e = LnK_f + \frac{1}{n}LnC_e$

Langmiur Equation

Irving Langmuir was the first to derive a scientifically based adsorption isotherm in 1918 (Czepirski *et al*., 2000). The model applies to gases adsorbed on solid surfaces. It is a semi-empirical isotherm with a kinetic basis and was derived based on statistical thermodynamics. It is the most common isotherm equation to use due to its simplicity and its ability to fit a variety of adsorption data. It is based on four assumptions:

1. All of the adsorption sites are equivalent, and each site can only accommodate one molecule.

2. The surface is energetically homogeneous, and adsorbed molecules do not interact.
3. There are no phase transitions.
4. At the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates.

These four assumptions are seldom all true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules to adsorb to a surface as for the last. The fourth condition is the most troublesome, as frequently more molecules will adsorb to the monolayer; this problem is addressed by the BET isotherm for relatively flat (non-microporous) surfaces. The Langmuir isotherm is nonetheless the first choice for most models of adsorption and has many applications in surface kinetics (usually called Langmuir–Hinshelwood kinetics) and thermodynamics.

Formula: $\frac{Ce}{qe} = \frac{1}{qm}C_e + \frac{1}{klqm}$

The term "clay" is applied both to materials having a particle size of less than 2 micrometers (25,400 micrometers = 1 inch) and to the family of minerals that has similar chemical compositions and common crystal structural characteristics (Velde, 1995) described in the next section. Clay minerals have a wide range of particle sizes from 10's of angstroms to millimeters. (An angstrom is a unit of measure at the scale of atoms.) Thus, clays may be composed of mixtures of finer grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides. Clays and clay minerals are found mainly on or near the surface of the Earth. (Velde, 1995) Water molecules are strongly attracted to clay mineral surfaces. When a little clay is added to water, a slurry forms because the clay distributes itself evenly throughout the water. This property of clay is used by the paint

industry to disperse pigment (color) evenly throughout a paint. Without clay to act as a carrier, it would be difficult to evenly mix the paint base and color pigment. A mixture of a lot of clay and a little water results in a mud that can be shaped and dried to form a relatively rigid solid. This property is exploited by potters and the ceramics industry to produce plates, cups, bowls, pipes, and so on. Environmental industries use both these properties to produce homogeneous liners for containment of waste. Blatt, H., Middleton, G., and Murray, R., 1980, Industrial minerals, such as clays, sand, gravel, and crushed stone, are raw materials used for building and maintaining infrastructure, agriculture, and mitigation of environmental problems. Because of the many uses for industrial minerals in our society, land management agencies have an increasing need for better geologic and mineralogic data on industrial minerals Hillier, S., 1995 Clay has a high content of clay minerals that give it its plasticity. Clay minerals are hydrous aluminium phyllosilicate minerals, composed of aluminium and silicon ions bonded into tiny, thin plates by interconnecting oxygen and hydroxyl ions. These plates are tough but flexible, and in moist clay, they adhere to each other. The resulting aggregates give clay the cohesion that makes it plastic. In kaolinite clay, the bonding between plates is provided by a film of water molecules that hydrogen bond the plates together. The bonds are weak enough to allow the plates to slip past each other when the clay is being moulded, but strong enough to hold the plates in place and allow the moulded clay to retain its shape after it is moulded. When the clay is dried, most of the water molecules are removed, and the plates hydrogen bond directly to each other, so that the dried clay is rigid but still fragile. If the clay is moistened again, it will once more become plastic. When the clay is fired to the earthenware stage, a dehydration reaction removes additional water from the clay, causing clay plates to irreversibly adhere to each other via stronger covalent bonding, which strengthens the material. The clay mineral, kaolin, is transformed into a non-clay material, meta kaolin, which remains rigid and hard if moistened again. Further firing through

the stoneware and porcelain stages further recrystallizes the metakaolin into yet stronger minerals such as mullite

Kaolinite:

The most prominent member of the 1: 1 type of clay minerals is kaolinite, in which one silica tetrahedral layer is joined with one aluminum octahedral layer when the top oxygen of the silica tetrahedral layer occupies the position of the oxygen of the aluminum octahedral layer and is common to the tetrahedral and octahedral layer as shown in Practically no isomorphous substitution of ions taken places. A weak negative charge develops on the surface of the basal oxygen of the silica tetrahedral layer and a weak positive charge develops on the surface of the hydrogen of the hydroxyl of the aluminum octahedral layer.

1.6 ORIGIN AND MODE OF CLAY

The Earth was created some 5,000 million years ago, according to scientific theory. At first it was a gaseous molten mass, which slowly contracted. While the mass was still molten, the heavier materials like iron and nickel sunk to the centre of the Earth. As the hot Earth gradually cooled, a layer of solid materials formed the crust. The crust feels very secure to us, but it is only about 40 km thick, floating on a 3000 km deep layer of molten materials

The terms 'primary' and 'residual' are applied to those clays which are found overlying or in close association with the rocks from which they have been derived, and distinguish them from the 'secondary' or 'transported' clays which have been carried some distance away from their place of origin.

Residual clays may be formed by the simple removal of other materials, the clay remaining behind, as in the decomposition of some argillaceous limestones, in which the calcareous matter has been removed by solution whilst the clay is unaffected. Such a clay is

not a primary one as it has probably been derived from some distant source and, having been deposited along with the limestone ooze, has formed an intimate mixture from which the limestone has, at a later geological epoch, been removed in the manner indicated. Residual clays are seldom pure, being often rich in iron compounds, though the white clays of Staffordshire and Derbyshire are highly refractory.

It is seldom necessary to distinguish residual clays from other secondary or transported ones

Primary clays, on the contrary, have been derived from rocks which have undergone chemical decomposition, one of the products being clay. The most important primary clays are the kaolins, which are derived from the decomposition of felspar, but other primary clays derived from other minerals are known, though less frequently mentioned

All the clay minerals, with the possible exception of halloysite have been synthesized from mixtures of oxides or hydroxides and water at moderately low temperatures and pressures. Kaolinite tends to form in alumina-silica systems without alkalies or alkaline earths. Illite is formed when potassium is added to such systems. And either smectite or chlorite results upon the addition of magnesium, depending on its concentration. The clay minerals can be synthesized at ordinary temperatures and pressures if the reactants are mixed together very slowly and in greatly diluted form.

clays or kaolins may usually be regarded as primary clays derived from granitic or other felspathic or felsitic rocks by chemical decomposition. Such clays are found near to their place of origin, are usually obtainable in a comparatively pure state and are generally deficient in plasticity. They may occur in beds of small or great depth, but these are not 'accumulations' in the ordinary meaning of that term.

Residual clays also form a distinct class, as unlike the majority of argillaceous materials they are left behind when other substances are removed, usually by some process of solution. In many cases, however, the residual clays are really secondary in character, having been transported from their place of origin, together with limestone or other minerals, the mixture deposited and subjected to pressure and possibly to heat, whereby a rock-like mass is formed. This mass has then been subjected to the solvent action of water containing carbon dioxide or other substances which dissolve out the bulk of the associated minerals and leave the residual clay behind. Some clay minerals may be expressed using ideal chemical formulas as the following: $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$ (kaolinite), $4SiO_2 \cdot Al_2O_3 \cdot H_2O$ (pyrophyllite), $4SiO_2 \cdot 3MgO \cdot H_2O$ (talc), and $3SiO_2 \cdot Al_2O_3 \cdot 5FeO \cdot 4H_2O$ (chamosite) The SiO_2 ratio in a formula is the key factor determining clay mineral types. These minerals can be classified on the basis of variations of chemical composition and atomic structure into nine groups: (1) kaolin-serpentine (kaolinite, halloysite, lizardite, chrysotile), pyrophyllite-talc, mica (illite, glauconite, celadonite), Grim, Ralph E. and Kodama, Hideomi. 20 Feb. 2014,

The structure of clay minerals has been determined largely by X-ray diffraction methods. The essential features of hydrous-layer silicates were revealed by various scientists including Charles Mauguin, Linus C. Pauling, W.W. Jackson, J. West, and John W. Gruner through the late 1920s to mid-1930s. These features are continuous two-dimensional tetrahedral sheets of composition Si_2O_5, with SiO_4 tetrahedrons

Kaolin-serpentine group

Minerals of this groups are 1:1 layer silicates. Their basic unit of structure consists of tetrahedral and octahedral sheets in which the anions at the exposed surface of the octahedral sheet are hydroxyls

Halloysite also has a composition close to that of kaolinite and is characterized by its tubular nature in contrast to the platy nature of kaolinite particles. Although tubular forms are the most common, other morphological varieties are also known: prismatic, rolled, pseudospherical, and platy forms. The structure of halloysite is believed to be similar to that of kaolinite, but no precise structure has been revealed yet. Halloysite has a hydrated form with a composition of $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$. This hydrated form irreversibly changes to a dehydrated variety at relatively low temperatures (60° C) or upon being exposed to conditions of low relative humidity.

Pyrophyllite-talc group

Minerals of this group have the simplest form of the 2:1 layer with a unit thickness of approximately 9.2 to 9.6 Å—i.e., the structure consists of an octahedral sheet sandwiched by two tetrahedral sheets . Pyrophyllite and talc represent the dioctahedral and trioctahedral members, respectively, of the group. In the ideal case, the structural formula is expressed by $Al_2Si_4O_{10}(OH)_2$ for pyrophyllite and by $Mg_3Si_4O_{10}(OH)_2$ for talc. Therefore, the 2:1 layers of these minerals are electrostatically neutral and are held together with van der Waals bonding. One-layer triclinic and two-layer monoclinic forms are known for polytypes of pyrophyllite and talc. The ferric iron analogue of pyrophyllite is called ferripyrophyllite.

Mica mineral group

Mica minerals have a basic structural unit of the 2:1 layer type like pyrophyllite and talc, but some of the silicon atoms (ideally one-fourth) are always replaced by those of aluminum. This results in a charge deficiency that is balanced by potassium ions between the unit layers. The sheet thickness (basal spacing or dimension along the direction normal to the basal plane) is fixed at about 10 Å. Typical examples are muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$, for

dioctahedral species, and phlogopite, $KMg_3(Si_3Al)O_{10}(OH)_2$, and biotite, $K(Mg, Fe)_3(Si_3Al)O_{10}(OH)_2$, for trioctahedral species. (Formulas rendered may vary slightly due to possible substitution within certain structural sites.) Various polytypes of the micas are known to occur. Among them, one-layer monoclinic (1M), two-layer monoclinic (2M, including $2M_1$ and $2M_2$), and three-layer trigonal (3T) polytypes are most common. The majority of clay-size micas are dioctahedral aluminous species; those similar to muscovite are called illite and generally occur in sediments. The illites are different from muscovite in that the amount of substitution of aluminum for silicon is less; sometimes only one-sixth of the silicon ions are replaced. This reduces a net unbalanced-charge deficiency from 1 to about 0.65 per unit chemical formula. As a result, the illites have a lower potassium content than the muscovites. To some extent, octahedral aluminum ions are replaced by magnesium (Mg^{2+}) and iron ions (Fe^{2+}, Fe^{3+}). In the illites, stacking disorders of the layers are common, but their polytypes are often unidentifiable.

Vermiculite

The vermiculite unit structure consists of sheets of trioctahedral mica or talc separated by layers of water molecules; these layers occupy a space about two water molecules thick (approximately 4.8 Å). Substitutions of aluminum cations (Al^{3+}) for silicon cations (Si^{4+}) constitute the chief imbalance, but the net charge deficiency may be partially balanced by other substitutions within the mica layer; there is always a residual net charge deficiency commonly in the range from 0.6 to 0.8 per $O_{10}(OH)_2$. This charge deficiency is satisfied with interlayer cations that are closely associated with the water molecules between the mica layers. In the natural mineral, the balancing cation is magnesium (Mg^{2+}). The interlayer cation, however, is readily replaced by other inorganic and organic cations

Smectite

The structural units of smectite can be derived from the structures of pyrophyllite and talc. Unlike pyrophyllite and talc, the 2:1 silicate layers of smectite have a slight negative charge owing to ionic substitutions in the octahedral and tetrahedral sheets. The net charge deficiency is normally smaller than that of vermiculite—from 0.2 to 0.6 per $O_{10}(OH)_2$—and is balanced by the interlayer cations as in vermiculite. This weak bond offers excellent cleavage between the layers. The distinguishing feature of the smectite structure is that water and other polar molecules (in the form of certain organic substances) can, by entering between the unit layers, cause the structure to expand in the direction normal to the basal plane. Thus this dimension may vary from about 9.6 Å, when there are no polar molecules between the unit layers, to nearly complete separation of the individual layers.

Chlorite

The structure of the chlorite minerals consists of alternate micalike layers and brucitelike hydroxide sheets about 14 Å thick. Structural formulas of most trioctahedral chlorites may be expressed by four end-member compositions:

$(Mg_5Al)(Si_3Al)O_{10}(OH)_8$ (clinochlore)

$(Fe_5^{2+}Al)(Si_3Al)O_{10}(OH)_8$ (chamosite)

$(Mn_5Al)(Si_3Al)O_{10}(OH)_8$ (pennantite)

$(Ni_5Al)(Si_3Al)O_{10}(OH)_8$ (nimite)

The unbalanced charge of the micalike layer is compensated by an excess charge of the hydroxide sheet that is caused by the substitution of trivalent cations (Al^{3+}, Fe^{3+}, etc.) for

divalent cations (Mg^{2+}, Fe^{2+}, etc.). Chlorites with a muscovite-like silicate layer and an aluminum hydroxide sheet are called donbassite and have the ideal formula of $Al_{4.33}(Si_3Al)O_{10}(OH)_8$ as an end-member for the dioctahedral chlorite. In many cases, the octahedral aluminum ions are partially replaced by magnesium, as in magnesium-rich aluminum dioctahedral chlorites called sudoite. Cookeite is another type of dioctahedral chlorite, in which lithium substitutes for aluminum in the octahedral sheets.

Chlorite structures are relatively thermally stable compared to kaolinite, vermiculite, and smectite minerals and are thus resistant to high temperatures. Because of this, after heat treatment at 500°–700° C, the presence of a characteristic X-ray diffraction peak at 14 Å is widely used to identify chlorite minerals.

HEAVY METALS

"Heavy metals" are natural elements characterized by their rather high atomic mass and their high density. Although typically occurring in rather low concentration, they can be found all through the crust of our planet. Commonly, a density of at least 5 g cm^{-3} is used to define a heavy metal and to differentiate it from other, "light" metals. r definitions for "heavy metals" require an atomic mass higher than 23 or an atomic number exceeding 20; these definitions are highly error prone and confusing. Both alternative definitions cause the inclusion even of nonmetals; resorting to the atomic mass criterion, the maximum number of elements (Verma N, 2005)

Heavy metal are commonly referred to as "trace elements" and is defined

as a group of elements that are in very low concentrations (mg/kg or less) present in most of the

soil, plants and living organisms. However, there is no authoritative definition in the relevant

literature, and until now no relevant authority, has not defined the term "heavy metals"

Lately there is an opinion that is the a more appropriate term instead of "heavy metals" for these

elements would be "toxic elements" or "microelements", bat no consemsus was achieved All in all, the heavy metals are an important group of environmental pollutants and a source of

toxicity (Moon, K.A., and Chae, H.K. (2007) Heavy metals from soil, can be intake by human body in the following ways: ingestion (intake

through water and food), inhalation, direct contact through the skin and indirect contact.

Excessive intake of heavy metals into living organisms causes many harmful consequences,

including death. Alloway B.J. (2013).

CHAPTER TWO

METHODOLOGY

2.0 MATERIAL

This are material used during my experimental studies

- Natural Dangara clay
- Distill water
- Ammonium metavanadate (NH_4VO_3).
- Conc sulphuric acid
- Sodium hydroxide

2.1 EQUIPMENT AND GLASSWARE

1000ml volumetric flask

100ml measuring cylinder

pH meter.

250ml Beaker

Analytical weighing balance

Atomic Adsorption Spectrophotomer

Stock solution

Funnel

Stirrer

METHODOLOGY

2.2 Adsorbent Preparation

The raw Dangara middle layer clay was used as the adsorbent. The clay was crushed in porcelain mortar to a fine texture and no further treatment was carried out on the clay.

2.3 ADSORBATE PREPARATION

1000mg/l standard solution of the required adsorbate was prepared dissolving in mass(in gram) of salt that contain the metal ion NH_4VO_3, determined by the stoichiometric calculation. Vanadium metavanadate (NH_4VO_3) (2.32g) was dissolved in 1000ml of distilled water to give 100mg/L NH_4VO_3 .

2.4 ADSORBENT DOSAGE PREPARATION

To determine adsorbent dosage on adsorption of NH_4VO_3 50ml of 10ppm of the stock solution was divided into 5places and clay of various mass 0.2g, 0.4g, 0.6, 0.8g and 1.og was added, agitated and placed in orbital shaker for 1hr . Which was then filtered and the filtrate was analyzed using SpectrAA lamp hollow cathode lamp 11c928 vanadium V for Atomic Adsorption Spectrophotometer and the values obtained were recorded.

2.5 Initial Concentration

50ml solutions with concentration 10ppm, 20ppm, 30pmm, 40ppm and 50ppm of aqueous solution 1ml, 2ml, 3ml, 4ml and 5ml respectively from the stock solution (1000ppm) and diluting with distilled water to 100ml mark. 1g of clay added into each measured solution agitated and then placed orbital shaker for 1hr. The mixtures were filtered and the filtrate was analyzed using SpectrAA lamp hollow cathode lamp 11c928 vanadium V for Atomic Adsorption Spectrophotometer and the values obtained were recorded.

2.6 CONTACT TIME

To determine the adsorption time, 10ml of the 10ppm solution was measured into 5 beakers and 1g of clay added into each beaker, Agitated and placed in the orbital shaker for different time interval; 10, 20, 30, 40 and 50 minutes respectively. The mixture was filtered and the filtrate was analyzed using SpectrAA lamp hollow cathode lamp 11c928 vanadium V for Atomic Adsorption Spectrophotometer and the values obtained were recorded.

2.6 Effect of pH

To determine the effect of pH, 50ml of 10ppm was measured into a beaker (5 beakers) and their pH was varied to obtain 3,5,7,8 and 9 using 0.1M NaOH and 0.1M HCl. 1g of clay was added to each solution, then placed in the orbital shaker for 1hr. The mixtures were filtered and the filtrates was analyzed using SpectrAA lamp hollow cathode lamp 11c928 vanadium V for Atomic Adsorption Spectrophotometer and the values obtained were recorded.
was analyzed using SpectrAA lamp hollow cathode lamp 11c928 vanadium V for Atomic Adsorption Spectrophotometer and the values obtained were recorded.

2.7 Effect of Temperature

To study the effect of temperature, 50ml of 10ppm of the aqueous solution was measured into five different beakers and 1g of clay was added into each and was heated to 20^0C, 30^0C, 40^0C, 50^0C and 80^0C respectively and allowed to settle before filtering. The filtrate was analyzed using using SpectrAA lamp hollow cathode lamp 11c928 vanadium V for Atomic Adsorption Spectrophotometer and the values obtained were recorded.

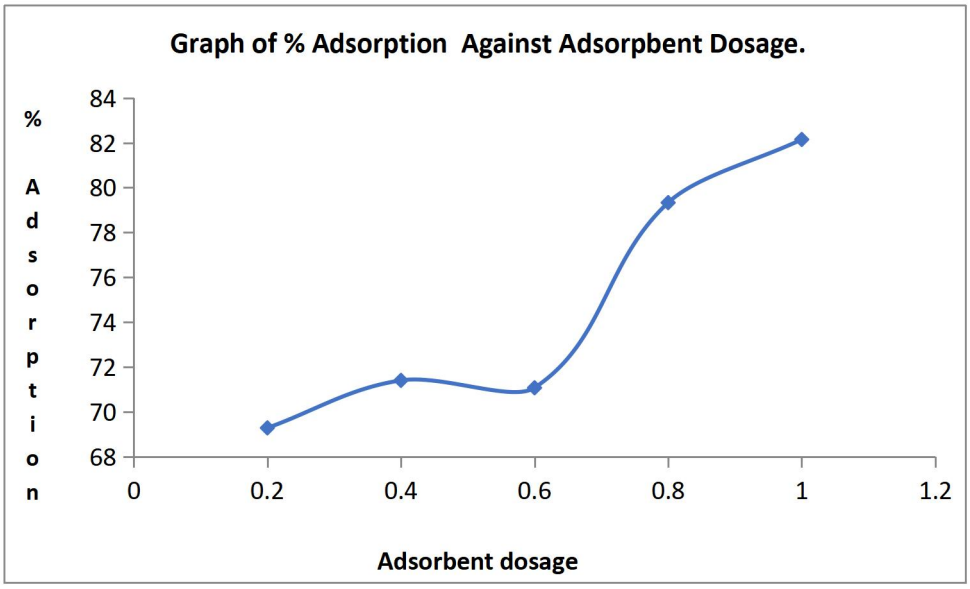
CHAPTER THREE

RESULT/ DISCUSSION

The table shows below are result obtained from the atomic adsorption spectrophotometer analysis carried out on the various filtrates obtained from the experiments

Table 3.1 Effect of adsorbent dosage on Adsorption

Adsorbent dosage (g)	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)	Adsorption %
0.2	3.072	1.732	69.28
0.4	2.86	0.893	71.4
0.6	2.893	0.592	71.07
0.8	2.067	0.496	79.33
1	1.785	0.411	82.15



3. Figure 1Graph Showing the Effect of Adsorbent Dosage on Adsorption Vanadium.

FIGURE 3.1: From the above discussion on Effect of Adsorbent Dosage on adsorption of vanadium ions from aqueous solution using Dangara clay as an Adsorbent, it was discover that the fraction of the metal removed from aqueous solution increased with an increasing in the adsorbent dosage. such behaviors are obvious since the metal uptake the capacity of the adsorbent increased as there is an increase in dosage. The reason was that, the number of the active sites available for metal uptake were more as the amount of the adsorbent increases. The maximum adsorption was 82.18% at 1.0g.

TABLE 3.2; Effect of initial concentration on adsorption of vanadium.

Below are result discussion on effect of initial concentration of vanadium using Dangara clay as an adsorbent

Initial concentration (mg/l)	**Equilibrum concentration (mg/l)**	**Amount adsorbed (mg/l)**	**Adsorption %**
10	**1.844**	**0.0408**	**81.56**
20	**1.722**	**0.0206**	**82.78**
30	**1.499**	**0.0142**	**85.01**
40	**1.593**	**0.0105**	**84.07**
50	**1.309**	**0.0087**	**86.91**

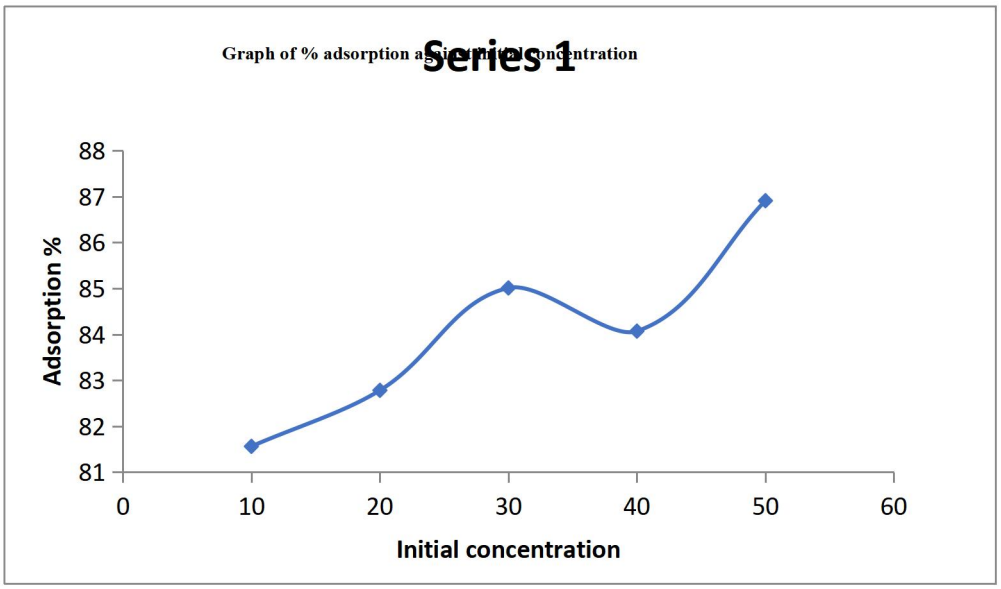


Figure3.2: Graph of % Adsorption Against initial concentration

From fig 3.2, above graph , the percentage removal of vanadium ion from aqueous solution was observed to increases with an increasing in initial concentration from 81.56 at 10g of adsorbent to 86.91 at 50g, the lower percentage adsorption was obtained at 10g (81.91) and maximum was obtained at 50g (86.91).

Table 3.3 Table of effect of ph on adsorption of vanadium.

pH	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)	Adsorption %
3	2.943	0.117	70.50
5	2.335	0.076	76.65
7	2.089	0.056	79.11
8	2.122	0.049	78.78
9	2.061	0.882	79.39

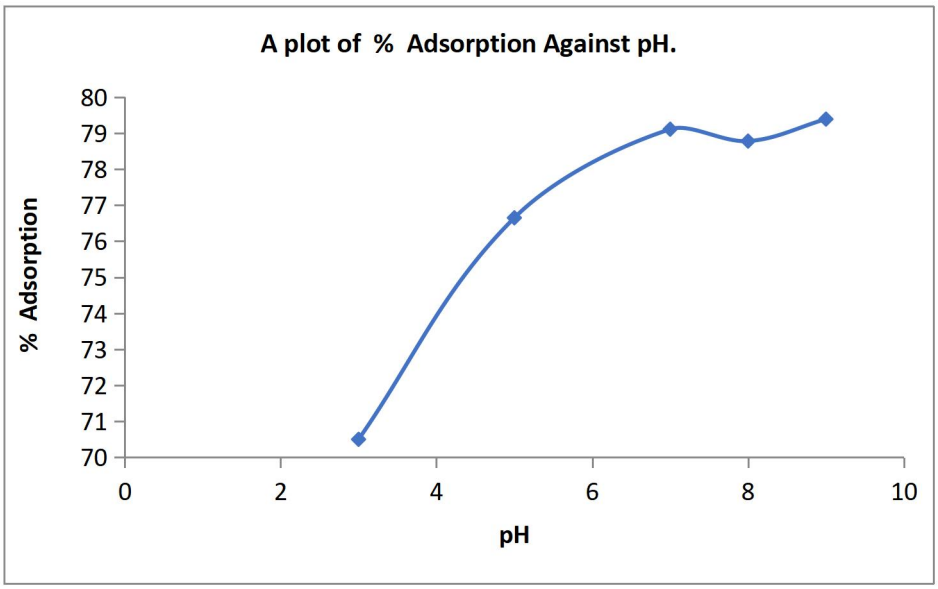


Figure 3.3 plot of % adsorption against pH

From above graph percentage Adsorption against pH, it was observed that % removal was increases with an increasing in pH. The result obtained indicated that % removal increases with an increasing in pH from 70.50 to 79.39 of % removal to pH 3 and 9, The maximum % removal was obtained at pH 9 (79.39) and the lower % removal was obtained at pH 3(70.50).

Table 3.4 Effect of contact time on adsorption of vanadium.

TIME (minutes)	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)	Adsorption %
10	**3.388**	**0.033**	**66.12**
20	**2.393**	**0.019**	**76.07**
30	**2.083**	**0.013**	**79.17**
40	**1.783**	**0.010**	**82.17**
50	**1.948**	**0.008**	**80.52**

Figure3.4 graph of % Adsorption against contact time

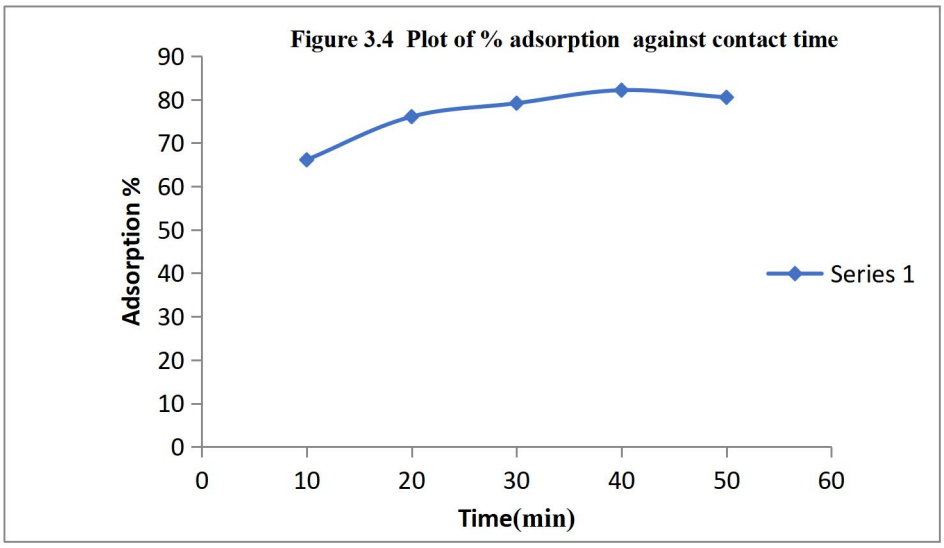


Figure3.4 graph of % Adsorption against contact time

From above fig 3.4, percentage removal of vanadium ion from aqueous solution was observed to increased with an increasing in contact time from 66.12 at 10mins time, to 80.52 at 50min time, maximum was obtained at 40mins (82.17).and the lower percentage adsorption was obtained at 10mins (10.12).

Table 3.5: The effect of temperature on adsorption of vanadium.

Temperature (°c)	Equilibrium concentration(mg/l)	Amount adsorbed (mg/l)	% Adsorption
20	2.133	0.0196	78.67
30	2.044	0.013	79.56
40	1.893	0.010	81.07
50	1.920	0.008	80.80
80	1.911	0.005	80.89

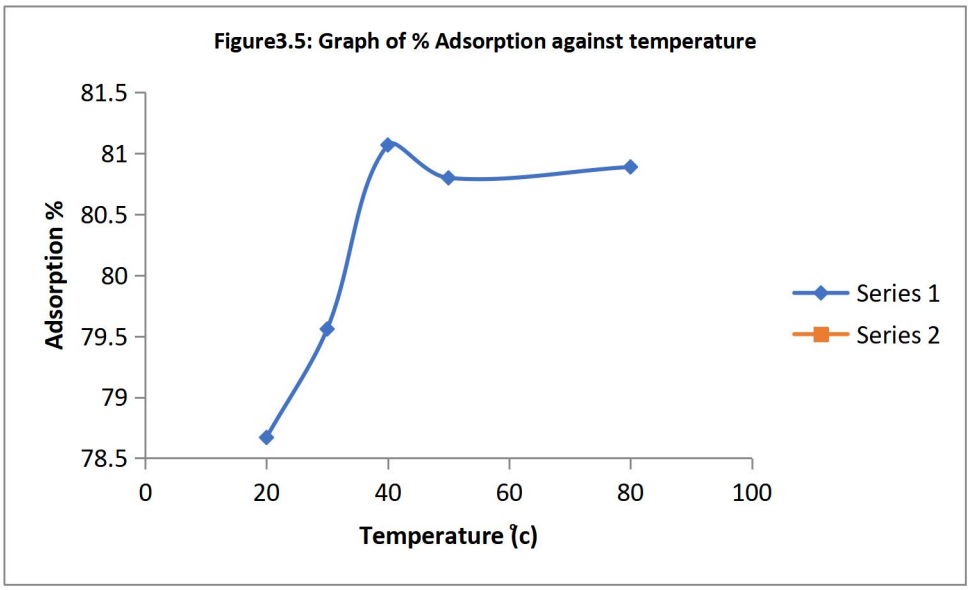


Figure3.5 plot of % adsorption against temperature

From above fig 3.5, percentage removal of vanadium ion from aqueous solution was observed to increases with an increasing in Temperature from 78.67 at 20^{O}c of Temperature to 80.89 at 80^{O}c, the maximum % removal was obtained at 40^{O}c (81.07). lower percentage adsorption was obtained at 20 (78.67).

Table 3.6 table of langmuir .

q_m	K_l	r2
0.354	-4.074	0.999

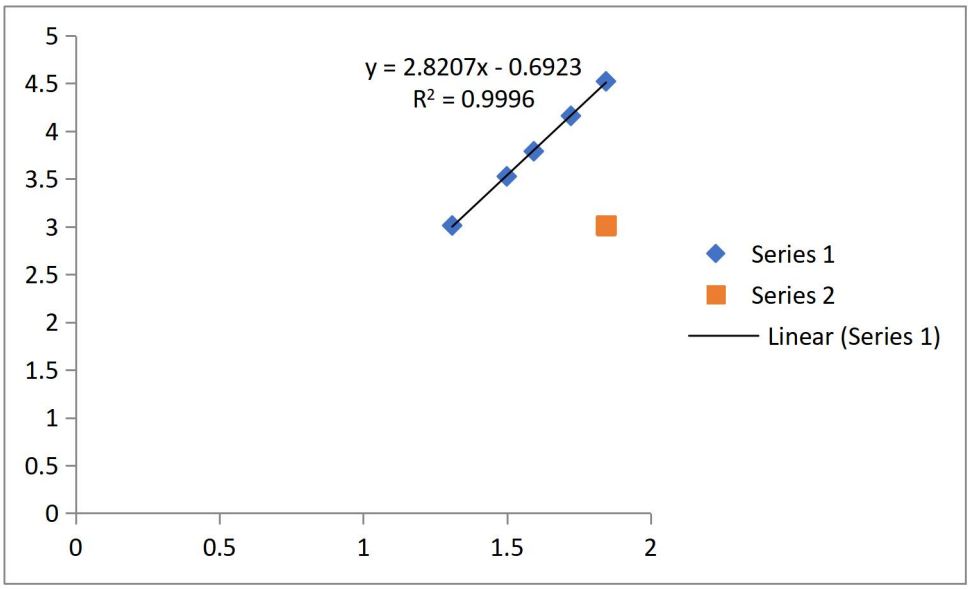


Figure 3.6: graph of Langmuir.

Table3.7 table of freundlich

k_f	N	r^2
0.457	**-5.41**	**0.995**

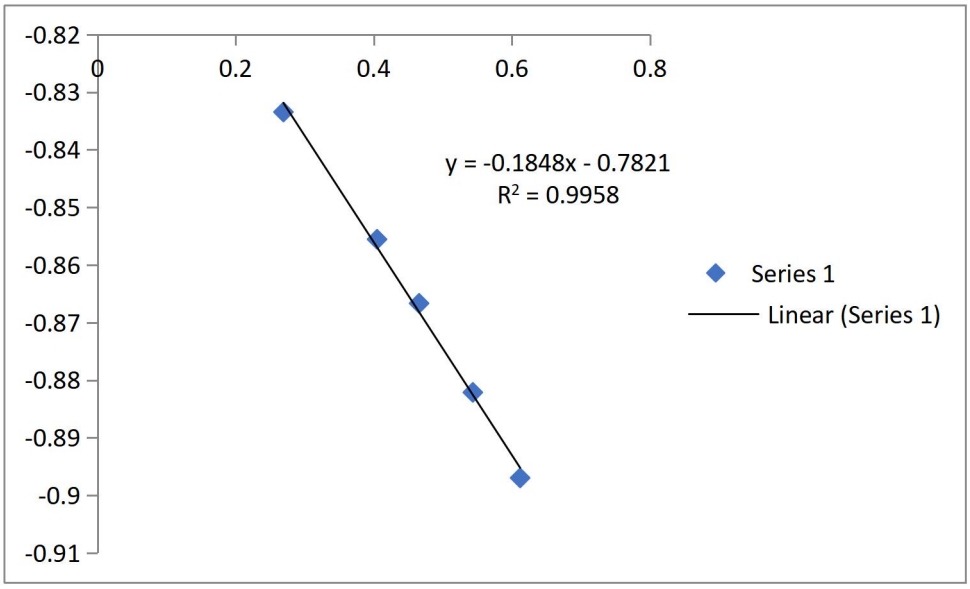


Fig 3.7 graph of freunlch.

CONCLUSION

The study examined the utilization of unmodified dangara clay for the removal of vanadium from aqueous solution. The study showed that as the process variable(pH, initial concentration, adsorbent dosage and temperature increase, the percentage removal of vanadium increased as well. The highest percentage removal was observed with varying concentration which was found to be 86% followed by adsorbent dosage at 82%, then temperature at 80% and pH at 79%. The Langmuir model was found to better described the adsorption behavior. Overall, the clay is not considered competent enough as an adsorbent for the removal of vanadium ions from aqueous solution because of low adsorption capacity calculated to be 0.345mg/g. Modification of the surface of the clay could improve its adsorption capacity.

REFERNCES

Adamson, A.W (1997). *Physical chemistry of surfaces*. p. 393

Appenroth, K.J. (2010). Definition of “Heavy Metals” and Their Role in Biological Systems,

Atkins, P. W.; De Paula, Julio; Keeler, James (2018). *Atkins' Physical chemistry* (Eleventh ed.). Oxford, United Kingdom.

Baird C. &Cann M. 2012, Environmental Chemistry, 5th ed., W. H. Freeman and Company, New York, ISBN 978-1-4292-7704-4.

Bergaya, F.; Lagaly, G. (2006). "Chapter 1 General Introduction: Clays, Clay Minerals, and Clay Science". *Developments in Clay Science*. **1**: 1–18.

*Bergaya, F.; Lagaly, G. (2006). "Chapter 1 General Introduction: Clays, Clay Minerals, and Clay Science". Developments in Clay Science. **1**: 1–18. doi:10.1016/S1572-4352(05)01001-9. ISBN 9780080441832.*

Berry L. G. & Mason B. 1959, *Mineralogy: Concepts, Descriptions, Determinations*, W. H. Freeman and Company, San Francisco.

Blatt, H., Middleton, G., and Murray, R., 1980, Origin of sedimentary rocks (2d ed.): Englewood Cliffs, N.J., Prentice-Hall, 766 p.

Boggs, Sam (2006). *Principles of sedimentology and stratigraphy* (4th ed.). Upper Saddle River, N.J.

Boylu, Feridun (1 April 2011). "Optimization of foundry sand characteristics of soda-activated calcium bentonite". *Applied Clay Science*. **52** (1): 104–108.

Bradl HB (2004). Adsorption of heavy metal ions on soils and soils constituents. J. Colloid Interface Sci., 277: 1-18

Breuer, Stephen (July 2012). "The chemistry of pottery" (PDF). Education in Chemistry: 17–20. Retrieved 8 December 2020.

Byerrum, R.U, Echardt, R.E, Hopkins, L.L, 1974 Vanadium.National Academic of Sciences, Washington,DC.

Chanturiya, V.A.; Minenko, V.G.; Makarov, D.V. (2018). "Advanced Techniques of Saponite Recovery from Diamond Processing Plant Water and Areas of Saponite Application". Minerals. **8** (12): 549.

Chen J. & Huang K. 2006, "A new technique for extraction of platinum group metals by pressure cyanidation", *Hydrometallurgy*, vol. 82, nos. 3–4, pp. 164–171,

Churchman, G. J.; Gates, W. P.; Theng, B. K. G.; Yuan, G. (2006). Faïza Bergaya, Benny K. G. Theng and Gerhard Lagaly (ed.). "Chapter 11.1 Clays and Clay Minerals for Pollution Control". *Developments in Clay Science*. Handbook of Clay Science. Elsevier. **1**: 625–675.

Cintas, Pedro (2004). "The Road to Chemical Names and Eponyms: Discovery, Priority, and Credit". *Angewandte Chemie International Edition*. **43** (44): 5888–94.

Cox P. A. 1997, *The elements: Their Origin, Abundance and Distribution*, Oxford University Press, Oxford,

Crundwell F. K., Moats M. S., Ramachandran V., Robinson T. G. & Davenport W. G. 2011, *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*, Elsevier, Kidlington, Oxford, p. 409.

Czelej, K.; Cwieka, K.; Colmenares, J.C.; Kurzydlowski, K.J. (2016). "Insight on the Interaction of Methanol-Selective Oxidation Intermediates with Au- or/and Pd-Containing Monometallic and Bimetallic Core@Shell Catalysts". *Langmuir*. **32** (30): 7493–7502.

Czelej, K.; Cwieka, K.; Kurzydlowski, K.J. (May 2016). "CO_2 stability on the Ni low-index surfaces: Van der Waals corrected DFT analysis". *Catalysis Communications*. **80** (5): 33–38.

Dadu, Ramona; Hu, Mimi I.; Cleeland, Charles; Busaidy, Naifa L.; Habra, Mouhammed; Waguespack, Steven G.; Sherman, Steven I.; Ying, Anita; Fox, Patricia; Cabanillas, Maria E. (October 2015). "Efficacy of the Natural Clay, Calcium Aluminosilicate Anti-Diarrheal, in Reducing Medullary Thyroid Cancer–Related

Diarrhea and Its Effects on Quality of Life: A Pilot Study". *Thyroid*. **25** (10): 1085–1090.

Diamond, Jared M. (1999). "Diamond on Geophagy". *ucla.edu*.

Duruibe JO, Ogwuegbu MOC, Egwurugwu JN. Heavy metal pollution and human biotoxic effects. International Journal of physical sciences. 2007;2(5):112-118

Ebert, John David (31 August 2011). *The New Media Invasion: Digital Technologies and the World They Unmake*. McFarland.

Eisenhour, D. D.; Brown, R. K. (1 April 2009). "Bentonite and Its Impact on Modern Life". *Elements*. **5** (2): 83–88.

Emsley J. 2011, *Nature's Building Blocks*, new edition, Oxford University Press, Oxford, pp. 47; 331; 138; 133.

Emsley J. 2011, *Nature's Building Blocks*, new edition, Oxford University Press, Oxford, pp. 32.

FAO/WHO Expert Committee on Food Additives (JECFA). (2004). Safety evaluation of certain food additives and contaminants. WHO Food Additives Series No 52.

Featherstonhaugh, George William (1831). "New Metal, provisionally called Vanadium". *The Monthly American Journal of Geology and Natural Science*: 69.

Fergusson JE (eds.) (1990) The Heavy Elements: Chemistry, Environmental Impact

Foley, Nora K. (September 1999). "Environmental Characteristics of Clays and Clay Mineral Deposits"

Forouzan, Firoozeh; Glover, Jeffrey B.; Williams, Frank; Deocampo, Daniel (1 December 2012). "Portable XRF analysis of zoomorphic figurines, "tokens," and sling bullets from Chogha Gavaneh, Iran". *Journal of Archaeological Science*. **39** (12): 3534–3541.

Freundlich, Herbert. Kapillarchemie, eine Darstellung der Chemie der Kolloide und verwandter Gebiete. Akademische Verlagsgesellschaft, 1909.

García-Sanchez, A.; Alvarez-Ayuso, E.; Rodriguez-Martin, F. (1 March 2002). "Sorption of As(V) by some oxyhydroxides and clay minerals. Application to its immobilization in two polluted mining soils". *Clay Minerals*. **37** (1): 187–194.

Grim R.E.(1953): Clay Mineralogy. McGraw-Hill, London.

Grim, Ralph (2016). "Clay mineral". *Encyclopædia Britannica*.

Grim, Ralph E. and Kodama, Hideomi, 20 Feb. 2014, "Clay mineral". *Encyclopedia Britannica*, 20 Feb. 2014, https://www.britannica.com/science/clay-mineral. Accessed 25 July 2021.

Guan, H.; Buchheit R. G. (2004). "Corrosion Protection of Aluminum Alloy 2024-T3 by Vanadate Conversion Coatings". *Corrosion*. **60** (3): 284–296.

Guggenheim, Stephen; Martin, R. T. (1995), "Definition of clay and clay mineral: Journal report of the AIPEA nomenclature and CMS nomenclature committees", *Clays and Clay Minerals*, **43** (2): 255–256,

Hadhazy A. 2016, "Galactic 'gold mine' explains the origin of nature's heaviest elements", *Science Spotlights*.

Hartmann W. K. 2005, *Moons & Planets*, 5th ed., Thomson Brooks/Cole, Belmont, California.

Hawkesworth, C. J., and Kemp, A. I. S. (2006). Evolution of the continental crust, Nature,

Hillier, S., 1995, Erosion, sedimentation and sedimentary origin of clays, in Velde, B., ed., Origin and mineralogy of clays: New York, Springer-Verlag, p. 162-219.

Hillier, S., 1995, Erosion, sedimentation and sedimentary origin of clays, in Velde, B., ed., Origin and mineralogy of clays: New York, Springer-Verlag, p. 162-219

Hodges, S.C. (2010). "Soil fertility basics" (PDF). Soil Science Extension, North Carolina State University.

in Korean Textbooks, Proceeding of the 2nd NICE Symposium, Taipei, TAIWAN. July 30-31.,

in: Soil Heavy Metals, Soil Biology, I. Sherameti and A. Varma (eds.), Chapter 2, 19-29 pages,

Joerissen, Ludwig; Garche, Juergen; Fabjan, Ch.; Tomazic G. (2004). "Possible use of vanadium redox-flow batteries for energy storage in small grids and stand-alone photovoltaic systems". *Journal of Power Sources*. **127** (1–2): 98–104.

K. Autumn; et al. (2000), "Adhesive force of a single gecko foot-hair", *Nature*, **405** (6787): 681–5.

Kariatsumari, Koji (February 2008). "Li-Ion Rechargeable Batteries Made Safer". Nikkei Business Publications, Inc. Archived from the original on 12 September 2011.

Kayser, Heinrich (1881). "Über die Verdichtung von Gasen an Oberflächen in ihrer Abhängigkeit von Druck und Temperatur". *Annalen der Physik und Chemie*. **248** (4): 526–537.

Kerr PF (1952). “Formation and Occurrence of Clay Minerals”.Clays and Clay Minerals.

Klein, Cornelis; Hurlbut, Cornelius S., Jr. (1993). *Manual of mineralogy : (after James D. Dana)* (21st ed.). New York: Wiley.

Koçkar, Mustafa K.; Akgün, Haluk; Aktürk, Özgür (November 2005). "Preliminary evaluation of a compacted bentonite / sand mixture as a landfill liner material (Abstract)]". *Department of Geological Engineering, Middle East Technical University, Ankara, Turkey*.

Leeder, M. R. (2011). *Sedimentology and sedimentary basins : from turbulence to tectonics* (2nd ed.). Chichester, West Sussex, UK: Wiley-Blackwell.

Lide D. R. (ed.) 2004, *CRC Handbook of Chemistry and Physics*, 85th ed., CRC Press, Boca Raton, Florida.

Litasov K. D. & Shatskiy A. F. 2016, "Composition of the Earth's core: A review", *Russian Geology and Geophysics*, vol. 57, no. 1, pp. 22–46,.

Lositskii, N. T.; Grigor'ev A. A.; Khitrova, G. V. (1966). "Welding of chemical equipment made from two-layer sheet with titanium protective layer (review of foreign literature)". *Chemical and Petroleum Engineering*. **2** (12): 854–856.

MacKay K. M., MacKay R. A. & Henderson W. 2002, *Introduction to Modern Inorganic Chemistry*, 6th ed., Nelson Thornes, Cheltenham, pp. 203–204.

Matsui, H.; Fukumoto, K.; Smith, D. L.; Chung, Hee M.; Witzenburg, W. van; Votinov, S. N. (1996). "Status of vanadium alloys for fusion reactors". *Journal of Nuclear Materials*. 233–237 (1): 92–99.

Moon, K.A., and Chae, H.K. (2007). What is the Meaning of Heavy Metals?: A Case Study

Moreno-Maroto, José Manuel; Alonso-Azcárate, Jacinto (September 2018). "What is clay? A new definition of "clay" based on plasticity and its impact on the most widespread soil classification systems". *Applied Clay Science*. **161**: 57–63.

Murray, H. (2002). "Industrial clays case study" (PDF). *Mining, Minerals and Sustainable Development*. **64**: 1–9.

Nesse, William D. (2000). *Introduction to mineralogy*. New York: Oxford University Press.

Nesse, William D. (2000). *Introduction to mineralogy*. New York: Oxford University Press.

Nriagu JO (1989) A global assessment of natural sources of atmospheric trace metals. Nature 338: 47-49

Olive, W.W.; Chleborad, A.F.; Frahme, C.W.; Shlocker, Julius; Schneider, R.R.; Schuster, R.L. (1989). "Swelling Clays Map of the Conterminous United States". *U.S. Geological Survey*

Miscellaneous Investigations Series Map. I-1940. Retrieved 8 December 2020.

Padmanabhan T. 2001, *Theoretical Astrophysics*, vol. 2, Stars and Stellar Systems, Cambridge University Press, Cambridge.

Pashkevich, M.A.; Alekseenko, A.V. (2020). "Reutilization Prospects of Diamond Clay Tailings at the Lomonosov Mine, Northwestern Russia". Minerals. **10** (6): 517.

Podosek F. A. 2011, "Noble gases", in H. D. Holland & K. K. Turekian (eds), *Isotope Geochemistry: From the Treatise on Geochemistry*, Elsevier, Amsterdam, pp. 467–492,

*Pourret, Olivier (August 2018). "On the Necessity of Banning the Term "Heavy Metal" from the Scientific Literature" (PDF). Sustainability. **10** (8): 2879.*

Preuss P. 17 July 2011, "What keeps the Earth cooking?," Berkeley Lab,

Rankin W. J. 2011, *Minerals, Metals and Sustainability: Meeting Future Material Needs*, CSIRO Publishing, Collingwood, Victoria.

Rao CRM, Reddi GS. Platinum group metals (PGM); occurrence, use and recent trends in their determination. TrAC Trends in Analytical Chemistry. 2000;19(9):565-586

Saıdi, M.Y.; Barker, J.; Huang, H.; Swoyer, J.L.; Adamson, G. (1 June 2003), "Performance characteristics of lithium vanadium phosphate as a cathode material for lithium-ion batteries", *Journal of Power Sources*, 119–121: 266–272.

Sajidu SMI (2008). Characterisation and interaction of mixed alkaline clays and moringa seeds with heavy metals in contaminated water, Doctoral dissertation, University of Malawi, Zomba, MalawiKabre TS, Traore K, Blanchart P (1998). Mineralogy of clay raw material from Burkina Faso and Niger used for ceramic wares. Appl. Clay Sci., 12: 463-477

Sanders R. 2003, "Radioactive potassium may be major heat source in Earth's core,

Scarre, C. (2005). *The Human Past*. London:

Science Learning Hub. University of Waikato. Archived from the original on 3 January 2016. Retrieved 10 January 2016.

Sefström, N. G. (1831). "Ueber das Vanadin, ein neues Metall, gefunden im Stangeneisen von Eckersholm, einer Eisenhütte, die ihr Erz von Taberg in Småland bezieht". *Annalen der Physik und Chemie*. **97** (1): 43–49.

The Brownfields and Land Revitalization Technology Support Center. Archived from the original on 2008-02-18. Retrieved 2009-12-21.

Velde, B., 1995, Composition and mineralogy of clay minerals, in Velde, B., ed., Origin and mineralogy of clays: New York, Springer-Verlag, p. 8-42.

Verma N, Singh M. Biosensors for heavy metals. Biometals. 2005;18(2):121-129

Vol 19, Springer-Verlag Berlin Heidelberg 492 p.

White, W.A. (1949). "Atterberg plastic limits of clay minerals" (PDF). *American Mineralogist: Journal of Earth and Planetary Materials*. **34** (7–8): 508–512.

Wiberg N. 2001, *Inorganic Chemistry*, Academic Press, San Diego,

Wiberg N. 2001, *Inorganic Chemistry*, Academic Press, San Diego, p. 1277

Wise, James M. (May 2018). "Remarkable folded dacitic dikes at Mina Ragra, Peru"

Yousif N. 2007, *Geochemistry of stream sediment from the state of Colorado using NURE data*, ETD Collection for the University of Texas, El Paso.

APPENDIX

CALCULATION FOR THE ADSORBENT DOSAGE

Formular for Calculation of Amount Adsorbed $\left(\frac{Co-Cf}{m}\right)v$

For 0.2g = $\left(\frac{10-3.072}{0.2}\right) \times 0.05 =$ 1.732

For 0.4g = $\left(\frac{10-2.86}{0.4}\right) \times 0.05 = 0.892$

For 0.6g = $\left(\frac{10-2.893}{0.6}\right) \times 0.05 = 0.592$

For o.8g = $\left(\frac{10-2.067}{0.8}\right) \times 0.05 = 0.496$

For 1.0g = $\left(\frac{10-1.785}{1.0}\right) \times 0.05 = 0.4107$

CALCULATION FOR % ABSORPTION.

For the Calculation of % Adsorption = $\left(\frac{Co-Cf}{Co}\right) \times 100$

For 0.2g = $\left(\frac{10-3.072}{10}\right) \times 100 =$ 69.28

For 0.4g = $\left(\frac{10-2.86}{10}\right) \times 100 = 71.4$

For 0.6g = $\left(\frac{10-2.893}{10}\right) \times 100 = 71.07$

For o.8g = $\left(\frac{10-2.067}{10}\right) \times 100 = 79.33$

For 1.0g = $\left(\frac{10-1.785}{10}\right) \times 100 = 82.15$

CALCULATION FOR INITIAL CONCENTRATION

Calculation for amount absorbed = $\left(\frac{Co-Cf}{m}\right)v$

For 10g = $\left(\frac{10-1.844}{10}\right) \times 0.05 = 0.041$

For 20g = $\left(\frac{10-1.722}{20}\right) \times 0.05 = 0.020$

For 30g = $\left(\frac{10-1.499}{30}\right) \times 0.05 = 0.014$

For 40g = $\left(\frac{10-1.593}{40}\right) \times 0.05 = 0.010$

For 50g = $\left(\frac{10-1.309}{50}\right) \times 0.05 = 0.008$

CALCULATION FOR ABSORPTION PERCENTAGE

Formular for the Calculation of % Adsorption = $\left(\frac{Co-Cf}{Co}\right) \times 100$

For 10 minutes = $\left(\frac{10-1.844}{10}\right) \times 100 = 81.5$

For 20 minutes = $\left(\frac{10-1.722}{10}\right) \times 100 = 82.78$

For 30 minutes = $\left(\frac{10-1.499}{10}\right) \times 100 = 85.01$

For 40 minutes = $\left(\frac{10-1.593}{10}\right) \times 100 = 84.07$

For 50 minutes = $\left(\frac{10-1.309}{10}\right) \times 100 = 17.38$

CALCULATION FOR EFFECT OF pH

Calculation for amount absorbed = $\left(\frac{Co-Cf}{m}\right)v$

For pH 3 $= \left(\frac{10-2.943}{3}\right) \times 0.05 = 0.117.$

For pH 5 = $\left(\frac{10-2.335}{5}\right) \times 0.05 = 0.076$

For pH 7 == $\left(\frac{10-2.089}{7}\right) \times 0.05 = 0.056.$

FOR pH 8 = $\left(\frac{10-2.122}{8}\right) \times 0.05 = 0.049$

For pH 9 = $\left(\frac{10-2.061}{9}\right) \times 0.05 = 0.044$

For % Adsorption

Calculation of % Adsorption $= \left(\frac{Co-Cf}{Co}\right) \times 100$

For pH 3 $= \left(\frac{10-2.943}{10}\right) \times 100 = 70.50$

For pH 5 = $\left(\frac{10-2.335}{10}\right) \times 100 = 76.65$

For pH 7 == $\left(\frac{10-2.089}{10}\right) \times 100 = 79.11.$

FOR pH 8 = $\left(\frac{10-2.122}{10}\right) \times 100 = 78.78$

For pH 9 = $\left(\frac{10-2.061}{10}\right) \times 100 = 79.39$

EFFECT OF CONTACT TIME.

Calculation for amount absorbed = $\left(\frac{Co-Cf}{m}\right) v$

CALCULATION FOR EFFECT CONTACT TIME.

Calculation for amount absorbed = $\left(\frac{Co-Cf}{m}\right) v$

For 10mins = $\left(\frac{10-3.388}{10}\right)\times 0.05 = 0.030.$

For 20mins = $\left(\frac{10-2.393}{20}\right) \times 0.05 = 0.019.$

For 30mins = $\left(\frac{10-2.083}{30}\right) \times 0.05 = 0.0131.$

For 40mins = $\left(\frac{10-1.783}{40}\right) \times 0.05 = 0.0102.$

For 50mins = $\left(\frac{10-1.948}{50}\right) \times 0.05 = 0.008.$

For the Calculation of % Adsorption = $\left(\frac{Co-Cf}{Co}\right) \times 100.$

For 10mins = $\left(\frac{10-3.388}{10}\right)\times 100 = 66.12$

For 20mins = $\left(\frac{10-2.393}{10}\right) \times \ 100 = 76.07$

For 30mins = $\left(\frac{10-2.083}{10}\right) \times 100 = 79.17$

For 40mins = $\left(\frac{10-1.783}{10}\right) \times 100 = 82.17.$

For 50mins = $\left(\frac{10-1.948}{10}\right) \times 100 = 80.52.$

EFFECT OF TEMPERATURE ON ADSORPTION

For amount Adsorbed=$\left(\frac{Co-Cf}{m}\right) v$

For $20^{O}C = \left(\frac{10-2.133}{20}\right) \times 0.05 = 0.019$

For $30^{O}C = \left(\frac{10-2.044}{30}\right) \times 0.05 = 0.013$

For $40^{O}C = \left(\frac{10-1.893}{40}\right) \times 0.05 = 0.010$

For $50^{O}C = \left(\frac{10-1.920}{50}\right) \times 0.05 = 0.008.$

For $80^{O}C = \left(\frac{10-1.911}{80}\right) \times 0.05 = 0.005$

FOR % ADSORPTION

For $20^{O}C = \left(\frac{10-2.133}{20}\right) \times 0.05 = 0.019$

For $30^{O}C = \left(\frac{10-2.044}{30}\right) \times 0.05 = 0.013$

For $40^{O}C = \left(\frac{10-1.893}{40}\right) \times 0.05 = 0.010$

For $50^{O}C = \left(\frac{10-1.920}{50}\right) \times 0.05 = 0.008.$

For $80^{O}C = \left(\frac{10-1.911}{80}\right) \times 0.05 = 0.005$

TABLE 3.6 TABLE OF LANGMUIR

C_e	q_e	C_e/ q_e
1.844	**0.4078**	**4.522**
1.722	**0.4139**	**4.160**
1.499	**0.42505**	**3.526**
1.593	**0.42035**	**3.789**

1.309	**0.43455**	**3.012**

CALCULATION FOR LANGMUIR FORMULAR

Qe=$\left(\frac{Ce-Qe}{m}\right)v$

For 10g =$Q_e\left(\frac{10-1.844}{1}\right) \times 0.05 = 0.408.$

For 20g =$\left(\frac{10-1.722}{1}\right) \times 0.05$=0.414.

For 30g =$\left(\frac{10-1.499}{1}\right) \times 0.05 = 0.425$

For 40g =$\left(\frac{10-1.593}{1}\right) \times$0.05= 0.420

Ln Ce	**Ln q_e**
0.611937	-0.89698
0.543486	-0.88213
0.404798	-0.85555
0.465619	-0.86667
0.269263	-0.83344

CALCULATION FOR FREUNDLICH

FOR C_e

Ln 1.844= 0.612

Ln1.722 = 0.543

Ln1.499 = 0.405

Ln 1.593 = 0.465

Ln 1.309 = 0.269

For q_e

Ln 0.408 = -0.896

Ln 0.441= -0.881

Ln 0.425 = -0.855

Ln 0.420 = -0.867

Ln 0.434 = -0.835

For Langmuir

$$\frac{ce}{qe} = \frac{1}{qm} C_e + \frac{1}{Kl\ qm}$$

$$M = \frac{1}{qm}$$

$$2.826 = \frac{1}{qm}$$

$$q_m = \frac{1}{2.820} = 0.354$$

(2) $\frac{1}{Kl\,qm} = C$

$\frac{1}{Klqm}$ = 0.692

$\frac{1}{Kl \times 0.354}$ =0.692

$\frac{1}{0.692 \times 0.354}$=Kl

Kl = -4.074

For freundlich

$(Lnk_{f)} = (Lnk_f) + (\frac{1}{n})(LnC_e)$

$Lnk_{f=C}$

$_{Ln}k_f$ = -0.782

k_f = EXP(-0.782)

k_f = 0.457

2) $\frac{1}{n} = m$

$\frac{1}{n} = -\ 0.184$

$n = \frac{1}{-0.184} = -\ 5.41$