ADDIS ABABA UNIVERSITY
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Synthesis and characterization of Iron nano particle using Eucalyptus (*Eucalyptus globulus*) for the removal of lead from aqueous solution

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A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in process Engineering.

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As members of Examining Board of the Final M.Sc. thesis open defense, we certify that we have read and evaluated the thesis prepared by Yemane G/medihn, entitled "Synthesis and characterization of Iron nano particle using Eucalyptus (*Eucalyptus globulus*) for the removal of lead ion from aqueous solution" and recommended that it can be accepted as fulfilling the thesis requirements for the Degree of Master of Science in Chemical Engineering (process Engineering).

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Declaration

I, the undersigned, declare that this thesis entitled "*Synthesis and characterization of Iron nano particle using Eucalyptus (Eucalyptus globulus) for the removal of lead (Pb^{2+}) from aqueous solution"* is my original work, and has not been presented by any other person for an award of a degree in this or any other University, and that all resources of materials used for this thesis have been duly acknowledged.

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Date of submission October 29, 2018

This thesis has been submitted to the University with my approval as the University Advisor.

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Dedication

This Research Paper is dedicated to my Mom

Acknowledgement

First and foremost, I would like to thank the Almighty God for His benevolence. His will has made the completion of this research achievable. Next to God, I would like to express my thanks and gratitude to my advisor, Dr. Anuradha Jabasingh. Her guidance, insightful feedback, experience and inspiration have been invaluable throughout my research. I am grateful to my mom, my elder brother and my sister in law for their patient support, understanding and their prayer. I am most grateful to my wife for giving me endless support, encouragement and being my close companion in yet another journey we made together. At last but not least to my fellow AAIT students, I am thankful for your support, friendship, and good humor. Your company made the challenges of graduate school less difficult. Your mentorship made me open to life and a better friend.

Abstract

The application of greenly synthesized ironl nano particle for the removal of lead from aqueous solution is what was studied in this thesis research. The FT-IR and X-RD results reveal that a greenly synthesized iron-polyphenol nano particle complex (GInP) with 80nm size was synthesized using eucalyptus leaf extract the specific surface area was found to be 59m^2/g. The deployment of GInP in the removal of lead was studied after this diminutive GInP had been procreated by reduction of ferric iron in presence of Eucalyptus globulus leaf extract. The lead removal capability of GInP was investigated for lead concentration ranging from 50ppm-250ppm. Batch experiments were performed to investigate the influence of lead concentration, contact time, dosage of GInP and pH on the removal process. A maximum lead removal percentage of 96.75 was observed at pH 4 for 100 ppm lead concentration in 45min using 0.8g dosage. Minitab response optimize technic was used to optimize the amount of lead concentration which has shown there was around 86% removal probability at 150 ppm lead concentration. The adsorption kinetics data were well fitted by the pseudo-first-order rate model with high regression coefficient (0.975). The intra particle diffusion of pb (II) on GInP represents the rate-limiting step. The lead removal process was found to be well fitted into the Langimure isotherm model with determination coefficient of 0.965. Desorption was observed to increase with time. The adsorption capacity was decreased with the increase of temperature, and thermodynamic calculations suggested that the adsorption of lead (II) ions onto GInP is an endothermic process. It has been found that GInPs show high selectivity's and adsorption capacities to removal of Pb^{2+} from aqueous solution.

Key terms: Iron nano particle, adsorption, heavy metal, percentage removal, leaf extract.

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Acronyms and Symbols

ANOVA	Analysis of variance
CCD	Central Composite Design
C_o	Initial metal concentration
C_e	Concentration of the sorbate at equilibrium
EPA	Environmental protection agency
ESID	Ethiopian sustainable industrial development
FT-IR	Fourier transforms infrared red
GInP	Greenly synthesized iron nano particle
IQ	Intelligent quotient
K_f	Freundlich adsorption capacity
K_L	Langmuir equilibrium constant
K_f	Pseudo first order rate constant
K_s	Pseudo second order rate constant
nZVI	Iron nano zero valent
pH_{pzc}	Point of zero charge
UNIDO	United Nation Industrial Development Organization
USEPA	United States Environmental Protection Agency
Uv vis	Ultra-Violate Visible
X-RD	X-Ray Diffraction

CHAPTER ONE

1. Introduction

The presence of heavy metal ions in the environment, especially in water sources, is major concern due to their non-biodegradability, toxicity, wide-spread presence, and tendency to accumulate in living organisms (Xu et al, 2008). In the light of these observations, it is not surprising that the issue of heavy metal contamination has taken on a sense of significance in environmental pollution control, and that it has been given the status of high priority on the list of problems requiring immediate solution. Lead, a main concern metal pollutant, is widely used in battery manufacturing, electroplating industry, painting and printing processes, plumbing and the combustion of automobile petrol (Z.hang et al, 2010).

Presence of lead, in the environment has been a serious problem, especially with rapid industrialization, which has created new uses for lead. The toxicity of lead to aquatic Life and humans and the stringent effluent standard to be - met by industries as specified by regulatory organizations has necessitated the development of innovative, effective and economical methods for treating lead-bearing wastewater. The U.S. Environmental Protection Agency (U.S.EPA) has set a permissible limit of 0 .01 5 mg /L in drinking water and has placed it on top of the priority list of toxic pollutants.Lead pollution can cause nervous system damage, renal kidney disease, mental retardation, cancer, and anemia in humans (Z.hang et al, 2010). Despite existence of huge number of potential sources of lead, most the drinking water of Ethiopia has never been studied for its content of lead. However an important study carried out on the rural and urban children incisors exfoliated in 1998-2000 showed higher concentrations of lead in the teeth of children (Tamene, & Duressa, 2008).

The deployment of diminutive particles for ecological remediation has received substantial monetary funding as well as courtesy of service providers and researchers of nanotechnology (Karn et al, 2009). This fact paved a way for an exponential release of scientific publications, patents and research projects that supplied knowledge about the development of new materials and new applications involving nanomaterials. One of these applications, nano remediation, is based on the use of reactive nanomaterial to degrade/transform/destroy contaminants located in distinct environmental compartments (namely soils and waters). Their extremely small size results in a high surface area to mass ratio, making them much more reactive compared to their more-coarse predecessors (Andrew, 2012).

Among the most common nanomaterials, iron nanoparticles are one of the most widely used and have proven to be extremely effective for the removal of a wide range of pollutants such as heavy metals (Machado et al, 2015). Two different approaches can be used to produce nano-sized iron particles these are, top-down and bottom-up methods. The former consists of the reduction of the iron particle size through mechanical and/or chemical processes, and includes milling, etching, and/or machining; while the latter promotes the growth of the particles through chemical reactions, positional and self-assembling. The top down method generally involves specific equipment and is associated with high energy costs (Li et al, 2006).

In the bottom up method materials are built up from the bottom like atom by atom, molecule by molecule, cluster by cluster sequence. The synthesis of iron nano particle by the recently developed green bottom-up method is extremely promising. However, the lack of information about the characteristics of the synthetized particles hinders a wider and more extensive application. Bottom up approach offers a better chance to get nanostructures with comparatively less defects, more homogenous chemical composition and better range of ordering as it is driven mainly by Gibb’s free energy. So the nanostructures produced by bottom up method are in a state of close to thermodynamic equilibrium (Gangadhar et al, 2012).

There are two distinct paths to be followed in the bottom-up approach: traditional and green production methods. The traditional method involves the reaction between iron (III) or iron (II) solutions with sodium borohydride. Although at first this seems like a very simple and fast procedure without the requirement of specific equipment, there are safety and health concerns associated with this method The use of a toxic compound such as sodium borohydride requires specific actions during the production process to protect operators, and the removal of the remaining toxic compound at the end of the synthesis. Besides this, in the traditional method, hydrogen is produced which also requires safety measures to reduce/eliminate the combustion/explosion risks (Li et al, 2006).

The toxicity and explosion risks are giving new opportunities to develop more cost-effective and environmentally acceptable environmental remediation technology. The property of having higher specific surface area leading to a higher capacity makes the nanoparticles one of the best adsorbents for the effective removal of heavy metals from waste water. They also exhibit various advantages such as fast kinetics, and preferable sorption toward heavy metals in effluent streams (Mahesh & Gupta, 2012). Research is needed using nanoscale science and technology to identify opportunities and applications to environmental problems, and to evaluate the potential environmental impacts of nanotechnology. Also, approaches are needed to offer new capabilities for preventing or treating highly toxic or persistent pollutants, which would result in the more effective monitoring of pollutants or their impact in the ways not currently possible. The greener capping agent method uses aqueous extracts with high reduction capacities which are obtained from natural products, such as tree leaves. In addition to serving as reducing agent, the polyphenolic matrix of these extracts can act as that protects the iron nanoparticles from premature oxidation (Machado et al, 2013).

The major advantage of green synthesisi methods over other methods are simple, less expensive, openly applicable without any binders, no need for toxic chemicals, no toxic byproducts and most it is environment friendly. In the biological approach, the synthesis of nanoparticles has been evolved from various sources that were available, enormously in the earth such as microorganisms and terrestrial plants. (Subha et al, 2015). This research study is aimed at the applicability and efficacy of greenly synthesized nano sized iron particles for the removal of lead from the aqueous system through adsorption process.

1.1. Statement of Problem

Among many problems that triggered the commencement of this thesis research was the toxicity of the reducing agents, which had been used for the chemical synthesis of iron nanoparticle and the health hazard of lead contaminated waste and drinking water. The type of reducing agents, sodium borohydride ($NaBH_4$) and Sodium dithionite ($Na_2S_2O_4$) used during the synthesis process are expensive and dangerous and cannot be easily separated from the nanoparticle and the by-product of the experimental procedures leads to undesired detrimental impacts on the environment, plant and animal.

Several methods have been employed for the chemical synthesis of iron nanoparticles but in addition to the toxicity of the reducing agent, it was recognized that the resulting nanoparticle tend to rapidly agglomerate due to the van der waals and magnetic forces. This problem can easily be handled by the utilization of plant leaf extract such as from Eucalyptus leaf as a reducing and stabilizing agent (Wang et al, 2014). Heavy metals can not be chemically or biologicaly degraded (Utomo et al 2016). Lead contamination of drinking water is a major global problem. Acute lead poisoning in children can cause anorexia, vomiting, malaise, convulsions and even, permanent brain damage (Khayat, 2013).

Despite the existence of huge number of potential sources of lead, most the drinking water of Ethiopia has never been studied for its content of lead. However, a study of lead assessment in Addis Ababa city showed higher concentrations of lead in the incisors of the children of the city (Tamene & Duressa, 2008).

1.2. Objective

❖ General objective

The general objective of this study is synthesis and characterization of iron nanoparticle using Eucalyptus (*Eucalyptus globulus*) leaf extracts for the removal of lead from aqueous solution.

❖ Specific objectives

- ✓ To prepare green synthesized iron nanoparticles (GInP) using Eucalyptus leaf extract as a reducing agent
- ✓ To characterize the (GInP) using X-Ray Diffraction (XRD) and Fourier Transform Infra-Red spectroscopy (FT-IR)
- ✓ To study the applicability of GInP for lead (Pb) removal from aqueous solution by adsorption mechanism
- ✓ To investigate the effect of parameters (time, pH, dosage, and Pb concentration) on the adsorption efficiency and adsorption capacity during the adsorption studies and to determine the optimum condition for the adsorption
- ✓ To investigate the adsorption kinetics, thermodynamics and isotherms.

1.3. Significance of the Study

In the environmental remediation process such as separating heavy metals from aqueous solution iron nano particles are more preferable because they are able to react longer, disperse better and reach locations farther than bigger particles. However, in real situations, since they have agglomeration tendency, the nanomaterials have a limited radius of influence, this thesis work has tried to expand their limited radius of influence to explore their enormous environmental remediation potential. Besides to avoid the toxicity of the reducing agent used in the chemical synthesis of iron nanoparticle, cost effective and eco-friendly synthesis method is the way forward in the 21st century. To this effect in this study, an attempt was made to deal with the investigation on the Eucalyptus globulus leaf extract as environmentally benign reducing agent for the green synthesis of iron nanoparticle. This nanoparticle was used for the removal of lead from aqueous solution. In addition, the effect of various parameters on the adsorption process were investigated.

The interesting features of this method are the methodology adopted for nanoparticle synthesis is quite simple, efficient and can be carried out in room temperature.The synthesized particles are biodegradable and non-toxic. This provides resourcefulness towards the application of Eucalyptus leaf. And this synthesis leads to an application which is the need of the hour, namely as removal of lead ions from aqueous solution.

CHAPTER TWO

2. Literature Review

We all depend on earth’s ecological and atmospheric balance for survival. But the increasing industrialization and urbanization has affected this balance by the introduction of pollutants. These hazardous pollutants consist of a variety of organic compounds and heavy metals, which pose serious risks to human health. Heavy metals are primarily a concern because they cannot be destroyed by degradation. The most common heavy metals at hazardous waste sites are cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), Nickel (Ni) and Zinc (Zn). Of these, lead and mercury are two of the most significant contaminants, posing serious and sometimes life threatening health hazard (Suhag et al, 2011). They can also be defined as the elements in the d-block in the periodic table such as cadmium (Cd), Lead (Pb), copper (Cu), and mercury (Hg). Heavy metals are elements of high density, and they are toxic at even low concentrations. .

2.1. Sources of lead containing wastewater

Lead is a naturally occurring element chiefly buried in the earth crus in in sold and biologically inoffensive forms. It is simply found as lead supplied (galena, PbS) and in Canada it is found as complex ores composed mainly of lead and zinc sulphides, with small inclusions of silver or silver sulphide materials. Enhanced industrialization and discovery of various uses for lead however have caused humans to disinter it, which has caused the release of large quantities of the by-product of little material into air, soils and surface waters. It is used as an industrial raw material in manufacturing of storage batteries, television tube, printing, paints, pigments, photography materials, fuels, matches and explosives. The manufacturing process of these materials produces lead-bearing wastewaters, which have to be treated and disposed of one of the largest consumers of lead is the storage battery industry fpollowed by the petroleum industry in producing gasoline additives. Lead concentrations in wastewater from battery manufacturing, acid mine drainage, tailing pond and steel production plants range from 0.5 to 25 mg/L (Patterson, 1985).

2.2. Lead Health Effects

Lead contamination of drinking water is a major global problem. Acute lead poisoning in children can cause anorexia, vomiting, malaise, convulsions and even, permanent brain damage. Chronic lead poisoning can cause weight loss, weakness and anaemia. Lead, symbolized Pb is located in group N of the periodic table, it has an atomic weight and Nurnberg of 207.19 g and 82, respectively. It has a melting point of 327°C and a density of 11.4g/m^3 (11.4t/m^3) and a remarkably high corrosion resistance to most acids, including sulphuric (H_2SO_4) and hydrochloric (HCI) acids with the exception of nitric acid (HNO_3).

Lead and lead compounds are generally toxic pollutants which has bioaccumulation property in tissues of human body (Khayat, 2013). Menstrual disorder, infertility and spontaneous abortion are caused by lead. Lead increases stillbirth risk. Mothers are less sensitive to lead poisoning than fetuses and are in general protected from lead poisoning by fetuses. A larger amount of lead per unit body weight (up to 40%) may be absorbed by children compared with adults. Therefore, children are generally more sensitive to lead poisoning than adults. behavioral changes and concentration disorder are the symptoms of lead poisoning. Leg tissue is where lead accumulates. Encephalopathy is a result of the most severe type of lead poisoning (Moezzi et al, 2017). Lead (II) salts are the most harmful from an eco-toxicological point of view Lead salts such as lead acetate, oxide, nitrate, and carbonate are associated with water hazard class 2 and are thus harmful.

Table 1: Standard guide line for metal limit in drinking (Raveendran, 2003)

Parameters	Guideline (µg/L)	Hardness in mg/L (as $CaCO_3$)
Lead	1	0-60
	2	60-120
	4	120-180
	7	>180
Cadmium	0.2	0-60
	0.8	60-120
	1.3	120-180
	1.8	>180
Nickel	25	0-60
	65	60-120
	110	120-180
	150	>180

Source: - Canadian Council of Resource and Environment Ministers, 1987

Chlorophyll synthesis inplants is decreased by lead (Gurpreet, 2012). However, up to 500 ppm of lead can be taken up by plants from the soil. Plant growth is adversely affected by high lead quantities. Lead enters food chains via plant uptake. As a result, the application of lead pesticide is banned in most countries. Lead is collected in organisms, sediments and sludge. Lead present in wastewater mostly originates from streets and roofs. The presence of lead in water may be due to the application of lead and PVC pipes in addition to spill of sewages from such industries as battery making, metal plating, electrical equipment, chemicals, steel, iron and copper (Hakim & Elwaer, 2006).

One of the popular methods to eliminate heavy metals is the use of reductants(Shi et al, 2009). Chemical oxidation is a fast, highly effective process which uses reductions to remove lead from water (Niu et al, 2005). Among available reductions, iron has priority due to it's abundance, low cost, non-toxicity, rapid reaction potential and high efficiency in decomposition of contaminants. Particle size and surface-to-volume ratio are of the great importance in reduction and elimination of pollutants by the particles (Dickinson, 2010). The major sources of lead in aquatic ecosystem including the ocean are domestic wastewater effluent, coal burning power plants, non-ferrous metal smelters, iron and steel plants and dumping of sewage sludge (Nriagu et al, 1973) demonstrated that urban runoff and disposa1 of treated wastewaters had an adverse effect on a river ecosystem. (Aubert, 1975) determined that the toxic threshold of $Pb(NO_3)_2$ in sea water for the aquatic worm (*Nereis diversico Zour)* was 8.3 ppm for eight days.

Lead has a significant role in many industries because it is ductile and easily shaped. It has been used in many sectors and products: batteries, petrol additives, chemical compounds, pigments, and cables. Accordingly, lead can find a pathway to human beings through drinking water, food, air, soil and dust. Overdoses of lead and long term exposure can tend to severe impacts especially on infants. High concentrations of lead may cause problems in the synthesis of haemoglobin, effects on the kidney, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system. According to the Environmental Protection Agency (EPA) the long-term exposure of lead can be severe and tends to decreased growth, hyperactivity, impaired hearing, and brain damage.

Recent studies have stated that lead may have an impact on mental and psychological developments in children; for instance children may lose up to 2 Intelligence Quotient (IQ) points if the blood lead level rises from 10 to 20 μg/L. Lead mainly can be found in foods from the deposition of dust and rain containing lead on crops and soil. It can also accumulate in the human body from point source emissions. For example, lead can exist in drinking water from old lead piping and from illegal discharging of industrial waste water of high concentrations into surface fresh water Heavy metals can reach surface water either through industrial and consumer wastewater discharged into water bodies or from acidic rain leached to the soils and releasing heavy metals into groundwater and surface water. Heavy metals are natural components of the Earth’s crust. Some heavy metals are vital to maintain the metabolism in our bodies at certain concentrations such as zinc. However, the excess of these heavy metals can lead to poisoning via drinking water contamination, high ambient air concentrations, or eating contaminated food. It’s well known also that the specific gravity of heavy metal elements is more than five times the specific gravity of water where the specific gravity of water is 1 at temperature 4°C. For instance, the specific gravity of some toxic heavy metals is: lead, 11.34; cadmium, 8.65; copper, 8.93; and mercury, 13.546 the potential use of plants to remediate contaminated soil and groundwater has recently received a great deal of interest. Up to this point the most widely used wastewater treatments such as trickling filters have been mechanical. Such plants have proven to be too complex, costly, and energy-intensive.

Wastewater treatment systems which are simple and require little or no maintenance must be developed to fulfill these needs. It is becoming evident that aquatic plants have great potential for wastewater treatment and reclamation. These plants can absorb nitrate, phosphate, heavy metals such as manganese, and other chemical compounds. They are generally used to provide secondary treatment of effluents, in small lagoons filled with cattails.There are now more than fifteen aquatic plant wastewater Water is referred to as polluted when it is either impaired by anthropogenic or natural contaminants making it unsuitable for human consumption, such as drinking or has lost its ability to support life as an aquatic biota (Dipak and Arti, 2011).

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from Industrial are a large amount of suspended organic solid Water pollution has been recognized as a problem for decades. The use of heavy metals in industries and their regular mining increases their concentration in water bodies. Unlike organic compounds, metals cannot degrade, and therefore effective cleanup requires their immobilization to reduce or remove toxicity.

2.3. Impact of lead on aquatic ecosystems

The unique physical properties of lead, including low melting point, corrosion resistance, malleability and high density have led to its use in a wide variety of industries and trade and consequently increased the potential of lead exposure in many occupations. Some of the occupations at the risk of lead exposure include battery makers, paint manufacturers, painters, lead miners and smelters, diamond polishers, electroplaters, musical instrument makers, pipe filters, match makers and welders among others Existence of lead in natural waters is greatly dependent on the atmosphere and earth surface that they are in direct contact. The major sources of lead in aquatic ecosystem including the ocean are domestic wastewater effluent, coal burning power plants, non-ferrous metal smelters, iron and steel plants and dumping of sewage sludge demonstrated that urban runoff and disposa1 of treated wastewaters had an adverse effect on a river ecosystem. They found acid extractable lead in river sediments in urban and rural drainage areas varied from 10 to 388 ppm respectively and that fishes were generally absent from urban drainage waters. Oyster, *Crczssortrea virginica*, could accumulate lead in concentrations of several hundreds to several thousand times greater than concentrations in seawater.

Lead accumulating ability of shell fish thus made them very useful as a means of monitoring lead pollution found that absorption and accumulation of lead by shell fish produced lethal and chronic effects even at 0.5 ppm in aqueous solution. Other smaller aquatic organisms also have ability to accumulate lead from their food as well as from their surrounding medium and these may attain lethal concentrations. The toxic threshold of $Pb(NO_3)_2$ in sea water for the aquatic worm (*Nereis diversico Zour)* was 8.3 ppm for eight days. It's been found that 50% mortality was reached in a group of 50 *Ophyotrocha Zabronica* maintained in sea water containing 1 ppm lead in about 600 hours.

There a linear relationship between lead concentration in sea water and the exposure time required for 50% mortality in groups of 50 brine shrirnp (Arteniasalina). fish taken from a marsh receiving dredge soi1 from a polluted industrialized harbour contained significantly higher levels of lead (4.5 ppm) than fish from a control marsh (0.2 -0.6 ppm). The acute lead toxicity resulted in production of copious amounts of fish epidermal mucus interferes with the gills and caused death by asphyxia. Under conditions of low pH and low water hardness, insoluble lead compounds can release $pb^{2+}$to levels toxic to fish.

2.4. Treatment methods for heavy metal-bearing wastewater

There exists numerous techniques for the removal of heavy metals from wastewater and these include chemical precipitation, ion exchange, adsorption, electrolytic recovery, electro dialysis, solvent extraction, reverse osmosis, membrane separation, ultrafiltration, ozonation, foam floatation, vapor recovery, gamma irradiation, freeze crystallization, and photochemical methods.(Patterson, 1985). Although some of these treatment methods can be successfully used for treating most wastewaters, others are quite limited in use. The application of chemical precipitation to dilute solutions (low concentration) an be difficult unless the addition of flocculating agents such as lime, caustic and sodium carbonate is employed However a bulky sludge is produced, and the disposal constitutes a problem (Thackston et al, 1980). Ion exchange and activated carbon adsorption are quite expensive and require recharge of resin or spent activated carbon as well as the disposal of substantial volume of used regeneration solution.

In addition to the fact that membrane technology is expensive, membranes are susceptible to attack by microorganisms, likewise other methods mentioned require elaborate and considerably hi& operation costs In general, factors to be considered in the choice of a method to be adopted for the treatment of heavy metal-bearing wastewater should include: high rate of removal, economic feasibility in terms of labor, materials, equipment and energy, applicability to small, intermediate and large scales, low productivity of highly enriched spent materials and capability of reducing heavy metal ion concentration to levels below established regulatory standards. Adsorption process is an effective process and adoption of economic and easily available adsorbents such as iron nanoparticle will make the process a considerably promising option by meeting the criteria stated above.(Peat, 2000).

2.5. Conventional heavy metals removal.

Several technologies have been used to treat metal containing aqueous solution for the last few decades(Wang and Chen, 2009). Commonly used methods for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. However, these methods proved either inefficient or expensive in case of low concentration (1-100 mg/l) of heavy metals prevailing in the environment and generate huge amount of sludge which are difficult to dispose.

2.5.1. Electro dialysis

In this process, the ionic components (heavy metals) are separated through the use of semipermeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane.

2.5.2. Reverse Osmosis

It is a process in which heavy metals are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is expensive.

2.5.3. Ultra-filtration

They are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge.

2.5.4. Ion-exchange

In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages include: high cost and partial removal of certain ions.

2.5.5. Chemical Precipitation

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage. the demerits in the above-mentioned techniques like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has led to look for cost-effective treatment method that is capable of removing heavy metals from aqueous effluents.

The contamination of water recourses by heavy metal is a serious worldwide environmental problem. Numerous metals such as cadmium, chromium, lead, etc. are known to be significantly toxic. Lead is well known for its extremely high toxicity. A very low concentration of lead in water may cause health hazard. Facts have motivated many physicochemical methods for heavy metal removal from aqueous solution, including chemical precipitation, membrane separation, electrochemical reduction, ion exchange, and adsorption. Among these methods, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness.

2.6. Adsorption of Heavy Metals

Adsorption was discovered from the 1700’s by C.W. Scheele for gases, while Lowitz in the late 1700’s discovered adsorption for other media (Kraemer, 1930). Now adsorption is a significant phenomenon in many applications. Adsorption on solids is commonly used for purification in water and wastewater, most often by using activated carbon. However, many other adsorbents are being used effectively such as silica gel, treated acid clay, agricultural wastes and metal oxides. For example, Smith (1998) used recycled iron to remove metals from aqueous solutions. The triple layer surface complexation model was used to characterize the equilibrium of lead, cadmium, and zinc adsorption by using a recycled iron-bearing material. The experiments were conducted using fixed bed and batch reactor systems. The uptake capacity of the recycled iron adsorbent was favourable relative to some commercial adsorbents.

Adsorption is one of the major unit operation used for removal of various pollutants from wastewater. The basic feature of a good adsorbent is a large specific surface area. The bigger the surface area, the more molecules are trapped on its surface. Generally, this means that a good adsorbent is very porous. The specific area of an adsorbent is the surface area available for adsorption per gram of the adsorbent. It offers flexibility in terms of selection of contacting devices and adsorbent material depending on the time, space and funds available for treatment of the wastewater. “Adsorption” may be defined as the process of accumulation of any substance giving higher concentration of molecular species on the surface of another substance as compared to that in the bulk. When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentrate at the surface. The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption. “Adsorption” is a well-established and powerful technique for treating domestic and industrial effluents.

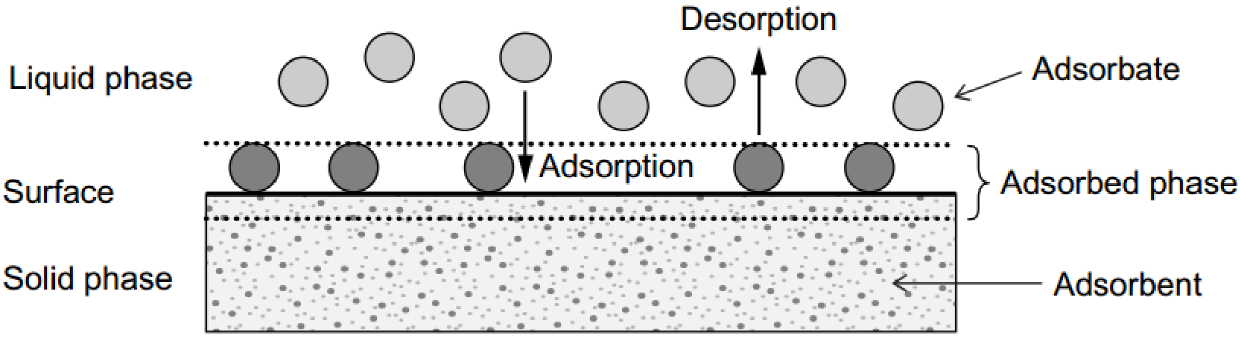

Figure 1: Schematic representation of adsorption

2.7. Types of Adsorption

Depending on the type of attractions between adsorbate and adsorbent, the adsorption can be divided into two types. Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Vander Waal forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types: Physical Adsorption or Chemical Adsorption.

2.7.1. Physical Adsorption

When the force of attraction existing between adsorbate and adsorbent are weak Vander Waal forces of attraction, the process is called Physical Adsorption. Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e. $\triangle H$ is 20-40KJ/mol (Habish, 2017). takes place at low temperature below boiling point of adsorbate. As the temperature increases the process of Physisorption decreases.

2.7.2. Characteristics of Physisorption Energetics and kinetics

Physisorption is an exothermic process however it is characterized by low enthalpy values (20–40 kJ mol-1), due to weak van der Waals forces of attraction. The activation energy for physisorption is also very low and hence it is practically a reversible process.

- ✓ **Effect of temperature:** Since physical adsorption is an exothermic process, it occurs more readily at lower temperatures and decreases with increase in temperature.
- ✓ **Effect of pressure:** In case of physisorption of gases over solids, the extent of adsorption increases with increase in pressure as the volume of the gases decrease during adsorption.

- ✓ **Specificity:** Since the van der Waals' forces are universal, a given surface of an adsorbent does not show any preference for an adsorbate in physisorption i.e. it is not specific with respect to adsorbent.

2.7.3. Chemical Adsorption or Chemisorption

When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemical Adsorption or Chemisorption. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption. With an increment of temperature, chemisorption first increases and then decreases.

2.7.4. Characteristics of Chemisorption

- **Energetics and kinetics**

Chemisorption is also an exothermic process and the enthalpy values are higher (80-240 kJ mol^{-1}) (Habish, 2017). As it involves formation of chemical bonds. However, the activation energy for chemisorption is high and occurs slowly. Hence it is also called activated adsorption. It is practically irreversible.

- **Effect of temperature**

Even though chemical adsorption is an exothermic process, it does not occur slowly at lower temperature due to high kinetic energy barrier. Hence, like most chemical changes, the extent of chemisorption increases with increase in temperature up to certain limit and then after that it starts decreasing. It is also observed that, in some cases, physisorption of a gas adsorbed at low temperature may change into chemisorption at high temperatures.

- **Effect of pressure**

The chemisorption is not appreciably affected by small changes in pressure. However, very high pressures are favourable for chemisorption.

- **High specificity**

Chemisorption is highly specific and occurs only if there is some possibility of chemical bonding between adsorbent and adsorbate.

- **Surface area**

Like physisorption, chemisorption also increases with increase of surface area of the adsorbent. In general Adsorption is one of the major unit operation used for removal of various pollutants from wastewater. It offers flexibility in terms of selection of contacting devices and adsorbent material depending on the time, space and funds available for treatment of the wastewater. Although this fact is widely recognized, pollution of water resources is a common occurrence. In particular, Potable water has become greatly affected, and in many instances has lost its original purpose.

There are many sources of water pollution, but two main general categories exist: direct and indirect contaminant sources. Direct sources include effluent outfalls from industries, refineries contaminants that enter to water supply from soils/ground water systems and from the atmosphere via rain water. Some organic water pollutants include industrial solvents, volatile organic compounds, insecticides, pesticides and food processing wastes, etc. Inorganic water pollutants include metals, fertilizers and acidity caused by industrial discharges, etc.

A major group of contaminants of concern are metals. Metals are extensively used in several industries, including mining, metallurgical, electronic, electroplating and metal finishing. The presence of metal ions in final industrial effluents is extremely undesirable, as they are toxic to both lower and higher organisms. Under certain environmental conditions, metals may accumulate to toxic levels and cause ecological damage. Of the important metals, mercury, lead, cadmium and chromium (VI) are regarded as toxic; whereas, others, such as copper, nickel, cobalt and zinc are not as toxic, but their extensive usage and increasing levels in the environment are of serious concerns radionuclides, such as uranium, possess high toxicity and radioactivity, and exhibit a serious threat, even at small concentrations.

Solid surfaces are characterized by active, energy-rich sites that are able to interact with solutes in the adjacent aqueous phase due to their specific electronic and spatial properties. Typically, the active sites have different energies, or – in other words – the surface is energetically heterogeneous. The solid material that provides the surface for adsorption is referred to as adsorbent; the species that will be adsorbed are named adsorbate. By changing the properties of the liquid phase (e.g. concentration, temperature, pH) adsorbed species can be released from the surface and transferred back into the liquid phase. This reverse process is referred to as desorption (Eckhard, 2012).

In recent years, the development of nanoscience and nanotechnology has shown remarkable potential for the remediation of environmental problems. Compared with traditional materials, nanostructure adsorbents have exhibited much higher efficiency and faster rates in water treatment. In the last decades nanotechnology has become increasingly important because it offers indisputable advantages to almost every area of expertise, including environmental remediation. The particles or matters falls within 1 - 100 nm or collection of atoms is nanoparticles or nanomaterials. A nanometre is said to be one billionth of a meter and approximately ten atoms fit inside one nanometre. Due to size reduction the matter or particles show unusual physical, chemical, electronic, optical and magnetic properties. Nanostructured materials have unique nanostructures and properties. It is used in cosmetics, medicine, food products, paints, fuel, catalyst, personal computers.Nanoparticles include zero-valent metals can generally be used to remove heavy metal ions from aqueous solution. (Sundarajan et al, 2013). The presence of heavy metal ions in the environment , especially in water resources , was becoming a major concern due to their non-biodegradability toxicity, wide-spread presence, and tendency to accumulate in living organisms (Xun et al, 2008).

Industrial effluents are one of the principal sources of heavy metals responsible for environmental pollution. Subsequently, contamination of soils, ground water, surface water and sediments with heavy metals is one of the major environmental problems. Textile industries are major sources of these effluents due to the nature of their operations which is chemical and water intensive – eventually resulting in high wastewater generation. In developing countries, untreated or partially-treated industrial wastewaters are directly discharged to the nearby wetland and /or water bodies (Ghoreishi, 2003) Ethiopian Environmental Protection Authority indicated that, most factories in Ethiopia, including textile and leather industries, have no effluent treatment plants (Tamene et al, 2003).

Lead, a main concern metal pollutant, is widely used in battery manufacturing , electroplating industry, painting and printing processes , plumbing and the combustion of automobile petrol (Lu et al 2010). The U.S. Environmental Protection Agency (U.S.EPA) has set a permissible limit of 0 .01 5 mg /L in drinking water and has placed it on top of the priority list of toxic pollutants (U.S.EPA, 2014). Lead pollution can cause nervous system damage, renal kidney disease, mental retardation, cancer, and anemia in humans (Zhang et al, 2010). Chemical reduction, ion exchange, chemical precipitation, mineral adsorption, membrane separation, and bio-sorption are the most frequently used treatment technologies for Pb^{2+} removal which are ex-situ techniques (Machida et al, 2006). Most of these methods are only suitable for the removal of Pb^{2+} in low concentrations and often require extensive processing as well as being too expensive.

Advancements in nanoscience and engineering are giving new opportunities to develop more cost-effective and environmentally acceptable water treatment technology. The property of having higher specific surface area leading to a higher capacity makes the nanoparticles one of the best adsorbents for the effective removal of heavy metals from waste water. They also exhibit various advantages such as fast kinetics, and preferable sorption toward heavy metals in effluent streams. Nanoparticles are reported to be successful in removing various heavy metal ions such as Pb(II), Ni(II), Zn(II),Cu(II), Co(II),Cd(II) from industrial wastewater. Some aspects such as the toxicity and cost effectiveness are to be studied in detail to make the process economically feasible on an industrial scale.

Nano zero valent iron particles could be used as reducing agents for the removing of wide range of pollutions, the reaction rates are 25 to 30 times faster, and the sorption capacity is much higher compared with granular iron (Zhang et al, 2010). The high reactivity of iron nano particle is the consequence of greater total surface area, higher density of reactive sites on the particle surface, and/or more intrinsic reactivity of the surface sites (Cundy, 2008). Iron nano particles have been extensively studied to remediate pollutants such as chlorinated compounds and metal ions (Rangsivek, 2005).

3.8. Lead removal and analysis

Lead has been determined by pulse polarography, NAA, ICP-AES, ICPMS and AAS. The first four methods are disadvantageous in terms of costs and instruments used in routine analysis. AAS is often lacking in sensitivity and affected by matrix conditions of samples such as salinity. The proposed method using dithizone in the presence of aqueous micellar solutions not only is one of the most sensitive methods for the determination of lead but also is excellent in terms of selectivity and simplicity. Therefore, this method will be successfully applied to the monitoring of trace amounts of lead in environmental, biological and soil samples.

3.8.1 Reagents and solutions

The samples were analysed to measure the concentrations of Pb^{2+} by using 1,5-diphenylthiocarbazone (dithizone) with H_2SO_4 can be used as a reagent in the determination of lead using UV spectrophotometer (Khan et al 2006).

3.8. 2. Lead (II) standard solutions

A 1000 ml stock solution (1 mg ml $^{-1}$) of divalent lead can be prepared by dissolving 1.59 mg of lead nitrate in de-ionized water. More dilute standard solutions can the be prepared from the prepared stock solution, as and when required (Zubir et al, 2014).

2.9. Synthesis of iron nano particles

The synthesis in laboratory scale has been the subject of research activities with the aim of modifying its properties focusing on particle size. A smaller particle size means higher surface area per unit mass making the material more reactive(Zang, et al, 1998). Several methods can be used for the production of these nanoparticles, namely: i) top-down methods (Li et al, 2006) such as vacuum sputtering (Kuhn et al, 2002) or the decomposition of iron pentacarbonyl ($Fe(CO)_5$) in organic solvents (Karlsson et al 2005); and ii) bottom-up methods that promote the 'growth' of the nanostructures via chemical synthesis, for example through the reaction of iron(II) or iron(III) salts with sodium borohydride (Wang and Zhang, 1997). However, these methods present several limitations and problems that is the conventional production of nano zero-valent iron includes the chemical reaction of NaBH4, as a reducing agent, with iron salts (Sun et al, 2006). However, by this method synthesized nZVI nanoparticles tend to either react with surrounding media or agglomerate into a chain-like structures, resulting in significant loss of reactivity of surface area (Sun et al, 2007).

The top-down methods are generally expensive and require specific and costly equipment while the drawbacks of the bottom-up approaches are related to safety issues due to the toxicity of sodium borohydride, the production of flammable hydrogen gas during the process and the tendency to form large agglomerates, very fast and at a high extent, and therefore have a reduced reactivity and degradation efficiency (Li et al, 2006).

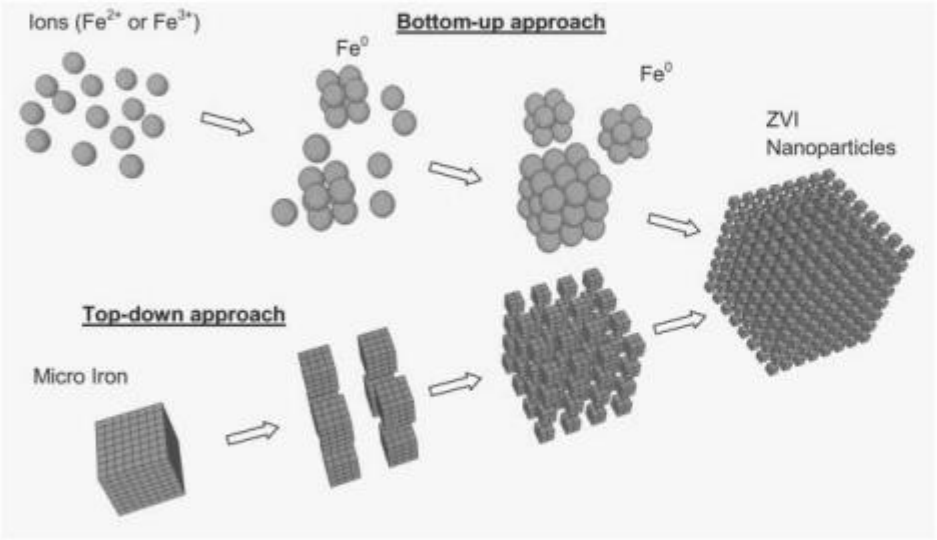

Figure 2: Conceptual models of bottom-up and top-down approaches for nanoparticle preparations (Li et al, 2006)

Bottom-up approach entails piecing together individual atoms or molecules to form nano sized structures. The top-down approach, on the other hand, is the process where large size materials are converted to iron nano particle with the aid of mechanical and chemical processes such as milling, etching, and/or machining. The synthesis methods can be also divided into two principal groups: physical methods and chemical methods. Generally, physical methods, such as gas condensation processes and ball milling, possess the advantages of simple operation and easy separation of products over chemical methods. However, chemical methods are thought to be potentially advantageous for iron nano particle manufacture and have been the focus of recent research studies, resulting in the development of a diverse range of chemical synthesis techniques of iron nano particle.

2.9.1. Physical methods of iron nano particle synthesis

Mechanical milling has rarely been applied for nanoparticle production, partly due to the limitation of the conventional equipment to achieve size reduction down to the nanometre scale. In addition, mechanical forces during milling introduce considerable dislocations, vacancies and strain to the products. However, precision ball milling (Li et al, 2009) in a high-speed rotary chamber with steel shot, using micro iron particles as raw materials, could effectively produce zero valent iron nanoparticles of uniform size and a high specific surface area. The method is nontoxic, free of secondary pollution and suitable for industrial scale supply. But, this method is energy-intensive and requires specialized equipment to achieve size reduction down to the nanometer scale. In addition, the product homogeneity of this method is not satisfactory (Lu et al, 2016).

In gas condensation processing, nano iron particles are obtained by condensing the vapour of iron atoms under an inert gas atmosphere via cooling with liquid nitrogen. This method enables good control of particle size, but highly restricted process conditions are required: high temperature, high pressure and substantial coolant. In addition, energy consumption is very high, while the yield is extremely low.

2.9.2. Chemical methods of iron nano particle synthesis

Among various chemical synthesis methods, chemical reduction is the most common for nZVI synthesis in both laboratories and large-scale applications due to its simplicity, productivity and chemical homogeneity of the product (Jamei & Khosravi, 2014). Most of other techniques for synthesizing nZVI are not feasible or cost-effective for industrial largescale production.

2.9.3. Borohydride reduction method.

The synthesis of nZVI can be achieved by reduction of ferrous or ferric ions in aqueous solutions using sodium borohydride ($NaBH_4$) under inert conditions. The method includes four steps:

a. preparation of supersaturated solution (ferric or ferrous salts),
b. nucleation of the nZVI cluster (reduction of Fe(II) or Fe(III) by reducting agent),
c. growth of nZVI nuclei, and
d. Agglomeration of nZVI.

Investigation showed that the last two steps have the most significant effects on shape and properties of nano particles (Hwang et al, 2010). Therefore, it is important to control the growth and agglomeration exposure time by controlling the reductant delivery rate, reductant concentration and other synthesis parameters (Zhang et al, 2010). Excess of borohydride is needed to speed up the synthesis reaction and to provide the uniform growth of iron nano particles. The reactions of the ferrous and ferric ions reduction in aqueous solutions using sodium borohydride can be represented by equations(Wang, 1997):

$$4Fe^{3+} + 3BH^{4-} + 9H_2O \rightarrow 4Fe^{0\downarrow} + 3B\,(OH)^{3+} + 9H^{+} + 6H_2 \qquad (1)$$

$$2Fe^{2+} + BH^{4-} + 3H_2O \rightarrow 2Fe^{0}(s) + B\,(OH)^{3+}\ 3H^{+} + 2H_2\,(g) \qquad (2)$$

In borohydride reduction, washing and drying processes are required in order to rinse out excess chemicals on nZVI surfaces and to prevent gradual oxidation and aging of nZVI by residual water on the surfaces, respectively (Woo et al, 2014). Deionized water is the most typical washing solution used in nZVI preparation, while some researchers have applied volatile solvents like ethanol and acetone. For drying, several methods have been employed to minimize nZVI oxidation during the process, including vacuum oven drying and freeze drying. Recent studies have reported alterations in the surface properties of nZVIs experiencing different washing and drying conditions.

2.9.4. Ultrasound assisted method

It was found that ultrasound affects the growth and coalescence of iron nanoparticles. The nZVI synthesized in this manner has a smaller particle size, a larger specific surface area and higher crystallinity than that synthesized by the conventional borohydride reduction method. It was also observed that under ultrasound, the morphology of nZVI particles was changed from spherical to plate and needle types by increasing the ultrasonic power (Li & Yan, 2009).

2.9.5. Carbothermal reduction

Generally, in carbo thermal reduction, C or CO is used to reduce iron oxide (natural iron ores, such as goethite), ferrous or ferric ions at elevated temperatures. Raw materials are inexpensive and widely available, leading to low production cost. However, the generation of carbon monoxide (CO), a flammable and toxic gas, is an unavoidable drawback of this method.

$$Fe\,(C_2H_3O_2)_2 + C \rightarrow Fe0 + 2CH_2CO + CO + H_2O \qquad (3)$$

$$Fe_2O_3 + 2C \rightarrow 2FeO + CO + CO \qquad (4)$$

2.9.6. Thermal decomposition method

High quality nZVI particles can be produced by thermal decomposition of an iron precursor. Organo metallic molecules containing iron, especially $Fe\,(CO)_5$, can be used as a starting material. Spherical nano iron particles can be generated by adding $Fe\,(CO)_5$ into trioctylphosphineoxide (TOPO) at 320 °C under an argon atmosphere:

$$Fe\,(CO)_5 \rightarrow Fe^0 + 5CO \qquad (5)$$

The product from this method has an extremely small size (2 nm) and good homogeneity. Nevertheless, this method also has some drawbacks: $Fe\,(CO)_5$ is highly toxic and unstable, the process is energy-intensive, and a considerable amount of carbon monoxide is generated as a by-product.

2.9.7. Thermal reduction method

Nano zero-valent particles can be produced by the reduction of goethite (α-FeOOH) or hematite (α-Fe_2O_3) at elevated temperature, by H_2. Depending on hydrogen reduction conditions, the complete reduction can be accomplished even at low temperature up to 380 °C in pure hydrogen. The reduction behaviour is strongly influenced by the particle size, crystallinity and the conditions of the temperature–time– pressure dependent reduction (Jozwiak et al, 2007).

2.9.8. Electrochemical method

In this method, cathodes are used to attract Fe^{2+}/Fe^{3+} ions from solution by help of electric current (Chen et al, 2004). The method is extremely simple, cheap, and fast in comparison to chemical reduction (Yoo et al, 2007). Produced FeO is gradually deposited on the cathode, but they often display a strong tendency towards aggregation and the formation of clusters. To counteract that phenomenon, cationic surfactants are used (Li & Yan, 2009), act as a stabilizing agent, and ultrasonic waves, which constitute a source of energy necessary for fast removal of iron nanoparticles from the cathode. The nZVI particles produced with the use of ultra-sonication can be between 1 and 20 nm and have a specific surface area of 25 m^2/g (Chen & Hsu, 2004). This method has the advantages of low cost, though the as-prepared product has shown a tendency to aggregate.

2.9.9. Green synthesis

Recently, a green method that uses natural, plant extracts in which the active substances are highly reductive compounds, such as polyphenol, has been developed (Machado et al, 2014). Green synthesis is not only environmentally friendly, but also inexpensive. Because there is no need to use high temperatures, pressure, or additional energy inputs, it is easy to implement on a large scale. The method included the preparation of a polyphenolic solution by heating plant extracts (coffee, green tea, black tea, lemon, balm, sorghum, bran, grape, Eucalyptus leaf etc.) in water to a temperature close to the boiling point.

Though there is no definite explanation for the formation of Fe^0 (ZVI), there are speculations that this is due to the reduction potential of polyphenols which are sufficient to reduce Fe^{2+}

to Fe^0 (Smuleac et al 2011). Mystrioti suggested the overall mechanism for the formation of Fe^0 using polyphenols as it is shown in eqn. 2.1).

$$nFe^{3+} + 3(A_r - OH)_n \rightarrow nFe^0 + 3n(A_r = O)^+ 3nH^+ \qquad 2.1$$

where Ar represents the aromatic ring and n is the number of groups oxidised by Fe^{3+}(Mystrioti et al, 2012).

Structural characterization of polyphenol-reduced nanoparticles revealed that they contain large amounts of α-Fe_2O_3 or iron ox hydroxide with only a less component of amorphous Fe^0, which explains their low reactivity in reduction applications and more applicability towards oxidative reactions with H_2O_2. In addition, presence of hydroxyl and phenol groups in these compounds affords them as good capping agents to stabilize the reactive surfaces of the nanoparticles and decreases their bio toxicity. These extracts have high reductive capacities and assure the reduction of iron(III)/(II) producing nZVI particles (Reddy et al, 2016).

One of the major drawbacks of using plant resources for nanoparticle synthesis is the destruction of plants and plant parts. A possible way to avoid this is value adding opportunity e.g. extract of Eucalyptus leaf (Wang et al, 2014) or extracts from various residues (skin, albedo, flesh) of such fruits as lemons, mandarins, limes, oranges or vine pomace (Machado et al, 2013). Depending upon plant type and concentration of phytochemicals, nanoparticles are synthesized within a few minutes or hours. In spite of the numerous advantages of using this method, green synthesis is still not commonly accepted. These results from insufficient knowledge of the reactivity, physicochemical properties, and agglomeration of the nanoparticles produced (Machado et al, 2013). The information available in the literature indicates that depending on the kind of plant extract used for the production of nZVI, we obtain nanoparticles with various sizes and values of specific surface area.:

Table 2: Environmental contaminants amenable to degradation by nZVI (Sharaf, 2013)

Chlorinated Methanes	Trihalomethanes
Carbon tetrachloride (CCl_4)	Bromoform ($CHBr_3$)
Chloroform ($CHCl_3$)	
Chlorinated Benzenes	Chlorinated Ethenes
Hexachlorobenzene (C_6Cl_6)	Tetrachloroethene (C_2Cl_4)
Pentachlorobenzene (C_6HCl_5)	Trichloroethene (C_2HCl_3)
Tetrachlorobenzenes ($C_6H_2Cl_4$)	cis-Dichloroethene ($C2H_2Cl_2$)
Organic Dyes	Other Organic Contaminants
Orange II ($C1_6H_{11}N_2NaO_4S$)	N-nitrosodiumethylamine ($C_4H_{10}N_2O$)
Chrysoidin ($C12H_{13}ClN_4$)	TNT ($C_7H_5N_3O_6$)
Tropaeolin O ($C1_2H_9N_2NaO_5S$)	
Heavy Metals	Other Inorganic Anions
Mercury (Hg^{2+})	Perchlorate (ClO^{4-})
Nickel (Ni^{2+})	Nitrate (NO^{3-})
Cadium (Cd^{2+})	Dichromate (Cr_2O7^{2-})
Lead (Pb^{2+})	Arsenate (AsO_4^{3-})

Green synthesis can also be limited by the incomplete reduction of iron to nZVI by plant extracts (Mystrioti C et al2015), resulting in the formation of other forms of iron, e.g. iron oxides of hydroxides, in the course of the process (Huang et al, 2014).

Zero valent iron nanoparticles (nZVI) have already proven their efficacy in the reductive disposal of a wide array of environmental contaminants in numerous laboratory and field trials. However, their large-scale application in remediation applications is hindered by the high costs and the legislative issues associated with the conventional nZVI synthesis method that relies on NaBH4 as a reducing agent. The two common strategies to replace sodium borohydride are totally "green" nZVI syntheses based on plant extracts, and "semi-green" nZVI synthesis based on less toxic and more cost-effective industrial chemical reducing agent (Kozma & Kukovecz, 2015).

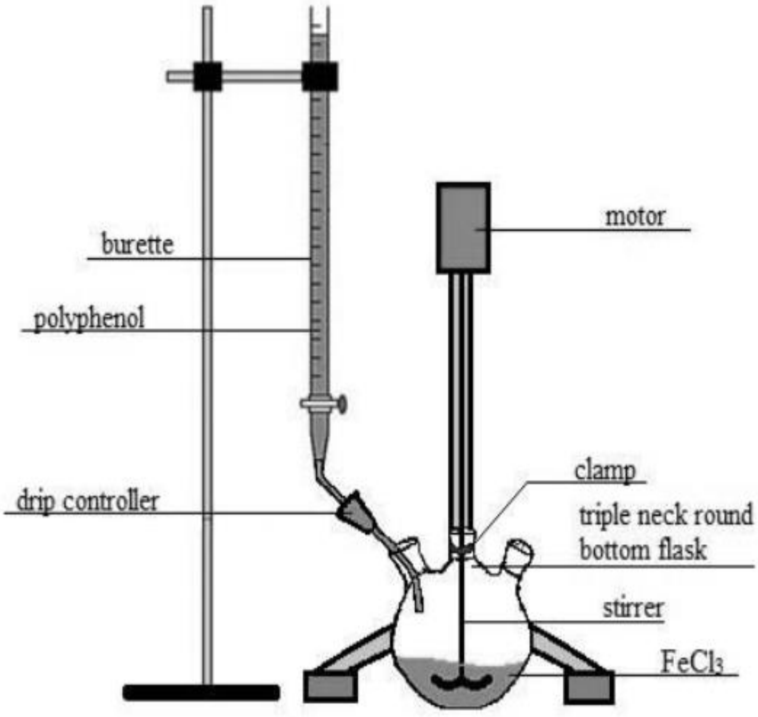

Figure 3: Schematic diagram of synthesis set-up ((Pattanayak & Nayak, 2013)

2.10. Eucalyptus (Eucalyptus *globulus*)

Several species of *Eucalyptus* leaves are used in traditional medicine as antiseptics, and against upper respiratory tract infections, such as common cold, influenza and sinus congestion(Williams & Stockley, 1998). The essential oil obtained from these plants has a therapeutic application in treatment of pulmonary infections by inhalation(Low, 1974). Leaf extracts of E. globulus are used as food additive for the prevention of many chronic diseases (Hasegawa et al, 2008).

Figure 4: Eucalyptus (*Eucalyptus globulus)* leaf

The main component responsible for these properties of Eucalyptus leaves is eucalyptol, which is also the most abundant component of the essential oil and the component that is responsible for its purifying and antiseptic properties. Other components of the essential oil enhance its antibacterial activity: α-pinene (antiacne, antiviral, antiseptic and antibacterial agent), β -pinene (antiseptic and candidacidal substance), α-phellandrene (antibacterial, anti-staphylococcal and fungicidal agent), γ- terpinene (acaricide), caffeic acid, linalol, geraniol and thymol.

Table 3: Components of Eucalyptus globulus leaf extract (Singab et al 2011)

No	R_T	Name of compound
1	5.352	α –pinene
2	6.918	D-Limonene
3	6.984	Eucalyptol
4	6.512	α –Terpineol
5	11.765	Terpinolene
6	14.904	N-Desmethyltapentadol

CHAPTER THREE

3. Materials and Methods

3.1 Materials

3.1.1 Chemicals

In this research, chemicals used to synthesize iron nanoparticles included ferric chloride (anhydrous.), sodium hydroxide (NaOH), 1.5 diphylthiocarbazone (dithiozone), hydrochloric acid (HCl). Lead nitrate (Pb $(NO_3)_2$), ethanol and Eucalyptus globulus leaf . All the solutions were prepared with deionized water and the chemicals used were of analytical grade. Lead nitrate and iron(III)chloride were products of Avi-chem industries (Mumbai,India) and Loba-chemie industries, (Mumbai, India) respectively and all the rest chemicals and reagenrts were products of Sigma-alorich,Germany and bought from Atomic chemicals plc. Addis Ababa, Ethiopa.. All chemicals used were of analytical grade.

3.1.2 Equipment

The major equipment employed to conduct the experiments of this research are triple neck round bottom flask, drip controller, beaker, burette, overhead stirrer, centrifuge, vacuum filter and magnetic bead.

3.1.3 Eucalyptus leaves extract preparation

Eucalyptus globulus leaves were brought from the Ethiopian agricultural institute and washed thoroughly with DI water to eliminate dust on the surface, after which the leaves were dried at room temperature. After the elimination of dusts by washing the leaves' size were reduced so as to facilitate the extract process using steam distillation.

3.1.4 Iron nano particles synthesis

The applied nanoparticles were prepared using reduction method in solution phase. It is known that the stability constant of ferrous iron is lower than that of ferric iron for a specific ligand (Pattanayak & Nayak, 2013). Thus, ferric iron complex will give more stable nanoparticle suspensions and smaller particle sizes; hence, the GInP was prepared by by a 0.1 M solution of ferric chloride (anhydrous) in 100 mL of distilled water. The water used was pre-cooled to a temperature of 25 ºC for 30 minutes to prevent the reductant from being consumed by the dissolved O_2. The ferric chloride solution was stirred for five minutes and then placed in a triple-neck flask.

The Eucalyptus globulus leaf extract was added to the ferric chloride solution by drop-wise addition to control the flow rate of the reducing agent because it has significant effect on the particle size of GInP and 8ml/min give smallest particle (Borja et al, 2015).While the leaf extract was added, the contents of the reactor were continuously stirred to increase reactivity using a mechanical stirrer (overhead stirrer) attached to the top of the flask. When all of the extract has been added, the stirring process was continued for 10 minutes. The immediate appearance of a black color indicated the formation of GInP. Then the resulting solution was centrifuged for 30 minutes at 5000 rpm.

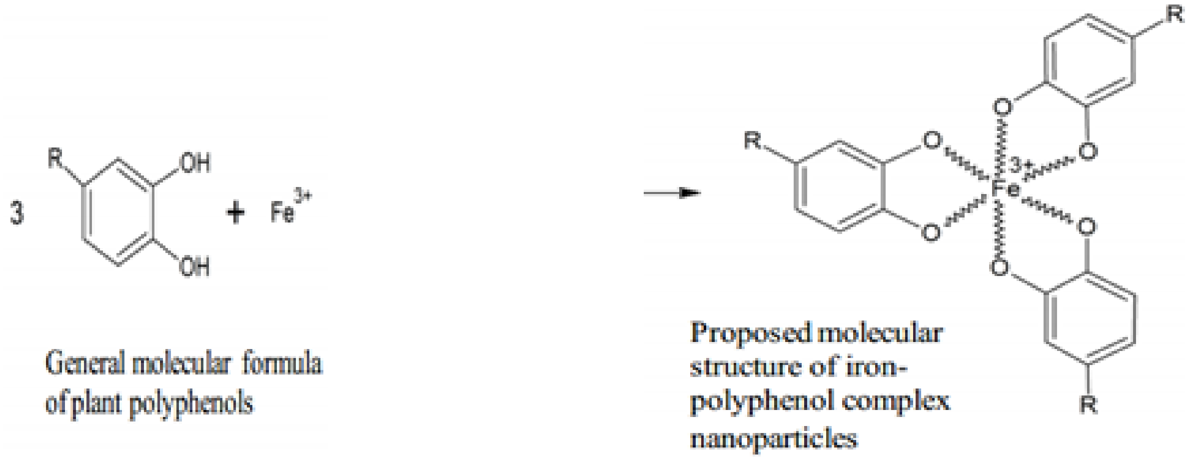

Figure 5: Schematic representation of iron nano particle synthesis from Eucalyptus leaf extract (Chrysochoou et al, 2012)

R groups are typically H, OH, galloyl esters, or carbohydrate groups, depending on the compound. Synthesis of iron nanoparticles using plant polyphenols has attracted much attention due to its environmental benignity, low cost, and simplicity

3.2. Characterization of the iron nano particle produced by greener method

3.2.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy analysis was carried out in order to identify the functional groups that might be involved in the binding of heavy metal ions. The functional groups were determined using FTIR spectroscopy at wave number range of 4000- 400 cm^{-1}. First, the dried adsorbent was mixed with KBr particles to make it suitable to infrared analysis. The mixture was then pressed to a small thickness, slightly below 1 mm, required for FTIR spectroscopy analysis. FTIR analysis was done at Addis Ababa University, College of Natural Science, and Chemistry Laboratory.

3.2.2. X ray Diffraction Spectroscopy

X-ray diffraction is a convenient method for determining the mean size of single-crystal nanoparticles or crystallites in nano crystalline bulk materials (Holzwarth & Gibson, 2011). The analyses was carried out at Addis Ababa university chemistry laboratory . The grain size calculation was carried out using Scherer's Formula which, can be expressed by the following relationship:

$$\mathrm{Dp}= \frac{(0.9X\lambda)}{\beta X Cos\theta} \tag{3.1}$$

Where, Dp = Average Crystallite size, β = Line broadening in radians, θ = Bragg angle, λ = X-ray wavelength.

3.3 Point of Zero Charge

The surface chemistry of any materialcan can be determined by the acidic or basic character of their surface charge. In this research, nine 250 ml of 0.1M NaCl solution conical flasks were prepared and their initial pH values were adjusted to 1.5, 2.5, 3.5, 4.5, 5.5, 6.5, 7.5, 8.5 and 9.5 by adding 0.1M HCl or NaOH as solution required by using a pH meter. 0.2 g of iron nano particle adsorbent was added into each solution. The solution mixtures were allowed to equilibrate in an encubater shaker at 200 rpm and room temperature for 1 hr. Then the solution was filtered using vacuum filter and the filtrates final pH was measured. The results were plotted as ΔpH against pH final curve. The $\mathrm{pH_{PZC}}$ values are estimated from the curve interceptions (from the plot of the ΔpH against final pH); the $\mathrm{pH_{pzc}}$ is the pH at which the change in pH is zero (Yadav, O. P., 2012).

3.4 Specific Surface Area

To determine the specific surface area one gram of iron nano particle was mixed with 250 ml of distilled water and 25 g NaCl. The mixture was shaken for five minutes. Its final pH was adjusted to 4 with 0.1 M HCl. It was then titrated against 0.1M NaOH to raise the pH from 4 to 9 and the volume (ml) of 0.1M NaOH used was measured in replicate and the average value was taken to calculate the surface area by the following equation. The volume of NaOH was found to be 2.625ml.

$$S = 32 \times V - 25 \qquad 3.2$$

Where, S is surface area of iron nano particle per gram V is volume (ml) of 0.1M NaOH required to raise the pH of the sample from 4 to 9 the numbers 32 and 25 are physical constants (Yadav et al, 2012).

3.5 Preparation of lead nitrate solution

Lead nitrate - $Pb(NO_3)_2$ salt was used in the preparation of stock solution. 500 ppm of Stock solution Pb (II) was prepared by dissolving accurately weighed amount of the salt 0.7995 g of $Pb(NO_3)_2$ in 500 ml distilled water. Working solution of different concentration was prepared from the stock solution by serial dilution with distilled water.

3.6 Batch Adsorption Experiments

All batch experiments were conducted out at a room temperature (25±2 °C). The designed solution pH was adjusted using 0.1 M NaOH or HCl. Lead nitrate ($Pb(NO_3)_2$), used as the source of Pb^{2+} in all experiments. A 0.1M of GInP was added to samples and was stirred by overhead stirrer at 250 rpm stirring speed, allowing sufficient exposure time for adsorption equilibrium. The effects of four main variables were investigated to determine the extent of lead removal; this was done by varying iron nanoparticle dose, contact time, initial lead concentration and pH of the solution in batch tests. Batch experiments were carried out in a flask at room temperature.

3.7 Analysis method

The samples were analysed to measure the concentrations of Pb^{2+} by using 1,5-diphenylthiocarbazone (dithizone). 50 mg (1, 5 DPC) was dissolved in 100 mL acetone solution. 15 mL sample was taken and 2mL of 3M H_2SO_4 and 1mL of DPC was added. Pb^{2+} concentration was estimated by absorbance formed and it was measured using UV spectrophotometer (JAZ Spectrometer) at 500nm, following the 1,5 DPC method (Khan et al 2006).

3.8 Thermodynamics Studies

Thermodynamic studies are basic tool in adsorption–adsorbate systems, to provide information on the feasibility (spontaneity), exo- or endo-thermicity of the adsorption and explain whether or not the randomness increases or decreases at the solid–solution interface. The Gibbs free energy change (ΔG^o) is an indication of spontaneity of an adsorption and therefore is one of the most important criteria. It is calculated as follows:

$$\Delta G^\circ = -RT \ln Ka \qquad (3.2)$$

Where: R is the universal gas constant (8.314 J/mol·K) and Ka is the equilibrium constant. Negative or positive values of ΔG^o indicate the spontaneity or non-spontaneity of adsorption process, respectively. Enthalpy change, ΔH^o, provides information about the energy release (exothermic process) or consumption (endothermic process) during adsorption process. Another thermodynamic parameter namely ΔS^o (entropy change) depending on the sign, indicates if the randomness increases (positive values) or decreases (negative values), during adsorption procedure. Therefore, the correct estimation of the thermodynamic parameters is essential in describing the adsorption process (Anastopoulos, 2016). For ΔG^o determination, it is necessary to estimate equilibrium constant Ka.

The determination of ΔH^o and ΔS^o performed by using van't Hoff equation as follows

$$\ln K_a = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (3.3)$$

In order to calculate ΔH^o and ΔS^o, adsorption data from two or more temperatures are bare necessities, i.e., the values of Ka for different temperatures should be determined. The values of ΔH^o and ΔS^o were determined from the slope and intercept of the linear plot of ln Ka vs. 1/T.

3.9 Adsorption Isotherms

When a solution is contacted with a solid adsorbent, molecules of adsorbate get transferred from the fluid to the solid until the concentration of adsorbate in solution as well as in the solid phase are in equilibrium. At equilibrium, equal amounts of solute eventually are being adsorbed and desorbed simultaneously. This is called adsorption equilibrium. The equilibrium data at a given temperature are represented by adsorption isotherm. Adsorption isotherm models such as Temkin, Langmuir and Freundlich models were used to fit the experimental data. It helps to find out the best fitting isotherm model in order to evaluate the efficiency of the prepared adsorbent and to develop a suitable batch absorber design. The adsorption capacity at equilibrium, Qe (mg/g) was calculated by the following relationship:

$$Qe = \frac{Co - \mathrm{Ce}}{W} * V \qquad (3.4)$$

Where qe is the equilibrium adsorption capacity (mg/g), Co and Ce are the initial and equilibrium liquid phase solute concentration (ppm), respectively; V is the liquid phase volume (L) and W is the amount of adsorbent (g). The removal percentage was determined b

$$\text{Percentage adsorption} = \frac{C - Co}{Co} * 100 \qquad (3.5)$$

Where, Co and C represent the initial concentration and final concentration (ppm) respectively. The lead mass adsorbed per gram of iron nano particle was calculated by difference between the Pb^{2+} concentration of the solution before equilibrium and in the equilibrium, multiplied by hundred.

3.10 Desorption experiments

Desorption studies are important since they contribute to explain the nature of adsorption process. In addition to this it is necessary to examine the possibility to recover metal ions and to regenerate and recycle the adsorbent. The experiments for desorption efficiency were carried out with dilute HNO_3 solutions. The desorption efficiency (DE) was determined using the following

$$DE = \frac{C * V}{q * m} * 100 \qquad (3.6)$$

Where, C (mg/L) is the concentration of lead ions in the desorption solution, V (L) is the volume of the desorption solution, q (mg/g) is the amount of lead ions adsorbed on the adsorbents before desorption experiment, and m (g) is the amount of the adsorbent used in the desorption experiments.

3.11. Kinetic Studies of the adsorption process of lead by iron nano particle

The adsorption kinetics of Pb^{2+} ions was studied to determine the required exposure time to achieve equilibrium adsorption of lead ions on the adsorbents. In this research, the kinetics was investigated experimentally under different values of initial Pb^{2+} concentration, solution pH, and iron nano particle dosage by using pseudo first-order reaction model since the pseudo first-order kinetic model was the most suitable which approves the best fit with the experimental data of Pb^{2+} removal compared to the rest number of kinetic models, such as pseudo first -order, pseudo second order and Intra particle diffusion kinetic models(Boparai et al 2011).

3.12. Experimental design for adsorption of lead by iron nano particle

Among the many experimental operating parameters that may influence the adsorption process, the most important factors include the solution pH, adsorbent dose time and metal ion concentration. For finding optimum conditions of the parameters for metal removal efficiency of iron nano particle data analysis was performed by minitab 17 software design. Central composite design was used to design the experiments because it minimise the number of runs and it also allows for efficient estimation of the terms in the regression model. The experiment was designed to investigate the single and interaction effects of selected optimum parameters. ANOVA was used to investigate the result of the experiments.

Table 4: Central composite design (CCD**)**

Parameters	Ranges and levels				
	-2	-1	0	+1	+2
Exposure time (min)	15	25	35	45	55
Dosage of sorbent (g)	0.2	0.4	0.6	0.8	1
Sorbate concentration(ppm)	50	100	150	200	250
pH	2	4	6	8	10

CHAPTER FOUR

4. Results and Discussion

4.1. Point of Zero Charge

The point of zero charge of adsorbent surface play a crucial role in adsorption processes, and the characterization of cation and anion preference of adsorbent material in aqueous media could be useful to explain adsorption mechanism. The pH of point of zero charge is the point at which the change of pH crosses the final pH and accordingly the pH_{pzc} of GInPis found to be at pH of 7.60, which revealed there was a specific adsorption of Pb^{2+} at the surface of the greenly synthesized iron nano particles because the point of zero charge can only be equal to the isoelectric point only if there is no specific adsorption of ions at the surface of the solid phase (Goldstein, 2012).

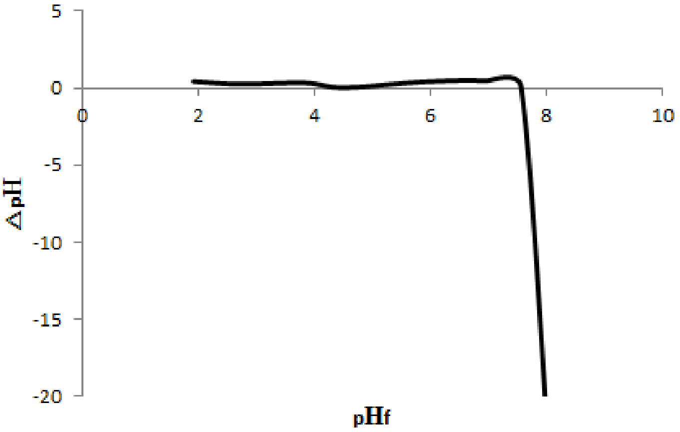

Figure 6: pHpzc determination plot

4.2. Characterization of GInP using FT-IR and X-RD

The morphology and size were verified by characterizing the sample by FTIR and X-RD analysis for studying the functional groups and diameter of the GInP.

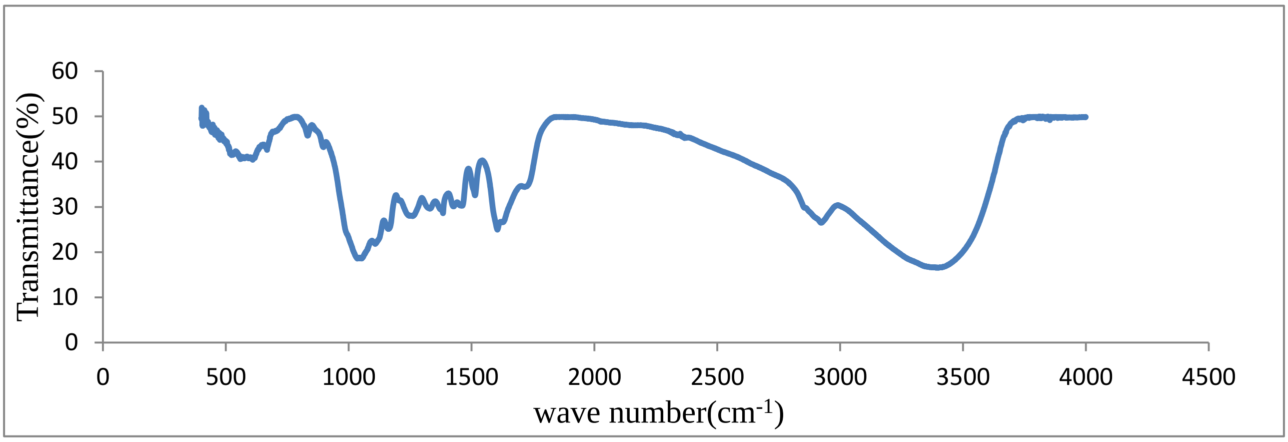

Figure 7: FT-IR plot of Eucalyptus globulus leaf extract

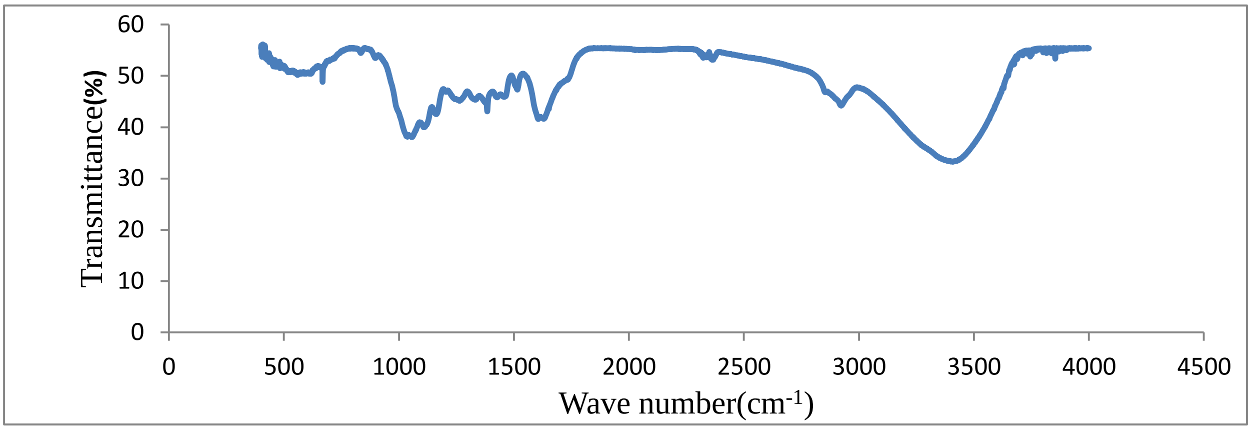

Figure 8: FT-IR plot of greenly synthesized iron nano particle (GInP)

FTIR analysis was carried out to identify the possible interaction between the biomolecules and iron ion during the reduction reactions. The FTIR data for GInP containing Eucalyptus leaf extract is shown in figure 8. The band at 3589 cm^{-1} is assigned for O-H stretching vibration of alcohol and phenol compounds and bands observed at1793.7 cm^{-1}, 1654 cm^{-1}, 983.93 cm^{-1} are due to the C-O stretching, C=O stretching mode of the carbonyl functional groups. The FT-IR result revealed that the carbonyl group from Water soluble heterocyclic compounds such as flavonoids, alkaloids were mainly responsible for the reduction and stabilization of NPs. This suggests that the molecules in Eucalyptus leaf extract could possibly perform the dual function of formation and stabilization of iron nano particles in the aqueous medium.

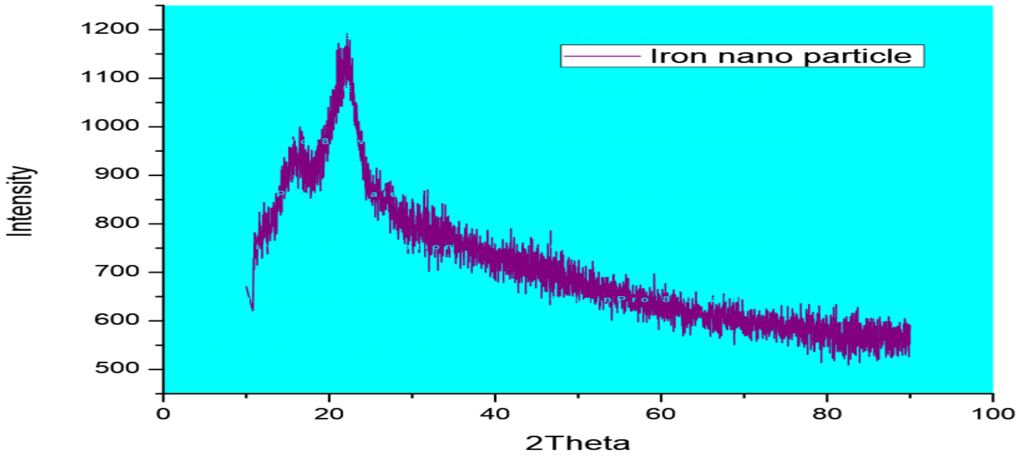

Figure 9: X-RD plot of greenly synthesized iron nano particle

X-RD analyses were performed on the synthesized green iron nano particle. The broad hump shoulder peak at 2 theta 25^{o} revealed that the synthesized iron nano particles were not necessary elemental iron nano paricle but iron nano particle-polyphenol complex i.e. organic materials of the eucalyptus leaf extract were attached to it as a capping/stabilizing agents (Wang et al, 2014). Theta and full width at half maximum were found to 12.5 and 17.7nm respectively. The default value for lambda in scherrer formula is 0.154nm. The Scherrer Formula revealed that the grain size of the GInP is 80nm. The surface of nanoparticles is capped mainly by C and O elements which indicate that the material has organic properties. The dried powder can remain stable on exposure to air for several hours, and then be partially oxidized to form iron oxides.

4.3. Effect of exposure time

Removal efficacy for lead at exposure time of 15-55 min was investigated. As the result in Fig.10 below showed, the optimum exposure time for Pb^{+2} removals by iron nano particle was obtained in 55 min. Therefore, the lead adsorption was found to increase with increase in time. The Pb^{+2}sorption in mentioned time was attributed to the surface junction between active surface groups and lead ion. Also, the further sorption at the described times can be illustrated with an increased availability in the active bounding sites on the sorbent surface area. The plot of percentage removal versus exposure tme was constructed at pH 4 ,25°C,150rpm and 150ppm using fitted empirical cumulative function plot to clearly understand the trend that the percentage removal with respect to exposure time increment.

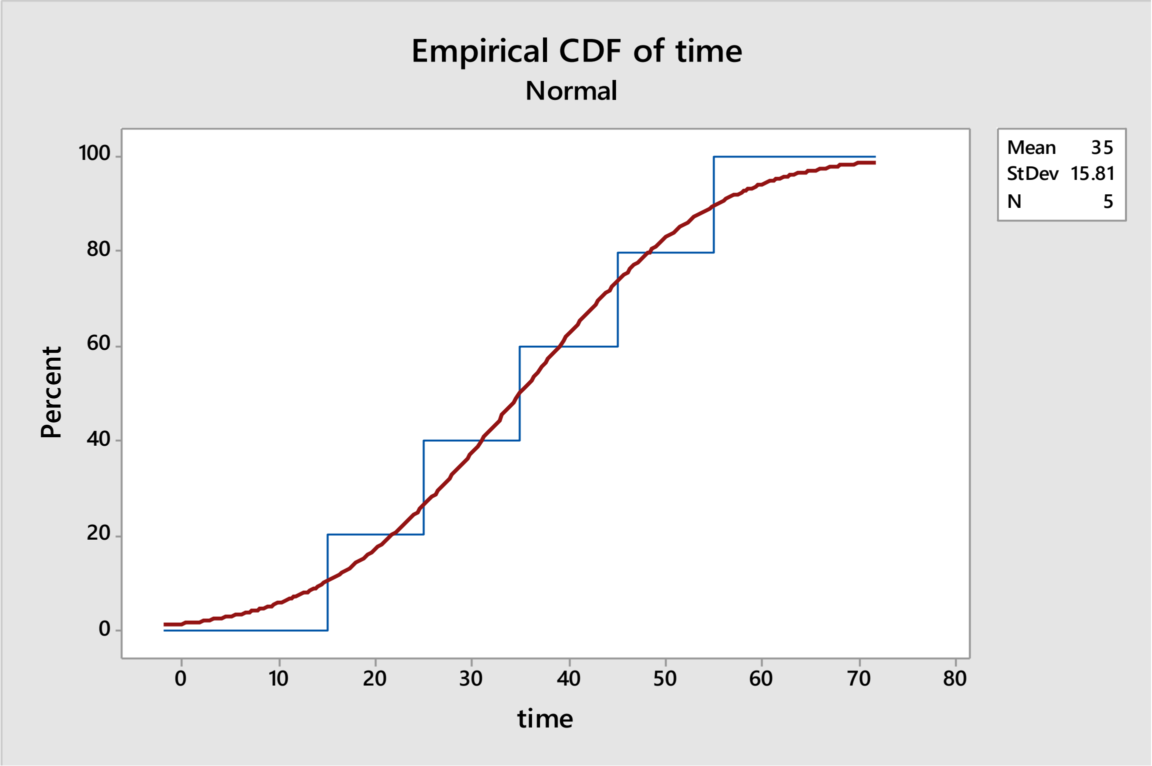

Figure 10: Plot of lead removal versus exposure time graph

4.4. Effect of Adsorbent dosage

The lead removal process found to be positively affected by the dosage of the iron nano particle. The plot of percentage removal versus adsorbent dosage was constructed at 100ppm, pH of 4 55min,25°C and 200rpm using fitted empirical cumulative function plot to clearly understand the trend that the percentage removal with respect to adsorbent dosage increment. As Fig.11 showes, the removal increased with increasing the amount of adsorbent dosage. These results indicate that removal efficiency is directly related to the number of available adsorption sites. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. Amount of adsorbent added to the solution determines the number of binding sites available for adsorption. Metals adsorption efficiency was increased with increase in adsorbent dose. This implies that the adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose..

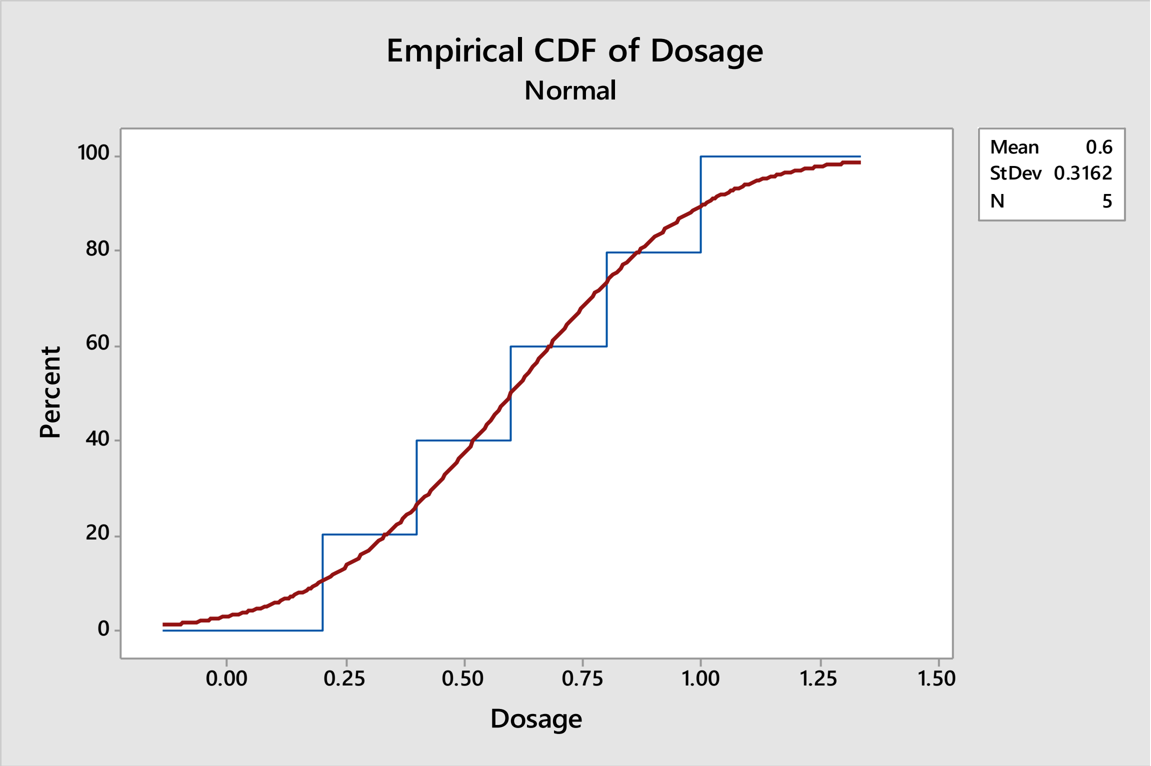

Figure 11: Plot of lead removal versus dosage

4.5. Effect of lead ions concentration

The effect of initial concentration of Pb^{2+} on removal efficiency was investigated in the range of 50 to 250 ppm.The adsorption process observed to be inverse affected by the initial lead ions concentration, the removal process decrease with increasing lead concentration. As Fig.12 clearly revealed, the removal efficiency of Pb^{2+} decreased as the initial Pb^{2+} concentration increased; so, the percentage of Pb^{2+} removed at an initial concentration of 50ppm was nearly 90%, and it was only 60% at an initial concentration of 250ppm. The plot of percentage removal versus lead concentration was constructed at pH 4, 55min, 25°C, 0.8g ,25°C and 200rpm using fitted empirical cumulative function plot to clearly understand the trend that the percentage removal with respect to lead concentration increment.

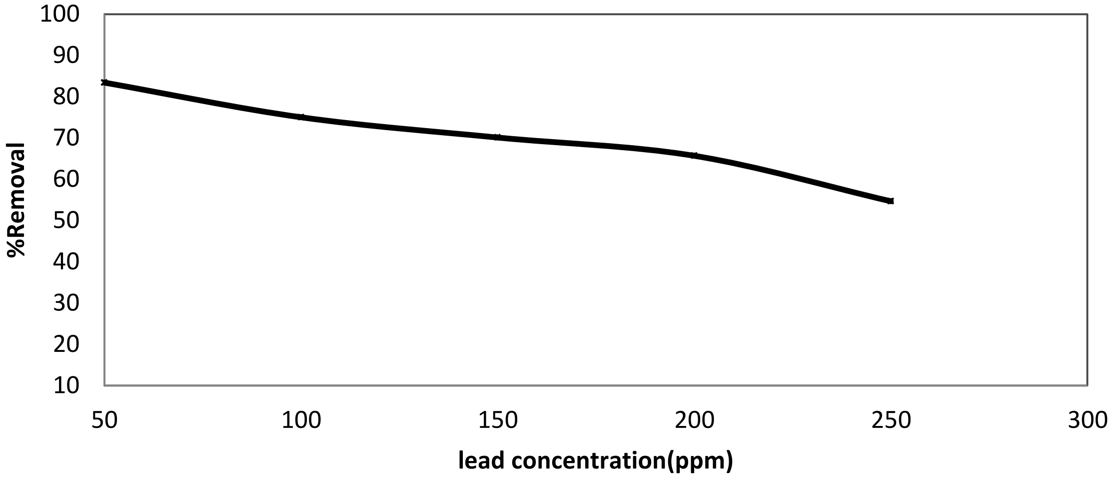

Figure 12: Lead ion concentration versus %removal plot

4.6. Effect of pH on the lead removal process

To determine the maximum pH at maximum lead removal occurs 0.1M was found by adjusting the pH of the stock solution using 0.1M HCl or NaOH. 0.4g nano particle of was added to each of the 200 mL Erlenmeyer flask containing 100 mL of lead solution with a concentration of about 100 ppm. The lead solution pH was adjusted from 2 to 10 in an increment of 2 units. The mixture was shaken at 200 rpm for 55min that is equilibrium exposure time and at room temperature the final pH results were recored after the equilibrium had been reached. The sample was filtered using vacuum filiter and the lead concentration in the filtrate was also measured. The experiments were conducted in duplicate and mean values were used. The plot of percentage removal versus adsorbent dosage was constructed using fitted empirical cumulative function plot to clearly understand the trend in Fig.13 shows that the percentage removal decrease with respect to pH increment.

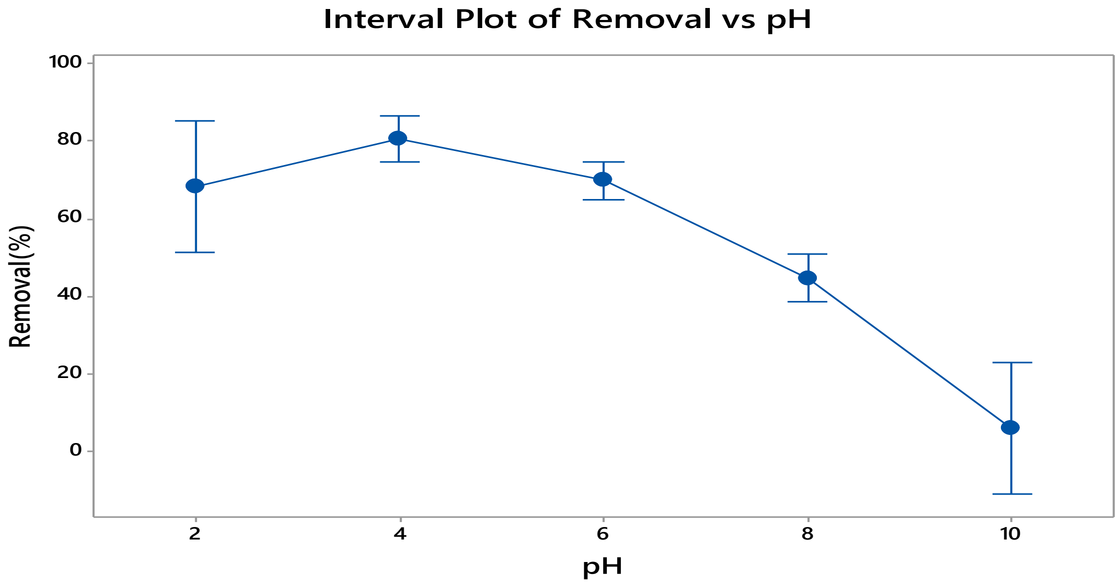

Figure 13: Plot pH versus percentage removal

4.7. Isotherm studies

The removal of Pb^{2+} by the iron NPs at different Pb^{+2}concentrations is depicted in Fig. 12. It was observed that the adsorption of Pb^{+2}onto the iron NPs decreased with rise in concentration of Pb^{2+} from 50 to 250 mg L^{-1}. This is attributed to the greater driving force through a higher concentration gradient at high metal ion concentration. Thus the developed iron NPs can be efficiently used for the removal of high concentration $Pb^{2+}$from aqueous solutions. The surface property and affinity of iron NPs for Pb^{2+}removal can be determined using the different adsorption isotherm models. The obtained equilibrium data from the adsorption of Pb^{+2}onto the iron NPs fitted to the linear equation of Langmuir,Freundlich and Isotherm models. The linear equation for Langmuir, Freundlich and Temkin isotherm models are expressed as follows:-

Langmuir isotherm: $\frac{Ce}{qe} = \frac{1}{Qo} + \frac{Ce}{Qo}$ (4.1)

$R_l = \frac{1}{1+klCo}$ (4.2)

Freundlich isotherm: $\log q_e = \log Kf + \frac{\log Ce}{n}$ (4.3)

Temkin isotherm: $qe = BlnAT + BlnCe$ (4.4)

$$B = \frac{RT}{bT} \quad (4.5)$$

Where

Ce is the Equilibrium concentration of adsorbate (ppm)

q_e is the adsorbed amount of adsorbate at equilibrium (mg/g)

Q_o is the maximum adsorption at monolayer (mg g^{-1})

K_L is a constant related to the affinity of the binding sites (L/mg).

R_l referred to as separation factor or equilibrium parameter (dimensionless)

C_o is initial concentration of the adsorbate(ppm)

K_f the adsorption capacity of the sorbent (mg/g (L/mg) 1/n)

N is the Adsorption favorableness indicator

A_T Temkin isotherm equilibrium binding constant (L/g)

b_T is Temkin isotherm constant

R is universal gas constant (8.314J/mol/K)

T is Temperature at 298K.

B is a Constant related to heat of sorption (J/mol)

The Langmuir model assumes that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the surface of the adsorbent, the energy of adsorption is fixed and molecules of the adsorbent will not migrate in the surface plane. The constants (K and Qo) were calculated as 0.041.50L/mg and 3.457mg/g respectively. With correlation coefficient of 0.965.

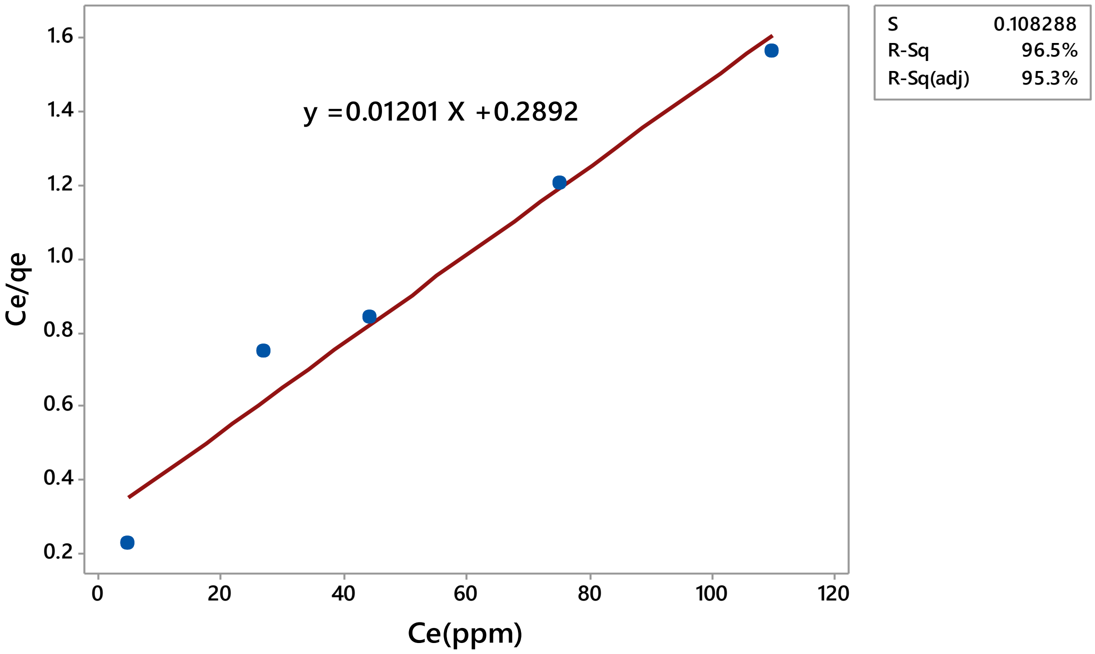

Figure 14: Langmuir for lead removal from aqueous solution

The Freundlich isotherm model was plotted as log Ce versus Ce on figure 4.10 to test the validity generate the values of freundlich constants K_f indicator of adsorption capacity and" n" adsorption intensity. The freundlich constants K_f and n were calculated as 10 mg g_{-}^{1}(mg L^{-1})$1^{/n}$ and 2.41 with a correlation coefficient 0.846.

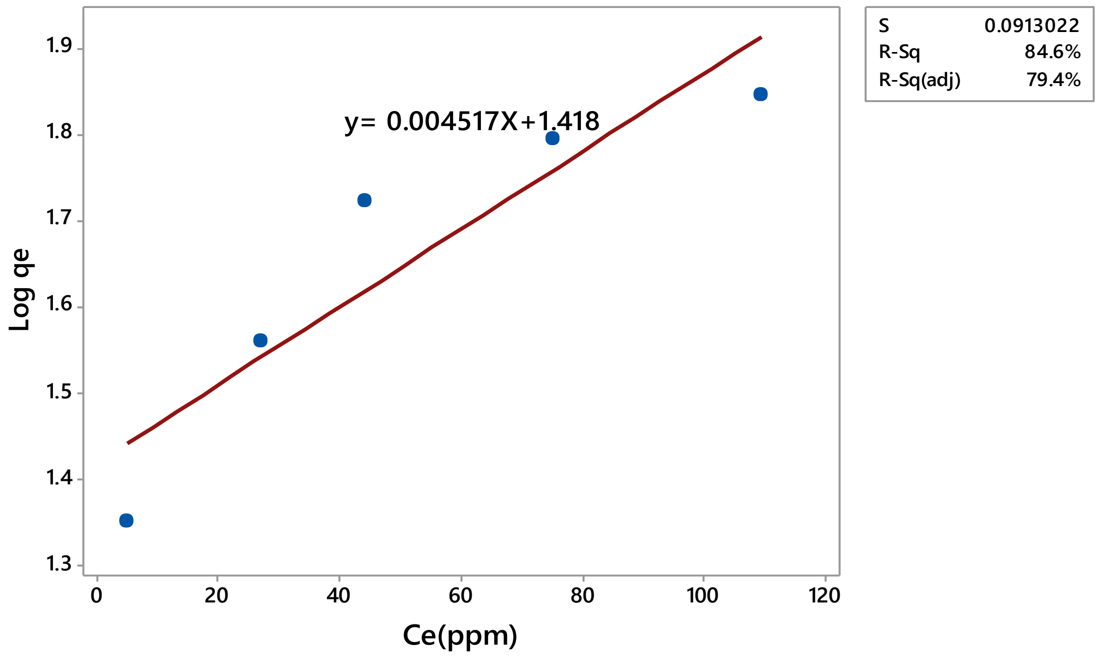

Figure 15: Freundlich isotherm for lead ion removal from aqueous solution

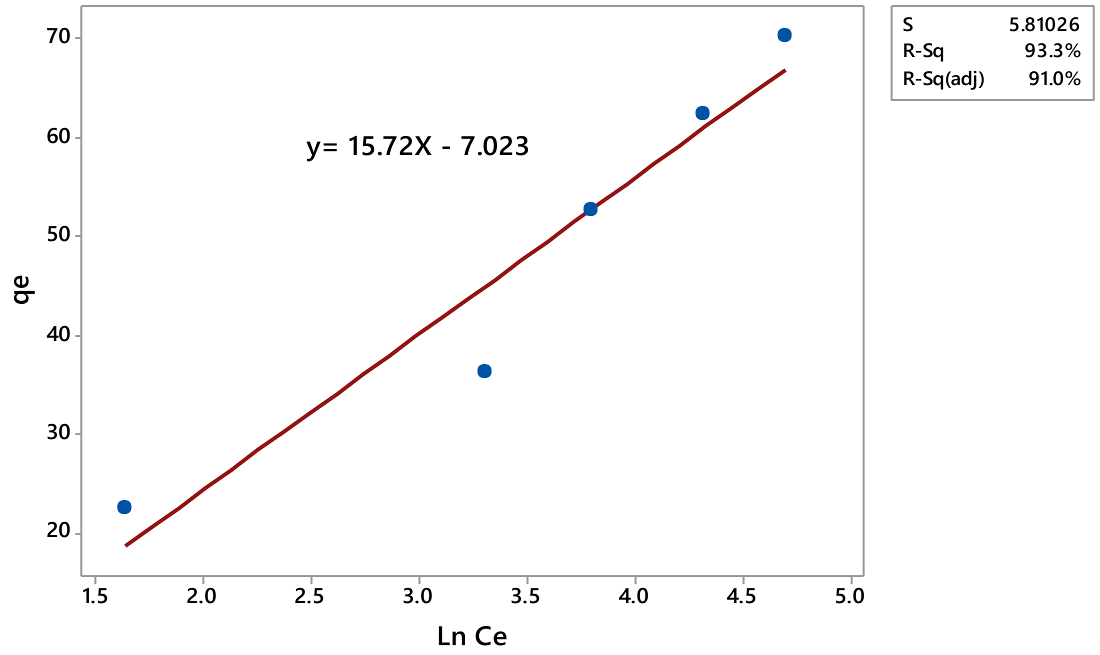

Figure 16: Temkin isotherm representation of lead ion removal from aqueous

The plot of *q*e versus ln *C*e is reveals t the validity of Temkin isotherm and determine the equilibrium constants.B_1 and K_T. K_T is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption. As seen on the graph below the R^2 values obtained are almost same with those obtained from freundlich isotherm. It can be concluded that the adsorption process followed all the adsorption isotherms but best fits to the Langmuir isotherm model. The values of Langmuir, Freundlich and Temkin isotherm model constants and correlation coefficients for adsorption of lead ion were found to be as follollws.

Table 5: Isotherm parameters of three isotherm models

Isotherm Model	Correlation coefficient (R^2)	Isotherm Parameters	Estimated Values
Langmuir	0.965	Q_o(mg/g)	3.457
		K_L (L/mg)	0.0415
Freundlich	0.846	K_f	10.50
		N	2.41
Temkin	0.933	A_T(L/g)	-33.87
		B(J/mol)	16.235

The Plot of adsorption capacity of GInP versus initial metal concentration GInP at exposure time = 55min , Adsorbent dosage= 0.2, pH = 6 in 100 ml of metal ion solution, agitation speed = 200 rpm, particle size 80nm and at room temprature reveals the synthesized nano particle has promising adsorption capacity.

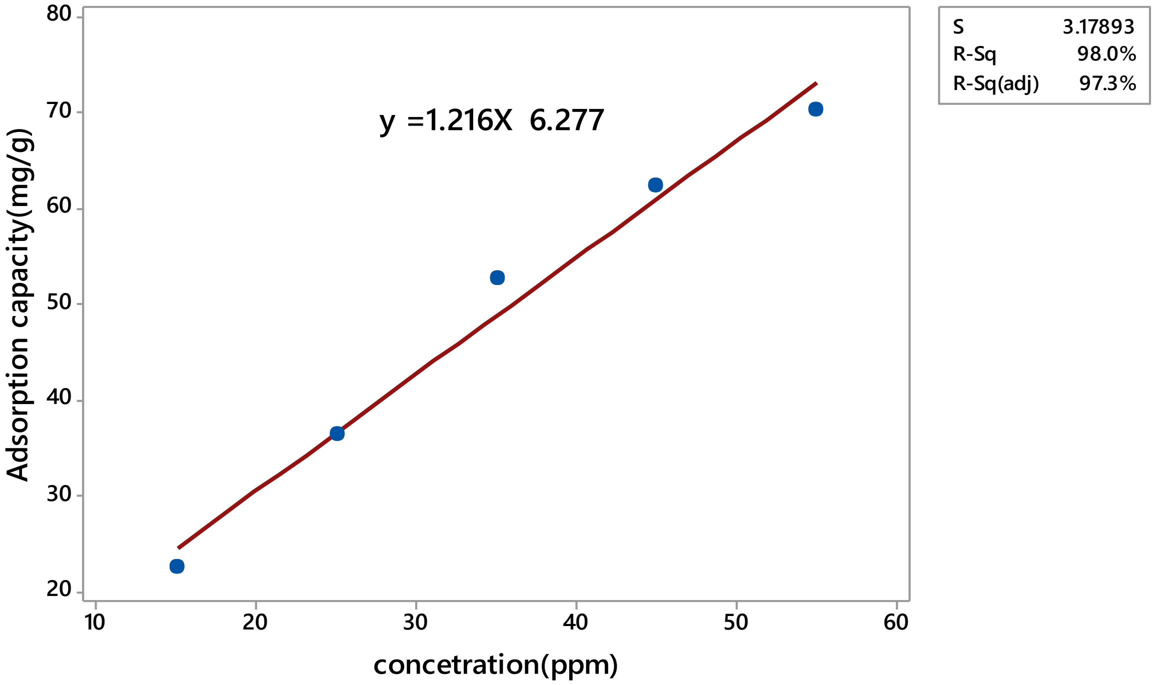

Figure 17: Plot of adsorption capacity of GInP versus initial lead concentration

4.8. Kinetics study

Aiming to study the adsorption kinetics of heavy lead ions different kinetic model were considered and the kinetics parameters such as The kinetic rate constants, adsorption capacities and correlation coefficient were calculated from the slope and intercept of their corresponding curves. The equations that describe the pseudo first order, second order and intra particle diffusion models are given in the following linear form:

Pseudo first order model

$$log(\mathrm{qe} - \mathrm{q}_t = \log \mathrm{q}_e - \frac{\mathrm{K}_t}{2.303} \qquad (4.6)$$

Pseudo second order model

$$\frac{t}{q_t} = \frac{1}{\mathrm{K}^2 \mathrm{qe}^2} + \frac{1}{qe}\mathrm{t} \tag{4.7}$$

Intra particle diffusion

$$\mathrm{q} = \mathrm{Ki}\ (\mathrm{t})^{0.5} + \mathrm{C} \tag{4.8}$$

Table 6: Kinetic parameters' values

Kinetic model	Parameters	Values	Correlation coefficient(R2)
Pseudo first order	Qo (mg/g)	54.20	0.975
	K_1 min-1	-0.017	
Pseudo second order	Qo (mg/g)	63.25	0.94
	K_2 g/(mg*min)	0.002	
Intra particle diffusion	Ki mg g-1 min$^{1/2}$	4.161	0.935
	C	-3.859	

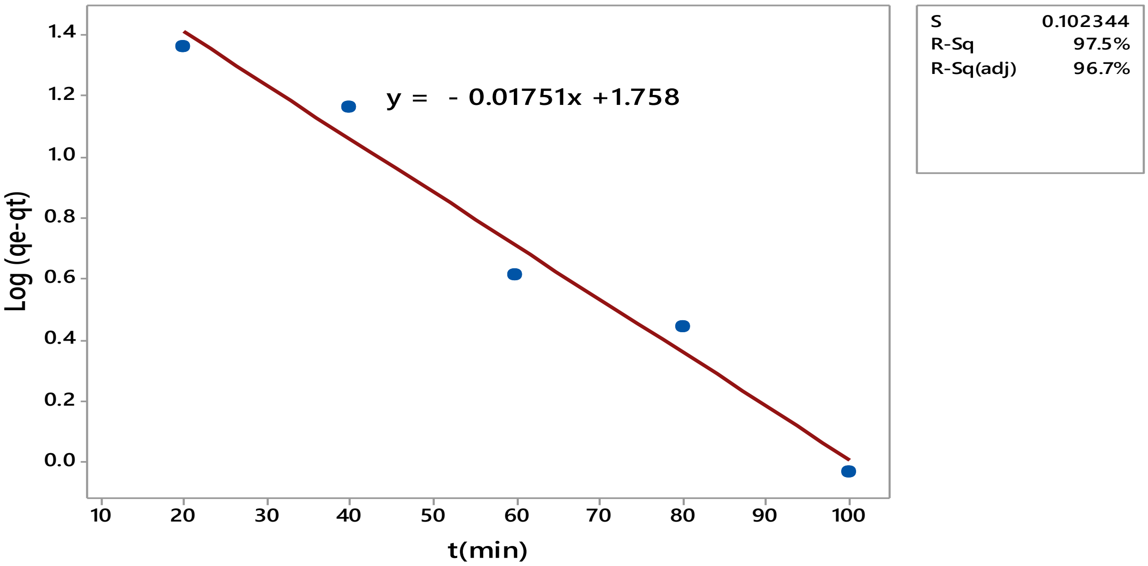

Figure 18: Plot of pseudo first order model

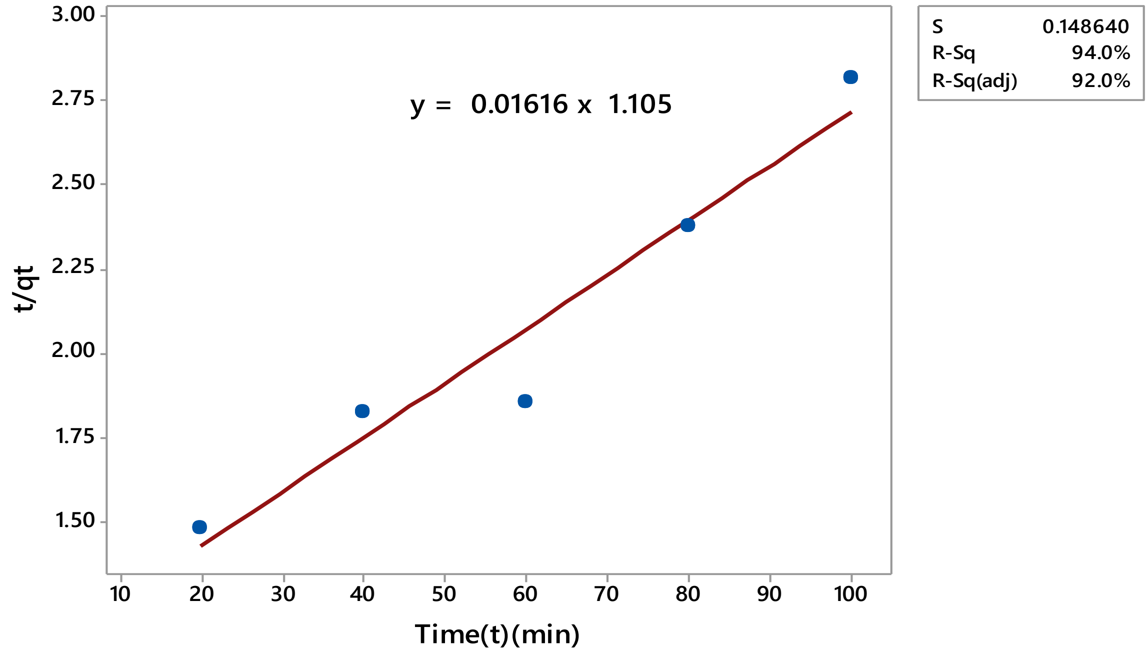

Figure 19: plot of pseudo second order model

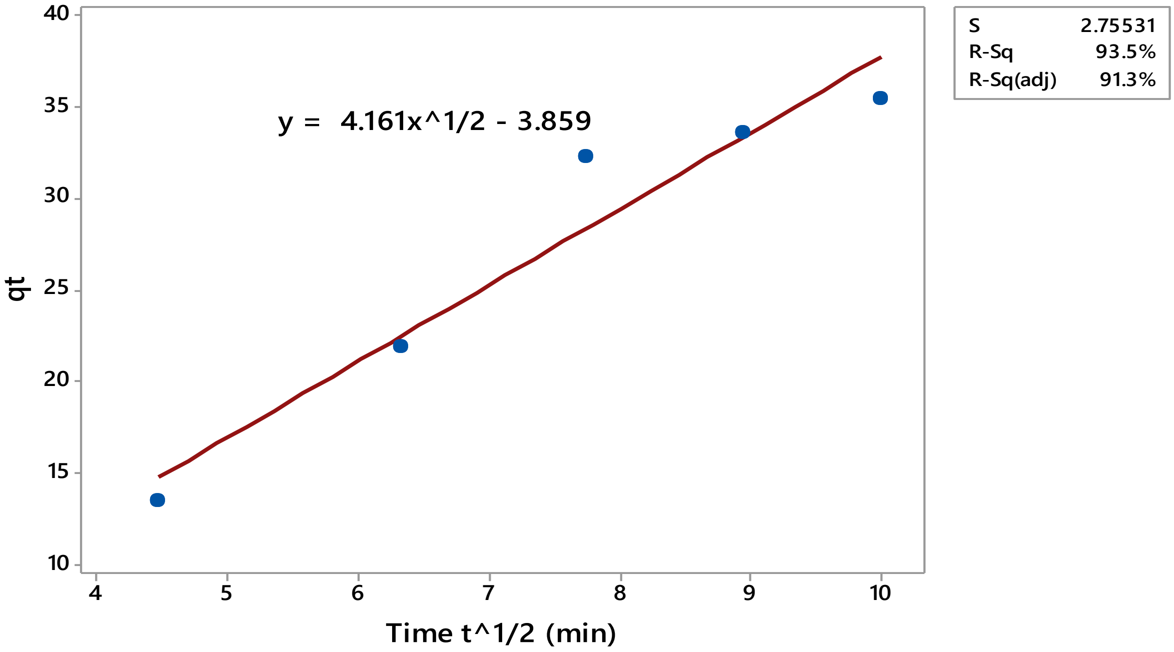

Figure 20: Intra particle diffusion kinetic model

4.9. Thermodynamic results

The Gibbs energy free (ΔG), enthalpy change and entropy change were determined using the adsorption equilibrium constants of the best fit model which was Langimur isotherm model. The values of the Langimur isotherm constants were calculated at four different temperatures

Table 7: Thermodynamic parameters

Temperature(k)	Langmuir isotherm K_L values	Gibbs free energy (-△G^0)(Kjoule/mol)	Enthalpy change(△H)(KJ/mol)	Entropy change(△S) (KJ/mol)
293	54.46	9.599	38.493	-98.430
298	41.50	9.230		
303	31.54	8.694		
308	16.14	8.134		

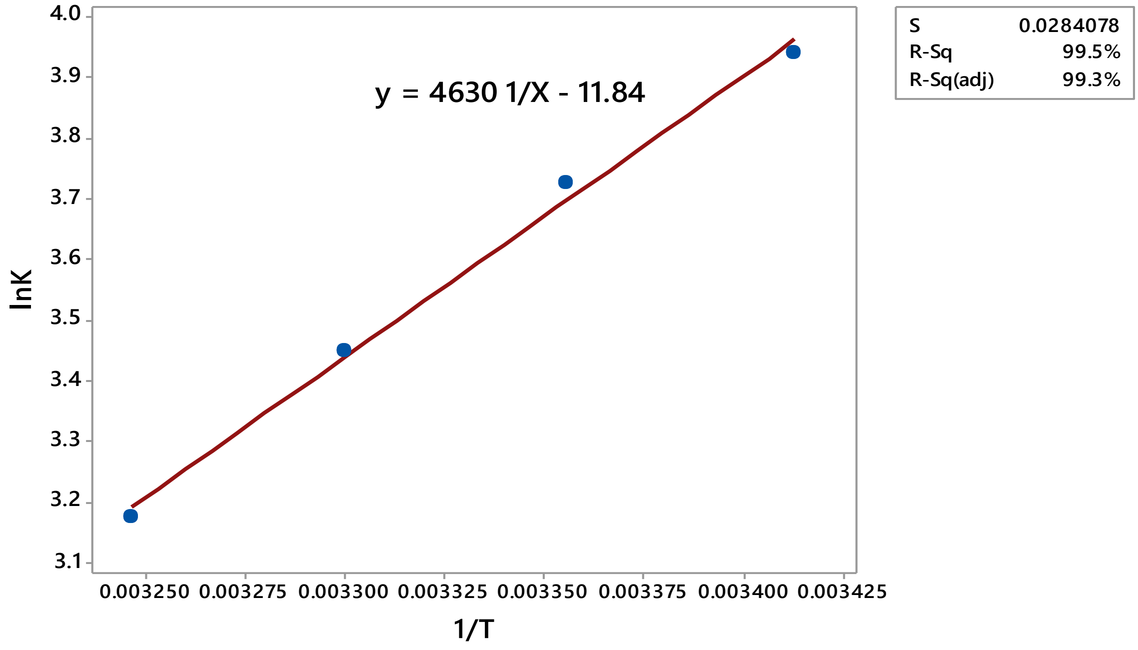

Figure 21: Vant Hoff's plot for removal of lead ion by GInP

4.10. Desorption studies

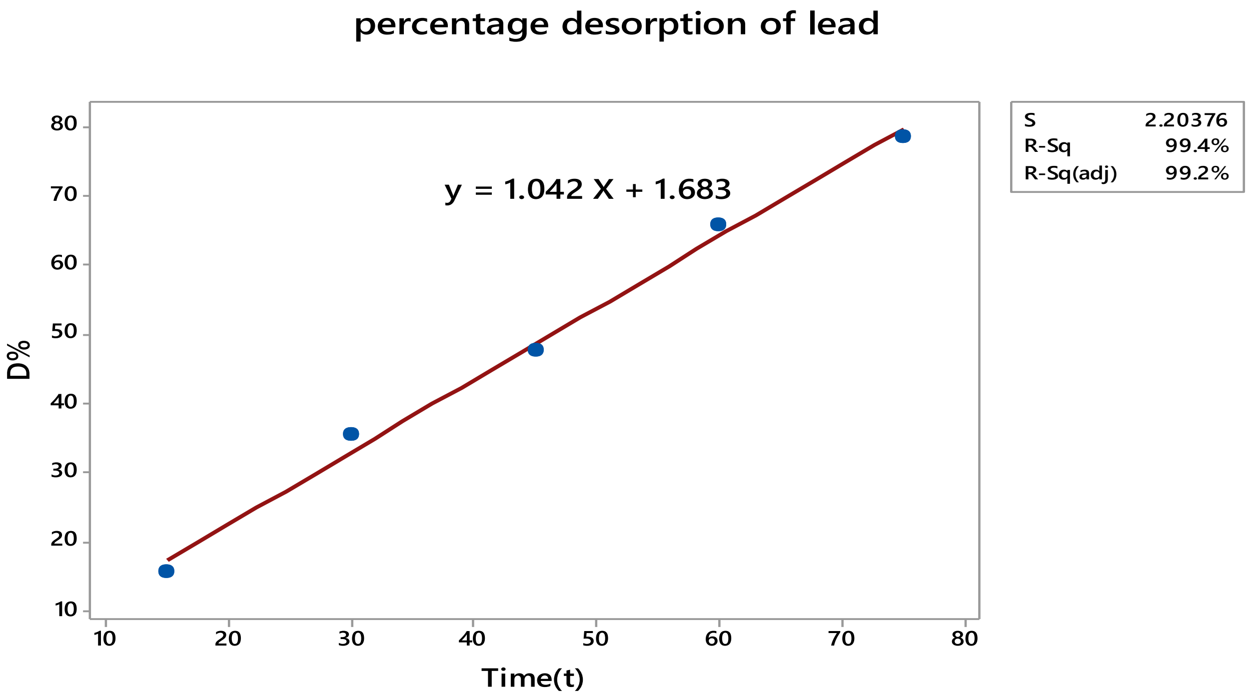

Figure 22: Lead desorption plot

4.11. Design expert analysis of the adsorption

In Figure 23; the normal probability plot revealed the data are normally distributed and the residual versus fit indicated that there was linear relationship between the predictors and the response (%lead removal) and also the residual versus order implied that the data were randomized. General the residual plots supported that the model met the requirements for model adequacy.

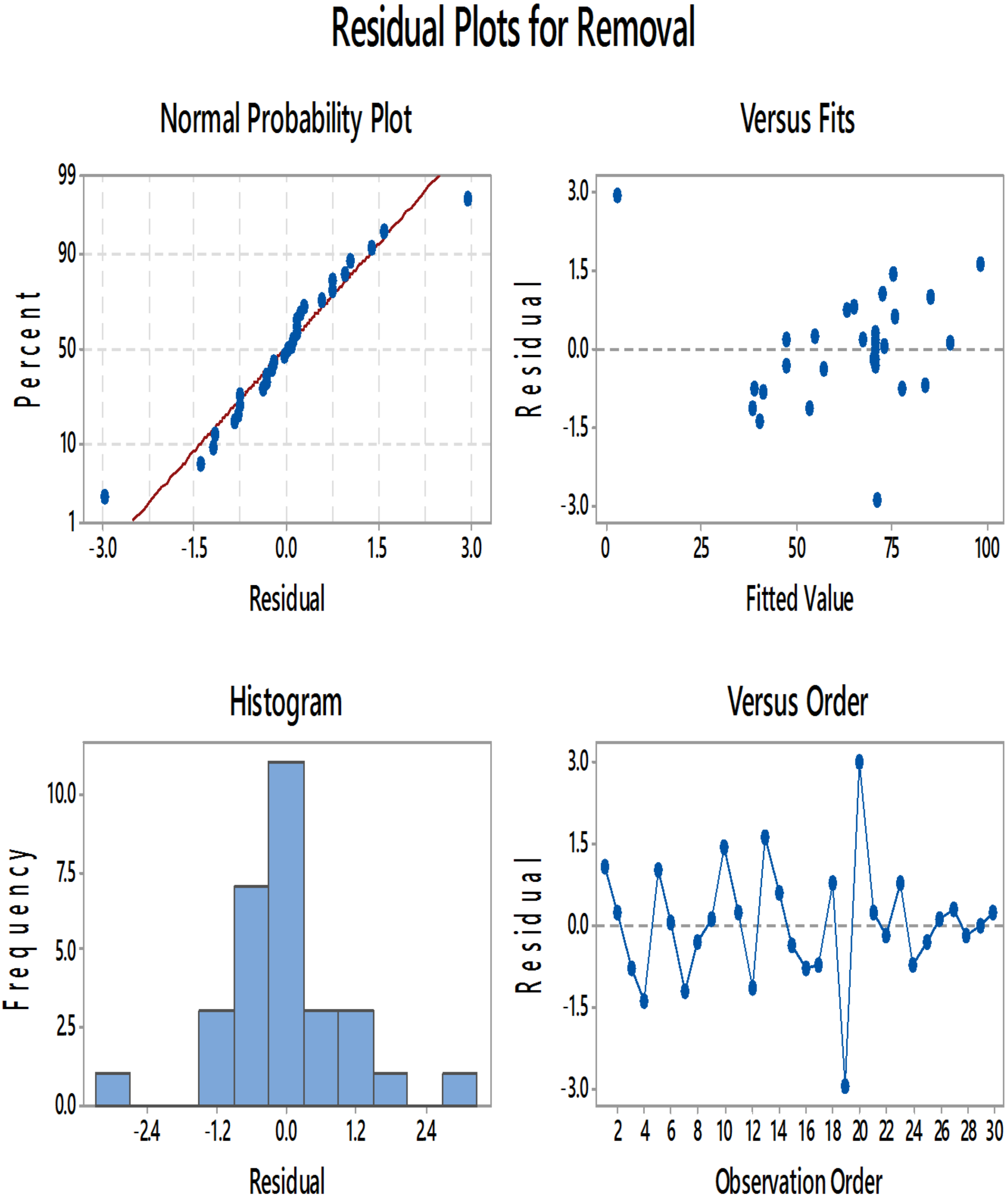

Figure 23: Residual plot for lead removal using GInP

Table 8: ANOVA plot of lead removal by GInP

Source	Sum of squares	DF	Mean Square	F Value	Prob > F
Model	9982.49	14	713.03	276.65	< 0.0001
A	325.11	1	325.11	126.14	< 0.0001
B	106.22	1	106.22	41.21	< 0.0001
C	662.24	1	662.24	256.94	< 0.0001
D	6108.59	1	6108.59	2370.11	< 0.0001
A2	97.61	1	97.61	37.87	< 0.0001
B2	0.92	1	0.92	0.36	0.5604
C2	0.16	1	0.16	0.063	0.8062
D2	393.07	1	393.07	152.51	< 0.0001
AB	14.58	1	14.58	5.66	0.0334
AC	50.52	1	50.52	19.60	0.0007
AD	1.87	1	1.87	0.73	0.4097
BC	100.65	1	100.65	39.05	< 0.0001
BD	64.75	1	64.75	25.12	0.0002
CD	38.84	1	38.84	15.07	0.0019
Residual	33.51	13	2.58		
Lack of Fit	43.24	8	5.405	3.02	0.0572

%Removal (Actual) = +72.44 +3.93 * A +3.18 * B -5.25 * C -17.06* D-2.02* A2 +0.20 * B2 +0.18 * C2 -8.94 * D2 -1.05* A * B -1.78* A * C +0.38* A * D -2.51* B * C -2.2 * B * D +1.56 * C * D

Table 9: Model adequacy check parameters

	Model	Adequacy check	
Std. Dev.	1.61	R-Squared	0.9967
Mean	63.97	Adj R-Squared	0.9931
C.V.	2.51	Pred R-Squared	0.9621
PRESS	379.33	Adeq Precision	78.905

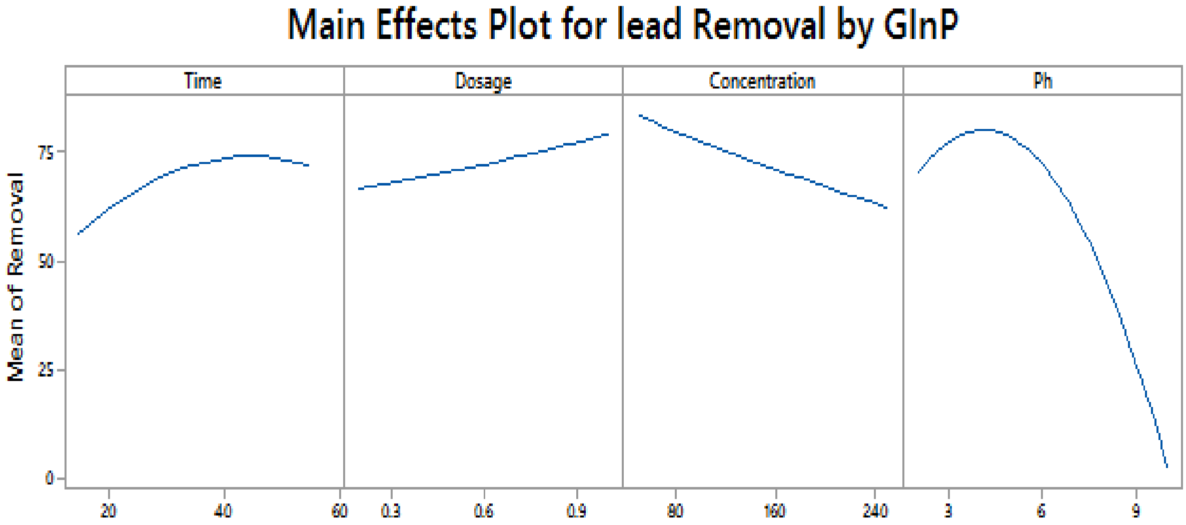

Figure 24: Main effects plot lead removal by GInP

4.12. Single and interaction

A maximum and minimum percentage removal of 70.30% and 55.00% was observed at exposure time equals to 55 and 15 min respectively, holding the remaining constant values of 0.6, 150 and 6 for dosage, concentration and pH respectively. The percentage removal of metals increased with increasing adsorbent dose. Minimum percent removal 77.10% was obtained at 1.0g adsorbent dose and maximum removal of 65.90% was at 0.2 g. In contrary the percentage removal of lead decreased with increasing initial metal ion concentration. Maximum removal of 83.40 % occurred at 50 ppm concentration and minimum removal of 57.36% was obtained at 200 mg/l. on the other hand the removal maximum (80.70%) lead removal was observed at pH of 4 and the minimum(10%) was observed at pH of 10.

4.13. Interaction effect

4.13.1. Exposure time versus Adsorbent dose

As exposure time increases the removal efficiency in all the lnes(pH values) increases but at different rate the values tend to converge and decrease as the exposure time exceeds 55 min and this indicates that the the two factores have interaction effect and since the p- value was found to be less than the α value their interaction effect is significant.

4.13.2. Exposure time versus concentration

As exposure time increases the lines for the three levels of dosage fan out(the removal efficiency) increases but at different rates. This indicates the tow factores have interaction effects.

4.13.3. Exposure time versus pH

The lines are nearly parallel revealing there is no interaction effect between the two factores.

4.13.4. Dosage versus concentration

As dosage increase the three line fan out that is the removal efficiency increases at different rates.and this implies that there is interaction effect between the two.

4.13.5. Dosage versus pH

As it can be seen clearly from the interaction plot matrix the parallel lines (with the exception when pH is 2) reveal that there is no interaction effect.

4.13.6. Concentration versus pH

As concentraton decreases with exception of pH of 2 the removal efficiency increases. This reveals there is an interaction effect between concentration and pH.

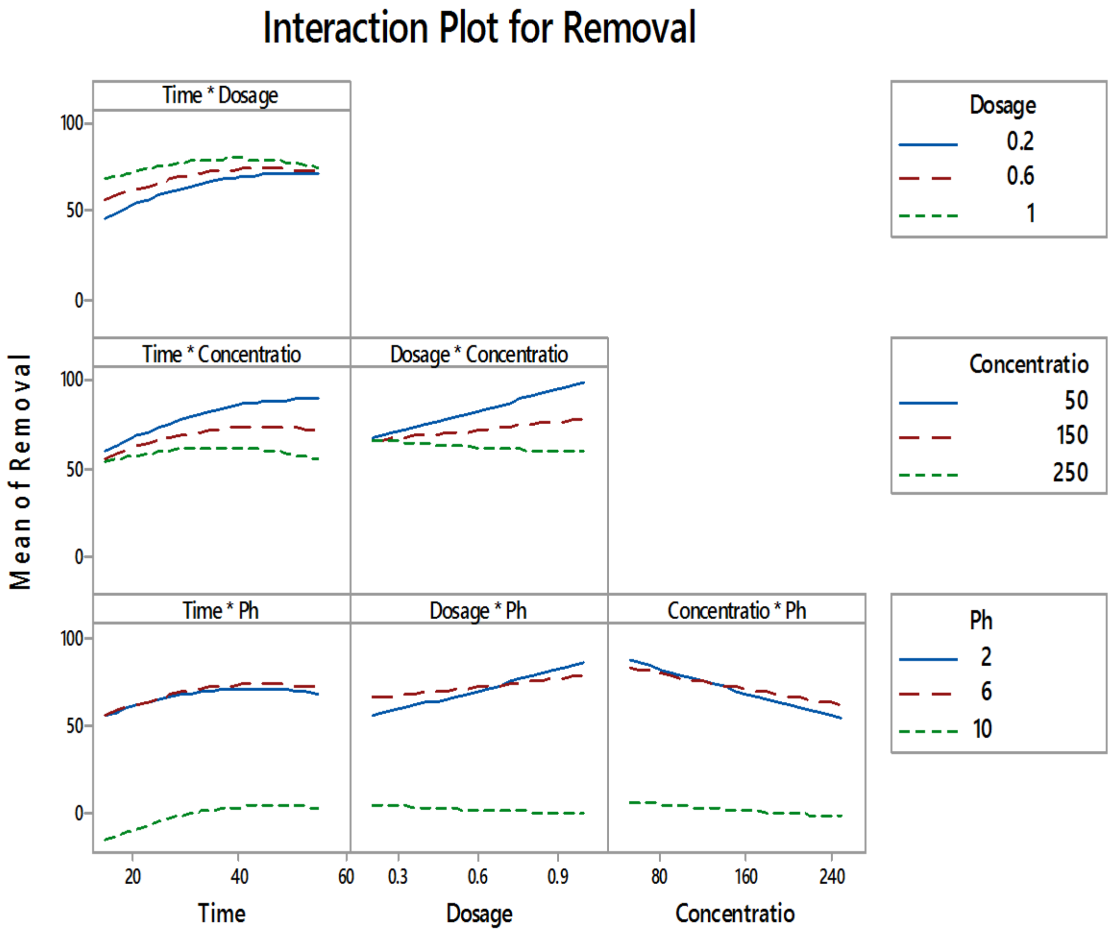

Figure 25: Interaction plot for lead removal

4.13.7.Optimal point determination

The constraints were taken in to account to determine the possible optimal points using Minitab response optimizer technic. Holding the concertation at three predetermined values and letting the remain three factors to vary the author was came across three optimum values for the response, among which one was the best optimal point with 89.13% lead removal.

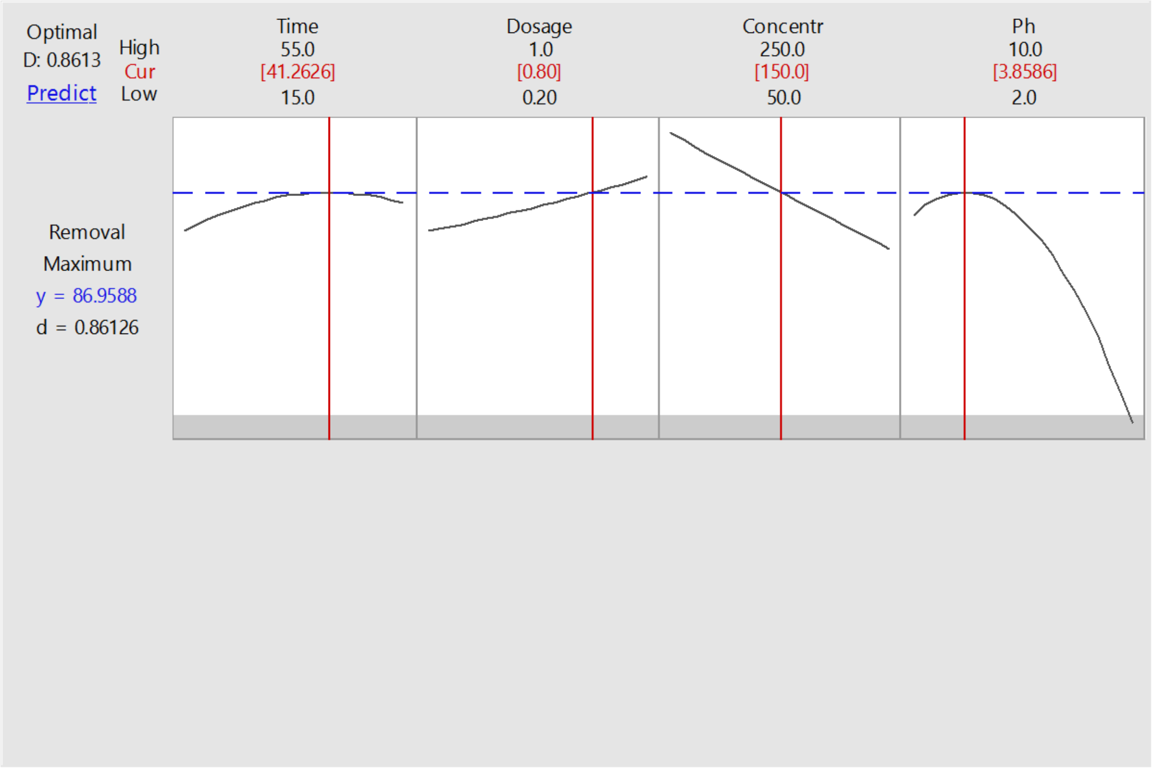

Figure 26: Response optimizer plot lead removal by GInP

CHAPTER FIVE

5. Conclusion and Recommendation

5.1. Conclusion

The study of Lead ion removal from aqueous solution using greenly synthesized iron nano particle (GInP) has shown GInP was a promising material for heavy metal removal particularly lead ion. A batch experiment to study the effect of exposure time, dosage, concentration and pH using central composite design with the help of minitab 17. Maximum removal percentage (96.75) was found at 0.8g, 100 ppm, 4 and 45min of dosage, concentration, pH, and exposure time respectively. The kinetic study reveals that the adsorption process was endothermic with positive enthalpy values and negative free Gibbs energy values. The Removal efficiency GInP increased with increase in temperature. The removal process was analyzed with Langmuir, Freundlich and Temkin adsorption isotherm models. Langmuir and Temkin model fitted very well to the data in concentration 50-250 ppm with correlation coefficient (R^2) value 0.965 and 0.933 respectively. Kinetic analysis of the removal process was carried out via pseudo first order, pseudo second order and intraparticle diffusion. The pseudo first order equation appeared to be the best fitting model than both second order and intra particle diffusion with highest correlation coefficient value of 0.975. It can be confirmed that this type of GInP material is a sustainable adsorbent that can effectively remove lead from aqueous solution. The final important point that could be made out of this research is because of the fast reaction kinetics and high Pb^{2+} removal capacity, GInP has the potential to become an effective remedial agent for the removal of lead ions from aqueous solution.

5.2. Recommendation

- Greenly synthesized iron nano particle is one of the most extensively studied and applied engineered nanomaterials for environmental remediation. Therefore further study should be conducted on the fundamental properties of GInPparticularly, its structure, surface composition,
- The study of lead and other heavy metals removal efficacy of GInPusing industrial effluents should be the way forward.

- More relevant detailed-studies should be carried out on this novel material so that its properties are understood better.
- The chemistry of the iron nano particle using eucalyptus leaf extract should be studied in detail.

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Appendices

Appendix A Isotherm value parameters

Initial lead concentration(mg/L)	Final concentration (Ce)	%Removal	Qe	Log C_e	Log q_e	Ln C_e	C_e/q_e	lnq_e
50	5.140	89.720	22.43	0.710	1.350	1.637	0.229	3.110
100	27.280	72.720	36.36	1.435	1.560	3.306	0.750	3.593
150	44.511	70.326	52.744	1.648	1.722	3.954	0.843	3.965
200	75.250	62.375	62.375	1.876	1.795	4.082	1.206	4.133
250	109.600	56.160	70.2	2.039	1.844	4.684	1.561	4.251

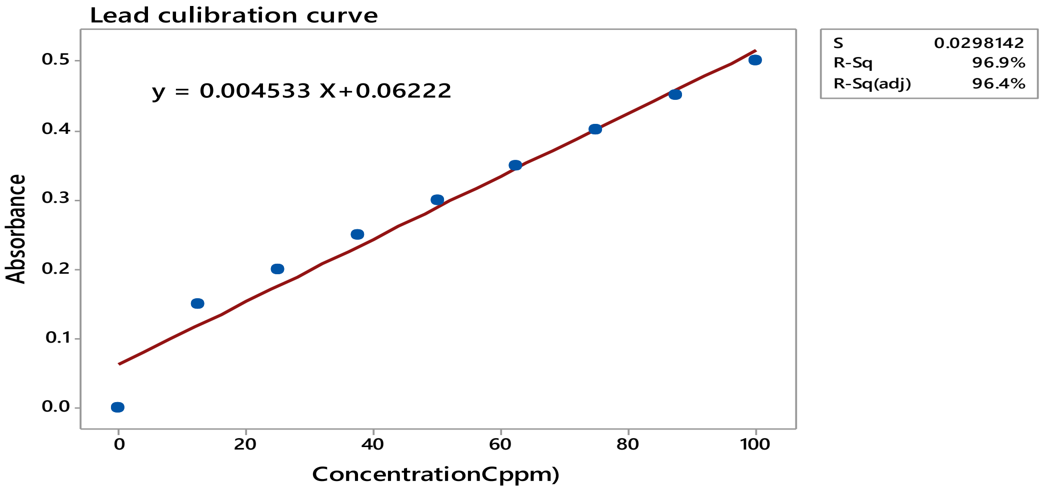
Appendix B: Kinetic value parameters

Time(t)(min)	Exposure time $t^{\wedge 1/2}$ (min)	C_o	C_{tf}	q_e	Q_t	t/q_t	q_e -q_t	Log (q_e-q_t)	t/q_e	$q_e^{\wedge 2}$
20	4.472	100	73.047	36.36	13.476	1.480	22.883	1.359	0.550	1322.05
40	6.324	100	56.191	36.36	21.904	1.826	14.455	1.160	1.100	1322.05
60	7.745	100	35.403	36.36	32.298	1.857	4.061	0.608	1.650	1322.05
80	8.944	100	17.011	36.36	33.589	2.381	2.771	0.442	2.200	1322.05
100	10.	100	13.865	36.36	35.432	2.822	0.928	-0.032	2.750	1322.05

Appendix C: Correlation table for FTIR results (Mystrioti et al 2015)

Ginp peaks(cm-1)	Functional Groups	Compounds Indicated
3589.00	O-H(H-bonded) stretch	Polyphenols
2050.00	C=C asymmetric stretch	Alkenes
1793.70	C=O stretch	Carbonyl Compounds
1654.00	C=O (H-bonded)	Carbonyl Compounds
1651.29	C=C(Symmetric)	Alkenes
1458.62	CH_2 and CH_3 deformation	Alkenes
1380.44	O-H bending (in plane)	Polyphenols
1319.01	O-C stretch	Ethers
1109.58	C-O stretch	Carbonyl Compounds
1042.57	C-O stretch	Carbonyl Compounds
983.93	C-O stretch	Carbonyl Compounds
947.63	=C-H and =CH_2 bending	Aromatics
877.82	=C-H and =CH_2 bending	Aromatics
833.14	=C-H and =CH_2 bending	Aromatics

Appendix D: Lead calibration curve

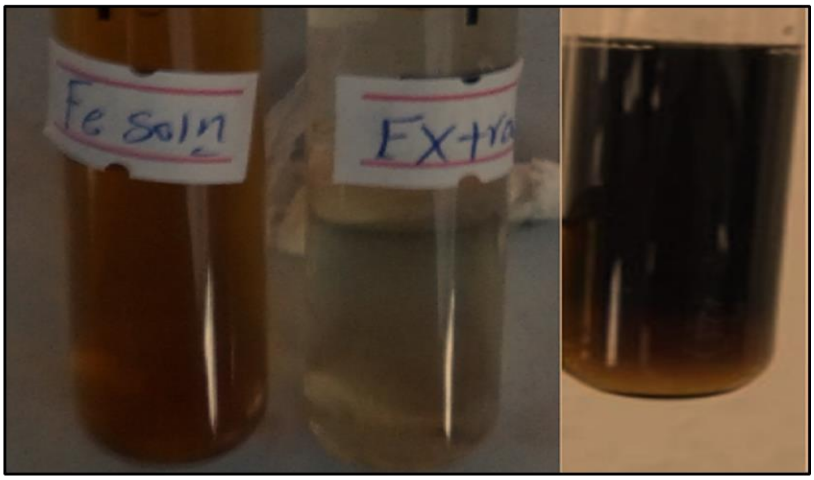


Appendix E: CCD led removal experiment results

			Factor 1	Factor 2	Factor 3	Factor 4	Response	
Std	Run	Block	A:Time	B: Dos.	C:Conc.	D:pH	%Removal (Actual)	%Removal (Predicted)
1	10	Block 1	25.00	0.80	200.00	4.00	76.9	74.909
2	9	Block 1	25.00	0.80	100.00	4.00	90.7	89.994
3	4	Block 1	25.00	0.40	200.00	8.00	38.9	39.587
4	2	Block 1	25.00	0.40	200.00	4.00	67.8	67.027
5	8	Block 1	45.00	0.40	200.00	8.00	47.1	47.010
6	1	Block 1	25.00	0.40	100.00	4.00	73.7	72.079
7	3	Block 1	25.00	0.40	100.00	8.00	38.3	38.407
8	7	Block 1	45.00	0.40	100.00	8.00	52.2	52.937
9	6	Block 1	45.00	0.40	200.00	4.00	73.3	72.567
10	5	Block 1	45.00	0.40	100.00	4.00	86.4	84.727
11	11	Block 2	25.00	0.80	100.00	8.00	47.6	47.079
12	19	Block 2	35.00	0.60	150.00	2.00	68.3	72.434
13	18	Block 2	35.00	0.60	250.00	6.00	63.9	64.192
14	13	Block 2	45.00	0.80	100.00	4.00	96.7	98.059
15	14	Block 2	45.00	0.80	200.00	4.00	76.8	75.867
16	20	Block 2	35.00	0.60	150.00	10.00	6	3.629
17	16	Block 2	45.00	0.80	200.00	8.00	40.7	41.067
18	12	Block 2	25.00	0.80	200.00	8.00	37.4	38.227
19	17	Block 2	35.00	0.60	50.00	6.00	83.4	85.204
20	15	Block 2	45.00	0.80	100.00	8.00	57.1	57.027
21	25	Block 3	35.00	0.60	150.00	6.00	70.4	70.7
22	26	Block 3	35.00	0.60	150.00	6.00	70.8	70.7
23	27	Block 3	35.00	0.60	150.00	6.00	71	70.7
24	23	Block 3	35.00	0.20	150.00	6.00	65.9	66.562
25	28	Block 3	35.00	0.60	150.00	6.00	70.5	70.7
26	30	Block 3	35.00	0.60	150.00	6.00	70.9	70.7
27	24	Block 3	35.00	1.00	150.00	6.00	77.1	78.534
28	21	Block 3	15.00	0.60	150.00	6.00	55	55.954
29	22	Block 3	55.00	0.60	150.00	6.00	70.3	71.442
30	29	Block 3	35.00	0.60	150.00	6.00	70.7	70.7

Appendix F: Images before and after the GInP synthesis

picture 1: Iron solution and *Eucalyptus globulus* leaf extract from left to right



picture2: Iron solution *Eucalyptus globulus* leaf extract and iron nano particle from left to right respectively