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SYNTHESIS AND CHARACTERIZATION OF BAMBOO SUPPORTED ZEROVALENT IRON FOR CHROMIUM ADSORPTION

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DECLARATION

I declare that this thesis for the M.Sc. Degree at Addis Ababa University, hereby submitted by me, is my original work and has not previously been submitted for the degree at this or any other university, and that all resources of materials used in this thesis have been duly acknowledged.

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List of Abbreviations and Acronyms

Cr (VI)	Hexavalent chromium
WHO	World Health Organization
NZVI	Nano Zero-Valent Iron
FeNPs	Iron nanoparticles
MCL	Maximum concentration limit
PAC	Polyaluminium chloride
XRD	X-ray diffraction
FTIR	Fourier transforms infrared spectra
NPs	Nano particle
Pzc	point of Zero charge
SEM	Scanning electron microscope
CI	Confidence interval
MB	Methylene blue
MO	Methyl orange
TGA	Thermo gravimetric analysis
SMNPs	Synthesized spherical magnetic nanoparticles
NZVI-AB	Bamboo supported avocado seed extract based nano zerovalent iron

Abstract

Chromium is an important industrial metal used in various production processes. Remediation of Chromium contaminated sites present both technological and economic challenges, as conventional methods are often too expensive and difficult to operate. Green synthesis provides advancement over chemical and physical method as it is cost effective, environment friendly, easily scaled up for large scale synthesis. In this study, bamboo supported Zero-valent iron (Fe^0) nanoparticles were synthesized, characterized, and were tested for adsorption of Cr (VI). Fe^0 nanoparticles were synthesized by the reduction of ferric chloride with avocado seed extract polyphenol and were characterized by UV–Visible spectro- photometer, FTIR (Fourier transform infrared) spectroscopy and XRD (X-ray diffraction). Batch experiments were performed using various concentrations of Fe^0 nanoparticles for reduction of Cr (VI). The synthesized nZVI-bamboo was subsequently applied to the adsorption of hexavalent chromium from aqueous solution. The adsorption of chromium was investigated under various experimental conditions such as pH, initial concentration of chromium and adsorbent dosage. The results showed that the synthesized nZVI-AB adsorbent was able to perform the maximum adsorption capacity of 18.913 mg/g. and at a concentration of 20 mg/L, pH of 3 and 1 g of nZVI bamboo adsorbent concentration which resulted in 92.38% and optimum removal percentage. The equilibrium data was best represented by Langmuir isotherm.

Keywords: Nanozerovalent iron, Green synthesis, polyphenol, FTIR and XRD.

1. Introduction

1.1 Background

Heavy metals are toxic substances and create hazards to the environment, because they are non-biodegradable and toxic at trace concentrations. Metal toxicity poses many human diseases, e.g., cancer, nervous disorder, organ failure, growth reduction and abdominal pain (Lee et al. 2012). In the environment, metal concentrations are found due to discharge of industrial effluents from many industries such as tanneries, textile, pulp and paper, chlore-alkali, electroplating, fertilizers, dying, battery manufacturing and mining operations which create metal toxicity (Manzoor et al. 2013). One of the most important and toxic heavy metals in wastewater is Chromium. Cr (VI) is released from different industrial operations, including metallurgy, leather tanning, paint, textile industries, chemical manufacturing, pulp production, ore and petroleum refining, metal corrosion, electroplating and the manufacture of products for corrosion protection. Chromium (VI) has been released to the environment via leakage, poor storage or improper disposal practices. Over the decades, extensive use of chromium in tanning industries have resulted in chromium contaminated soil and ground water at production sites which pose a serious threat to human health, fish and other aquatic biodiversity.

According to the World Health Organization (WHO, 2008) drinking water guidelines, the maximum recommended limit for total chromium is 0.05 mg/L, whereas, according to BIS (Bureau of Indian Standards) the maximum acceptable limit for Cr (VI) in drinking water is 0.05 mg/L. The recommended limit of Cr (VI) in waste water is only 0.05 mg/Chromium (Cr), which is one of the most toxic and important heavy metals usually found in wastewater due to industrial activities of tanning and electroplating industries. In nature, chromium occurs either as Cr (VI) or as Cr (III). In aqueous solution most commonly formed as Cr (VI) or Cr (III). These two oxidation states are drastically different in charge, physicochemical properties as well as chemical and biochemical reactivity.

During the last two decades, there has been important interest in using Nano Zero-Valent Iron (NZVI) particles as a Cr (VI) reducing agent. According to researcher amongst various technologies which are available to remove heavy metals from water, use of NZVI particles is reported as an ideal technique for in-situ remediation due to its large active surface area and high heavy metal adsorption capacity. Under oxidizing condition, chromium is present as Cr (VI) and has the highest mobility whereas chromium early precipitation as Cr (III) oxides has limited solubility makes chromium relatively immobile. In recent years, the use of Nano Zero-Valent Iron (NZVI) particles has been gaining increasing interest in the area of environmental remediation. Due to its larger specific surface area, higher surface reactivity, and unique catalytic activity.

Various studies have been reported on the use of NZVI particles for removing Cr (VI) in aqueous solutions. The mechanism of Cr (VI) removal from aqueous solutions by NZVI particles consists of the reduction, complexation, adsorption, precipitation or co- precipitation. Chromium is widely used in a variety of industrial processes such as metal electroplating, leather tanning, manufacturing of products for corrosion protection and wood preservation. The contamination of groundwater, surface waters and soils by hexavalent Chromium, due to accidents or inefficient waste management practices related with the above industrial activities, has become a high priority environmental problem. Hexavalent Chromium presents high toxicity and can cause severe health problems due to its strong oxidizing properties. On the contrary, trivalent Chromium (Cr (III)) is not toxic and presents lower water solubility and mobility than Cr (VI). Furthermore, Cr (III) is referred to be an essential micro-nutrient for many living organisms (Ghejou 2011). Consequently the chemical reduction of Cr (VI) to Cr (III) is an effective method for Cr (VI) remediation.

Nano scale zero valent iron has been studied extensively during the last 15 years as a remarkable reductant for a variety of pollutants, including Cr (VI). Metallic iron, at Nano scale, combines many properties such as, small particle size, large specific surface area and high surface reactivity. As a consequence, it can reduce the pollutants at a rate several orders of magnitude higher compared to the rates observed with granular ZVI particles (Ghejou, 2011). Also the

colloidal suspensions of nZVI can be injected directly inside the hotspot area of contaminated aquifer, a technique which is considered to ensure lower costs and shorter remediation time compared to other remediation options, such as pump and treat methods or permeable reactive barriers (He, 2009).

Nanotechnology is the ability to measure, see, manipulate and manufacture things on an atomic or molecular scale, usually between one and 100 nanometers. These tiny products also have a large surface area to volume ratio, which is their most important feature responsible for the wide spread use of nanomaterial in mechanics, optics, electronics, biotechnology, microbiology, environmental remediation, medicine, numerous engineering fields and material science.

Different protocols have been designed for the production of metallic nanoparticles. Currently, two main approaches are used to synthesize nanoparticles, referred to as the top-down and bottom-up approaches. Briefly, in the top-down approach, nanoparticles are produced by the size reduction of bulk material by lithographic techniques and by mechanical techniques such as machining and grinding, etc., while, in bottom-up approach, small building blocks are assembled into a larger structure, e.g., chemical synthesis. However, the most acceptable and effective approach for nanoparticle preparation is the bottom-up approach, where a nanoparticle is "grown" from simpler molecules known as reaction precursors. In this way, it is likely possible to control the size and shape of the nanoparticle depending on the subsequent application through variation in precursor concentrations and reaction conditions (temperature, pH, etc.)

Physical and chemical methods are being used extensively for production of metal and metal oxide nanoparticles. However, this production requires the use of very reactive and toxic reducing agents, nano materials prepared using sodium borohydride and hydrazine hydrate cause undesired detrimental impacts on the environment, plant and animal life it supports. Researchers continue efforts to develop facile, effective and reliable green chemistry processes for the production of nanomaterial. Various organisms act as clean, eco-friendly and sustainable precursors to produce the stable and well functionalized nanoparticles. These may include bacteria, *actinomycetes*, fungi, yeast, viruses, etc. Thus, it is vitally important to explore a more

reliable and sustainable process for the synthesis of nanomaterials. Economic viability, environmental sustainability, and social adaptability as well as the availability of local resources are a matter of concern in the production of nanomaterials. The green nanotechnology-based production processes operate under green conditions without the intervention of toxic chemicals. Many recent studies have indicated the potential of iron nanoparticles (NPs) for environmental remediation. Nano scale materials such as nano adsorbents, nano catalysts, Nano filtration, and nano biocides such as metal and metal oxide nanoparticles are currently being employed for remediation of water and wastewater pollutants. Among these metallic nanoparticles, iron nanoparticles (FeNPs) have promising advantages that can combat environmental pollution. The interest in nano scale zero-valent iron (nZVI) in environmental remediation is increasing due to the reactivity of nano-scale iron having a large surface area to volume ratio. The production of iron nanomaterials, such as metallic iron and oxide of iron via a more convenient greener route, is a great step forward in the development of nanomaterials.

At present, the search for low-cost and easily available adsorbents has led many researchers to explore more economic and efficient techniques of using the natural and synthetic materials as adsorbents. Among them, nanomaterial represents a promising application in a variety of fields due to the special properties (Jain et al., 2010). One of its properties is that most of the atoms of the nanoparticle are on the surface. The surface atoms are unsaturated and can therefore bind with other atoms, possess highly chemical activity and adsorption ability (Han et al, 2009). over the last few years, various synthetic methods have been developed to produce iron nanoparticles modify the nanoparticle surface properties and enhance the efficiency for field delivery and reactions.

Bamboo is a low cost agricultural waste material, readily available, and its composition with nZVI will improve some of its physicochemical properties and also serve as a means for conversion of the agricultural waste (bamboo) to economical use, through its application in the preparation of nano adsorbents. Moreover, bamboo supported nZVI overcome some of the disadvantages inherent existing in the use of nZVI which reduces its efficiency and usability, these are rapid oxidation, tendency of agglomeration into larger particles and the separation and

recovery of the fine particles after usage. Various chemical and physical methods have been used to produce Fe NPs, such as through the reaction of iron (II) or iron (III) salts with sodium borohydride (Wang et al., 2013), which generally require special equipment or high energy, thus they are expensive. Chemical substances that are toxic, corrosive and flammable, such as $NaBH_4$ or organic solvents are involved during this process, and can create environmental problems. Furthermore, the rapid agglomeration or reaction with the oxidisable media (e.g., dissolved oxygen or water) using these conventional methods could lead to the reduced reactivity and stability of these nanoparticles (Wang et al., 2013). Consequently, new processes have been devised in the green synthesis of Fe NPs using extracts of natural products in the last few years A promising approach to overcome this need is to harness the biological sources for synthesis of metal nanoparticles. Over the past several years, plants and their different products have come up as a low-cost, energy-efficient and non-toxic approach for synthesis of metal nanoparticles which is stable and can be used for large-scale production (Kumar et al., 2013; Machado et al., 2013).

Avocado seed extract is a large portion of the fruit with a phenolic content in which capable of reducing heavy metals due to its antioxidant and reducing agent activity (Salgado et al., 2008). The seed of avocado represents one of the under-utilized non-edible parts of the fruit which are usually discarded as residues it involves an important reduction in the production of wastes and the fact that the non-edible parts of many fruits concentrates high levels of valuable bioactive compounds, particularly natural antioxidants. Although the seed represents about 100 to 300 g/kg of the fruit which is a considerable percentage scientific research on the nutritional compositions, phyto-chemistry and biological effects of avocado seeds is still at the nascent stage. However, studies have shown that the seeds from avocado pear contain oil with considerable nutritional values. The oil content of the fruit depends upon its ecological origin and on the cultivator. The oil content of an avocado pear varies from species to species (Banji Adaramola et al., 2016).

1.1 Statement of the Problem

Zerovalent iron (ZVI) particles are inexpensive and environmentally friendly reducing agents that can be used to remediate many environmental contaminants. Introduction of ZVI to treat wastewater and a contaminated soil has become a prominent environmental technology in recent years. Due to their relatively large surface area and high reactivity, however, fine sized ZVI particles are unstable in aqueous solutions, which may present challenges to their environmental application (Zhang, 2003) and the application of nZVI works best under anaerobic conditions since it is otherwise quickly transformed to iron oxides under aerobic conditions. The large surface area of the nZVI is the strength of this technique as the degradation reaction occurs on the surface of the particles. Any modification to the surface such as oxidation would therefore affect the performance of the particles. Some of the major challenges identified with the use of nZVI are the rapid aggregation of the particles, passivation (quick oxidation by non-target compounds), and sorption to aquifer materials and rapid sedimentation that consequently limits the mobility of nanoparticles in the aquatic environment. This also makes long term storage of nano iron particles materials not feasible as they must be used soon after production unless they are stabilized on a support to inhibit oxidation nZVI also has the potential to treat recalcitrant pollutants such as chlorinated organic compounds, nitrates and hexavalent chromium. But the high reactivity of nZVI alone is not enough to make it an effective remediation agent, the Nano iron particles should also be able to form stable dispersions and migrate to contaminated plumes. These expected additional Properties are seen to be missing as the nZVI quickly agglomerates and oxidizes once released into the environment. Further, attention is focused on how these nZVI particles are synthesized on carriers and the results obtained when used to treat chromium by modifying it and enhancing its adsorption capacity. Thus, several stabilization methods have been developed to facilitate the use of fine ZVI. Recent studies have showed that ZVI particles can be supported by porous materials including clays, resins, and carbon materials, to enhance their dispersion and stability(Shu et al., 2010; Sunkara et al., 2010). Moreover, the study focuses on the production of bamboo supported nZVI because of the need to overcome some of the disadvantages inherent in the use of nZVI which reduces its efficiency and usability, such as

rapid oxidation, a strong tendency to agglomerate into larger particles and also the separation and recovery of the fine particles after usage.

Physical and chemical methods are being used extensively for production of metal and metal oxide nanoparticles. However, this production requires the use of very reactive and toxic reducing agents such as sodium borohydride and hydrazine hydrate, which cause undesired detrimental impacts on the environment, plant and animal life it supports, so the implementation of green chemistry principles for the production of nanoparticles and for Nano technological applications in standard chemical engineering will lead to a great reduction in waste generation, less hazardous chemical syntheses, improved catalysis and finally an inherently safer chemistry, this is carried out by employing polyphenols in place of toxic reducing agents. (Albrecht et al., 2006).

1.3 Objectives

1.3.1 General Objective

To synthesize and characterize bamboo supported Nano zero valent iron for its application as an adsorbent for the removal of chromium ions from aqueous solution.

1.3.2 Specific Objectives

- To synthesize nano zerovalent Iron using polyphenols from avocado.
- To characterize nZVI - bamboo adsorbent.
- To Investigate the application of nZVI - bamboo adsorbent for the adsorption of Chromium (VI).
- To Optimize parameters including the pH, concentration and adsorbent dosage for the Cr (VI) adsorption on to nZVI - bamboo adsorbent.

1.4 Significance of the study

- Results from this study can be used to assess the utility of green synthesis nZVI-bamboo supported for heavy metal removal, in particular chromium adsorption.
- This study will enhance the economic value of bamboo tree, as one of the raw material for the synthesis of nZVI-Bamboo.
- Extraction of polyphenols from the avocado seeds will enhance its value that is thrown as waste valuable.
- The study will facilitate environmentally friendly nano zerovalent iron (nZVI).

2. Literature Review

2.1 Industrial wastewater sources

Industrial wastewater streams containing heavy metals are produced from different industries. Electroplating, tannery processing factories and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, electro less depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another significant source of heavy metals wastes result from printed circuit board (PCB) manufacturing. Other sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and Ferro cyanide. All of these generators produce a large quantity of wastewaters, residues, and sludge that can be categorized as hazardous wastes requiring extensive waste treatment (Some and Lagerkvist, 2002).

2.1.1 Heavy metals in industrial wastewater.

Heavy metals are generally considered to be those whose density exceeds 5 g per cubic centimeter. A large number of elements fall into this category, Arsenics usually regarded as a hazardous heavy metal even though it is actually a semi-metal. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage. Wastewater regulations were established to

minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater.

Table 2.1. The MCL standards for the most hazardous heavy metals (Babel and Kurniawan, 2003).

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human Carcinogen	0.2
Zinc	Depression, lethargy, neurological signs and increased thirst	0.8
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.06
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

2.1.2 Toxicity of Chromium

Chromium has a 'chronic' toxic effect upon aquatic life (UNIDO, 2000). Dichromates are toxic to fish life since they rapidly penetrate cell walls. They are mainly absorbed through the gills and the effect is accumulative. Concentration of chromium in natural water that has not been affected by waste disposal commonly ranges from 0.1-0.6 µg/mL (Perk, 2006). The WHO standard for

the acceptable amount of Chromium in drinking water is 0.05 mg/L and 0.2mg/L in river water. The EEPA standard for the acceptable amount of Chromium in industrial wastewater effluent is 2 mg/L. Average daily intake of 50-200 µg/day of Cr (III) is safe and adequate for adults. Cr (III) is an essential nutrient, required for normal energy metabolisms in animals. However the consumption of contaminated fish, other foodstuffs and drinking water could increase the daily intake levels far beyond those recommended levels. Ingesting small amounts of Cr (both Cr^{+3} and Cr^{+6} forms) will generally not harm, however ingesting above recommended levels over long periods of time can result in adverse health effects including gastro-intestinal irritation, stomach ulcers, heart burning, respiratory tract infection, sever cough, fever and loss of eyesight. Lung cancer and kidney failure were the reported causes of death in many cases (Perk, 2006). Skin contact may result in systemic poisoning, damage or even severe burns, interference with the healing of cut or scrapes which, if not treated properly, may lead to ulceration and severe chronic allergies. Eye exposure may cause permanent damage. In general, Cr (VI) is more toxic, more soluble, more mobile and hence absorbed into cells more readily than Cr (III) (James, 1996). This chromium can replace other metals in biological systems with toxic effects and its accumulation throughout the food chain leads to serious ecological and health problems (UNIDO, 2000). Investigations have been performed on fish under conditions of exposure insufficient to cause severe toxicity, yet sufficient to cause visible changes in behavior at a dosages of 0.2 mg/L. It is understood however, that daphnia are even more susceptible at this dosage, thus posing a potential hazard to the food chain for fish. Chromium is also toxic to agronomic plants at about 5 to 100 µg/g of available Cr in the soil. Plants absorb Cr (VI) better than Cr (III); whereas Cr (VI) is more toxic. Plant growth studies of solution cultures with low levels of Cr have indicated that Cr is not an essential component of plant nutrition (Huffman and Alloway, 1973). Although some crops are not affected by low concentration of Cr, it is toxic at high concentration or may reduce yield.

2.2 Wastewater treatment techniques

Due to increasing awareness about the environment and stringent environmental regulations, Wastewater treatment has always been a key aspect of research. Water is a vital component for the economic prosperity of any country. In coming years, the economic importance of water is expected to grow with the global economic growth, industrial development and urbanization. Industrial wastewater contains the variety of inorganic compounds which are characterized as toxic, carcinogenic and mutagenic which when persist in the environment have the potential to cause adverse effect on man and vegetation. The heavy metals present in the industrial waste water such as Pb, Cd, Cr, Ni, Zn, and As, are the most toxic and perilous materials among the other toxic materials from the chemical and allied industries (Bernard et. al., 2013). Hence, there is burning need for the removal of heavy metals from the wastewater. Various technologies that are currently used for the removal of heavy metals are evaporation, Ion exchange, precipitation, membrane filtration, and adsorption (Fenglian et.al. 2011). Among all these technologies, adsorption process appears to be more favorable technology as it is low cost, require low maintenance, economical and is energy efficient.

2.2.1 Chemical precipitation

Chemical precipitation is effective and by far the most widely used process in industry (Ku and Jung, 2001) because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The formed precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation. Adjustment of pH to the basic conditions (pH 9–11) is the major parameter that significantly improves heavy metal removal by chemical precipitation. Lime and limestone are the most commonly employed precipitation agents due to their availability and low-cost in most countries (Aziz et al., 2008). Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of

the process, inexpensive equipment requirement, and convenient and safe operations. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Aziz et al., 2008).

2.2.2 Ion Exchange

Ion-exchange processes have been widely used to remove heavy metals from wastewater due to Their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Kang et al., 2004). Ion-exchange resin, either synthetic or natural solidres in, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Alyüz and Veli, 2009).The most common cation exchangers are strongly acidic resins with sulfonic acid groups (SO_3H) and weakly acid resins with carboxylic acid groups (COOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion-exchange process: The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time (Gode and Pehlivan, 2006). Ionic charge also plays an important role in ion-exchange process. Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluent. Ion exchange is a physical process in which an ion with a high affinity for the resin material of the ion exchange column replaces an ion with a lower affinity that was previously bound to the column resin. As water flows through, dissolved Cr (VI) ions bind to the resin and displace the previously bound ions usually (Cl^- or OH^-) ions. The resins used for Cr sequestration are typically either a naturally occurring inorganic zeolite or a synthetic weak base or strong base anion exchanger resin. Once the resins have accumulated Cr on enough exchange sites that breakthrough surpasses a threshold value, they must be regenerated. Ion exchange resins are capable of reducing Cr (VI) concentrations to less than the

detection limit. Resins are typically most effective at low pH values, because Cr(VI) will be present as $HCrO_4$– and $Cr_2O_7^{2-}$, not as CrO_4^{2-}.Anion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to the pH of the solution. Electrolytic recovery or electro-winning is one of the many technologies used to remove metals from process water streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantage was that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced (Kurniawan et al., 2006).

2.2.3 Membrane filtration

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency, easy operation and space saving. The membrane processes used to remove metals from the wastewater are ultrafiltration, reverse osmosis, nano filtration and electro dialysis. Semipermeable membrane filters are used in water treatment to filter soluble compound anions and cations from water, including $HCrO_4^-$ andCrO_4^{2-}. The flux of water through the membrane is proportional to the pressure that is applied. The flux of solute (Cr) can be related to the flux of water, the concentration of Cr ion and other empirically derived membrane parameters.

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, Nano filtration and reverse osmosis can be employed for heavy metal removal from wastewater. Ultrafiltration (UF) utilizes

permeable membrane to separate heavy metals, macromolecules and suspended solids from in organic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000–100,000 Da). These unique specialties enable UF to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane (Vigneswaran et al., 2004).

2.2.4 Coagulation and flocculation

Coagulation and flocculation followed by sedimentation and filtration is also employed to remove heavy metal from waste waters. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Many coagulants are widely used in the conventional wastewater treatment processes such as aluminum, ferrous sulfate and ferric chloride, resulting in the effective removal of wastewater particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates.

Coagulation is one of the most important methods for waste water treatment, but the main objects of coagulation are only the hydrophobic colloids and suspended particles. In order to remove both soluble heavy metal and insoluble substances efficiently by coagulation, sodium xanthogenate group was grafted to polyethylene mine (Chang and Wang, 2007). This new kind of coagulant was an amphoteric polyelectrolyte. When the pH of water sample is lower, the colloidal substances with negative charges can be coagulated by it, but the cationic charges cannot be removed very well. When the pH of water sample is higher, the turbidity removal decreases, and the cationic removal increases.

Flocculation is the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. Once suspended, particles are flocculated into larger particles; they can usually be removed or separated by filtration, straining or floatation. Today many kinds of flocculants, such as PAC, polyferricsulfate (PFS) and polyacrylamide (PAM), are widely used

in the treatment of waste water; however, it is nearly impracticable to remove heavy metal very well from wastewater directly by the recurrent flocculants.

2.2.5 Electro dialysis

Electro dialysis (ED) is another membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving force. In most ED processes, ion-exchange membranes are used. The membranes are actually of two basic types: cation-exchange and anion-exchange membranes. This process has been widely used for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents and salt production. ED has also proven a promising method in heavy metal wastewater treatment. Electro dialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cat ion-exchange membranes (Chen, 2004).

2.2.6 Electrochemical treatment

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies involve relatively large capital investment and the expensive electricity supply, so they haven't been widely applied. However, with the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades (Wang et al., 2007).

2.2.7 Adsorption

Adsorption is now recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases

will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process. Recently, adsorption has become one of the alternative treatment techniques for waste water laden with heavy metals. Adsorption is a process where the atoms, ions or molecules of dissolved solids from liquid grips on the surface of solid; i.e. it is a process of mass transfer in which the dissolved solid from liquid gets deposited on the surface of solid because of physical or chemical interaction (Babel et. al., 2003).

Among all these techniques, adsorption seems efficient, low cost in operation, simple in design, rapid in nature and effective at lower concentrations (Aksu and Yener, 2001). In adsorbent, bio adsorbents have potential in wastewater treatment processes; these are present in nature in different forms such as plant waste and forest waste. Adsorption has several advantages over conventional treatment methods viz. metal regeneration capability, reuse of material, effectiveness at trace concentrations and low cost in nature (Demirbas, 2008). It encompasses a solid phase (sorbent) and a liquid phase (solvent) containing the metal/dyes or other species as bio sorbent. The major factors of this method are the technical applicability and the cost effectiveness that needs to be considering while selecting adsorbent to treat wastewater. Adsorbents are of different types and are classified as natural materials, industrial waste, agricultural and biological waste.

Alternative sorbents have been proposed for removing Cr (VI), in order to save money and/or recycle waste material. Materials tested so far have ranged from used automobile tires to seaweed. Researchers have tested living and dead bio sorbents, including bacteria, yeasts, milled peat, microalgae, fungi and seaweed. Other natural materials tested include clays, peat moss, and plant litter. Low cost sorbents are not regenerated, but are disposed off as soon as significant breakthrough occurs. Since adsorption is an equilibrium process, the mass of Cr (VI) sorbed to the surface depends on both the concentration of Cr (VI) in the aqueous phase and the affinity of the sorbent for the Cr. This in turn depends on the types of chemical attractions between the sorbent and the Cr (such as ionic bonding, electrostatic attraction, and hydrogen bonding), which can vary with pH and the presence/absence of competing molecule.

2.3 NANOTECHNOLOGY

Nanotechnology is a field of applied science, focused on the design, synthesis, characterization and application of materials and devices on the Nano scale. This branch of knowledge is a sub-classification of technology in colloidal science, biology, physics, chemistry and other scientific fields and involves the study of phenomena and manipulation of materials in the Nano scale (Mansoor and Soelaiman, 2005). This results in materials and systems that often exhibit novel and significantly changing physical, chemical and biological properties due to their size and structure. Nano materials have been used extensively in many fields of science and technology, including catalysis, drug delivery, medical diagnostics, enzyme immobilization, sensors and pollution control (Kong et al., 2000). Currently, many industries have been engaged in the manufacturing of nanoparticles throughout the world. Nanotechnology sectors are growing rapidly and expected to exceed $1 trillion annually and to explore about 2 million employment opportunity worldwide during the next 10 years (Roco and Bainbridge, 2001). Pollution prevention by nanotechnology refers on the one hand to a reduction in the use of raw materials, water or other resources and the elimination or reduction of waste and on the other hand to more efficient use of energy or involvement in energy production. The implementation of green chemistry principles for the production of nanoparticles and for nano technological applications in standard chemical engineering will lead to a great reduction in waste generation, less hazardous chemical syntheses, improved catalysis and finally an inherently safer chemistry (Albrecht et al., 2006). However, there are very few data that actually show quantitatively that these claims are true and that replacing traditional materials with nanoparticles really does result in less energy and materials consumption and that unwanted or unanticipated side effects do not occur. Nano materials can be substituted for conventional materials that require more raw materials, are more energy intensive to produce or are known to be environmentally harmful. Also, a unique aspect of nanotechnology is the "vastly increased ratio of surface area to volume", present in many Nano scale materials, which opens new possibilities in surface-based sciences (Zhang and Masciangioli, 2003). Similar to nanotechnology's success in consumer products and other sectors, Nano scale materials have the potential to improve the environment, both through

direct applications of those materials to detect, prevent, and remove pollutants, as well as indirectly by using nanotechnology to design cleaner industrial processes and create environmentally responsible products. For example, iron nanoparticle can remove contaminants from soil and ground water; and nano sized sensors hold promise for improved detection and tracking of contaminants.

Behavior of materials at nano scale is not necessarily predictable from what we know at macro scale. At the nano scale, often highly desirable, properties are created due to size confinement, dominance of interfacial phenomena, and quantum effects. These new and unique properties of nanostructured materials, nanoparticles, and other related nanotechnologies lead to improved catalysts, tunable photo activity, increased strength, and many other interesting characteristics (Mansoori et al, 2005). As the exciting field of nanotechnology develops, the broader environmental impacts of nanotechnology will also need to be considered. Such considerations might include: the environmental implications of the cost, size and availability of advanced technological devices; models to determine potential benefits of reduction or prevention of pollutants from environmental sources; potential new directions in environmental science due to advanced sensors; effects of rapid advances in health care and health management as related to the environment; impact of artificial nanoparticles in the atmosphere; and impacts from the development of Nano machines (Hutchison and James 2001).

Early application of nanotechnology is remediation using nano scale iron particles. Zero-valent iron nanoparticles are deployed in situ to remediate soil and water contaminated with chlorinated compounds and heavy metals. Among the many applications of nanotechnology that have environmental implications, remediation of contaminated ground water using nanoparticles containing zero-valent iron is one of the most prominent examples of a rapidly emerging technology with considerable potential benefits. One of the main environmental applications of nanotechnology is in the water sector. As freshwater sources become increasingly scarce due to overconsumption and contamination, scientists have begun to consider seawater as another source for drinking water.

The majority of the world's water supply has too much salt for human consumption and desalination is an option but expensive method for removing the salt to create new sources of drinking water. Carbon nanotube membranes have the potential to reduce desalination costs. Similarly, nano filters could be used to remediate or clean up ground water or surface water contaminated with chemicals and hazardous substances. Overall, there is a multitude of promising environmental applications for nanotechnology. Much of the current research is focused on energy and water technologies. Environmental remediation includes the degradation, sequestration, or other related approaches that result in reduced risks to human and environmental receptors posed by chemical and radiological contaminants. The benefits, which arise from the application of Nano materials for remediation, would be more rapid or cost-effective cleanup of wastes. Cost-effective remediation techniques pose a major challenge in the development of adequate remediation methods that protect the environment. Substances of significant concern in remediation of soils, sediment, and groundwater include heavy metals (e.g., mercury, lead, cadmium) and organic compounds (e.g., benzene, chlorinated solvents, creosote, and toluene). Specific control and design of materials at the molecular level may impart increased affinity, capacity, and selectivity for pollutants.

Minimizing quantities and exposure of hazardous wastes to the air and water and providing safe drinking water are among the environmental protection agencies' goals. In this regards, nanotechnology could play a key role in pollution prevention technologies (Shahsav and Ahmadpour, 2004). Nanoparticles could provide very high flexibility for both in situ and ex situ remediations. For example, nanoparticles are easily deployed in ex-situ slurry reactors for the treatment of contaminated soils, sediments, and solid wastes. Alternatively, they can be anchored onto a solid matrix such as carbon, zeolite, or membrane for enhanced treatment of water, wastewater, or gaseous process streams. Direct subsurface injection of Nano scale iron particles, whether under gravity-feed or pressurized conditions, has already been shown to effectively degrade chlorinated organics such as trichloroethylene, to environmentally benign compounds. The technology also holds great promise for immobilizing heavy metals and radionuclides.

2.3.1 Nano Adsorbents

Adsorption processes and membrane separations are dominating technologies and increasingly being applied in developing new adsorbents and membranes from nano materials for various environmental applications showed that adsorbents of the traditional types such as commercially available activated carbon, zeolite, silica gels, and activated alumina have an estimated worldwide market exceedingUS$1.5 billion per year (Lu and Zhao, 2004). But the nano size particles show much higher efficiency as adsorbents than their macro sizes, and thus might have a wider market to be explored in the future.

The unique properties of nano materials, in particular as sorbents, have promisingly exhibited in solving many environmental issues. The high surface area to mass ratio, high surface reactivity and unique catalytic activity are the most important properties of a nanomaterial and led to increased efficiency as an adsorbent compare to macro sized of the material. A number of researches were conducted on batch adsorption experiments using different nano sizes metal oxide adsorbents for removal of arsenic from water (Auffan et al., 2008). The results of the studies revealed that TiO_2, Fe_2O_3 and NiO nanoparticles adsorbent showed more than 98% removal capacity from water matrix. The use of nanoparticles may have advantages over conventional materials due to the much larger surface area of nanoparticles on a mass basis. In addition, the unique structure and electronic properties of some nanoparticles can make them especially powerful adsorbents. Many materials have properties that are dependent on size (Hochella et al.,2002) Hematite particles with a diameter of 7 nm, for example, adsorbed Cu ions at lower pH values than particles of 25 or 88nm diameter, indicating the uniqueness of surface reactivity for iron oxides particles with decreasing diameter (Madden, 2006). Several types of nanoparticles have been investigated as adsorbents: metal-containing particles, mainly oxides, carbon nanotubes and fullerenes, organic nanomaterial and zeolites. For the removal of metals and other inorganic ions, mainly nano sized metal oxides but also natural Nano sized clays have been investigated. Also, oxidized and hydroxylated CNTs are good absorbers for metals. This has been found for various metals such as Cu, Ni, Cd and Pb Adsorption of organometallic

compounds on pristine multi-walled CNTs was found to be stronger than for carbon black (Munoz, et al., 2005).

2.3.2 Iron-Nano adsorbent

Iron is one of the most prevalent elements in the earth. The facileness of resource and ease in synthesis renders nanosized ferric oxides to be low-cost adsorbents for noxious metal sorption. Since iron is ecofriendly, nanosized ferric oxides can be pumped directly to contaminated sites with negligible risks of secondary contamination (Li et al., 2003).

In 2000, the first field trial of nano zero valent iron (nZVI) for the treatment of trichloroethylene in groundwater at a manufacturing site in Trenton, New Jersey, USA, was documented. NZVI is a promising material for groundwater in situ remediation because of its high surface area, high reactivity, fast kinetics, small particle size, and magnetic property that is beneficial for separating and recovering tiny particles from wastewater. Though the definition of Nano particles sets the threshold size at 100 nm, a review of applications in literature indicates the average particles size is approximately 60 nm(>90%) while the critical diameter below which specific Nano effect occurs is 30 nm. The high specific surface area allows nZVI to be 10 to 1000 times highly reactive than the granular ZVI, and the sorption capacity is also much higher there by creating a greater reductive capacity per gram. Thus smaller amounts of nZVI would be needed to treat a contaminated plume that would further reduce costs. The use of zero-valent iron (ZVI or Fe^0) for in situ remedial treatment has been expanded to include all different kinds of contaminants (Ponder et al., 2000).

Zero-valent iron removes aqueous contaminants by reductive DE chlorination, in the case of chlorinated solvents, or by reducing to an insoluble from, in the case of aqueous metal ions. Iron also undergoes “Redox” reactions with dissolved oxygen and water Nano powder of zero-valent iron (ZVI or Fe0) was used for the removal of nitrate in water. These nanoparticles have a large ratio of surface area to mass ($31.4 m^2/g$). Nano scale ZVI was employed by (Lowry et al., 2004). More recently, it was demonstrated that nano-sized zero-valent iron (nZVI) oxidizes organic

compounds in the presence of oxygen. The high surface area of nano scale nZVI may allow for more efficient generation of oxidants.

A decrease in reactivity is expected with the build-up of iron oxides on the surface, particularly at high ph. (Feitz et al., 2004).investigated the oxidization of herbicide molinate by Nano scale zero-valent iron (nZVI), when it is used in the presence of oxygen. The principal potential benefits of nZVI are the speed of contaminant degradation due to its high surface area and reactivity that reduces remediation time. It also has the potential of treating recalcitrant pollutants such as chlorinated organic compounds, nitrates and hexavalent Chromium that can be found in aquatic environments. There is almost complete degradation process eliminating the formation of toxic intermediate products and it has the potential for synergistic application with bioremediation techniques.Fe^0 has standard reduction potential (E^0) of -0.440 V for half-reaction between the Fe^2+/Fe^0 couple which confirms that it is an effective electron donor regardless of its particle size. Reduction potential measures the probability of chemical species being reduced. Thus a higher reduction potential means a higher probability of the species to be reduced. This means that theoretically Fe^0 can reduce any pollutant that has a higher reduction potential than receptors are water and to some extent residual dissolved oxygen Since the oxidation of Fe consumes H^+ and produces OH^- ions , there is an increase in solution pH and an associated decline in solution potential (E_h).

The high surface free energy of nZVI coupled with the dissociative adsorption of water on the iron surface results in the formation of surface bound hydroxyl species. Thus before reacting with target pollutants, the nZVI rapidly reacts with water and/or oxygen in its surrounding condition, resulting in the formation of passive oxidation layers. The structure of the nanoparticle is therefore made up of an inner core which exhibits characteristics of a metallic iron (reluctant) and an oxidized shell with characteristics of an iron oxide (sorbent).The principal mechanism of the core is to act as an electron source for the reduction of pollutants.

Iron oxides however can strongly adsorb metals in soils thus immobilizing metallic contaminants in soil but not much is known about the efficiency of the treatment in soils that are not saturated with water. It also serves as the barrier for electron passage from the core.

The high reactivity of nZVI alone is not enough to make it an effective remediation agent, the Nano iron particles should also be able to form stable dispersions and migrate to contaminated plume. Nano scale iron particles represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. Nano scale iron particles have large surface areas and high surface reactivity. Equally important, they provide enormous flexibility for in situ applications. Research has shown that Nano scale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as heavy metals chlorinated organic solvents, organo-chlorine pesticides, and PCBs. Modified iron nanoparticles, such as catalyzed and supported nanoparticles have been synthesized to further enhance the speed and efficiency of remediation.

2.3.3 Green Synthesis of Metallic Nanoparticles.

According to Kalaiarasi et al., 2010. green synthesis of metallic nanoparticles by different plant parts such as the leaf, stem, seed and root is the simplest, most cost effective and reproducible approach. Plants certainly produce more stable metal nanoparticles and have proved to be the best candidates for fast and large-scale synthesis as compared to microorganisms. The preference for plants and their derivatives in nanomaterial production lies in the plants' natural composition of different organic reducing compounds, which easily adapt to the synthesis of nanoparticles. Different herbs and plant sources occlude higher antioxidants that are available as phytochemical constituents in seeds, fruits, leaves and stems. Therefore, the utility of plant-based phytochemicals in the overall synthesis and architecture of nanoparticles creates an important symbiosis between natural/plant sciences and nanotechnology. This association gives a characteristically green approach to nanotechnology, referred to as green nanotechnology. These production processes can be carried out without significant environmental pollution, thereby

setting new standards in highly sustainable and economically viable clean and green technologies. It has long been known that plants have the potential to hyper-accumulate and biologically reduce metallic ions. Because of these interesting properties, plants have been considered a more environment-friendly route for biologically synthesizing metallic nanoparticles and for detoxification applications. Plant extracts containing bioactive alkaloids, phenolic acids, polyphenols, proteins, sugars, and terpenoids are believed to have an important role in first reducing the metallic ions and then stabilizing them. The variation in composition and concentration of these active biomolecules between different plants and their subsequent interaction with aqueous metal ions is believed to be the main contributing factors to the diversity of nanoparticle sizes and shapes produced. Importantly, the synthesis of nanoparticles from reducing metal salts via plants is a relatively straightforward room temperature process. The process begins by mixing a sample of plant extract with a metal salt solution. Biochemical reduction of the salts starts immediately and the formation of nanoparticles is indicated by a change in the color of the reaction mixture. During the synthesis, there is an initial activation period when process metal ions are converted from their mono or divalent oxidation states to zero-valent states and nucleation of the reduced metal atoms takes place. This is immediately followed by a period of growth when smaller neighboring particles amalgamate to form larger nanoparticles that are thermodynamically more stable while further biological reduction of metal ion stakes place. As growth progresses nanoparticles aggregate to form a variety of morphologies such as cubes, spheres, triangles, hexagons, pentagons, rods, and wires. In the final stage of synthesis, the plant extracts ability to stabilize the nanoparticle ultimately determines it's most energetically favorable and stable morphology. Properties of the plants extract such as its concentration, metal salt concentration, reaction time, reaction solution pH, and temperature significantly influence the quality, size, and morphology of the synthesized nanoparticle.

Table 2.2 Size and morphology of the synthesized nanoparticles from different plants source (Sadia Saif et al., 2016).

Plant origin	Nanoparticle	Size (nm)	Morphology
Avena sativa (oat)	Gold	5–20 (pH 3 & 4),25-85 (pH 2)	rod-shaped
Black tea leaf extracts	gold & silver	20	spherical, prism
Azadirachta indica (neem)	gold, silver & silver-gold alloys	5–35 & 50–100	spherical, triangular, hexagonal
Cinnamonzeylanicum(cinnamon	Silver	31–40	cubic, hexagonal
Medicago sativa (alfalfa)	iron oxide	2–10	Crystalline
Jatropha curcas (seed extract)	Silver	15–50	Spherical
Salvia officinalis Leaf	Silver	5–25 nm	Spherical

Synthesis of nanoparticles using plants has drawn the attention of researchers as a rapid, low-cost, eco-friendly and single-step method. The plant system can be harnessed both intracellular and extra-cellularly for synthesis of nanoparticles. The intracellular methods for synthesis of nanoparticles include growing plants in metal-rich organic media, metal-rich soil and metal-rich hydroponic solution etc. whereas, extracellular methods for synthesis of nanoparticles include use of leaf extract prepared by boiling or crushing of leaves. Use of different plant parts like fruits, latex have been reported for biosynthesis of nanoparticles. The use of these different methods for synthesis of nanoparticles yielded positive results in all the cases.

The synthesis of nanoparticles using plants is relatively fast compared with the other systems and can be visually observed because of the change in coloration from light-green to dark-brown. Shape and size of the nanoparticles can be modulated by a slight change in pH and temperature of the nanoparticles.

The exact mechanism for synthesis of nanoparticles is yet to be elucidated but the possible mechanisms suggest that the presence of protective and reductive biomolecules in the plant act as a major factor in synthesis of nanoparticles, (Thakkar et al., 2009). The nanoparticles synthesized using the plant system can be utilized for different commercial applications like pharmaceuticals, drugs, therapeutics etc.

Shankar et al, 2010. Used the leaf extract of neem (*Azadirachta indica*) for synthesis of nanoparticles. The ultraviolet (UV)–visible absorption spectra showed peak at 450 nm, whereas the TEM images depicted the synthesis of polydisperse and predominantly spherical nanoparticles. The X-ray diffraction (XRD) spectra confirmed the crystalline nature of nanoparticles. The Fourier transform infrared (FTIR) spectra showed the presence of reducing sugars and flavones or terpenoids in the sample.

In another recent study, Xiao et al., 2016 effectively employed plant mediated iron nanoparticles for removal of chromium, synthesized by various leaf extracts. Plant were selected on the basis of their reduction potential, i.e., selected from high to low antioxidant potential such as *S. jambos (L.) Alston (SJA)* extract with strong reducing ability, Oolong tea (OT) extract with moderate reducing ability and *A. moluccana (L.)Willd (AMW)* extract with weak reducing ability. The study shows that removal of chromium (VI) was consistent with reducing capacity of plants extracts. One milliliter of SJA-Fe NPs colloidal were able to remove 91.9% of the Cr(VI) in 5 min and 100% in 60 min. TEM image of the SJA-Fe NPs showed that NPs were spherical with diameter about to 5 nm and amorphous in nature when studied by XRD.

2.3.4 Synthesis of Iron Nanoparticles from Plant materials.

Physical and chemical methods are being used extensively for production of metal and metal oxide nanoparticles. However, this production requires the use of very reactive and toxic reducing agents nanomaterials such as sodium borohydride and hydrazine hydrate, which cause undesired detrimental impacts on the environment, plant and animal life it supports. Researchers continue efforts to develop facile, effective and reliable green chemistry processes for the

production of nanomaterials. Various organisms act as clean, eco-friendly and sustainable precursors to produce the stable and well functionalized nanoparticles. These may include bacteria, *actinomycetes*, fungi, yeast, viruses, etc. Thus, it is vitally important to explore a more reliable and sustainable process for the synthesis of nanomaterials. Economic viability, environmental sustainability, and social adaptability as well as the availability of local resources are a matter of concern in the production of nanomaterials.

- **Synthesis by leaf extract:**

The green synthesis of iron nanoparticles using various plant extracts has been reported by many researchers. Biosynthesis of iron nanoparticles (Fe NPs) has been mainly performed using extract of green tea which is a cheap and local resource. Hoag et al, 2010 synthesized nZVI utilizing green tea (*Camellia sinensis*) extract containing a range of polyphenols. Without the addition of any surfactant or polymer, the stable nanoparticles were obtained at room temperature. Polyphenols in plant act as a reducing agent and a capping agent, resulting instable green Nano scale zero-valent iron particles with unique properties. Green tea was used for preparation of extract. A solution of 0.1 M $FeCl_3$ was added to green tea extract in a 2:1 volume ratio resulting in spherical nanoparticles with diameter of 5–10 nm.

Moreover, Markova et al., 2014 Prepared the iron (II, III)-polyphenol complex nanoparticles with a diameter of 70 nm-sized by adding Fe $(NO_3)^{3-}$ $9H_2O$ to the green tea extract. Fe-based nanoparticles were prepared by introducing 0.5MFe $(NO_3)^{3-}$ $9H_2O$ into green tea extract in a 1:5 volume ratio under nitrogen atmosphere.

Researcher's produced zero valent iron and iron (II, III) polyphenol complex nanoparticles by utilizing green tea extract in different studies. Hence, production of nano iron with different size and properties are due to change in synthesis procedure, and most important ratio of extract to salt. Similar findings were found in study of Nadagouda et al, 2010, they evaluated the effect of extract concentration on size of iron nanoparticles. Nano scale zero valent iron (nZVI) synthesis was done at room temperature using different volumes of tea extract and Fe $(NO_3)_3$ solution. It

was found that size and morphology of particles could be changed by changing the concentration of extract as well as iron salt.

Machado et al, 2013, evaluated the feasibility of several tree leaves for production of nZVI. In addition, the antioxidant capacity of leaf extracts was also estimated. The results reveal that dried leaves produce extracts with higher antioxidant capacities than non-dried leaves. Leaves of oak, pomegranate and green tea produced the richest extracts, and TEM analysis confirmed that nZVIs (d = 10–20 nm) can be produced utilizing these plant resources.

In another study, Pattanayak and Nayak, 2015, used a low-cost reductant for synthesizing Nano scale zero-valent iron (nZVI) by *Azadirachta indica* (neem) leaves extract under atmospheric conditions. The UV-Vis spectroscopy of synthesized iron nanoparticles were in the range of 216–265 nm. The size of spherical iron nanoparticles was predominantly found within the range of 50–100 nm.

Stable iron-polyphenol complex nanoparticles (Fe-P NPs) using leaf extract of eucalyptus were synthesized by Wang et al, 2014. Three different plants i.e., *MelaleuEucalyptus tereticornis, ca nesophila* and *Rosemarinus officinalis* were used to produce iron ions polyphenols complex nanoparticles (Fe-P NPs) ranging in sizes from 50 to 80 nm.

Luo et al, 2011 Produced FeNPs with an average size of 60 nm by utilizing methanolic grape leaf extract. Gas chromatography-mass spectrometry (GC-MS) analysis confirmed the presence of biomolecules including phytols, terpenoids, and antioxidants which involved in synthesis of nanoparticles. Plants materials are capable of synthesizing crystalline magnetite nanoparticles. Crystalline mono-disperse magnetite (Fe_3O_4) nanoparticles were synthesized by the carob leaf in a one-step reaction. An aqueous solution of ferric chloride hexahydrate and ferrous chloride tetra hydrate (2/1 molar ratio) was mixed, and magnetite nanoparticles with an average diameter of 8 nm were obtained.

Remarkable changes in color and pH were observed during the reduction of iron salt by extracts. Such rapidly processed plant-mediated iron metallic nanoparticles is an alternative to chemical

synthesis protocols and can serve as a low cost reductant for synthesizing iron nanoparticles. Rapid synthesis of crystalline iron oxide nanoparticles (Fe_3O_4) was performed by reduction of ferric chloride ($FeCl_3$) with leaf extract of *Tridax procumbens*.

The water extract of *T. procumbens* contains water soluble carbohydrate compounds. Carbohydrates containing aldehyde groups may reduce the Fe^{3+} of ferric chloride to Fe_3O_4 nanoparticles Fe0/Fe_3O_4 nanoparticles were successfully synthesized using pomegranate (*Punica granatum*) leaf extract by Rao et al, 2013. Makarov et al, 2014 reported the synthesis of iron oxide nanoparticles using aqueous extract of *Hordeum vulgare* and *Rumex acetosa*. *Hordeum vulgare* produced the amorphous iron oxide (Fe_3O_4) nanoparticles with a particle size up to 30 nm. The role of pH was considerable in the stability of iron nanoparticles. The authors of this paper found that the stability of *H. vulgare* synthesized iron nanoparticles was increased by adding 40 mM of citrate buffer with pH 3.0. Similarly, amorphous iron nanoparticles with a diameter of 10–40 nm was produced by extract of *Rumex acetosa*. *R.acetosa* extract synthesized iron nanoparticles were highly stable due to low pH (ph. = 3.7) as compared to *H. vulgare* (pH = 5.8).

In recent study, Prasad et al, 2014 Produced iron (III) oxide Nano crystals with leaf extract of Garlic Vine and $FeSO_4$.7H2O. The bio-precipitation was accelerated by adding a few drops of 1 MNaOH to obtain pH 6. The reaction resulted in formation of β-Fe_2O_3 of nano crystals with size of 18.22 nm.

- **Fruit extract:**

Some researchers use fruits for synthesis of iron nanomaterials. Mohan Kumaret al, 2013 synthesized palladium and iron NPs using aqueous fruit extract of *Terminalia chebula*. Redox potential of polyphenol rich *T. chebula* aqueous extract was 0.63 V. Such a reduction helps to reduce the iron precursors to iron NPs. Remarkable stable iron nanoparticles were synthesized via simultaneous reduction of $FeSO_4.7H_2O$ solution by *T. chebula* extract containing complexation of polyphenols. A 5:1 ratio of extract to metal salt solution was used and solid

product was separated out by centrifugation followed by ethanolic washing. X-ray diffraction (XRD) and transmission electron microscope (TEM) analyses revealed that amorphous iron NPs were within a size of less than 80 nm.

In another study, (Kumar et al., 2013 Synthesized Fe_3O_4 nanoparticles by the fruit extract of *Passiflora tripartitavar mollissima* and studied their catalytic effect on the synthesis of 2-arylbenzimidazole under room temperature.

Using aqueous extract of *Passiflora tripartitavar, mollissima* fruit spherical iron oxide nanoparticles of 22.3±3 nm size were synthesised. The synthesized Nano catalyst is highly active for the synthesis of biologically significant 2-arylbenzimidazoles. Benz imidazole moiety is a structural is ostere of naturally occurring nucleotides; hence, it has been useful in creating intermediates in the development of molecules for pharmaceutical and biological purposes. The one-pot synthesis of 2-arylbenzimidazole derivatives using Fe_3O_4 nanoparticles is environmentally benign, selective, and easy to manipulate.

- **Seed extract:**

Seed extract of *Syzygium cumin* was used as a reducing agent and sodium acetate as an electrostatic stabilizing agent for the synthesis of iron oxide nanoparticles by Venkateswarlu et al, 2014. The XRD study reveals that the synthesized spherical magnetic nanoparticles (SMNPs) had inverse spinel face-centered cubic structure 9–20 nm in diameter as shown by TEM. The presence of polyphenols, flavonoids, and other biomolecules in the *S. cumini* seed was confirmed by Fourier transform infrared (FTIR) spectroscopy technique. The Brunauer–Emmett–Teller (BET) surface area of the Fe_3O_4 particles was found to be 3.517 m^2/g, and the particles were classified as mesoporous. The average pore size for the Fe_3O_4 was determined according to the single-point adsorption total volume at a relative pressure P/PO = 0.9905 cm^3/g. By virtue of this property, the synthesized nanoparticles can be used in the field of environmental remediation for the removal of toxic metals and dyes.

2.4 Possible Mechanism of Nanoparticles Synthesis

Actual mechanism of nanoparticles synthesis by living organisms is not yet clear, however, Studies shows that enzymes produced from bacteria and fungi and biomolecules especially phenolic compounds in plant products cause the production of metallic iron nanoparticle. Becerra et al, 2007 utilized tannin powder, a green reagent for synthesis of iron oxide NPs. *Tannins* consist of non-toxic polyphenolic compounds which act as reducing and stabilizing agents for the production of iron oxide NPs. According to them, most likely the presence of phenolic-OH groups and ortho-dihydroxyphenyl groups in chemical structure of tannins are involved in the formation of complexes with iron and also take part in redox reactions. In the formation of iron oxide NPs by tannins, the reactions undergo changes in electron structure. Tannins are oxidized to quinines and, by this reaction; iron salt is reduced to iron oxide nanoparticles.

Likewise, presence of biomolecules or combinations of chemically complex biomolecules, e.g. Enzymes, amino acids, proteins, vitamins, and polysaccharides, and organic acids such as citrates, may act as reducing and capping agents in nanoparticle synthesis. The mechanism behind plant extract mediated metallic nanoparticle formation has not been clearly defined up until now. Not a single biomolecule of plant extract was involved in the fabrication of nanoparticles. Various plant components are rich in secondary metabolites and responsible for synthesis of metallic nanoparticles. Secondary metabolites include the polyphenols, flavonoids, tannic acid, terpenoids, ascorbic acids, carboxylic acids, aldehydes and amides. Many reducing sugars are commonly found in plants, and their presence is confirmed by the IR spectroscopic technique in different studies. Phyto-chemicals in plant extracts possess ideal redox properties that allow efficient reduction of metal precursors for conversion into their corresponding metallic nanoparticles.

Becerra et al, 2007, utilized the *tannin of alfalfa*. According to the assumption, tannins associated to alfalfa, derivate into radical tannins "R" causes reduction of metal under the

influence of pH. The bio reduction process can be induced in the following way :(Becerra et al, 2007).

$$FeCl_3 + H_2O \rightarrow [Fe\ (H_2O)_n]^{3+} + H_2O \quad (2.1)$$

$$R + [Fe\ (H_2O)_n]^{3+} + H_2O \rightarrow [Fe\ (H_2O)_n]^{2+} + H^+ + R\text{–}OH \quad (2.2)$$

$$[Fe\ (H_2O)_n]^{2+} + 2R^- + H^+ + OH^- \rightarrow Fe^{2+}O^{2-} + Fe^{2+}Fe^{3+}O^{2-} + R\text{–}H + R\text{–}OH^- \quad (2.3)$$

Wang proposed the iron-polyphenol complex nanoparticles (Fe-P NPs), synthesized by Eucalyptus leaves. Reduction potential in Eucalyptus extract is due to polyphenols which make it able to reduce Fe^{3+} into Fe^{2+}. However, extract does not completely reduce the Fe^{2+} to zero-valent iron. Fe^{2+} strongly stabilizes due to polyphenols ligands but rapidly oxidize in the presence of oxygen to give Fe^{3+}-polyphenol complexes, this phenomenon commonly known as auto-oxidation. Thus, on reaction of iron metal solution with plants extract yields a black Nano-iron colloid. X-ray absorption (XAS) spectroscopy technique investigation suggested that plant polyphenols made chelate with ferric ion (Fe^{3+}) and found in globular position (Figure 2.1). Similar reaction mechanism was proposed for Sage (*Salvia officinalis*) mediated iron-polyphenol complex nanoparticles by Wang et al, 2015. Plant polyphenols and can be cross-linked by condensation of polyphenol on reaction between $FeCl_3$ and plant polyphenol, as can be seen in (Figure 2.2).

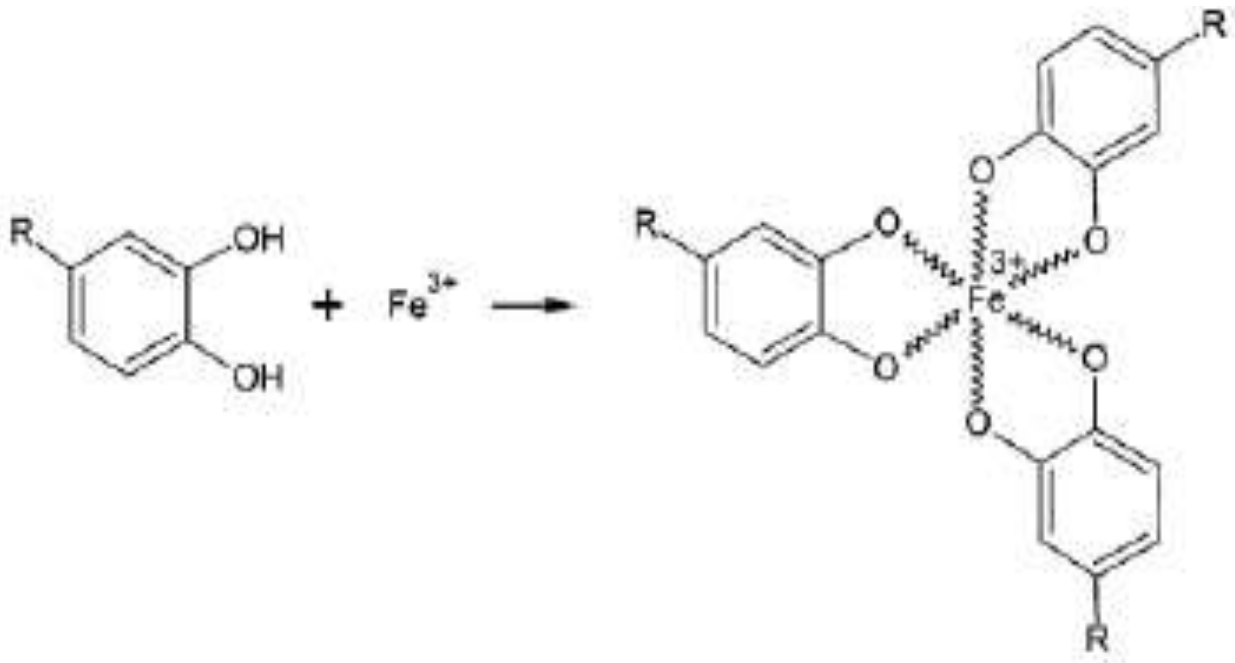

Figure 2.1 Proposed chemical structure of Fe-P NPs

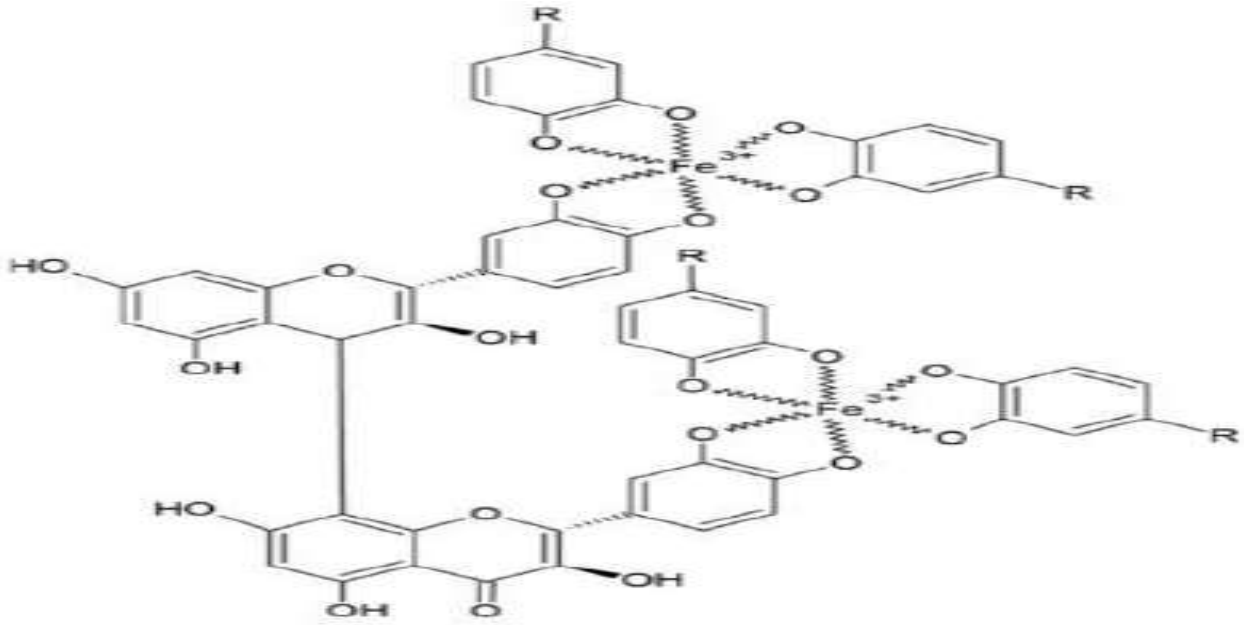

Figure 2.2. Proposed condensation mechanism of Fe-polyphenol

The mechanisms of Cr (VI) reduction by Fe^0 is a cyclic and consists of multiple reactions of electrochemical corrosion. The reduction rate of Cr (VI) by Fe^0 produces ferric ion (Fe (III)) and chromium ion (Cr (III)) (equation 2.4). Chromium (III) may be removed through the precipitation or co-precipitation in terms of mixed Fe (III) and Cr (III) hydroxide as shown in equations below: (Ensiye Fadaei1et al., 2013).

$$Cr^{6+} + Fe^0 \rightarrow Cr^{3+} + Fe^{3+} \quad (2.4)$$

$$(1\text{-}x)Fe^{3+} + (x)\ Cr^{3+} + 3H_2O \rightarrow (CrxFe\ (1\text{-}x))\ (OH)_3\ (s) + 3H^+ \quad (2.5)$$

$$(1\text{-}x)Fe^{3+} + (x)\ Cr^{3+} + 2H_2O \rightarrow Fe\ (1\text{-}x)\ CrxOOH\ (s) + 3H^+ \quad (2.6)$$

Retention occurs through the reduction of Cr (VI) in the trivalent state under the action of ZVI nanoparticles, and the precipitation of Cr (III) in the form of mixed Fe-Cr oxyhydroxides. A typical reaction describing the reductive precipitation of Cr (VI) is given in Equation below.

$$CrO^- + Fe^0 + 2H^+ + 2H_2O \rightarrow Fe(OH)_3 \cdot Cr(OH)_3\ (s) \quad (2.7)$$

The acidity of nZVI suspension is due to the generation of H^+ during the reduction of Fe (III) to the elemental state, Fe (0), as shown in reaction below.

$$nFe^{3+} + 3(Ar\text{-}OH)\ n \rightarrow nFe^0 + 3nAr{=}O + 3nH^+ \quad (2.8)$$

Where (Ar-OH) n represents polyphenols.

The reduction of adsorption with the increase of pH may be ascribed to the decrease in electrostatic force of attraction between the sorbent and the sorbate ions. Cr (VI) ions mostly exist as $H_2Cr_2O_4$ form at high acidic medium (pH =1). At pH 2-6 there is equilibrium between $Cr_2O_7^{-2}$ and $HCrO_4^-$ species, if the Cr (VI) concentration is less than 0.02 M, $HCrO_4^-$ is predominant form, when Cr (VI) concentration is greater than 0.02 M the dichromate ion (Cr_2O_7) is the predominant species and under alkaline condition (pH>8) it exists as chromate CrO_4^{-2} anion. The improved removal of Cr at low pH is probably due to reduction of hexavalent Cr to trivalent Cr.

At low pH: $Cr_2O_7^{-2} + 14H+ + 6e- \rightarrow 2Cr^{+3} + 7H$ (2.9)

At moderate pH: $HCrO_4^- + 7H^+ + 3e- \rightarrow Cr^{+3} + 4H_2O$ (2.10)

At low pH, there is presence of a large number of H^+ ions, which in turn neutralizes the negatively charged adsorbent surface thereby reducing hindrance to diffusion of dichromate ion. It is anticipated that the effect of pH on adsorption is also governed by the development of an electrical double layer on the adsorbent. The polarity of the double layer at the adsorbent surface may be changed from positive to negative as the H^+-ion concentration changes from acidic to basic with the increase of pH. It was found that at lower pH the system attained equilibrium faster and the percentage of chromium adsorbed increased. (Mystrioti et al., 2014).

2.5 Environmental Applications of Green Iron Nanoparticles

Many recent studies have indicated the potential of iron nanoparticles (NPs) for environmental remediation. Nano scale materials such as Nano adsorbents, Nano catalysts, Nano filtration, and Nano biocides such as metal and metal oxide nanoparticles are currently being employed for remediation of water and wastewater pollutants. Among these metallic nanoparticles, iron nanoparticles (FeNPs) have promising advantages that can combat environmental pollution. The interest in nano scale zero-valent iron (nZVI) in environmental remediation is increasing due to the reactivity of nano scale iron having a large surface area to volume ratio. The production of iron nanomaterial, such as metallic iron and oxide of iron via a more convenient greener route, is a great step forward in the development of nanomaterials.

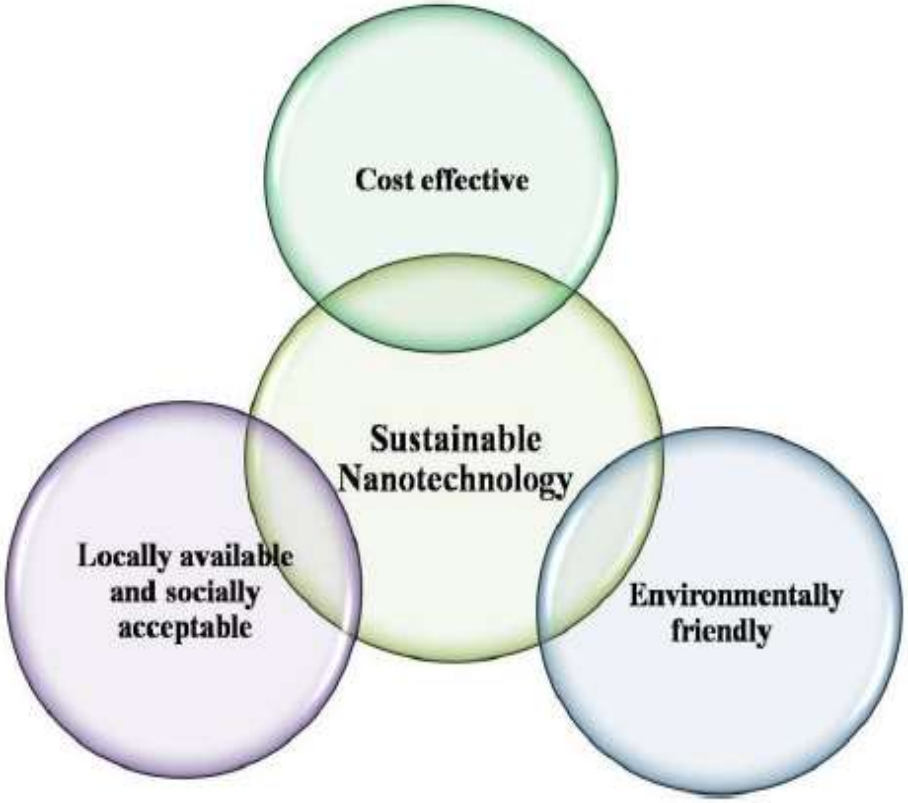

Figure 2.3. Sustainable green nanotechnology (Sadia Saif et al., 2016)

There are several green approaches to synthesize iron-based nanomaterials using different bio-chemicals and bio-reducing agents. Iron nanomaterials are significantly important for abatement of environmental pollution such as degradation of organic dyes, chlorinated organic pollutants and heavy metals removal, e.g., arsenic. Details about environmental applications of greener iron nanoparticles are as follows.

2.5.1 **Degradation of Dyes**

Hoag et al, 2009 Employed green tea (GT) synthesized iron nanoparticles to catalyze hydrogen Peroxide for the degradation of the organic contaminant bromothymol blue. From experiments, it was observed that by increasing concentrations of GT-nZVI, more hydrogen peroxide catalyzed, which ultimately increased the degradation of bromothymol blue. Similarly, the reactivity of iron nanoparticles synthesized by aqueous sorghum bran extracts was tested for degradation of dye

bromothymol blue by Njagi et al, 2011. In presence of iron nanoparticles and H_2O_2, Bromothymol blue degrades rapidly, demonstrating that the iron nanoparticles catalyzes the reaction for production of free radicals from H_2O_2. The catalysis of H_2O_2 prompting the rate of reaction ultimately increases the rate of degradation of bromothymol blue. In another report, green tea synthesized nZVI (Fe0) nanoparticles were employed for catalytic degradation of methylene blue (MB) and methyl orange (MO) dyes. The results indicate that the complete removal of methylene blue (MB) and methyl orange (MO) dyes from water was achieved at a concentration of 10–200 mg/L. As compared to MO, MB removed instantaneously as 80% of MB removed is first 5 min of reaction while 80% of MO dye removed after 1 h of reaction. Almost complete removal of the dyes was achieved after 200 min for MB and 350 min for MO, under the studied conditions. Green tea synthesized Fe nanoparticles proved to be more effective as a Fenton-like catalyst both in terms of kinetics and percentage removal compared to iron nanoparticles produced by borohydride reduction.

Huang et al, 2013.used *oolong tea* extract for synthesis of iron nanoparticles (OT-Fe NP) further employed to degrade malachite green (MG). The results also showed that: first, polyphenols/caffeine in oolong tea extract acted as both reducing and capping agents in synthesis of Fe nanoparticles, leading to reduced aggregation and to increased reactivity of OT-Fe NP. Second, OT-Fe NP proved to be efficient in the degradation of MG, resulting in 75.5% of MG (50 mg/L) being removed.

Kuang et al, 2013 used extracts of three different teas i.e., green tea (GT), oolong tea (OT), and black tea (BT) separately for synthesis of iron nanoparticles. Synthesized iron nanoparticles were used as a catalyst for Fenton-like oxidation of monochlorobenzene (MCB). Highest degradation rate was achieved by green tea synthesized Fe NPs and was attributed to high polyphenol present in extract. Sixty-nine percent degradation was observed for GT-Fe NPs while 53% by OT-Fe NPs and 39% by BT-Fe NPs in180 min. Oxidative degradation mechanism was proposed for green tea synthesized iron nanoparticles and as follows. At first, the MCB adsorbs onto the surface of Fe NPs and iron oxide formed in the Fe corrosion. As described in Equations (2.4) and (2.5).

- Adsorption process:

$$MCB + Fe\ NPs \rightarrow MCB/Fe\ NPs \quad (2.11)$$

$$MCB + \gamma\text{-}Fe_2O_3\ /Fe_3O_4 \rightarrow MCB/\gamma\text{-}Fe_2O_3/Fe_3O_4 \quad (2.12)$$

Fe^{2+} and Fe^{3+} leach from Fe^0 and iron oxides on the surface of Fe NPs, as shown in the equations below, and this process accelerates the decomposition of H_2O_2 and generates highly oxidative OH radicals when Fe^{2+} was oxidized by H_2O_2 into Fe^{3+}.

- The process of generating hydroxyl radicals' species:

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2HO\text{-} \quad (2.13)$$

$$Fe_2O_3/Fe_3O_4 + H+ \rightarrow Fe2+/Fe^{3+} + H_2O \quad (2.14)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + OH^- \quad (2.15)$$

In the meantime, generated Fe^{2+} and Fe^{3+} in the solution will react with H_2O and yield Oxy hydroxide equation which can also adsorb MCB. Furthermore, Fe^{3+} on the surface of FeNPs was converted into Fe^{2+} and HO^{2-} and the generated HO^{2-}. Possibly further react with Fe^{3+} and favored the decomposition of H_2O_2. Meanwhile, the generation of radical species rapidly reacts with the adsorbed MCB and also attacks MCB, resulting in mineralization of some part of MCB on surface of Fe NPs into CO_2 and H_2O, which also involve in removal of COD (chemical oxygen demand). In reaction time of 180 min, the rate of dye degradation (81%) was high then and removal of COD (31%). The study illustrates that the complete mineralization during Fenton-like process is not possible when COD content is high.

Iron ions polyphenol complex nanoparticles were effectively applied for degradation of dyes. Wang employed stable colloidal iron-polyphenol complex nanoparticles (Fe-P NPs) mediated by eucalyptus for adsorption-flocculation against Acid black 194 dyes was tested. It was observed that Acid black 194 adsorbed at 1.6 g per gram of Fe-P NPs at temperature 25^{o}C, Iron

polyphenol nanoparticles (Fe-P NPs) mediated by three different plants i.e., *E. tereticornis, M. nesophila* and R. officinalis were compared for decolonization of dye by Wang et al. About 100% of Acid black dye was decolorized, and 87% removal of total organic carbon (TOC) was achieved by Fe-P NPs. *E. tereticornis* Fe-P NPs showed good activity against dye degradation as compared to other nanoparticles and attributed to small size and good dispersibility of particles when analyzed under SEM.

Huang et al, 2013. Studied the experimental factors such as the volume ratio of Fe^{2+} and tea Extract, temperature, and pH to understand the influence of these factors on nanoparticles synthesis. Results show that there was a decline in the concentrations of Fe NPs with an increase in leaf extract because of decreasing Fe^{2+} concentration. Further studied the reactivity of synthesized nanoparticles for degradation of dye, malachite green (MG) was studied. Degradation of MG by Fe NPs was influenced synthesized condition, pH whereas the high temperature also influenced on reactivity.

Luo et al, 2014 utilized grape leaf extract mediated Fe NP for degradation of dye, acid Orange II. In this study, it was found that the reactivity of plant mediated Fe NP was greater than the methanolic extract of grape leaves and Fe^{2+} solution both in water and methanol. Hence, the above studies show that the plant mediated iron nanoparticles were significantly effective for the degradation of various types of dyes under different experimental conditions. As compared to the conventional Fenton reaction, the Fenton-like reaction with plant mediated iron NPs takes place in a more sustainable manner. Plant mediated nanoparticles act as Fenton-catalyst with H_2O_2. Generally, oxidation depends on the activity of the hydroxyl radical (OH^-) which produce in aqueous solution and due to reaction of Fe^{2+} and hydrogen peroxide, H_2O_2. However, reaction pathway may be varying for different catalysts, or may depend on chemical nature of the catalyst as well as for the dye.

2.5.2 **Removal of heavy metals**

Polyphenols enriched green tea extract plays dual role in synthesis of nZVI, since they have capability to reduce ferric cations, meanwhile shield nZVI from being oxidized and agglomerated, functioning as capping agents. Column tests were performed at different flow rates in order to analyze the effect of contact time between the nZVI attached on porous media and the flow-over solution on reduction of Cr (VI). According to the results of the study, reduction and removal of Cr (VI) from the aqueous phase can be increased by increasing contact time. Leaching tests indicate that chromium in precipitated form is insoluble. In the tested soil material, the total amount of precipitated Cr was observed to being the range between 280 and 890 mg/kg of soil, whereas the soluble Cr was less than 1.4 mg/kg of soil, which was most likely due to the presence of residual Cr (VI) solution in the porous soil. Nano zero-valent suspension is a very conducive to remediation of a contaminated aquifer, and the use of stable nanoparticles makes this technique successful. Metals adsorbed on nanoparticles via redox reaction, co-precipitation or surface adsorption process (Mystrioti et al., 2016).

Madhavi et al., 2013 reported a single-step synthesis of zero-valent iron nanoparticles at room temperature using the Eucalyptus globules leaf extract. The reaction for synthesis of iron nanoparticles was increased by adding more extract. FTIR spectroscopy provided the information about the vibrational state of adsorbed molecules and, hence, the nature of surface complexes. The phytogenic Fe^0 nanoparticles were further used for the adsorption of Cr (VI) metal. Adsorption parameters such as dose of adsorbent, initial concentration of Cr (VI) and kinetics were also studied by batch experiments. The highest adsorption efficiency was 98.1% at reaction time of 30 min, and dosage of was 0.8 g/L. One occurrence of particular interest was that phyto-synthesised iron nanoparticles were stabilized and remained in that state for up to two months after preparation. Sava sari et al., 2015 expand this using by ascorbic acid, which was employed for reduction of Cd (II) from aqueous and ascorbic acid synthesized nanoparticles proved to be stable and efficient.

In two different studies, Mystrioti et al, 2014. produced stable colloidal suspensions of nZVI coated with polyphenol of green tea and studied their chromium removal efficiency from groundwater as well as their transport characteristics through representative porous media The effectiveness of the resulting GT-nZVI suspension with diameter of 5–10 nm was evaluated for the removal of hexavalent chromium Cr (VI) from polluted groundwater flowing through the permeable soil bed. Green tea extract is characterized as a higher antioxidant compound due to presence of polyphenols. Polyphenols enriched green tea extract plays dual role in synthesis of nZVI, since they have capability to reduce ferric cations, meanwhile shield nZVI from being oxidized and agglomerated, functioning as capping agents. Column tests were performed at different flow rates in order to analyze the effect of contact time between the nZVI attached on porous media and the flow-over solution on reduction of Cr (VI).

The reactivity of iron nanoparticles based on different factors which ultimate influence on removal mechanism , e.g. iron nanoparticles with variable oxidation states, possess different chemical characteristics as well as their mechanism of reaction with contaminants might be dissimilar as described by Tang and Lo 2013. Heterogeneous reduction reaction takes place during in-situ remediation of chromium.

2.5.3 **Wastewater Treatment**

Chrysochoou et al, 2012 investigated the attributes related to the transportation of iron Nanoparticles synthesized with polyphenol enrich solution of green tea utilizing two granular media, refined silica sand, as well as sand-coated with aluminum hydroxide. The green tea nZVI (GT-nZVI) injection caused a rapid decline in the pH of effluent from 8.5 to 2 owing to the presence of residuary discharged Fe^{3+} in the solution along with corresponding hydrolysis reactions. The elevation in the redox potential from 150 mV to 550 mV was reported despite the fact that GT-nZVI holds reducing Fe^{0}. This phenomenon is the characteristic feature related to the oxidation of polyphenols available in green tea. The elevation in redox potential can be an indicator of transport of GT-nZVI in the subsurface when used as an in situ reactant.

He et al, 2011 Employed starch mediated bimetallic Fe/Pd nanoparticles for the degradation of TCE (trichloroethylene). Results from this study demonstrated that the starched Fe nanoparticles showed considerably less agglomeration however, higher DE chlorination power than those produced without a stabilizer. At dosage of 0.1 g/L of the starched nanoparticles were able to degrade 98% of TCE within1 h in water.

Wang et al, 2014 employed biosynthesized iron nanoparticles for treatment of eutrophic wastewater. This study first synthesized iron nanoparticles through a one-step room-temperature biosynthetic route using eucalyptus leaf extracts. To the best of the author's knowledge, this is the first study to report on green tea synthesized nanomaterial utilized for remediation of eutrophic wastewater.

Synthesized poly-dispersed iron nanoparticles employed eucalyptus leaf extract obtained from its leaf litter. Due to the presence of different phytochemicals, each with varied reducing power in the extract form, the nanoparticles were poly-dispersed unlike the more common practice where nanoparticles are synthesized using a chemical reducing agent. For the first time, biologically synthesized nanoparticles were used for the treatment of eutrophic wastewater. After 21 days, percentage removal of total nitrogen, total phosphorus, and COD was 71.7%, 30.4%, and 84.5%, respectively. The reason for very low phosphorus removal was assigned to the absence of precipitating agents such as calcium, magnesium or aluminum.

In another study, Wang et al, 2013 utilized the leaf extracts of green tea and eucalyptus separately for the formation of iron nanoparticles (Fe NPs) and employed for the efficient removal of nitrate from wastewater. Synthesis of spheroidal iron nanoparticles (Fe NPs) was confirmed by employing characterization techniques.

A comparison study was conducted between plant-synthesized and chemically-synthesized iron materials. Green tea and eucalyptus mediated Fe NPs were able to remove 59.7% and 41.4% of nitrate from waste water, respectively, compared to 87.6% and 11.7% removal of nitrate by nZVI

and Fe_3O_4 nanoparticles, respectively. Despite the higher removal efficiency of nZVI, the green synthesized Fe NPs were found to be more stable in nature.

2.5.4 **Antibacterial Activity**

Various studies confirm that iron nanoparticles possess good antimicrobial properties. The antibacterial effect of *Tridax Procumbent* synthesized iron oxide (Fe_3O_4) nanoparticles was investigated by Senthil and Ramesh, 2012 against gram negative bacteria *Pseudomonas aeruginaso*. Kiruba Daniel et al, 2012 used the leaf extract of *Dodonaea viscosa* for the synthesis of Cu, ZVI and Ag nanoparticles. The reduction of iron salt (ferric chloride) to ZVI nanoparticles was observed according to recorded instantaneous changes of reaction from yellow to greenish-black at room temperature. Iron zero-valent synthesized nanoparticles showed spherical morphology with an average particle size of 27 nm. The Fourier transform infrared (FTIR) study confirmed that the biomolecules in *D. viscos* leaves such as flavonoids perform the reduction of metals salts, and their tannins, and *saponins mayact* as capping agents. Capping of NPs with plant biomolecules prevent the oxidation of NPs to their oxide. Antimicrobial activity of biosynthesized NPs were evaluated against human pathogens *viz.gram-negative* bacteria *Escherichia coli, Klebsiella pneumonia, Pseudomonas fluorescens* and gram-positive bacteria *Staphylococcus aureus* and *Bacillus subtilis*. These biosynthesized NPs were proved as effective antimicrobial agents against specific human pathogens.

Table 2.3. Size, morphology and environmental application of $Fe^0/Fe_2O_3/Fe_3O_4$ nanoparticles synthesized by different parts of plants and plants material (Sadia Saif et al., 2016)

Plants	Plant Parts Used	Size and morphology	Environmental application
Green tea	Leaf	40–60nm amorphous	Degradation of aqueous cationic and anionic dyes
Grape	Leaf	15–100nmquasi-spherical shape amorphous	Azo dyes such as acid Orange
Tridax Procumbents	Leaf	80–100 nm crystalline irregular sphere shapes	Antibacterial against gram negative bacteria
Sorghum	Bran	40–50 nm spherical Amorphous	Degradation of bromothymol blue
Oolong tea	Leaf	40–50 nm spherical	Degradation of malachite green
Eucalyptus Globules	Leaf	50 to 80 nm spherical	Adsorption of hexavalent chromium
Green tea and Eucalyptus	Leaf	20–80nm quasi-spherical	Nitrates removal
Eucalyptus	Leaf	20–80nm amorphous	Treatment of eutrophic Wastewater

3. Methods

3.1 Raw material processing

3.1.1 Preparation of bamboo twigs

- The bamboo twigs were washed with 0.1 M HCl solution, dried and ground into fine powder and the physiochemical properties of the raw bamboo was analyzed based on ASTM D1762-84 and indicated in the Table 3.1.

Table 3.1. Proximate analysis of bamboo.

No.of run	1	2	3	average
Moisture content	10.10	9.51	10.2	9.936
Volatile mtter	80.3	81	81.52	80.94
Ash content	1.21	1.8	1.51	1.51
Fixed careben	18.49	16.84	16.97	17.1

3.1.2 Extraction of avocado seed

In this study to extract the oil the of avocado fruits were washed with distilled water and the seeds were separated from other edible parts, and then cut open with a knife and the seeds as well as the seed coverings were manually removed. The seeds were then chopped into smaller sizes, oven dried at 50ºC for 48 hours and then ground with laboratory grinder. The powdered samples were packaged in waterproof polyethylene bags and stored until required for analysis.

Figure 3.1. Avocado fruit and seed

Figure 3.2. Ground avocado seed powder

3.2 Extraction of polyphenol from avocado seed

Lyophilized 3g powder of was blend with 60% of solvent concentration. This mixture was placed in a water bath by stirring at the temperature of 60°C for 25 minutes. It was further cooled in a refrigerator and centrifuged at 2500 rpm for 10 minute; then the lost solvent was replaced by using vacuum filtration. The polyphenol extract was thus saved for further studies.

.

Figure 3.3. Polyphenol extracted from avocado seed.

3.3 Synthesis of Nano zerovalent Iron adsorbent

For the synthesis of Nano zerovalent iron treated and ground bamboo powder of 5g was weighed and added into a 5g solution of $FeCl_3$ in a beaker and stirred on a magnetic stirrer for 2 h to ensure thorough mixture of both materials and then poured into a three neck flask before addition of polyphenol extract from the avocado seed. Then, 2.5mL of polyphenol extract was dissolved in 100ml distilled water. Varying amounts of the polyphenol extract was taken in the burette and added drop-wise to the ferric chloride solution and black solid particles appeared immediately. During the addition, the contents of the flask was continuously stirred using a mechanical stirrer attached to the top of the flask. After the addition of the extract, the stirring was continued for 10 minutes. The resulting solution was then centrifuged for 30 minutes at 1000 rpm. The precipitate generated was collected and placed in test tubes. And then the precipitate was oven dried in at 50°C for 24 hours. After drying, the dried particles were stored inside sealed plastic bag. Thus the synthesized bamboo and avocado polyphenol extract based nanozerovalent iron was named as NZVI-AB.

Figure 3.4. Synthesis of NZVI-AB

Figure 3.5. Synthesized NZVI-AB

3.4 Preparation of stock Cr (VI) solution

The stock solutions of Cr (VI) of concentration 1 g/L was prepared by dissolving 2.8 g of analytical grade of $K_2Cr_2O_7$ in 1 L of distilled water. The stock solution was further diluted with distilled water to desired concentration for obtaining the standard solutions for absorbance measurement. The initial pH of the test solutions was adjusted to the desired value by using dilute solutions of HCl and NaOH. The required lower concentrations were prepared by dilution of the stock solution. All precautions were taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

3.4.1 UV spectrophotometer analysis of Cr (VI) concentration with Dpc

After experiments of adsorption performed the concentrations of Cr (VI) was determined via 1, 5-diphenylcarbazide (DPC) colorimetric method by measuring the absorbance using UV/VIS spectrophotometer at a wavelength of 540 nm. Diphenylcarbazide (DPC) solution was prepared by dissolving 250mg of DPC in 50ml of acetone in a 100ml volumetric flask. 0.2mL of sulfuric acid was added to 4mL of standard sample containing known concentration of chromium, pH was adjusted using 0.1M hydrochloric acid and sodium hydroxide. The solution was mixed well and then diluted in a volumetric flask using distilled water. Further 0.2 mL of DPC solution was added and mixed well. After full color development for 10 min, 4mL of this solution was used in an absorption cell and the concentrations were measured spectrometrically at 540nm in UV spectrophotometer (Lambda 950 UV/Vis spectrometer). The calibration curve is prepared by measuring the absorbance of different known concentrations of chromium solutions and plotting a graph between concentrations versus absorbance.

3.5 Characterization of Synthesized NZVI-AB

3.5.1 FTIR spectrum analysis

FT-IR analysis was used to understand the existence of surface functional groups in metallic interactions and the synthesized NZVI-AB particle was analyzed before and after the adsorption experiments using prinks Elmer spectrum 65 FT-IR at Addis Ababa university of 4 kilo campus.

3.5.2 XRD analysis of NZVI-AB

The X- ray diffraction studies of Zero-Valent Iron nanoparticles was performed with XRD analytical instrument equipped with a mono achromatized operated at 40 kV and a current of 15 mA with Cu α radiation (λ=0.154060 nm). A scan mode was used to collect 2θ data from 10^{o} to 90^{o}.

3.5.3 Point of zero charge

The point of zero charge (pzc), in physical chemistry, is a concept relating to the phenomenon of adsorption, and it describes the condition when the electrical charge density on a surface is zero. It is usually determined in relation to an electrolyte's pH, and the pzc value is assigned to a given substrate or colloidal particle. The value of pH is used to describe pzc only for systems in which H^{+}/OH^{-} are the potential-determining ions (which is the common case). Generally, pzc is the value of the negative decimal logarithm of the activity of the potential-determining ion in the bulk fluid. When the pH is lower than the pzc value, the system is said to be "below the pzc." Below the pzc, the acidic water donates more protons than hydroxide groups, and so the adsorbent surface is positively charged (attracting anions). Conversely, above pzc the surface is negatively charged (attracting cations/repelling anions).

Point of zero charge is of fundamental importance in surface science. For example, in the field of environmental science, it determines how easily a substrate is able to adsorb potentially harmful ions. It also has countless applications in technology of colloids, e.g., flotation of minerals. At

pzc, the colloidal system exhibits zero zeta potential (i.e., the particles remain stationary in an electric field), minimum stability (i.e., exhibits maximum coagulation/flocculation rate), maximum solubility of the solid phase, maximum viscosity of the dispersion, and others.

The pzc is typically obtained by acid-base titrations of colloidal dispersions while monitoring the electrophoretic mobility of the particles and the pH of the suspension. Several titrations are required to distinguish pzc using different electrolytes (including varying the electrolyte ionic strength). Once satisfactory graphs are obtained (acid/base amount-pH, and pH-zeta potential), the pzc is established as the common intersection point (cip) of the lines. (Kosmulski, 2009).

3.6 Cr (VI) Adsorption studies using NZVI-AB

Experimental solutions of the desired concentrations 20mg/l, 25 mg/l, and 30mg/l, of chromium were obtained by successive dilutions. All adsorption experiments were conducted at room temperature (25◦C). In each experiment, 100ml of Cr (VI) solution of known concentration was added to NZVI-AB particles at different dosages (0.1, 0.5 and 1 g), initial Cr (VI) concentration of (20, 25 and 30 mg/L) and initial pH of (3, 5, and 8) were employed in the adsorption studies which was performed using conical flasks by shaking it in rotary shaker with 200rpm for 60 minutes and all the experiments were carried out with two replications for each Cr (VI) solution and optimum experimental conditions were determined.

Figure 3.6. Diluted chromium solution

Figure 3.7. Solution of chrome and NZVI-AB

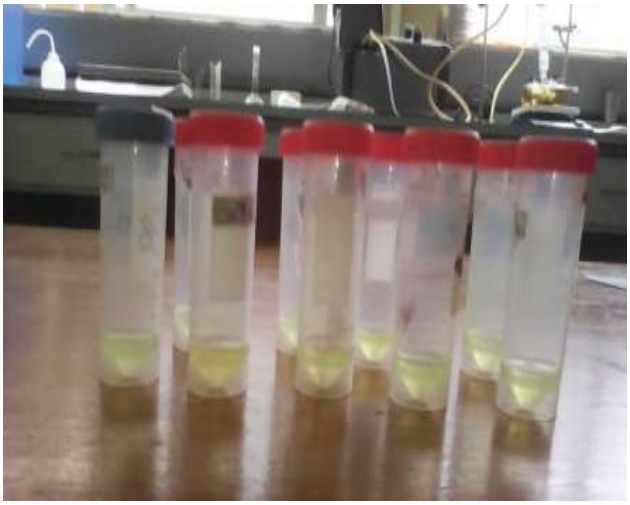

Figure 3.8. Filtrate solution after adsorption

3.6.1 Reduction of Cr (VI) by NZVI-AB

The extent of heavy metal removal was investigated separately by changing adsorption dose, contact time, initial chromium concentration and changing pH of the solution. After adsorption, the adsorbent was separated from the solutions using vacuum filter and the initial and final metal concentrations were determined. Effluent after the sorption was treated with 0.2 % DPC in acid medium to determine the final concentrations of Cr (VI). Hexavalent chromium reacts with DPC under acid conditions to form a red-violet color (diphenylcarbazide-dichromate complex) quantified using Perkin-Elmer UV-visible spectrophotometer.

The Cr (VI) removal percentage (R) was calculated spectro-photo metrically

Using the formula given equation (3.1):

Removal percentage

$$(R) = (Co - Ce / Co) * 100 \qquad (3.1)$$

Where C_0 and C_e are the initial and equilibrium liquid phase solute concentration (mg/L), respectively. The chromium mass adsorbed per gram of NZVI-AB adsorbent was calculated by difference between the Cr^{6+} concentration of the solution before equilibrium and in the equilibrium, multiplied by the chromium volume used in batch experiment and divided by the adsorbent mass adsorption capacity was obtained by the equation (3.2):

$$q_e = \frac{C_0 - C_e}{M} \times V \qquad (3.2)$$

Where V (L) represents the volume of chromium solution, M (mg) stands for the mass of the used NZVI particles.

3.7 Adsorption Isotherms:

A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm.

3.7.1 Freundlich Adsorption Isotherm

It is an empirical relation between the amount of an adsorbate adsorbed per unit weight of adsorbent and the adsorbate equilibrium concentration (C_e) in the fluid as follows:

$$X/M = K\, C_e^{\,n} \qquad (3.3)$$

Where, K and n are Freundlich coefficients

X = weight of adsorbate adsorbed on m unit weight of adsorbent

C_e = equilibrium concentration of adsorbate

From equation, for equilibrium conditions:

$$\text{Log (qe)} = \log (\text{kf}) + 1/\text{n}\log (\text{Ce}) \qquad (3.4)$$

Where, qe, is mass of adsorbate adsorbed over adsorbent (mg/g); Kf, is Freundlich capacity factor (units determined by q_e); C_e, is equilibrium concentration of adsorbate in liquid phase after adsorption (mg/L); *n*, is Freundlich intensity parameter. The coefficients K and n can be determined from the intercept and slope of a plot of log (qe) versus logC_e.

3.7.2 Langmuir Adsorption Isotherm

In the Langmuir model the adsorbent surface is considered to possess a number of active interaction sites for adsorption. Langmuir derived a relation between adsorbed material and its equilibrium concentration. Considering the processes of adsorption and desorption of the molecules on the surface, the Langmuir adsorption isotherm may be obtained as follows:

$$\frac{\text{Ce}}{\text{qe}} = \frac{1}{\text{bqmax}} + \frac{\text{Ce}}{\text{qmax}} \qquad (3.5)$$

Where, qe, is mass of adsorbate adsorbed over adsorbent (mg/g); C_e, is equilibrium concentration of adsorbate in liquid phase after adsorption (mg/L); qmax, is maximum amount of adsorbate that can be adsorbed (mg/kg); *b*, is Langmuir isotherm constant. Further, from empirical constant *b*, separation factor *R* (dimensionless) also called as *R* factor or equilibrium parameter was also determined using the Equation:

$$(R) = 1/(1 + bCo) \qquad (3.6)$$

the value of *R* gives insight into the suitability of adsorbent for the adsorption i.e., affinity between adsorbate and adsorbent. If, R < 1.0 it represents favorable adsorption; R > 1.0 it represents unfavorable adsorption; and R = 0 irreversible adsorption.

3.8 Design of Experiments

Data analysis was carried out by Design Expert version 7.0 software to evaluate (general factorial) the effects of the process variables; dosage (0.1g,0.5g ,and 1g), metal concentration (20mg/L, 25mg/L and 30 mg/L) and solution pH (3,5 and 8).. A 27 full factorial experimental design were employed and the experiment was performed with two replications. The response variable was removal percentage. This design of the experiment helps us to optimize and set combination of process parameters .Significance of the result was set from analysis of variance (ANOVA).

Table 3.2. Selected values of parameters

Factors	Minimum	Center point	Maximum
Dosage(g)	0.1	0.5	1
Concentration (mg/L)	20	25	30
PH	3	5.5	8

4. RESULTS AND DISCUSSIONS

4.1 Characterization of NZVI particles

4.1.1 FT-IR spectra of NZVI Nano Zero-Valent Iron

FT-IR analysis was used to understand the existence of surface functional groups in metallic interactions. Figure represented the FTIR spectrum nanovalent iron particles between 4000 to 400 cm−1 of NZVI-AB. As the band observed in the figure below the wave length at 420 cm^{-1}indicated to the presence of hematite (α-Fe_2O_3). The peaks at 3405 and 1609cm−1 were assigned to the O–H stretching vibration of polyphenols, partly were due to the O–H stretching vibration of FeOOH. the band at 670 cm-1 is due to the symmetric Fe-O stretch, and the broad band near 2923 cm^{-1} is attributable to the stretching mode of the bulk hydroxyl groups in the goethite(α -FeOOH) structure. The bands around 800 and cm^{-1} can be assigned to the bending modes of bulk hydroxyl groups in the goethite structure. In addition to magnetite (Fe_3O_4) and mag-hemite (γ-Fe_2O_3) exhibit bands at 784 and 667 cm^{-1}, respectively, which can be assigned to the Fe−O stretching modes of the tetrahedral and octahedral sites in their inverse spinel structure and the peaks at 1048 indicate the presence of γ-FeOOH-lepidocrocite. So finally I can conclude that the surface of fresh nZVI is covered by the mixture of different iron oxides. (Airong Liu, and Weixian Zhang, 2014).

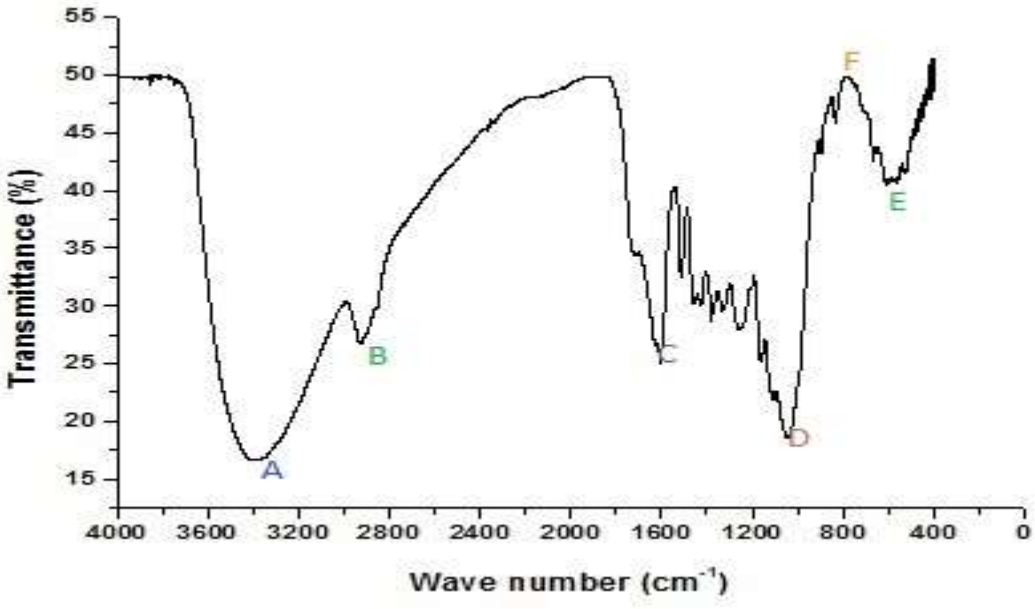

Figure 4.1. FT-IR spectrum of NZVI-AB particles before adsorption.

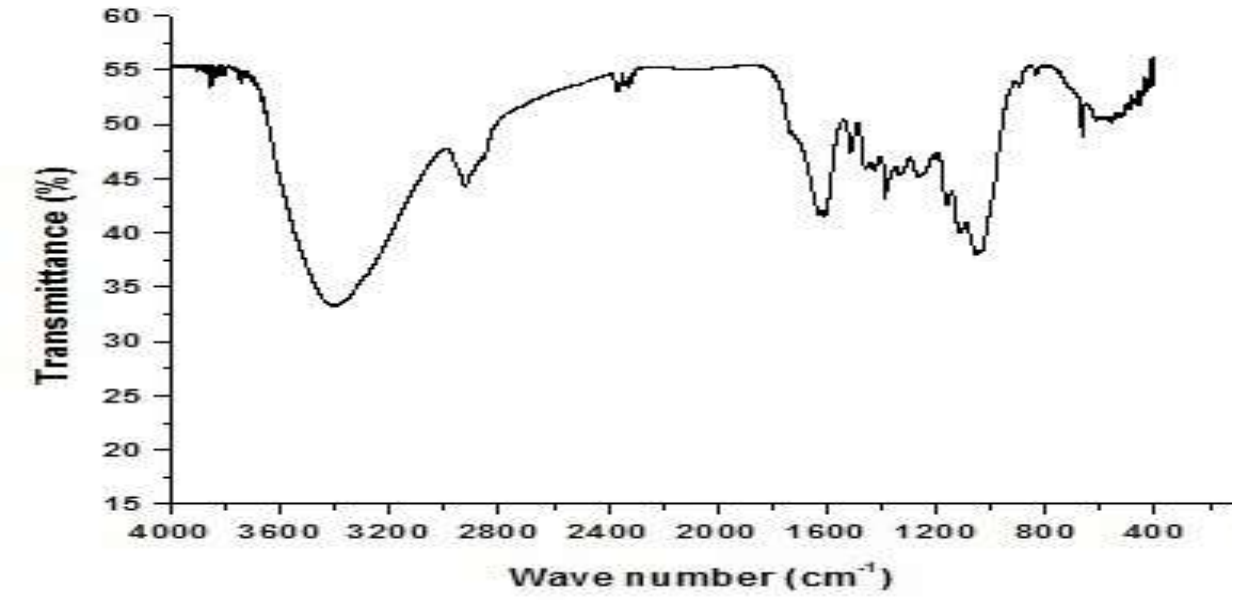

Figure 4.2. FT-IR spectrum of NZVI-AB particles after adsorption

Table 4.1.Changes in the FTIR peaks of NZVI-AB before and after adsorption

Peaks	Wave number before adsorption	Wave number after adsorption
A	3405.02	3395.98
B	2923.43	2915.83
C	1609.83	1595.98
D	1048.57	1046.13
E	800	795.65
F	667.08	662.79

4.1.2 X-Ray Diffraction Structure Analysis of NZVI-AB:

The method of X-ray diffraction (XRD) was used to investigate the material structure of iron nanoparticles. So according to the XRD of the particle indicated in figure 4.1.2, the broad peak reveals the existence of an amorphous phase of iron. And the peak around 2θ of 22.78° indicates the presence of zero-valent iron (α-Fe) crystalline phases, and also the broad peaks at 25° and above indicate the presence of iron oxide (FeO) phases, but the iron oxide phase in the oxide layer seems not to be perfect crystalline. (Airong Liu, and Weixian Zhang, 2014)

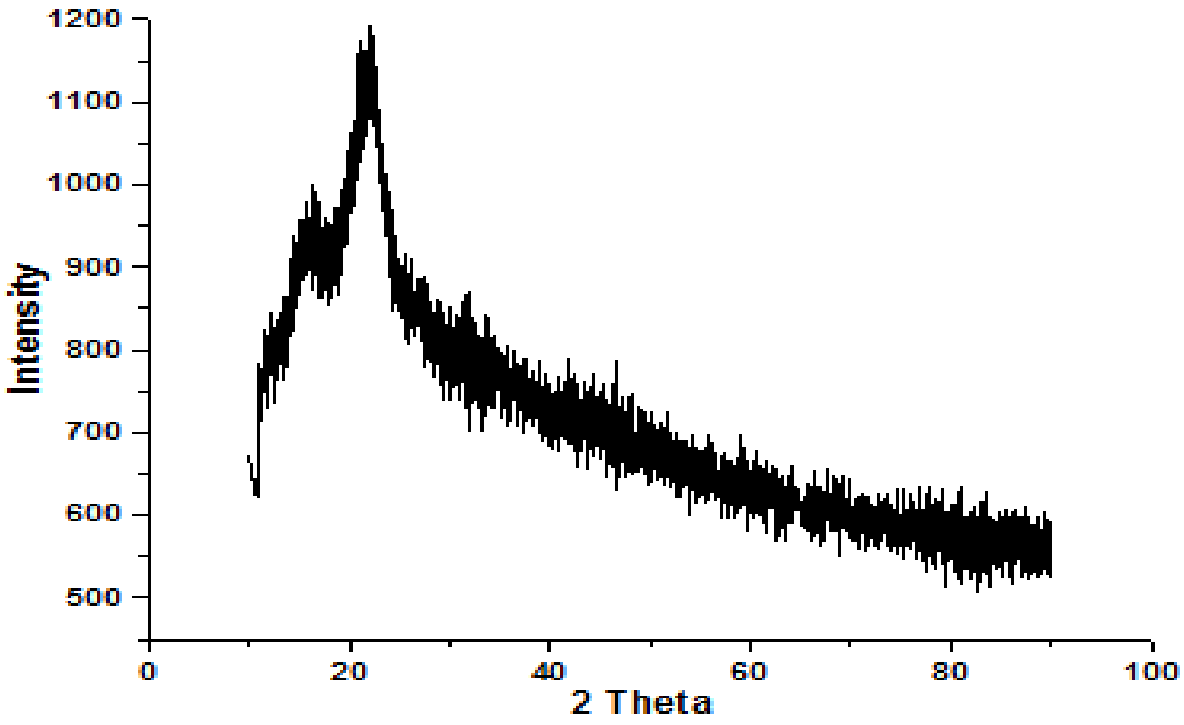

Figure 4.3. XRD graph of NZVI-AB

4.1.3 Point of zero charge

The pzc was obtained by acid-base titrations of colloidal dispersions of the particle in the solution of salt solution by monitoring the particles and the pH of the suspension at the values of 1, 3 and 5, of varying the electrolyte ionic strength and shaking it with 250 rpm for 6h and the measuring the pH of the solution after shaking it. The graph was plotted by taking the difference between the initial pH of solution and the suspension solution which contains the NZVI-AB after shaked it for 6h. Once satisfactory graphs were obtained (acid/base amount-pH, and pH-zeta potential), the pzc was established as the common intersection point (cip) of the lines. The PZC s graph shows the intersection point around an ionic strength of approximately 2.8.

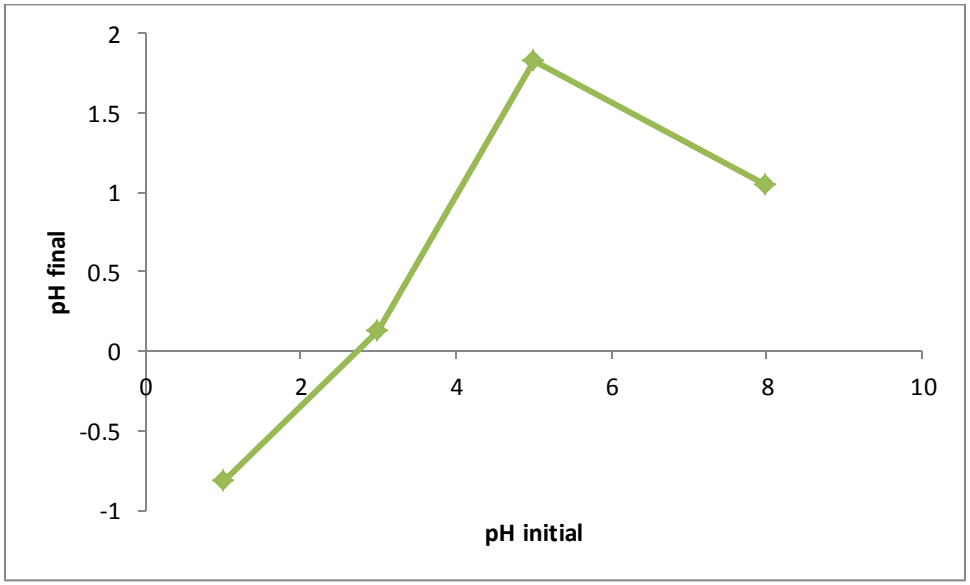

Figure 4.4. Point of zero charge determination

4.2 Cr (VI) Reduction Studies:

At the end of reduction/adsorption, the suspension was separated by using filtration. And after adsorption, the chromium concentrations were determined by UV–vis spectrophotometer. All the experiments were done in two replications with different the combination of the parameters. And the average values of the results have been presented.

Table 4.2. Experimental results of adsorption experiments

Run	Dosage (g)	Concentrations (mg/L)	pH	Absorbance	Replicate absorbance	Average absorbance
1	0.1	20	3	0.089	0.091	0.09
2	0.1	25	3	0.107	0.103	0.105
3	0.1	30	3	0.117	0.122	0.118
4	0.5	20	3	0.085	0.088	0.086
5	0.5	25	3	0.099	0.102	0.100
6	0.5	30	3	0.110	0.108	0.109
7	1	20	3	0.069	0.071	0.07
8	1	25	3	0.090	0.091	0.090
9	1	30	3	0.101	0.100	0.1005
10	0.1	20	3	0.09	0.093	0.091
11	0.1	25	5	0.103	0.101	0.102
12	0.1	30	5	0.114	0.121	0.117
13	0.5	20	5	0.091	0.089	0.09
14	0.5	25	5	0.108	0.11	0.109
15	0.5	30	5	0.121	0.124	0.122
16	1	20	5	0.077	0.079	0.078
17	1	25	5	0.095	0.093	0.094
18	1	30	5	0.107	0.104	0.105

19	0.1	20	8	0.101	0.10	0.1005
20	0.1	25	8	0.112	0.117	0.114
21	0.1	30	8	0.128	0.131	0.129
22	0.5	20	8	0.099	0.111	0.1
23	0.5	25	8	0.111	0.115	0.113
24	0.5	30	8	0.131	0.129	0.13
25	1	20	8	0.087	0.09	0.088
26	1	25	8	0.097	0.1	0.098
27	1	30	8	0.115	0.11	0.112

Based on the above results of the different parameters I have been studied the relationship and the interaction of the combination of these parameters on the removal efficiency graphically and drew the calibration curve by performing UV analysis on the range of the concentrations in the adsorption experiments as indicated below.

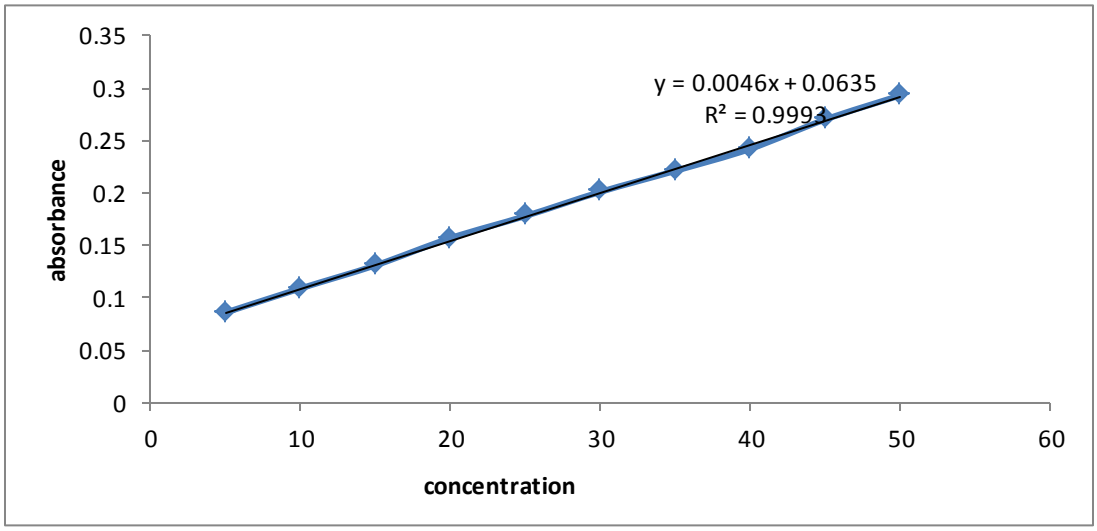

Figure 4.5. Calibration curve graph

4.2.1 Effect of pH on Cr (VI) Removal:

The adsorption of chromium from aqueous solution using NZVI-AB particles in this research was found to be a highly pH dependent process. PH of solution in fact determines the chemistry and speciation of chromium ions and also affects the surface charge of the adsorbent. In this experiment, the adsorption behavior of Cr (VI) ions was studied at different pH values, using 1g of NZVI-AB particles with a fixed concentration of chromium (20 mg/L). The results obtained are shown in Fig.4.6 which shows that removal of Cr (VI) ions increases with decreasing pH that indicates removal efficiency of chromium ion and pH of the solution has indirect relationship. And on the values of initial pH taken such as 3, 5 and 8, the Cr (VI) reduction rates were 92.38%,83.69%and71.82%respectively..

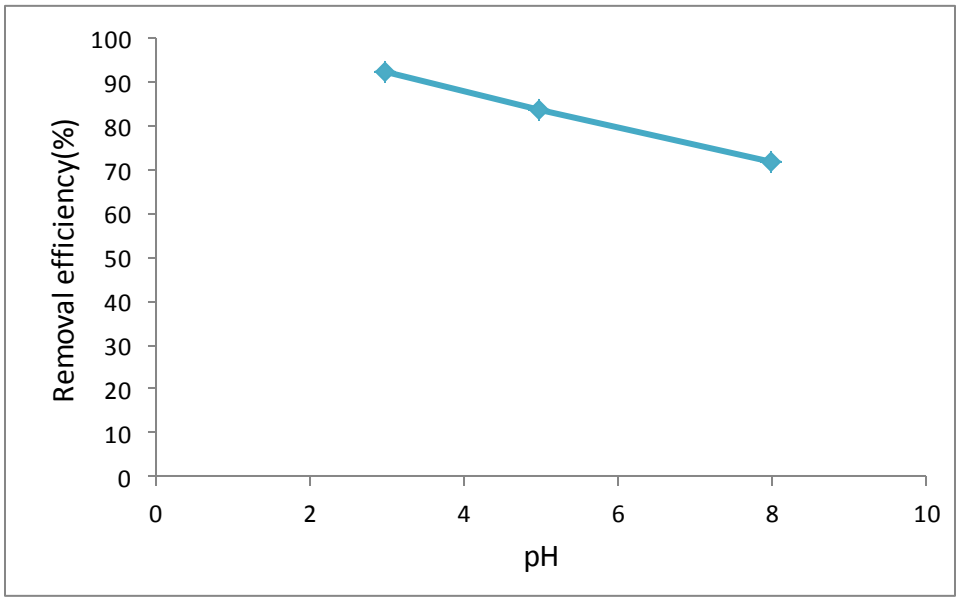

Figure 4.6. Effect of initial pH at initial concentration of 20mg/L and doze of 1g.

As it is observed from the fig.4.6 that the Maximum removal of Cr occurred at about pH=3.The Cr (VI) removal rate depends significantly on the pH of the solution, because the solubility of precipitate is strongly reliant on pH. Cr (VI) removal was insignificant except when the solution pH was low enough to dissolve the passive oxide layers. It is indicated that the NZVI-AB particles have a high reactivity at pH=3. In contrast, the plots for pH greater than 3 shows less

rapid removal efficiency decrement. This may be because of the formation of mixed Fe and Cr oxy hydroxides at high pH values on the iron surfaces. Solution of pH has an important effect on the reduction of Cr (VI) by NZVI particles. The pH value of solution changed slightly during the reaction process. It is evident that the reduction rate of Cr (VI) was greatly reduced under alkaline conditions because at a low pH (pH=3), the dominant form of Cr (VI) is $HCrO_4^-$ and the surface of the adsorbent is positively charged. By increasing of pH, the $HCrO_4^-$ species shifts to other forms CrO_4^{2-} and $Cr_2O_7^{2-}$ .The decrease in adsorption of Cr (VI) by increasing the pH is due to the competition between the anions CrO_4^{2-} and OH^-.

4.2.2 Effect of initial concentration:

Effect of initial concentrations of Cr (VI) on the removal efficiency of NZVI-AB particles had been studied for three different concentrations of 20, 25 and 30 mg/L through batch experiment mode at initial pH of 3 and adsorbent dosage of 1 g., and according to the fig. 4.7. The removal efficiency was found to be 92.38%, 76.07 % and 72.82% respectively for different concentrations of chromium as taken above. As the graph shown the adsorption was high at the initial low concentrations of Cr (VI) solution and thereafter the increase becomes more and more insignificant. The decrease in the percentage removal of Cr (VI) can be explained with the fact that the NZVI-AB particles had limited active sites, which would have become saturated at high Cr (VI) concentrations.

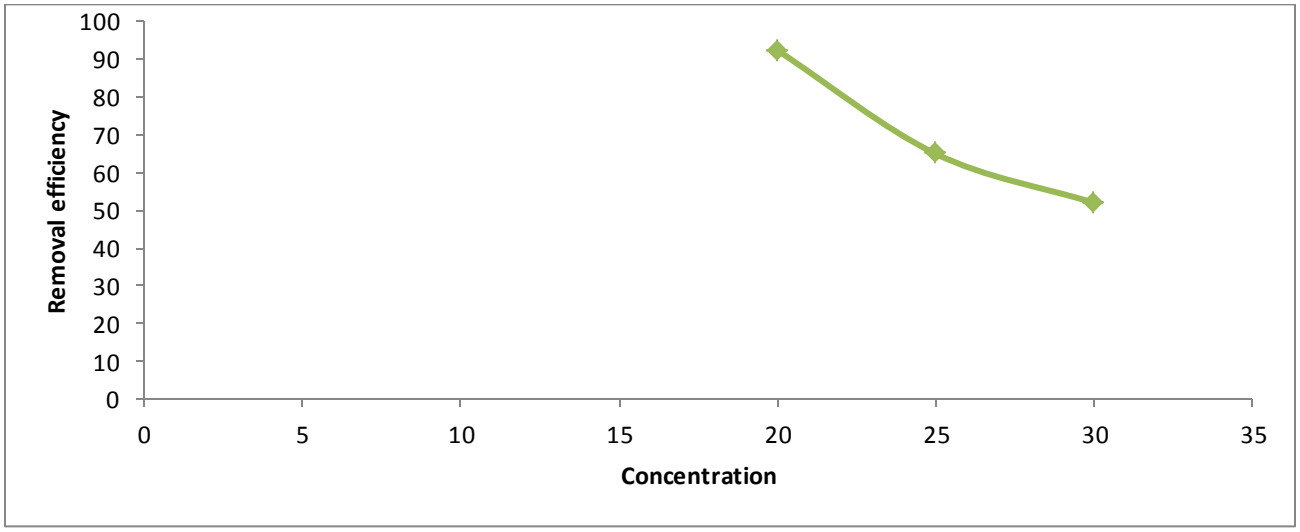

Figure 4.7. Effect of initial concentration of chromium on removal percentage.

4.2.3 Effect of NZVI –AB Concentration on Cr (VI) Reduction:

The effect of NZVI particle concentration on the adsorption of Cr (VI) ions in aqueous solution was studied by varying the NZVI particle concentration from 0.1 g to 1 g for constant initial concentration and pH of the solution. from fig.4.8 the adsorption removal percentage increases with an increased in adsorbent dose, and for this case the percentage removal of Cr (VI) increased from 70.6%,74.44% and 92.38% respectively for the selected particle doses of 0.1g, 0.5 and 1 g. As the adsorbent dosage increases, the number of sites available for adsorption increases.. Increase in NZVI-AB particle concentration increases the level of adsorption of Cr (VI) ions because of an overall increase in surface of the NZVI-AB particle which in turn increase the number of binding sites, leading to the increase of Cr (VI) removal efficiency. Therefore more NZVI-AB particles provide more iron surface-active sites for collision with Cr (VI) molecules, to accelerate the Cr (VI) removal efficiency.

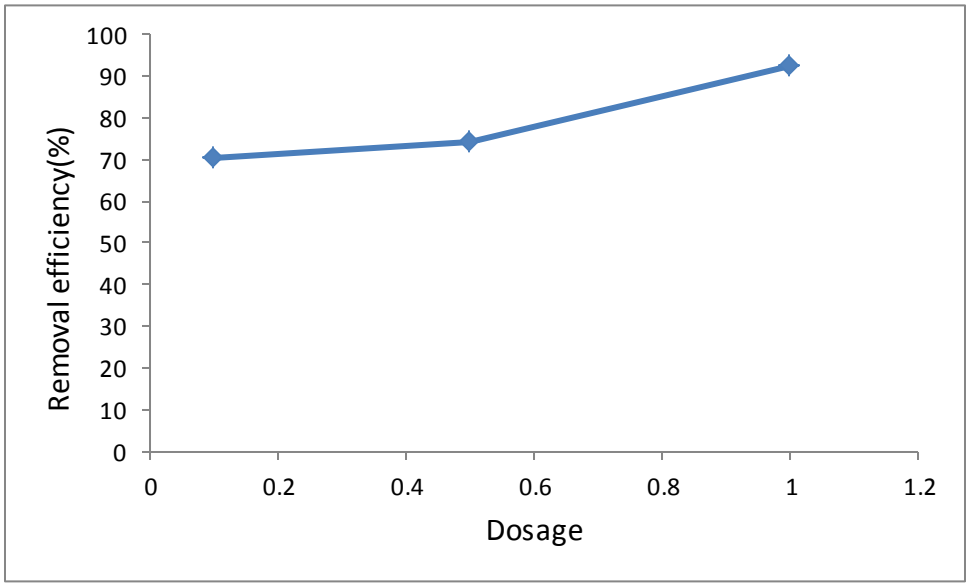

Figure 4.8. Effect of adsorbent dose on the removal efficiency.

4.3 Freundlich and Langmuir Adsorption Isotherms:

The equilibrium data was fitted to both Freundlich and Langmuir models. Plotting the experimental data using equations 3.5 and 3.6 the figures 4.9 and 4.10 shown below indicates that both Freundlich and Langmuir models give good fit for the data. The isotherms constants were calculated and presented in the Table 4.3.

Freundlich and Langmuir isotherm equations and parameters for the adsorption of Cr (VI) on to the synthesized adsorbent of correlation coefficients (R^2) indicate that both the adsorption isotherm models match satisfactorily with the experimental data obtained from the experiment. The Langmuir isotherm describes the experimental data better than Freundlich isotherm. The value of R obtained shows the favorable adsorption of Cr on NZVI-AB.

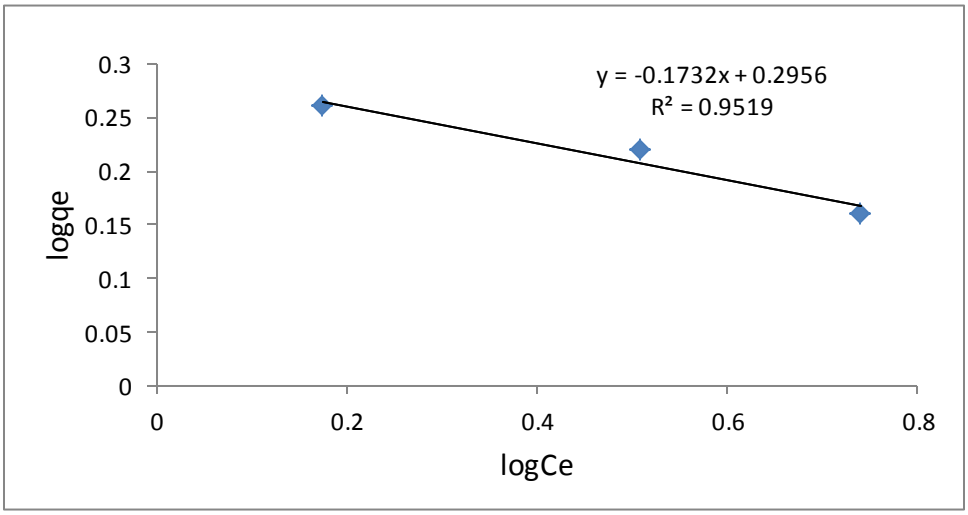

Figure 4.9. Freundlich isotherm model

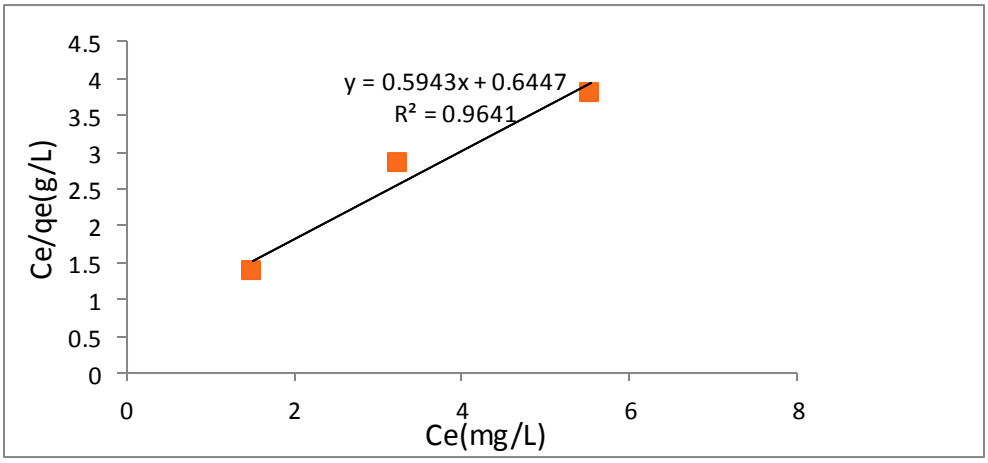

Figure 4.10. Langmuir isotherm model.

Table 4.3. Data showing the R_L values obtained for the adsorption of Cr (VI) ions by NZVI-AB.

Initial Concentration (mg/L)	R_L Value
20	0.0385
25	0.0311
30	0.026

To know the feasibility of Langmuir isotherm, the essential features of Langmuir model can be expressed in terms of R_L. The values of R_L indicate the shapes of isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) the calculated R_L values (0.0385, 0.0311 and 0.026) indicates favorability of the adsorption of chromium on to NZVI-AB.

Table 4.4**.** Adsorption isotherm constants for Cr (VI) reduction by NZVI-AB.

Isotherm	Parameters	Values
Langmuir	b (L/mg)	1.2456
	R_L	0.0386
	R^2	0.9641
Freundlih	K_F (mg/g(L/mg)1/n)	0.205
	n	19.22
	R^2	0.9519

4.4. Statistical and Graphical analysis of experimental results.

4.4.1. Analysis of variance (ANOVA)

The results found during absorption experiments were analyzed on ANOVA by taking the average results of replicated experiments from the experimental data in the absorption studies of Cr (VI). Anova analysis of the experimental data was done using general factorial design with three parametrs and three levels of the experiment in two replications.

Table 4.5. Analysis of variance (ANOVA) for selected quadratic Factorial Model.

Source	Sum of squares	Df	Mean square	F-value	P-value prob>f	Significance
Model	4402.39	9	489.15	73.70	< 0.0001	Significant
A-concentration	1035.59	1	1035.59	156.02	< 0.0001	
B-dose	1583.64	1	1583.64	238.59	< 0.0001	
C-pH	1203.48	1	1203.48	181.32	< 0.0001	
AB	38.74	1	38.74	5.84	0.0199	
AC	43.13	1	43.13	6.50	0.0144	
BC	9.40	1	9.40	1.42	0.2404	
A^2	57.70	1	57.70	8.69	0.0051	
B^2	260.13	1	260.13	39.19	< 0.0001	
C^2	2.51	1	2.51	0.38	0.5420	
Residuals	292.05	44	6.64	-	-	-

Lack of fit	186.36	17	10.96	2.80	0.082	Not significant
Pure error	105.69	27	3.91	-	-	-
CORE TOTAL	4694.44	53	-	-	-	

The analysis of variance of the regression model was a significant model, From Table 4.5 described above it was observed that the Values of "Prob > F" less than 0.0500 indicates that the model terms are significant accordingly A, B, C, AC, AB, A^2, and B^2, are significant model terms.The regression coefficients and the corresponding 95% CI (Confidence Interval) High and Low were presented in table 4.6 below. If zero was in the range High and Low 95% Confidence interval, the factors has no effect. From the 95% CI High and Low values of each model term, it could be concluded that the regression coefficients of concentration, dosage, pH and the interaction parameters of dosage and pH have highly significant effect in the adsorption of chromium.

Table 4.6. Regression coefficients and the corresponding 95% CI High and Low.

Terms	Coefficient estimate	Df	Standard	95% CI Low	95% CI High
Intercept	61.80	1	0.95	59.87	63.72
A	-5.39	1	0.43	-6.26	-4.52
B	6.65	1	0.43	5.79	7.52
C	-5.79	1	0.43	-6.65	-4.92
AB	-1.27	1	0.52	-2.33	-0.21

AC	1.33	1	0.52	0.28	2.38
BC	-0.62	1	0.52	-1.67	0.43
A^2	2.19	1	0.74	0.69	3.69
B^2	4.72	1	0.75	3.20	6.24
C^2	-0.48	1	0.78	-2.05	1.09

- Final Equation in Terms of Actual Factors:

$$\textit{Removal efficiency} = +158.1178 - 5.73891 * concentration + 6.24743 * dosage - 3.83168 * ph - 0.56348 * concentration * dosage + 0.10654 * concentration * ph - 0.55154 * dosage * ph + 0.087711 * concentration^2 + 23.32747 * dosage^2 - 0.076685 * ph^2$$

Table 4.7. Model adequacy measures

STD.Dev	2.03	R-Squared	0.9378
MEAN	66.24	ADJ R-Squared	0.9251
C.V.%	3.06	PRED R-Squared	0.9068
PRESS	375.14	ADEQ Precision	32.549

The "Pred R-Squared" of 0.9068 is in reasonable agreement with the "Adj R-Squared" of. 0.9251 The regression coefficient (R^2) quantitatively evaluates the correlation between the experimental data and the predicted responses. Results of R^2= 0.9378 and Adj-R^2=0.9251 obtained explicates that the predicted values were found to be in good agreement with the experimental values. Since the R^2 value is closer to 1.0. It indicates that the regression line perfectly fits the data. Similar to that in this investigation, R^2 obtained 0.9378 was close to 1 which imply that the predicted values were found to be in good agreement with experimental values (R^2=0.9378 and Adj-

R^2=0.9251), indicating the achievement of the model. The models goodness of fit was checked by regression coefficient (R^2). In this case, the value of the coefficient (R^2 =0.9378) from Table 4.7 indicated that only 6.22% of the total variance was not explained by the developed regression model. The obtained R^2 values suggest good adjustments to the experimental results. The adjusted determination coefficient (Adj-R^2=0.9251) was also satisfactory for confirming the significance of the model. Predicted R-Squared indicating that the model will probably explain a high percentage (about 90.68%) of the variability in new data. "Adeq precision" measures the signal to noise ratio. A ratio greater than 4 is desirable and in this study 32.549 indicates an adequate signal.

4.4.1 Graphical analysis of one factor and interaction effects on ANOVA.

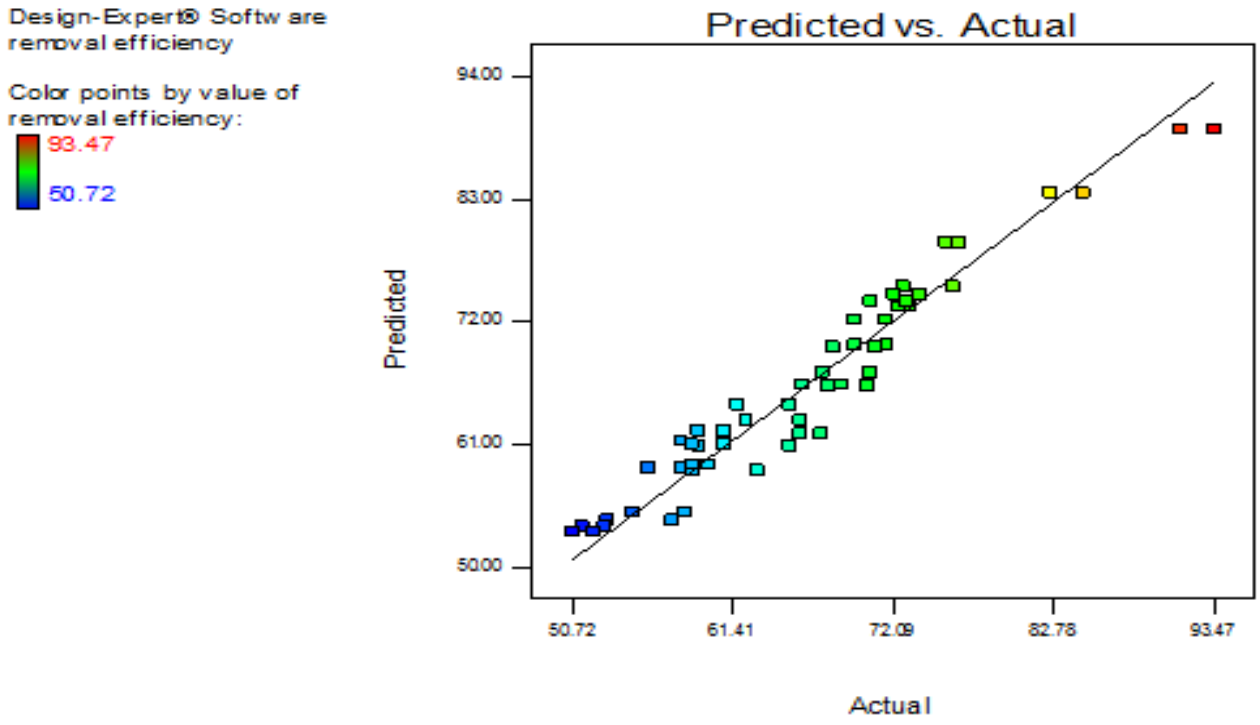

Figure 4.11 graph of Predicted and actual values

From the plot as shown above, the normal probability plot indicates the predicted following by the actual value distribution, in the case of this experimental data the points in the plots shows fitted to the straight line in the figure, this shows both the actual experimental values and the predicted values are approximate and the model satisfies the assumptions analysis of variance (ANOVA) i.e. the error distribution is approximately normal.

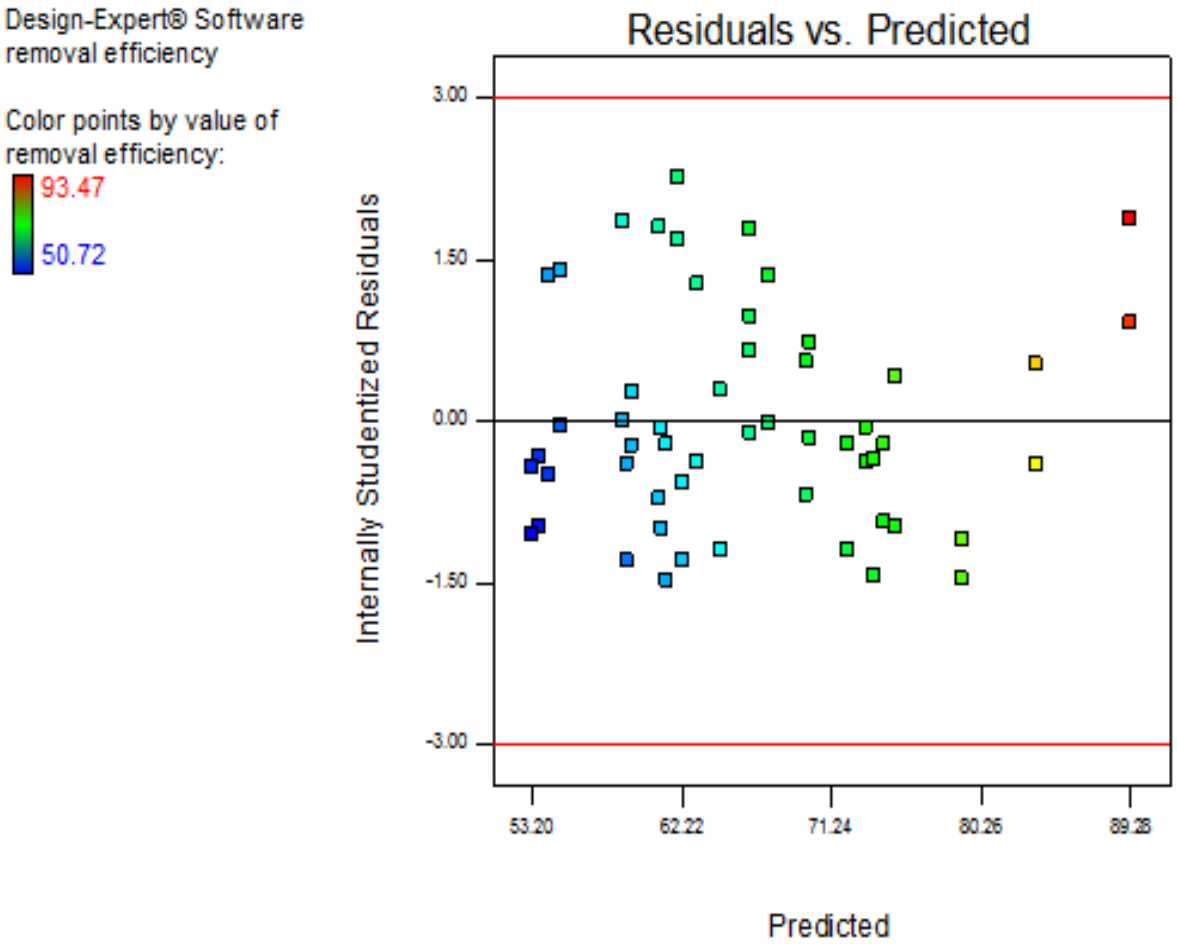

Figure 4.12. Graph of residual and predicted points

If the model is correct and the assumptions are satisfied, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals

versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

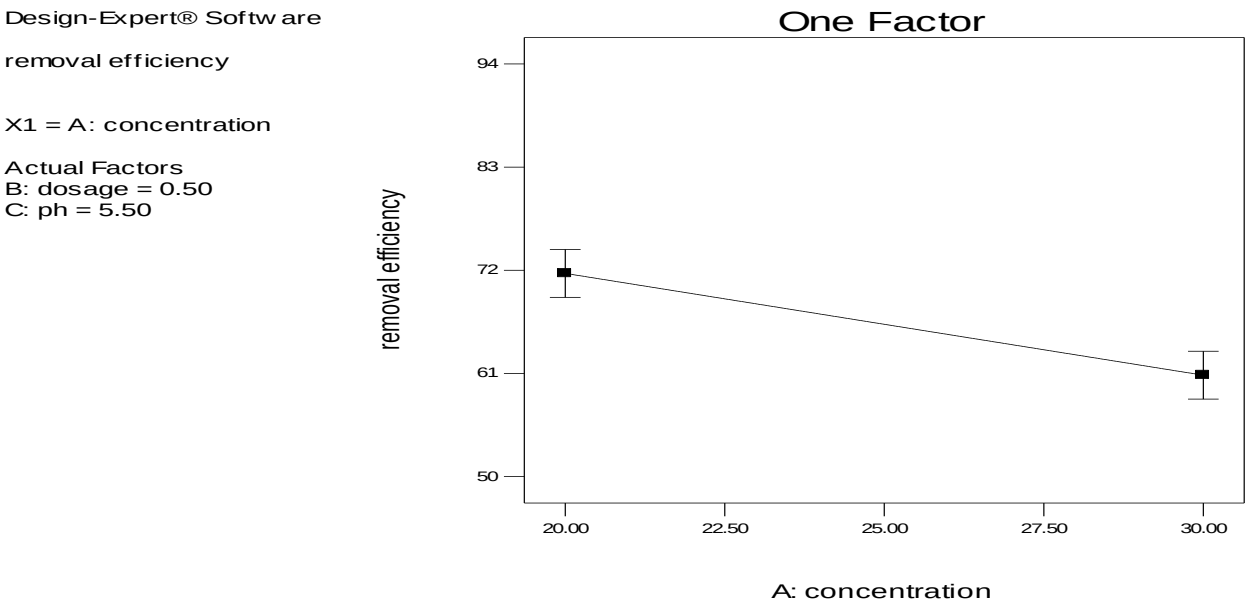

Figure 4.13. Effect of concentration on removal efficiency at center points.

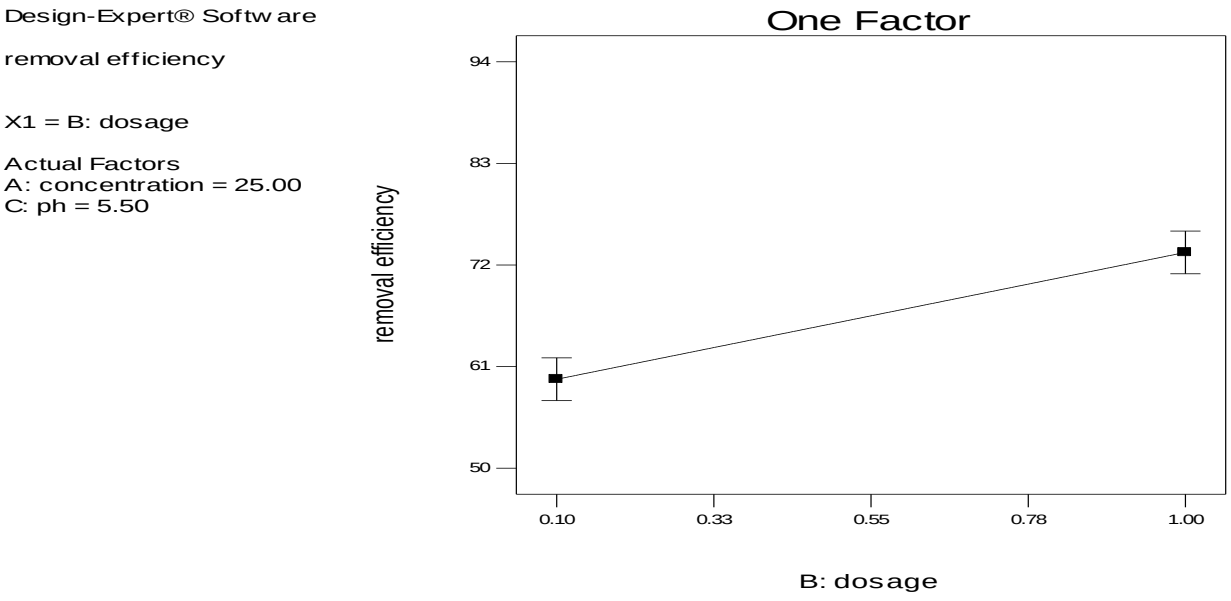

Figure 4.14. Effect of adsorbent dosage on removal efficiency at center point

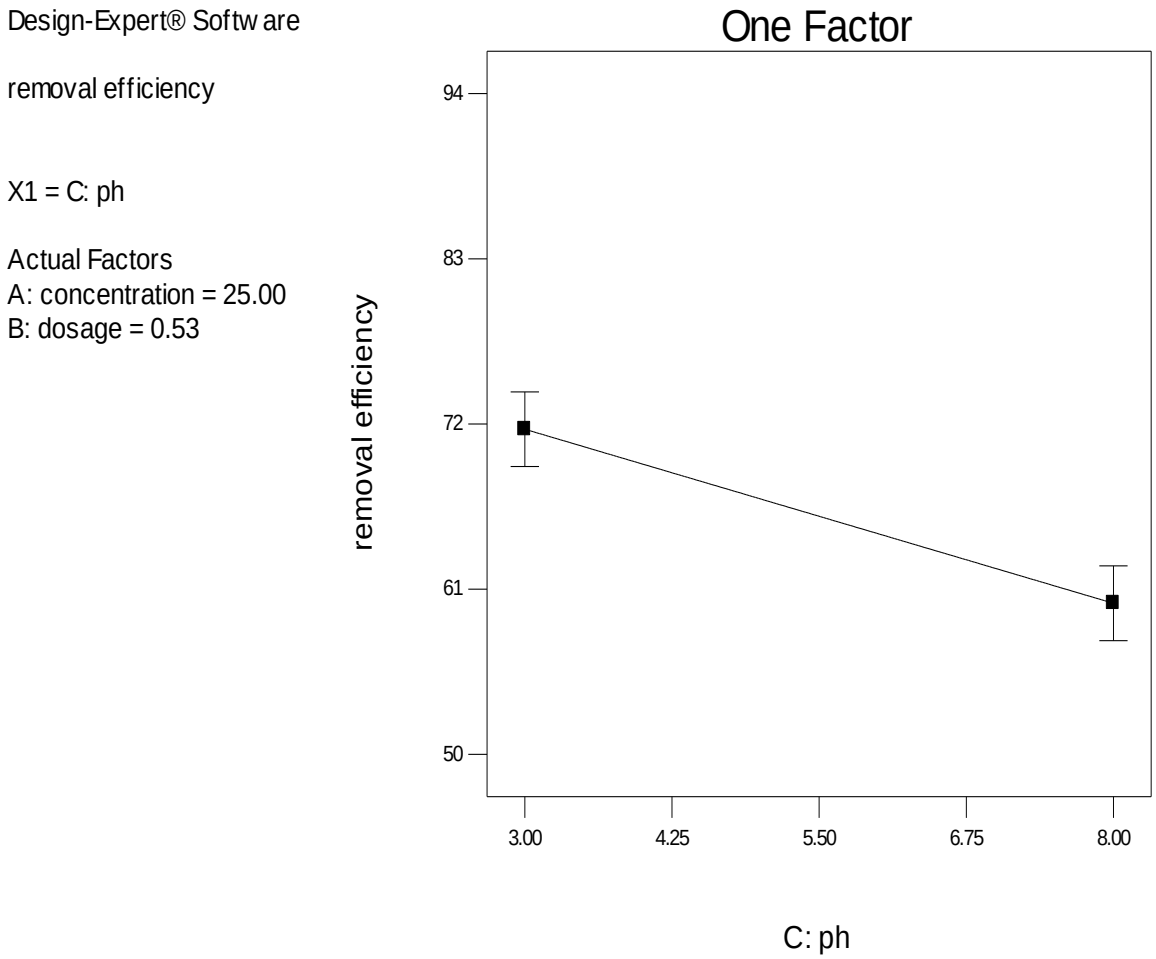

Figure 4.15. Effect of pH on removal efficiency at center point

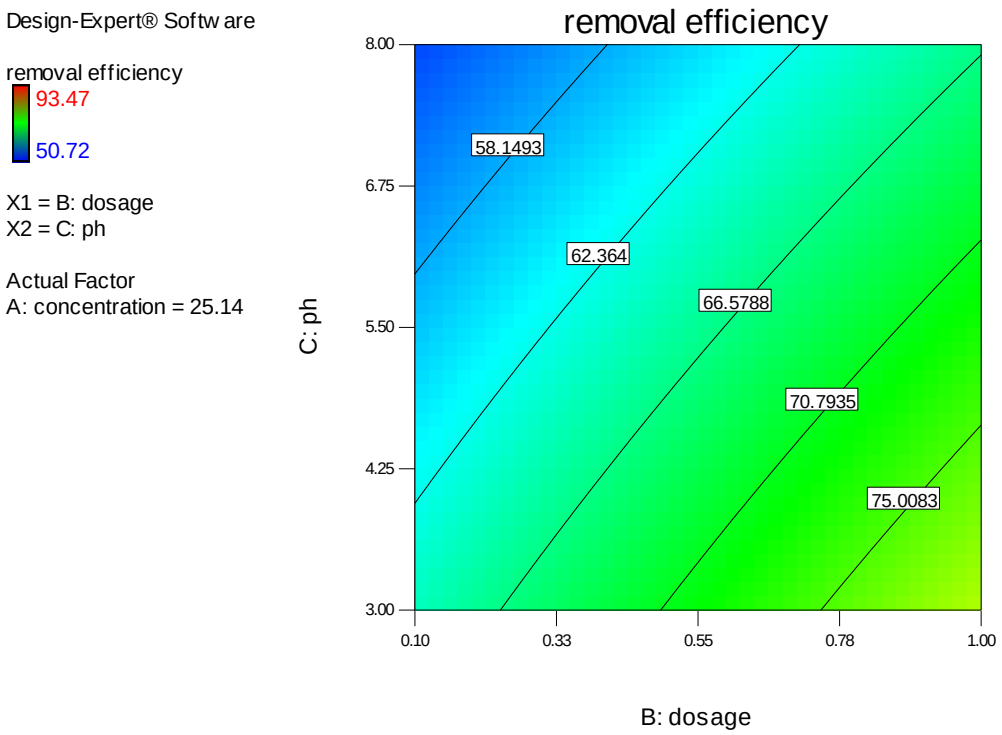

Figure 4.16. Interaction effect of pH and Doze on removal efficiency.

At constant concentration the percentage removal capacity have higher efficiency values with an increase in dosage and low pH values.

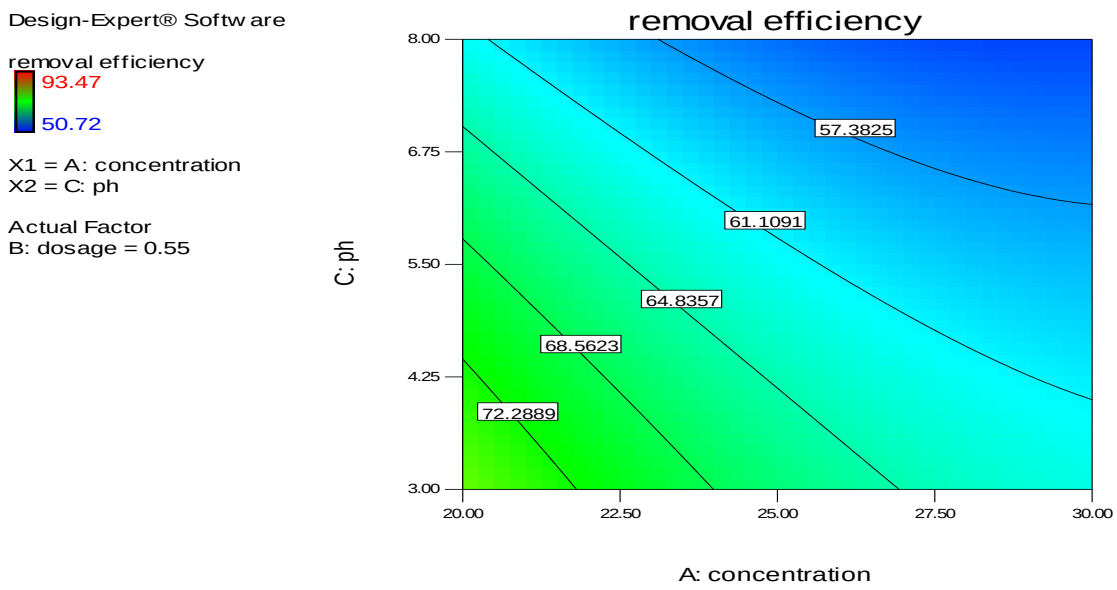

Figure 4.17. Interaction effects of pH and concentration on removal efficiency

As the interaction graph of pH. and concentration indicated above in figure 4.16 for constant value of adsorbent dosage the chromium removal efficiency exhibits high for low concentrations nd low pH values..

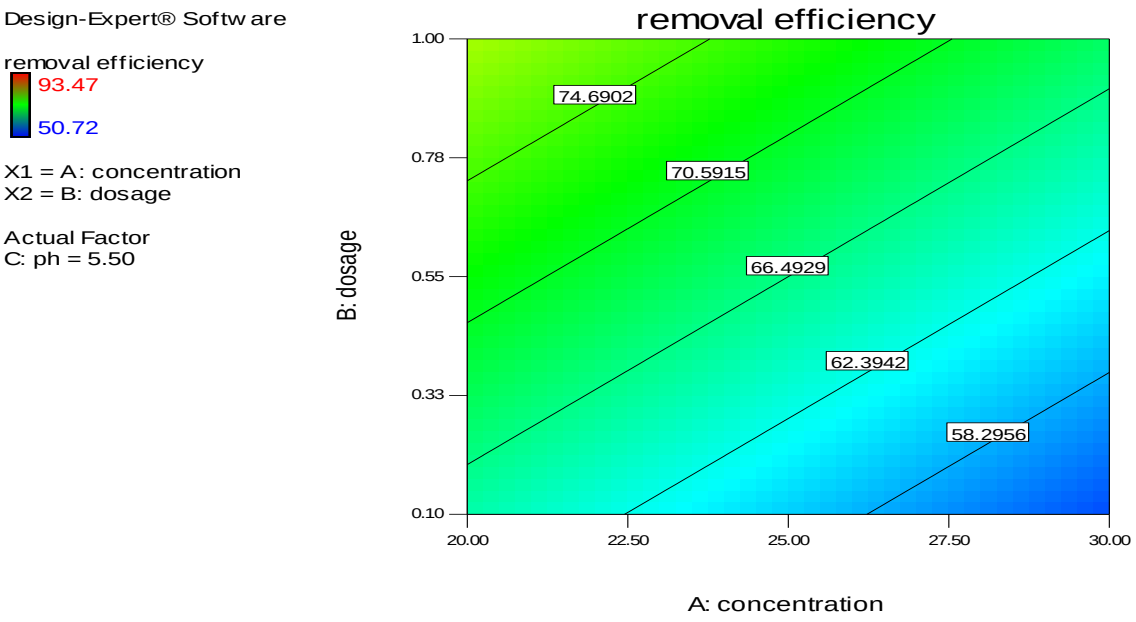

Figure 4.18. Interaction effect of doze and concentration on removal efficiency

As indicated in the graph in figure 4.17 at the fixed pH value there is high removal efficiency with the corresponding decreasing values of concentration of chromium and increasing values of dosage.

4.4.3 Optimization of parameters for Cr (VI) adsorption by NZVI-AB

In order to develop an adsorption process, a number of factors influencing the process such as Cr (VI) concentration, adsorbent dose and pH are to be studied. But the studying of the each and every factor is quite tedious and time consuming. Thus, a factorial design can minimize the above difficulties by optimizing all the affecting parameters collectively at a time. Factorial design is employed to reduce the total number of experiments in order to achieve the best overall optimization of the process. The design determines the effect of each factor on response as well as how the effect of each factor varies with the change in level of the other factors. Interaction effects of different factors could be attained using design of experiments only. Factorial design comprises the greater precision in estimating the overall main factor effects and interactions of

different factors. The optimization of adsorption parameters for the adsorption of Cr (VI) using NZVI-AB are summarized as follows:

Table 4.8.Goal of Parameters for the optimal removal efficiency of Cr (VI) adsorption.

Parameters	Goal	Minimum	Maximum
concentration	In range	20	30
dosage	In range	0.1	1
pH	In range	3	8
Removal efficiency	maximum	51.44	92.38

Table 4.9.Optimal possible solutions of factorial design.

Number	Concentration	Dosage	pH	Removal efficiency	Desirability	
1	20.00	1.00	3.00	89.2817	0.902	selected
2	20.00	1.00	3.03	89.2024	0.900	
3	20.11	1.00	3.00	89.0091	0.896	
4	20.00	0.99	3.00	88.9964	0.895	
5	20.20	1.00	3.00	88.8	0.891	
6	20.25	1.00	3.01	88.6465	0.887	
7	20.00	1.00	3.29	88.4841	0.883	
8	20.33	1.00	3.00	88.4661	0.883	
9	20.00	1.00	3.48	87.9563	0.871	
10	20.59	1.00	3.00	87.845	0.868	

11	20.85	1.00	3.00	87.2407	0.854	
12	20.00	1.00	3.84	86.963	0.848	
13	20.00	1.00	3.87	86.8551	0.845	
14	20.00	1.00	4.35	85.4922	0.813	
15	21.72	1.00	3.00	85.2752	0.808	
16	23.17	1.00	3.00	82.3229	0.739	
17	24.69	1.00	3.00	79.5999	0.676	
18	20.00	1.00	6.27	79.5796	0.675	
20	20.00	0.70	3.00	79.3376	0.669	
21	20.00	1.00	6.80	77.8725	0.635	
22	28.01	1.00	3.00	75.0848	0.570	
23	20.00	0.10	3.00	72.1944	0.502	

Based on the results the optimum possible solutions in adsorption of chromium are presented in table 4.9. The predicted optimum removal efficiency was 89.2817% observed at possible parameters of 20 mg/L, 1g and 3, concentration ,dosage and pH respectively. Under these conditions the experimental removal efficiency was 92.38% which is close to the general factorial design optimal result of 89.2817%, and this shows that the experimental values were found to be close to the predicted values and hence the model validation of the optimal solutions.

5. Conclusions and Recommendations

5.1 Conclusions

In this study, green synthesis method using avocado seed extract has been used for successful preparation of NZVI particles. And Potassium dichromate as a model synthetic contaminant in water is used for evaluation of adsorption of hexavalent chromium by NZVI particles. Thus the experimental condition result support that reduction rate of Cr (VI) is significantly affected by Concentration of NZVI particles, concentration of chromium and pH of the solution. It was found that the percentage adsorption of Cr (VI) decreased with the increase in the initial Cr (VI) concentration. This was expected due to the fact that for a fixed adsorbent dosage, the total available adsorption sites were limited thus leading to a decrease in percentage removal of the adsorbate corresponding to an increase initial adsorbate concentration. Cr (VI) reduction efficiency is strongly affected by pH of reaction mixture with decreasing initial pH & decreasing in initial Cr (VI) concentration that resulted an increase in removal percentage of chromium and also The removal efficiency of Cr (VI) was increased by increasing the adsorbent amount consequently the maximum amount of removal efficiency was found to be 92.38 in the corresponding values of pH=3, initial chromium concentration of 20 mg/l and adsorbent dosage of 1g. The produced adsorbent was characterized with FTIR and XRD and the equilibrium data was fitted to both Langmuir and Freundlich adsorption isotherm models but Langmuir isotherm was fitted better than the Freundlich isotherms.

5.2 Recommendations

Based on this study I would like to forward that;

- Synthesization of zerovalent iron using plant extracts is effective and environmentally friendly unlike chemical agents as reducing agent for the synthesis of nano materials.
- The amount of polyphenol content in the plant extract will also affect the synthesis process so I would like to recommend investigating this during green synthesis of nano adsorbents.
- In the synthesis of nano the adsorbent the ratio of extract and ferric chloride solution also considered in most studies so I suggest to take into account as one case of the process.
- Since The green nanotechnology-based production processes of nano particles operate under green conditions without the intervention of toxic chemicals we can rely on it in the synthesis of iron nano particles.
- Most of the green materials are capable of in synthesizing nanomaterials since the contain biological components which can be reduce heavy metals in nano scale. So since there are many types of green materials that are considered as waste but have value as such it is better to use them.
- Using different types of support materials to compensate the defects of the nano materials will enhance the effectiveness of the particles by for better efficiency.

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Appendix

Appendix A: synthesis of nano zerovalent iron

Figure A_1: Solution of ferric chloride and bamboo powder.

Figure A_2: Synthesis of nanozerovalent iron

Appendix B ; UV analysis

Figure B_1: Concentration analysis of chrome with DPC

Figure B_2: UV analysis of absorbance

Appendix C: Actual design of general factorial design.

Table C1: Actual design of design expert data and average response.

Std	Run	Block	Factor1 A:Concentration	Factor 2 B:Dosage	Factor3 C:PH	Response1 Removal efficiency (%) (average)
1	11	Block 1	20	0.1	3	70.6
2	2	Block 1	25	0.1	3	63.48
3	16	Block 1	30	0.1	3	59.38
4	6	Block 1	20	0.5	3	74.44
5	15	Block 1	25	0.5	3	67.38
6	19	Block 1	30	0.5	3	66.62
7	8	Block 1	20	1	3	92.38
8	13	Block 1	25	1	3	76.07
9	21	Block 1	30	1	3	72.82
10	12	Block 1	20	0.1	5	69
11	25	Block 1	25	0.1	5	62.16
12	9	Block 1	30	0.1	5	60.89
13	27	Block 1	20	0.5	5	70.63
14	24	Block 1	25	0.5	5	59.99

15	1	Block 1	30	0.5	5	56.88
16	18	Block 1	20	1	5	83.69
17	3	Block 1	25	1	5	73.04
18	23	Block 1	30	1	5	69.55
19	5	Block 1	20	0.1	8	59.23
20	14	Block 1	25	0.1	8	55.21
21	20	Block 1	30	0.1	8	52.16
22	10	Block 1	20	0.5	8	71.82
23	22	Block 1	25	0.5	8	69.11
24	26	Block 1	30	0.5	8	64.13
25	4	Block 1	20	1	8	59.77
26	17	Block 1	25	1	8	56.52
27	7	Block 1	30	1	8	51.44