JIMMA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

JIMMA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL ENGINEERING

Development and Application of Teff Straw Supported Nano Zero-valent Iron for Removal of Hexavalent Chromium from Aqueous Solution

By

Fekadu Abera

A Thesis Submitted to Jimma University, Jimma Institute of Technology, School of Chemical Engineering in Partial Fulfillment of the Requirement for the Degree of Masters of Science in Chemical Engineering (Process Engineering)

January, 2020

Jimma, Ethiopia

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Advisor: Dr.Eng. Hundessa Dessalegn

Co-advisor: Mr. Desalegn Abdisa

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PROCESS ENGINEERING STREAM

This is to certify that the thesis prepared by **Fekadu Abera**, entitled *"**Development and Application of Teff Straw supported Nano Zero-valent Iron for Removal of Hexavalent Chromium from Aqueous Solution**"* submitted in partial fulfillment of the requirement for the degree of Master of Science Chemical Engineering (Process Engineering) complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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The following process engineering post graduate program member and advisor of this thesis with the title **“Development and Application of Teff Straw supported Nano Zero-valent Iron for Removal of Hexavalent Chromium from Aqueous Solution”** and I confirm that this thesis work is approved as degree of masters of process engineering thesis for the student.

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ABSTRACT

Waste water released to the environment is causing adverse effect on our ecosystem. There are various toxic heavy metals that are released with industrial waste water to the environment, hence worsening the life of biodiversity and increasing environmental pollution. Hexavalent Chromium (Cr(VI)) is a highly toxic pollutant which needs to be removed from the waste water. Conventional methods for remediation of Cr(VI) are usually costly and difficult to operate. Green synthesis provides advancement over chemical and physical method because it is cost effective, environmentally friendly, easily scaled up for large scale synthesis. In this study, zero valent iron, a strong reducing agent that transforms Cr(VI) to nontoxic trivalent chromium (Cr(III)), was synthesized, characterized and tested for adsorption of Cr(VI). Zero valent iron (Fe^0*) nanoparticles were synthesized by reduction of Ferrous Sulphate (*$FeSO_4.7H_2O$*) in the presence of polyphenol extracted from Eucalyptus Camaldulensis leaves. The synthesized particles were identified as iron nanoparticles using UV visible spectrophotometer. X-ray Diffraction (XRD) was used to determine the crystallinity of synthesized nano zero valent iron (nZVI) particles, hence, the formed polyphenol based iron nanoparticles have no crystalline structure. FT-IR spectra revealed the existence of -OH stretching vibration of polyphenols and Fe-O bond formation in the prepared nanomaterials. The batch adsorption experiments for the removal of hexavalent chromium has been conducted using nZVI-TS dosage, initial concentrations of Cr(VI), solution pH and contact time as parameters and the process was significantly affected by these parameters. The highest removal efficiency obtained was 99.79%. Langmuir isotherm model was better to fit to the experimental data and favored adsorption process. Response Surface Methodology using Central Composite Design was applied to analyze statistical experimental analysis for the data obtained from laboratory experiments and its optimal condition was identified. The optimal conditions selected using design tool were nZVI-TS dosage of 0.972 g/100 ml, initial Cr(VI) concentration of 21.034 mg/1000 ml, pH of 4.166, and contact time of 6.99 min providing predicted value of 99.984% removal efficiency.*

Key words: *characterization, Chromium, green synthesis, nZVI-TS, Teff straw, waste water*

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ABBREVIATIONS

Adeq. Precision	Adequate precision
Adj. R^2	Adjusted R^2
ANOVA	Analysis of variances
CCD	Central Composite Design
Cor.total	Totals of all information corrected for the mean
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
C.V	Coefficient of variation
df	Degrees of freedom
Fe NPs	Iron Nano Particles
FTIR	Fourier Transform Infrared Spectroscopy
MCL	Maximum contaminant level
NPs	Nano Particles
nZVI	Nano Zero-valent Iron
nZVI-TS	Teff straw supported Nano Zero-valent Iron
Pred. R^2	Predicted R^2
R^2	Correlation coefficient
RSM	Response Surface Methodology
UV	Ultra Violet
XRD	X-ray diffraction
ZVI	Zero-valent Iron

1. INTRODUCTION

1.1 Background of the study

Heavy metals can be classified into three subgroups: toxic metals, precious metals, and radionuclide metals (Fu & Wang, 2011); (Lakherwal, 2014); (Tangahu, et al., 2011). They are not biodegradable, and need to be removed physically or chemically via converting it into nontoxic substance, otherwise they tend to accumulate in living organisms by entering the food chain or water resources which affect cells' function (Macaskie & Dean, 1989); (Abas, et al., 2013).

Heavy metal like hexavalent chromium which is used in a variety of industrial applications is highly toxic to humans, animals, plants and microorganisms (Gheju, 2011). Chromium contamination of aqueous solution has received increasing attention because of its severe impact on public health. Common hexavalent chromium (Cr(VI)) exposure has several contact pathways such as ingestion, inhalation and derma. It has significant effect on human health such as gastrointestinal, respiratory and immunological systems, which can also cause reproductive and development problems. According to the World Health Organization (WHO, 2008) and BIS (Bureau of Indian Standards) drinking water guidelines, the maximum recommended limit for total chromium is 0.05 mg/L. Therefore, it should be removed from contaminated waters. Its reduction to trivalent chromium can be advantageous because a more mobile and more toxic chromium species is converted to a less mobile and less toxic form. Several treatment technologies have been reported for the removal of Cr(VI), including phytoremediation, microbial remediation, chemical reduction, physical sorption (using ion exchange resin, activated carbon etc.) and membrane filtration (ultra-filtration, nanofiltration and reverse osmosis) (Owlad , et al., 2009).

Considering the rapid development in nanoscale science and engineering, unprecedented opportunities have been raised to develop more cost effective and environmentally acceptable remediation processes. Generally, nanotechnology can clean up the water through various methods, including nanofiltration membranes to improve water quality, nanoscale biosensors to detect pollution in water, the design of environmentally friendly methods for cleaning groundwater and improving the efficiency of chemical and photo-catalytic processes.

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. 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.

Among the various nanoparticles for removing heavy metals, applying zero valent iron (ZVI) is one of the most promising and effective remediation technologies because of its extremely small particle size, large surface area, and high reactivity. Nano zero valent iron is also a powerful reducing agent and a remarkable adsorbent that can be used for in situ and non-in situ groundwater remediation. These properties enable nZVI to reduce and immobilize the mineral contaminants such as heavy metals, metalloids, perchlorate, nitrate, and others (Matheson & Tratnyek, 1994).

The direct mechanism of Cr(VI) reduction is based on the capacity of nZVI to serve as electron donor. Additionally, ferrous iron released during Cr(VI) reduction by nZVI, as well as molecular hydrogen, atomic active hydrogen and solid minerals containing Fe (II) generated as products of nZVI corrosion, may also contribute to the reduction process. The rate of Cr(VI) reduction varies significantly depending on experimental conditions such as nZVI type, dose and pretreatment, pH, water composition, temperature and Cr(VI) concentration. The high remediation efficiency of nZVI is mainly attributed to its high surface area, high levels of surface defects, high density and decent intrinsic reactivity of surface sites, which make the nanoparticles very reactive in the degradation of contaminants (Singh , et al., 2011).

Nevertheless, nZVI particles synthesized from traditional methods tend to agglomerate rapidly in water via Van der Waals and magnetic attraction forces, forming particles with diameters ranging from several microns to several millimeters. In addition, conventional nZVI particles can react with the surrounding media (e.g., dissolved oxygen, water and other oxidizing agents), leading to the rapid loss of reactivity (He & Zhao, 2005); (Choi, et al., 2009); (Alidokht , et al., 2011).

Researchers proceed with efforts to develop facile, effective and reliable green chemistry processes for the production of nanomaterial. Various organisms act as clean, ecofriendly and sustainable precursors to produce the stable and well functionalized nanoparticles. 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 production processes using green nanotechnology operate under green conditions without the intervention of toxic chemicals. Recently, many studies have indicated the potential of iron nanoparticles (NPs) for environmental remediation. The interest in nZVI in environmental remediation is increasing due to the reactivity of nano-scale iron having a large surface area to volume ratio. The makeup 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.

These days, 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., 2009). 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, different synthetic methods have been developed to produce iron nanoparticles to modify the properties of nanoparticle surface and enhance the efficiency for field delivery and reactions.

Teff straw is a solid agricultural waste which is low cost and locally available biomass. It is cost effective technology that is used as bio adsorbent to remove heavy metals from aqueous solutions (Chojnacka , et al., 2005). Its composition with nano zero valent iron improves the adsorption efficiency and its economic use. Furthermore, Teff straw supported nano zero valent overcome some of the disadvantages inherent in the use of conventional methods which reduces efficiency, stability i.e. rapid oxidation, tendency of agglomeration into larger particles and the separation and recovery of fine particles after usage.

1.2 Statement of the problem

Water pollution is one of the largest environment problems in several countries. It mainly arises from wastewater released from household, industrial and agricultural processes. These effluents typically contain high concentrations of organic and inorganic chemicals such as hydrocarbon solvents, heavy metals, pesticides, dyes and so on. The toxicity, persistency and concentration of the contaminants result in serious environmental, public health and economic impacts. Industrial effluents from tanning, electroplating, paint, textile industries, etc. contains chromium species above the maximum contaminant level (MCL). Chromium exists in industrial wastewater due to the presence of both trivalent and hexavalent forms of. The toxicity caused by hexavalent chromium is high and hazardous due to its significant effect on human health such as cancer, gastrointestinal, skin irritation, mental illness, etc. It is also toxic to plants, animals and microorganisms (Gheju, 2011). Therefore, its removal from aqueous solution is necessary. Yet various techniques used for removal of Cr(VI) from industrial wastewater include chemical precipitation, filtration, electro deposition and membrane systems or even ion exchange process. The process of chemical precipitation and reduction needs other separation techniques for the treatment and disposal of high quantities of waste metal residual sludge produced. In addition, the application of membrane systems for the wastewater treatment has major problems like membrane scaling, fouling and blocking. The disadvantage of the ion exchange process is the high cost of the resin while the electro deposition method is more energy intensive than other methods (Gupta & Babu, 2009); (Kobya, 2004); (Sharma, 2003).

Zero valent iron (ZVI) nanoparticles 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 & Masciangioli, 2003). 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. 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.

Moreover, the study focused on the green synthesis of nZVI using polyphenol and to remove hexavalent chromium from aqueous solution by adsorption supported by Teff straw which is porous biomass. The nZVI synthesized using this method overcomes some of the disadvantages inherent in the use of nZVI which improves its stability, removes its aggregation and reduces its oxidation reaction with non-target compounds. This methodology is simpler, economic and has not been reported, hence, it is a green synthesis of nZVI from sustainable materials.

1.3 Objectives

1.3.1 General objective

The general objective of this research was to synthesize and characterize Teff Straw supported nano Zero-valent Iron for its application as an adsorbent for removal of hexavalent chromium from aqueous solution.

1.3.2 Specific objectives

- Synthesis of zero valent iron nanoparticles using Polyphenol extracted from Eucalyptus Camaldulensis tree leaves
- Characterization of physico-chemical and crystalline structure of synthesized zero valent iron nanoparticles.
- To evaluate removal efficiency of hexavalent chromium from aqueous solution by Teff straw supported zero valent iron nanoparticles.
- Optimization of adsorption parameters including pH, concentration of hexavalent chromium and nano zero-valent iron dosage.

1.4 Research questions

1. What are the materials and methods used to synthesize nZVI?
2. How the synthesized nZVI was characterized?
3. How removal of hexavalent chromium was accomplished? What the factors affected the process?
4. Why optimization of parameters is important?

1.5 Justification

The thesis work comprises green synthesis of zero valent iron nano particles supported by Teff straw by using Ferrous Sulphate solution (FeSO4.7H2O), Polyphenol extract, Distilled water and Teff straw as the main raw materials. A strong reducing agent property of Ferrous Sulphate solution provides an ability to adsorb the heavy toxic metals especially hexavalent chromium. The production of polyphenol from Eucalyptus Camaldulensis tree leaves using distilled water is economical and simple; the use of polyphenol extract for the synthesis of zero valent iron nanoparticles is economical and ecofriendly. The use Teff straw, which is porous and abundant biomass, adds more capacity to nZVI for adsorbing hexavalent chromium from aqueous solution. This biomass also adds stability for nZVI produced and inhibits the formation of corrosion reaction in the solution. Therefore, the use of both biomasses (Eucalyptus Camaldulensis and Teff straw) enhances their economic use and helps to replace commercial chemical products or synthetic products.

1.5 Significance of the study

The study addresses the development and application of Teff straw supported nano zero-valent iron for removal of hexavalent chromium from the aqueous solution to enhance the work for environmental protection. By doing so this investigation provides:

- Green synthesis of nZVI using polyphenol for the adsorption of Cr(VI)
- Enhancement of the economic value of Teff straw, as the raw material for supporting nZVI to adsorb Cr(VI) and increase removal efficiency
- Environmentally friendly synthesized nZVI

1.6 Scope of the study

The work of this paper generally covers synthesis of nZVI, characterization of the synthesized nZVI, and study of the adsorption of Cr(VI) by nZVI-TS. The removal of Cr(VI) was investigated at different adsorption dosage, contact time, initial chromium concentration and pH of the solution. The study focused on the removal of Cr(VI) from aqueous solution and it was conducted at Jimma university.

2. LITERATURE REVIEW

2.1 Industrial wastewater sources

Industrial wastewater streams containing heavy metals are produced from several industries. The processes such as electroplating, tannery processing factories and metal surface treatment 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 enclose milling, electroplating, electro less depositions, conversion-coating, anodizing-cleaning, and etching. Another significant source of heavy metals waste results from printed circuit board (PCB) manufacturing. Other sources for the metal wastes include; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic containing wastes; 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 (Sörme & Lagerkvist, 2002).

2.1.1 Heavy metals in industrial wastewater

Several heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in treatment of wastewater include chromium, copper, nickel, mercury, cadmium and lead. They can cause serious health effects, including reduced growth and development, organ damage, cancer, 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 shall 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 amounts, heavy metals can lead to irreversible brain damage. Hexavalent chromium (Cr(VI)) is a commonly identified contaminant from the metallurgy, leather tanning, and electroplating industries. Cr(VI) is toxic, carcinogenic, and its high subsurface mobility does great harm to the environment (Cissoko, et al., 2009).

Regulations were established for release of wastewater 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 1 Effects of heavy metals

Element	Problem	Allowable concentration (mg/L)
Arsenic	Highly toxic, cause DNA breakdown and death, visceral cancers, vascular disease	0.05
Cadmium	Carcinogen, renal disorder, kidney dysfunction	0.01
Chromium	Mental illness, diarrhea, skin irritation, nausea, vomiting and lung carcinoma, carcinogenic	0.05
Copper	Convulsions, cramps, and spasms that can lead to death, Wilson disease, insomnia	0.25
Lead	Damage to the central nervous system, kidney, liver and reproductive system, basic cellular processes and brain functions, anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages	0.006
Mercury	Impairment of pulmonary and kidney function, chest pain and dyspnea, neurological and renal disturbances, affect photosynthesis and oxidative metabolism	0.00003
Nickel	Lung, kidney, skin problems, vomiting, nausea, anemia, pulmonary fibrosis and skin dermatitis	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80

Source: (Gunatilake, 2015)

2.1.2 Toxicity of Chromium

Chromium occurs in the environment basically in two valence states, hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Exposure to this heavy metal may occur from natural or industrial sources of chromium. Cr(VI) is much more toxic than Cr(III). Chromium is a naturally occurring element in rocks, plants, animals, soil, and volcanic dust and gases. It occurs in the environment predominantly in one of two valence states. The first one is as trivalent chromium (Cr(III)), which occurs naturally and is an essential nutrient. The other is as hexavalent chromium (Cr(VI)), which, along with the less common metallic chromium (Cr^0), is most commonly produced by industrial processes (Kaplan & Gilmore, 2004).

The most essential industrial sources of chromium in the atmosphere are those connected to ferrochrome production. The other processes that have a contribution to the atmospheric burden of chromium are ore refining, chemical and refractory processing, cement-producing plants, automobile brake lining and catalytic converters for automobiles, leather tanneries, and chrome pigments. Societies are exposed to chromium (generally Cr(III)) by eating food, drinking water, and inhaling air that contains the chemical. The average daily intake from air, water, and food is estimated to be less than 0.2 to 0.4 micrograms (µg), 2.0 µg, and 60 µg, respectively. Our derma may be exposed to chromium that may occur during the use of consumer products that contain chromium, such as wood treated with copper dichromate or leather tanned with chromic sulfate. The industry workers (occupational) exposure to chromium occurs from chromate production, chrome plating, stainless-steel production, and working in tanning industries; occupational exposure can be two orders of magnitude higher than exposure to the general population. People who live in the proximity of chromium waste disposal sites or manufacturing of chromium and processing plants have a greater probability of elevated chromium exposure than the general population. These exposures are generally to mixed Cr(VI) and Cr(III) ((ATSDR), 1998).

2.2 Methods of removal of heavy metals

2.2.1 Physico-chemical processes

Physico-chemical processes involve different technologies such as adsorption, membrane filtration, ion exchange, reverse osmosis, and electrochemical treatments. These processes discussed as follow:

2.2.1.1 Adsorption

Adsorption is a surface-based process in which atoms, molecules, or ions from a liquid, dissolved solid, or gas are transferred to the surface of an adsorbent and established by physical or chemical interactions (Babel & Kurniawan, 2003). Physical adsorption resulting from attractive intermolecular forces between adsorbent and adsorbate is a reversible phenomenon, while chemisorption is derived from chemical interaction and is irreversible. Various parameters such as pH of solution, heavy metal concentration, temperature, nZVI dosage, and the reaction time have a crucial effect on the performance of the adsorption process. However, adsorption is considered an economical and efficient process for removing heavy metal pollutants. The flexibility in design, simple operation, and the effectiveness of reducing heavy metals concentration are the main features that make this method preferred (Abas, et al., 2013). Different adsorbents that are derived from industrial byproducts, agricultural waste, natural materials, or modified biopolymers, have been recently developed and applied for the removal of toxic heavy metals. Activated carbon with a high surface area is a favorite adsorbent that can also be modified by adding some additive compounds such as alginate, tannic acid, and surfactants (Kang, et al., 2008). Another appropriate promising candidate for adsorption of heavy metals is carbon nanotubes, which are widely studied because of their remarkable properties (Lin, et al., 2010). Biosorption is also a new and effective removal process in which removing pollutants from the environment is carried out by biological material such as crab shells, algae, bacteria, fungi, and yeast (Fu & Wang, 2011).

2.2.1.2 Chemical precipitation

This method is a process based on reacting heavy metal ions with a suitable compound to settle out sedimentation from a solution. The mechanism of this process is based on producing insoluble metal precipitation. In this regard, the conventional precipitation processes produce insoluble precipitates of heavy metals such as hydroxide, sulfide, and carbonate. Hydroxide is widely used to flocculate heavy metals ions such as Cu(II) and Cr(VI) by using NaOH and $Ca(OH)_2$ because of low cost and simplicity. This method can also be applied for removing Zn, Cd, Mn, and Mg at the optimum pH of more than 9.5. However, sludge production, slow and relatively poor metal precipitation, and environmental impacts of sludge disposal are the disadvantages of this process (Fu & Wang, 2011); (Abas, et al., 2013). Sulfide precipitation is another effective method in which iron sulfide from Pyrite can remove Cu^{2+}, Cd^{2+} and Pb^{2+} at pH lower than 3 (Ozverdi & Erdem, 2006). However, it should be noted that performing the sulfide precipitation in acidic conditions leads to the production of H_2S fumes, which is extremely dangerous. This process is still faced with isolation of colloidal sludge problems. Carbonate precipitation of heavy metals has been shown to be more effective treatment as compared to hydroxide precipitation. In this process, soda ash (sodium carbonate) or sodium bicarbonate can be used to precipitate heavy metals (Matlock, et al., 2002).

2.2.1.3 Membrane filtration

Filtration is a process that membranes with the pore size between 0.1 and 0.001 µm are used to separate high molecular weight, polymeric, and colloidal contaminates. This process, which is performed under pressure, can be affected by electrical charge and surface chemistry of the membrane (Lakherwal, 2014). Sometimes, by adding polymeric ligands to effluent, metal ions bind to the ligands and make macromolecular complexes with the size larger than membrane pores that can be separated by ultrafiltration (Rether & Schuster, 2003). The addition of surfactants to wastewater is another method in which surfactants bind to metal ions, making large molecules which can be removed by ultrafiltration (Landaburu-Aguirre, et al., 2009).

2.2.1.4 Electrochemical treatments

In this process, heavy metal ions are deposited by applying electrical current from a couple of electrodes in a weak acidic or neutralized solution. Electro-deposition, electrocoagulation, electro flotation, and electro oxidation can be categorized in this process. Some important parameters in the electrochemical treatment involve distance between electrodes, electrode surface area, current density, ion concentration, and pH. In the electro-flotation process, contaminant particles are floated out by hydrogen or oxygen bubbles produced during electrolysis. However, this process is an expensive method that needs massive investment and high electricity power consumption, so it isn’t widely used. Another weakness of this method is the consumption of large amounts of chemicals, slow metal precipitation, production of huge amounts of sludge, and its disposal problem (Fu & Wang, 2011); (Gunatilake, 2015).

2.2.2 Biological processes

These processes involve the processes associate with phytoremediation and activated sludge.

2.2.2.1 Phytoremediation

This is an affordable and environmentally friendly method using plants to clean up the pollution of water and soil. This technique is a suitable remediation technology that utilizes the inherent potential of living plants to reduce the volume, mobility, or toxicity of contaminants in soil, groundwater, or other contaminated media ((USEPA), 2000). Some of the plants absorb heavy metals such as Pb, Cd, and Cr by their roots.

There are several advantages of phytoremediation. This method is less disruptive than conventional techniques, effective, affordable, and applicable for a wide range of heavy metals. This is a fairly inexpensive method when compared with other methods. However, this method is time-consuming and depends on the depth of roots, age of the plant, and the contamination level (Tangahu, et al., 2011); (Mohsenzadeh & Rad, 2012).

2.2.2.2 Activated sludge

In this method, dried activated sludge is used as an eco-adsorbent to remove heavy metals contamination from effluent of wastewater discharge. In addition, this method can be used to break down organic pollutants using microorganisms. Activated sludge containing-bacteria is continually re-circulated back to the aeration basin to increase the rate of organic decomposition. The application of nanotechnology in the treatment of wastewater is a relatively new approach that has received much attention recently. Materials show some unprecedented properties when their size decreases to the nanometer scale, such as high specific surface area, compressibility without surface area reduction, reusability, increasing the adsorption sites significantly, etc. It seems that nanotechnology has supreme potential for improving environmental conditions, especially wastewaters. Of course, this approach faces major challenges that require investigation, such as the performance of nanoscale methods, the long-term effects on the environment, and cost-effectiveness (Rebeca & Rodriguez, 2015).

2.3 Nanotechnology

Nanotechnology is a discipline 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, physics, biology, chemistry and other scientific fields and involves the study of phenomena and manipulation of materials in the nanoscale. This results in materials and systems that often exhibit novel and noticeably changing physical, chemical and biological properties due to their size and structure. With the rapid development in nanoscale science and engineering, unprecedented opportunities have been raised to develop more cost effective and environmentally acceptable remediation processes. Generally, nanotechnology can clean up the water through various methods, including nanofiltration membranes to improve water quality, nanoscale biosensors to detect pollution in water, the design of environmentally friendly methods for cleaning groundwater and improving the efficiency of chemical and photo-catalytic processes.

2.3.1 Nano adsorbents

Adsorption processes and membrane separations are dominating technologies and increasingly being applied in developing new adsorbents and membranes from nanomaterials 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 exceeding US$1.5 billion per year. However, 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 (Sewunet Abebayehu, 2017).

The special properties of nanomaterials, 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 outcomes of the studies showed 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. Furthermore, some nanoparticles unique structure and electronic properties can make them especially powerful adsorbents. Many materials have properties that are dependent on size. Hematite particles with a 7 nm diameter, for example, adsorbed Cu ions at lower pH values than particles of 25 or 88 nm diameters, indicating the uniqueness of surface reactivity for iron oxides particles with decreasing diameter. 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 (Sewunet Abebayehu, 2017).

2.3.2 Nano zero valent iron and its application

Zero-valent iron (ZVI) is one of the most promising and effective remediation technologies because of its extremely small particle size, large surface area, and high reactivity. Nano-zero-valent iron is also a powerful reducing agent and a remarkable adsorbent that can be used for in situ and non-in situ groundwater remediation.

Figure 1 Schematic model of reaction mechanism of ZVI with different contaminants

Source: (Fu, et al., 2014)

These properties enable nZVI to reduce and immobilize the mineral contaminants such as heavy metals, metalloids, perchlorate, nitrate, and others (Matheson & Tratnyek, 1994). As zero-valent iron is a strong reducer, it has been used to remove several contaminants as shown in Table 2.

Table 2 Removal of Different contaminants using nZVI

Organic compounds		**Inorganic compounds**	
Methanes	Tetrachloromethane	**Trace metals**	Arsenic
	Trichloromethane		Cadmium
	Dichloromethane		Chromium
Ethanes	Hexachloroethane		Cobalt
	1,1,1-trichloroethane		Copper
	1,1,2-trichloroethane		Lead
	1,1-dichloroethane		Manganese
	1,2-dibromoethane		Nickel
Ethenes	Tetrachloroethene		Selenium
	Trichloroethene		Uranium
	cis-1,2-dichloroethene		Zinc
	trans-1,2-dichloroethene	**Anion contaminants**	Nitrate
	1,1-dichloroethene		Phosphate
	Vinyl chloride		Sulfate
	1,2,3-trichloropropane		
Propanes	1,2-dichloropropane		
	Benzene		
Aromatics	Toluene		
	Ethylbenzene		
	Hexachlorobutadiene		
Others	Freon 113 n-nitrosodimethylamine		

Source: (Sivavec & Horney, 1995)

2.3.3 Methods of Nano Zero valent iron synthesis

Various physical and chemical methods have been developed to produce nZVI that could proceed in solid, gas, and liquid status. Some of the important physical methods are abrasion and grinding as well as lithography (Shan, et al., 2009); (Nalwa, 2004).

Away from the physical methods mentioned above, chemical methods for the synthesis of nZVI have been developed. The nZVI can be obtained using sodium borohydride ($NaBH_4$) as a reducing agent, according to the following reaction (Wang & Zhang, 1997).

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0\downarrow + 3B(OH)_3 + 10.5H_2 \qquad \textbf{(2.1)}$$

Using sodium borohydride ($NaBH_4$) as a reducing agent, reduction of goethite (α-FeOOH) or hematite (α Fe_2O_3) at an elevated temperature and decomposition of iron pentacarbonyl [$Fe(CO)_5$]) in organic solvents or in argon are some of the chemical methods for the synthesis of nZVI (Stefaniuk, et al., 2016). These methods use very toxic and expensive chemical substances such as $NaBH_4$, organic solvents, stabilizing agents and dispersing agents, thus, result in accumulation of toxic chemicals on the surface of nanoparticles and synthesized nanocrystalline colloids are not stable and are vulnerable to aggregation (Desalegn, et al., 2019).

Due to its simplicity, chemical reduction is the most frequently used method for obtaining nZVI. In addition, the product obtained is characterized by a homogeneous structure that displays high reactivity (Jamei , et al., 2013).

2.3.4 Green synthesis

Due to various drawbacks of conventional methods, research focus has recently shifted towards the development of clean and ecofriendly synthesis protocols. Nanoparticles can also be biosynthesized (green synthesis), based on the use of plant extracts which are responsible for the reduction of metal compounds to suitable nanoparticles. Green synthesis is an environmentally friendly and inexpensive technology. Because there is no need to use high temperatures, pressure, or additional energy inputs, it is easy to implement on a large scale. Although it has numerous advantages of using this method, green synthesis is still not commonly accepted. These result from insufficient knowledge of the reactivity, physicochemical properties, and agglomeration of the nanoparticles produced (Machado , et al., 2013).

2.4 Possible Mechanism of Nanoparticles Synthesis

Actual mechanism of living organisms based nanoparticles synthesis is not yet clear, however, studies reveal 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 iron oxide NPs production. According to them, most probably the occurrence of phenolic-OH groups and ortho-dihydroxyphenyl groups in chemical structure of tannins are participated in the formation of complexes with iron and also involve in redox reactions. In the iron oxide NPs formation 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. amino acids, proteins, enzymes, vitamins, and polysaccharides, and organic acids such as citrates, may act as reducing and capping agents in nanoparticle synthesis. The process behind plant extract mediated metallic nanoparticle formation has not been clearly defined up until now. A plenty biomolecule of plant extract was involved in the fabrication of nanoparticles. Several plant components are rich in secondary metabolites and responsible for synthesis of metallic nanoparticles. Secondary metabolites include the flavonoids, polyphenols, terpenoids, tannic acid, ascorbic acids, carboxylic acids, aldehydes and amides. Plants commonly rich in reducing sugars, and their presence is confirmed by the IR spectroscopic technique in different studies. Phyto-chemicals in plant extracts exhibit ideal redox properties that allow efficient reduction of metal precursors for conversion into their corresponding metallic nanoparticles.

Becerra et al, utilized the tannin of alfalfa. From the assumption, tannins associated to alfalfa, derivate into radical tannins ‘R’ causes deoxidation of metal under the influence of pH (Becerra, et al., 2007). The bio reduction process can be induced in the following way:

$$FeCl_3 + H_2O \rightarrow [Fe(H_2O)_n]^{3+} + H_2O \tag{2.2}$$

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

$$[Fe(H_2O)_n]^{2+} + 2R^- + H^+ + OH^- \rightarrow Fe^{2+}O^{2-} + Fe^{2+}Fe^{3+}O^{2-} + R - H + R - OH^- \tag{2.4}$$

Wang proposed the iron-polyphenol complex nanoparticles (Fe-P NPs), synthesized by Eucalyptus leaves. Reduction possibility in Eucalyptus extract is as a result of polyphenols which make it able to reduce Fe^{3+} into Fe^{2+}. However, extract does not completely deoxidize 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. Hence, 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). Similar reaction mechanism was proposed for Sage (Salvia officinalis) mediated iron-polyphenol complex nanoparticles (Wang , et al., 2015). Plant polyphenols can form complexes by condensation of polyphenol on reaction between $FeCl_3$ and plant polyphenol as can be seen in (Figure 3 and 4).

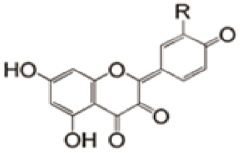


Figure 2 Polyphenol chemical structures

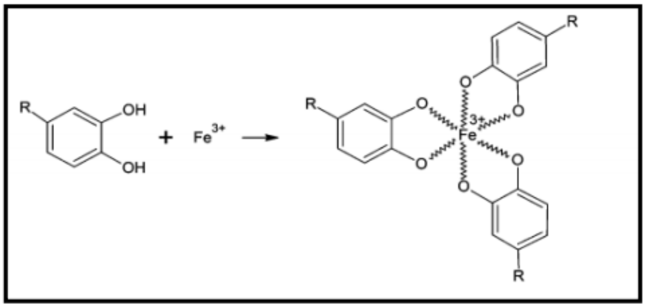


Figure 3 Proposed chemical structure of Iron-Polyphenol nano particles

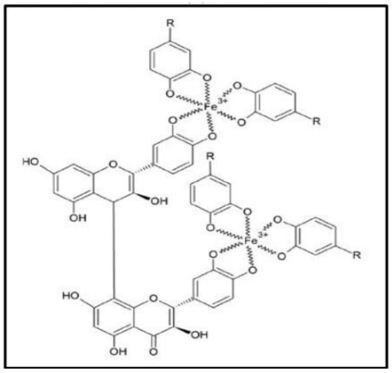


Figure 4 Proposed condensation mechanism of Iron-Polyphenol

Source: (Wang , et al., 2015)

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 2.6). 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).

$$Cr^{6+} + Fe^0 \rightarrow Cr^{3+} + Fe^{3+} \qquad \textbf{(2.5)}$$

$$(1\text{-}x)\ Fe^{3+} + (x)\ Cr^{3+} + 3H_2O \rightarrow (CrxFe\ (1\text{-}x))\ (OH)_3\ (s) + 3H^+ \qquad \textbf{(2.6)}$$

$$(1\text{-}x)\ Fe^{3+} + (x)\ Cr^{3+} + 2H_2O \rightarrow Fe\ (1\text{-}x)\ CrxOOH\ (s) + 3H^+ \qquad \textbf{(2.7)}$$

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.

$$CrO^- + Fe^0 + 2H^+ + 2H_2O \rightarrow Fe(OH)_3{\cdot}Cr\ (OH)_3 \qquad \textbf{(2.8)}$$

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.

$$nFe^{3+} + 3(Ar\text{-}OH)\ n \rightarrow nFe^0 + 3nAr{=}O + 3nH^+ \qquad \textbf{(2.9)}$$

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 $HCrO_4^-$ and $Cr_2O_7^{-2}$ species, if the Cr(VI) concentration is less than 0.02 M $HCrO4^-$ 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 chromium to trivalent chromium.

At low pH: $Cr_2O_7^{-2} + 14H+ + 6e- \rightarrow 2Cr^{+3} + 7H$ **(2.10)**

At moderate pH: $HCrO4^- + 7H^+ + 3e- \rightarrow Cr^{+3} + 4H_2O$ **(2.11)**

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

For the production of metal and metal oxide several physical and chemical methods are being used extensively. Nevertheless, these techniques require the use of very reactive and toxic reducing agents such as sodium borohydride and hydrazine hydrate, that cause severe impacts on ecosystems. The efforts toward the development of facile, effective and reliable green synthesis processes continue to produce nanomaterials using various organisms (Mandal, et al., 2006) (Jebali, et al., 2011). Hence, it is vitally important to explore a more reliable and sustainable process for the synthesis of nanomaterials for its economic viability, environmental sustainability, and social adaptability as well as the availability of local resources. In order to retain the prices of the final finished nanotechnology based products affordable to consumers, industries must uphold a delicate balance between environmentally sound green processes and their sustainability.

The green nanotechnology based production processes function under green conditions without the toxic chemicals intervention.

Many current studies have showed the potential of iron nanoparticles (NPs) for environmental remediation. Nanoscale materials such as nanoadsorbents, nanofiltration, nanocatalysts, and nanobiocides such as metal and metal oxide nanoparticles are recently being employed for remediation of water and wastewater pollutants. From these metallic nanoparticles, iron nanoparticles (FeNPs) have promising advantages that can withstand environmental pollution. The interest in nanoscale zero valent iron (nZVI) for environmental remediation is growing due to the reactivity of nanoscale iron having a large surface area to volume ratio. The synthesis of iron nanomaterials, such as metallic iron and oxide of iron via a more expedient greener route, is a great step forward in the development of nanomaterials (Lin , et al., 2008) (Gui , et al., 2012).

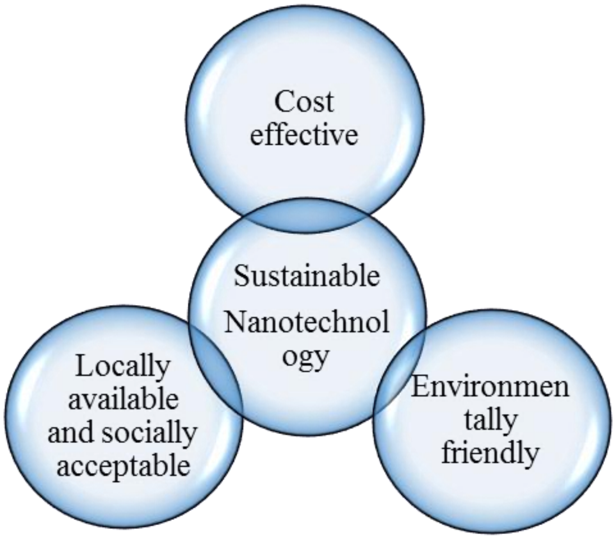


Figure 5 Sustainable green nanotechnologies

Source: (Saif, et al., 2016)

Some environmental applications of greener iron nanoparticles are degradation of dyes, removal of heavy metals, wastewater treatment, antibacterial activity, degradation of pollutant, etc. For example, complete methylene blue (MB) and methyl orange (MO) dyes removal from water was achieved using green tea synthesized nZVI (Fe^0)

nanoparticles (Shahwan, et al., 2011). According to the report of Madhavi et al, zero valent iron nanoparticles (ZVNI) synthesized using Eucalyptus globules leaf extract at room temperature were able to remove Cr(VI) metal and the highest adsorption efficiency was 98.1% at reaction time of 30 min, and ZVNI dosage of 0.8 g/L (Madhavi, et al., 2013). nZVI synthesized using green tea extract able to remove Cr(VI) from aqueous phase by column tests and efficiency was increased by increasing contact time. For the remediation of a contaminated aquifer, nano zero valent suspension is a very conducive, and the use of stable nanoparticles makes this technique successful (Mystrioti , et al., 2014).

Iron nanoparticles mediated by S. jambos (L.) Alston (SJA) extract were able to remove 91.9% of the Cr(VI) in 5 min and 100% in 60 min. As shown in the study, Cr(VI) removal was consistent with reducing capacity of plant extracts (Xiao, et al., 2016).

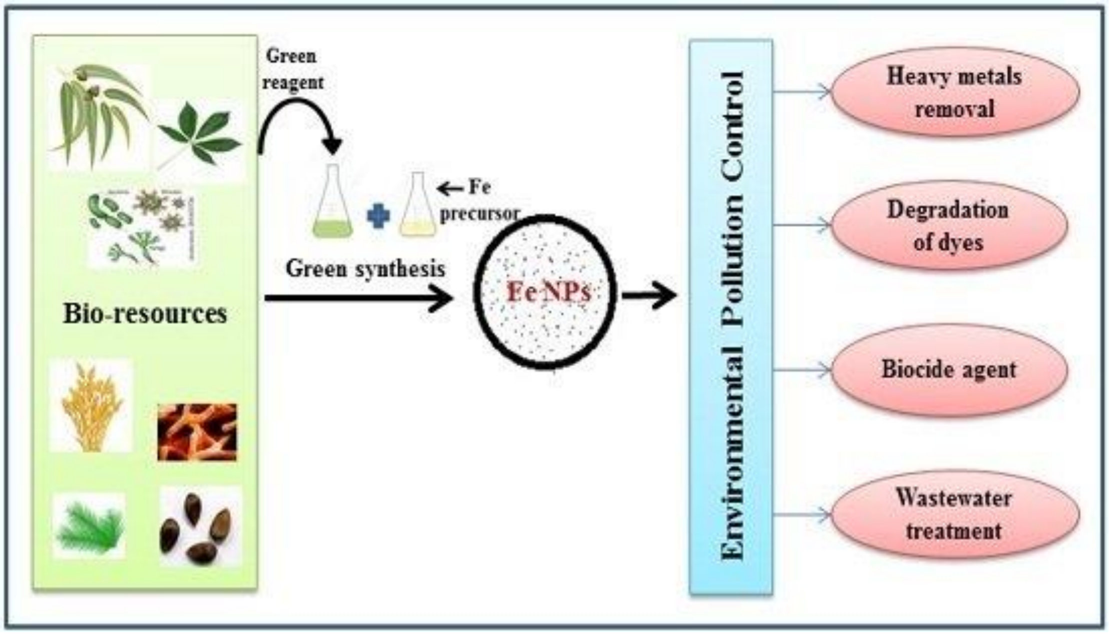


Figure 6 Green synthesis of iron nanoparticles and their application

3. MATERIALS AND METHODS

3.1 Chemicals collection and Equipment setup

All the necessary chemicals were purchased from chemicals suppliers in Addis Ababa and some of them were collected from chemical engineering, material science and engineering, chemistry and drug quality control laboratories in Jimma University. These chemicals are those prepared for research purpose and they are produced for laboratory scale.

The setup of the equipment necessary for experiment was made at chemical engineering and environmental engineering research laboratory for the preparation of the samples. The characterization of samples was done at material science and engineering Jimma institute of technology.

3.2 Preparation of the Teff Straw samples

The dry Teff straw sample was collected from the farm using cleaned plastic bag. The sample was reduced in size by cutting into smaller pieces. Then it was washed using distilled water and diluted sulphuric acid to remove unnecessary soluble impurities. The straw was dried and grounded using an electric miller and allowed to pass through a sieve with the size of 0.063mm. The powdered straw was dried at 110°C for 21 hours in an oven to obtain the powder with constant mass.

Figure 7 Preparation of Teff straw powder

3.3 Methodological Design

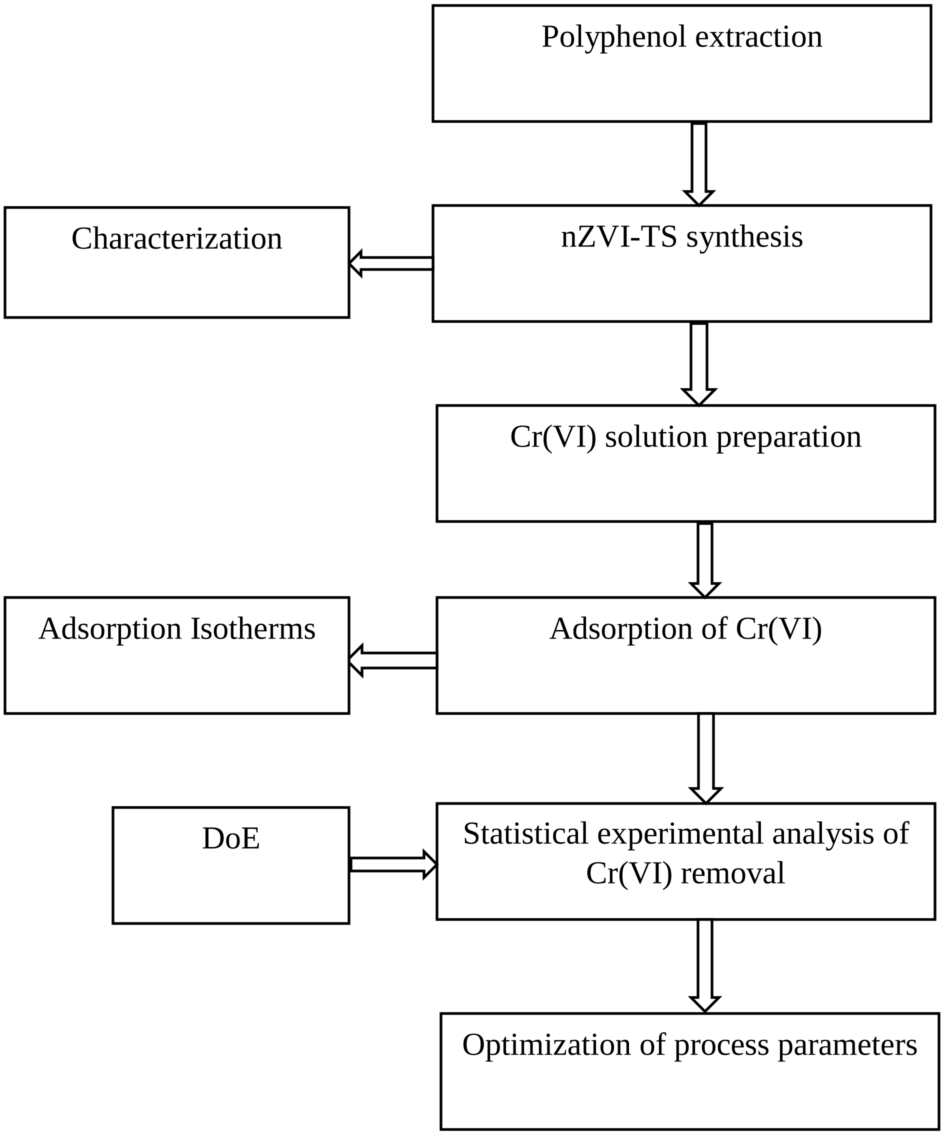


Figure 8 Diagram showing adsorption process

3.4 Polyphenol preparation

Leaves of Eucalyptus Camaldulensis were collected using cleaned plastic bag. The leaves were reduced into smaller sizes and washed using distilled water and diluted sulphuric acid to remove unnecessary impurities. Then the leaves were dried at 50 °C for 48 hours in an oven drier. The dried leaves were milled to make a powder with a size of 0.1mm, 0.25mm and 0.5mm. 2.4 g of powder was measured and added to a conical flask. After that 100ml of deionized water was added to a flask and placed in a water bath heated to 80 °C for 40 minutes. The mixture was filtered using a filter paper and polyphenol extract was collected.

Figure 9 Extracted polyphenol

3.5 Synthesis of Nano Zero-valent Iron and Teff straw supported Nano Zero-valent Iron

Nano Zero-valent Iron (nZVI) was produced by reduction of $FeSO_4$ solution ($FeSO_4.7H_2O$) in the presence of polyphenol extract. 0.5406 g of $FeSO_4.7H_2O$ was measured and added into a flask and stirred in well manner followed by the addition of 10 ml of polyphenol extract. The $FeSO_4$ solution was immediately changed to black color after the addition of polyphenol extract. This change shows the reduction of the iron into zero-valent iron and the formation of iron nanoparticles. The black colored sample was incubated in dark for 24 hours and measured for its maximum absorbance using UV-Visible spectrophotometer. The sample was filtered using vacuum filter and the black solid particle left on the filter paper was collected and dried in an oven at 50°C for 24 hours. After drying, the dried particles were stored in appropriate place for characterization and adsorption of Cr(VI) from aqueous solution.

The preparation of Teff straw supported nano zero valent iron particles were formed by mixing equal amount of both synthesized iron nanoparticles and powdered Teff straw. Then the prepared mixture was named as Teff straw supported nano zero valent iron and abbreviated as nZVI-TS.

Figure 10 Synthesized nZVI using polyphenol

3.6 Characterization of Synthesized nano Zero-valent Iron

3.6.1 UV-Visible spectrophotometer analysis

The black colored sample formed from the mixture of $FeSO_4$ solution and polyphenol extract was measured for its maximum absorbance to analyze the iron reduction and formation of iron nanoparticles. The measurement was done by ignoring the absorbance of distilled water and polyphenol extract.

3.6.2 X-ray diffraction (XRD) analysis of nano Zero-valent Iron

The nZVI particles X- ray diffraction studies were performed with XRD analytical instrument equipped with a monochromator operated at 40 kV and a current of 15 mA with Cu Kα radiation (λ=0.154060 nm). A scan mode was used to collect 2θ data from 10^o to 70^o.

3.6.3 Fourier Transform Infrared (FT-IR) spectrum analysis

FT-IR analysis was used to understand the existence of surface functional groups in metallic interactions and the synthesized nZVI particle was analyzed before and after the adsorption experiments using FT-IR in the spectral range 4000-450 cm^{-1} . The samples used for analysis were pelletized by a very small amount of sample and Potassium Bromide (KBr). The mixtures were added to the mold and 25 kN force was applied by CBR tester equipment to prepare the pellets.

3.7 Preparation of Cr(VI) solution and chemicals

The solutions were prepared by dissolving the adequate quantities of the compounds in distilled water. Stock solution Cr(VI) was prepared by dissolving of $K_2Cr_2O_7$ into distilled water. An experimental solution of the desired concentrations was obtained by successive dilutions and was determined in 540 nm by UV/vis spectrophotometer. Then 10-30 mg/1000 ml of initial Cr(VI) concentrations were prepared. NaOH and HCl were used for the adjustment of pH and controlled by pH meter. The experiments were carried out at room temperature. For all batch experiments, glassware and bottles were washed and rinsed before the use with HNO_3 and then by distilled water.

Figure 11 Prepared Cr(VI) stock solution

3.8 Adsorption experiments

In each adsorption experiment, Cr(VI) solution of known concentration and pH was added to nZVI-TS in Erlenmeyer flaks. The solution in the beaker was mixed by magnetic stirrer at room temperature for different time. After given period of time, the sample was centrifuged. Then the solution was filtered through Whiteman filter paper and analyzed for Cr(VI). The residual Cr(VI) was analyzed by a spectrophotometer at a wavelength of 540 nm. The experiments were done by different dosage of nZVI–TS (0.1, 0.25, 0.5, 1.0 g/100 ml), initial Cr(VI) concentration (10, 15, 20, 25, and 30 mg/1000 ml), initial pH (3, 4.75, 6.5, 8.25 and 10) in contact time (2, 5.25, 8.5, 11.75 and 15 minutes).

Figure 12 Adsorption of Cr(VI)

The removal efficiency ($E_{removal}$) of Cr(VI) was calculated by

$$E_{removal} = 1 - \frac{C_e}{C_o} * 100 \tag{3.1}$$

Where, Co and Ce are initial and equilibrium liquid phase solute concentration in mg/L respectively.

The chromium mass adsorbed per gram of nZVI adsorbent was calculated by difference between the Cr(VI) 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.

$$q_e = \frac{C_o - C_e}{C_o} * V \tag{3.2}$$

Where, q_e is the amount of Cr(VI) adsorbed at equilibrium, V is the volume of chromium solution.

3.9 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.

3.9.1 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 (Ce) in the fluid as follows:

$$\frac{X}{M} = KC_e^n \tag{3.3}$$

Where, K and n are Freundlich coefficients

X is the weight of adsorbate adsorbed on m unit weight of adsorbent

C_e is equilibrium concentration of adsorbate

From equation, for equilibrium conditions:

$$\log(q_e) = \log(k_f) + \frac{1}{n}\log(C_e) \tag{3.4}$$

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

3.9.2 Langmuir Adsorption Isotherm

In the Langmuir model the adsorbent surface was 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:

$$\frac{C_e}{q_e} = \frac{1}{b_{q_{\max}}} + \frac{C_e}{q_{\max}} \qquad \textbf{(3.5)}$$

Where q_e is mass of adsorbate adsorbed over adsorbent (mg/g); C_e, is equilibrium concentration of adsorbate in liquid phase after adsorption (mg/ml); q_{max} is maximum amount of adsorbate that can be adsorbed (mg/g); b is Langmuir isotherm constant. Further, from empirical constant b, separation factor (dimensionless) also called as R factor or equilibrium parameter will also be determined using the equation:

$$R = \frac{1}{1 + bC_o} \qquad \textbf{(3.6)}$$

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; $R=1$ at $b=0$ represents linear adsorption; $R>1.0$ it represents unfavorable adsorption; and $R = 0$ represents irreversible adsorption.

3.10 Design of Experiments

Data analysis was carried out by Design-Expert version 11.1.2.0 software tool by Response Surface Methodology using Central Composite Design to evaluate the effects of the process variables. Central composite design (CCD) is a common and efficient design in RSM; it was selected as a designing tool to investigate the interactive effect of process variables and in building mathematical models to describe the overall hexavalent chromium adsorption process. To study the process parameters, four major factors: nZVI-TS dosage (0.1-1.0 g/100 ml), initial Cr(VI) concentration (10-30 mg/1000 ml), solution pH (3-10) and contact time (2-15 minutes) were selected. Ranges of factors were selected by considering the previous related works The response variable was removal percentage. The design of the experiment helps to optimize and set of combination of process parameters. Significance of the result was set from analysis of variance (ANOVA).

Table 3 Selected values of parameters

Factors	Minimum	Maximum
Dosage(g/100 ml)	0.1	1
Concentration(mg/1000 ml)	10	30
pH	3	10
Time (min)	2	15

The total number of the experiments (N) was estimated using equation 3.7. The experiments were conducted using four independent process variables consisting 16 factorial points, 8 axial points, and 6 center points.

$$N = 2^n + 2n + n_c \tag{3.7}$$

$$N=2^4+2*4+6=16+8+6=\mathbf{30}$$

The optimum conditions obtained using CCD model were validated by conducting laboratory experiments. Statistically, the optimum conditions were obtained by the following model equation:

$$Y = \beta_o + \sum_{i=1}^{k} B_i X_i + \sum_{i=1}^{k} B_i X_i^2 + \sum_{i>j}^{k} \sum_{j}^{k} B_{ij} X_i X_j + \varepsilon \tag{3.8}$$

Where Y is a response of the process, i stands for linear coefficient and j represents quadratic coefficients, x_i and x_j are the independent variables, β_0 is standing for regression coefficient, k is the number of factors in the design, and ε represents an error.

4. RESULT AND DISCUSSION

4.1 Characterization of nano zerovalent iron

4.1.1 UV visible spectrophotometer analysis

The spectrum of UV visible spectrum of iron nanoparticle showed that the absorption peak at wave length of 293.753 nm in polyphenol extract indicates the formation of iron nanoparticles. This is due to visible UV spectra of Eucalyptus Camaldulensis in the wave length of 200-400 nm and the surface plasmon resonance peak at < 300 nm is conforming the phenolic acid and their derivatives. According to Wang et al., 2014 the absorption peak at 300 nm in polyphenol extract formed iron nanoparticles that have no metal properties on the particle surfaces due to polyphenols capping (Wang, et al., 2014). So the formation of the peak at 293.753 nm exhibits the formation of iron nanoparticles and confirms with the works of Wang et al.

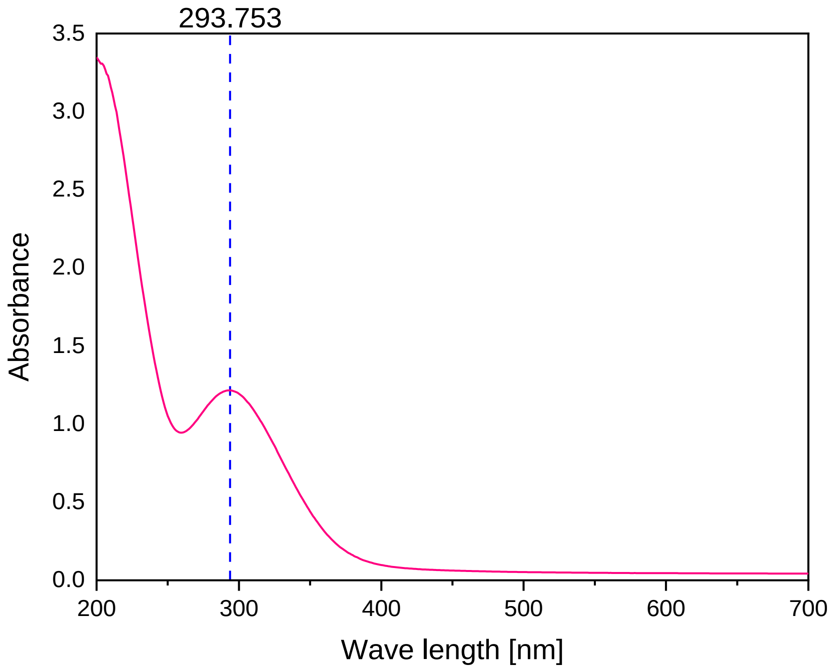


Figure 13 UV visible spectrum of iron nanoparticle

4.1.2 X-ray Diffraction analysis of iron nanoparticles

The patterns of XRD were recorded using a diffract meter with Cu Kα radiation (λ=0.154060nm) from 10° to 70° at a rate of 0.2°/s. the tube current was 15mA and its voltage was 40kV.

The patterns for the polyphenol based iron nanoparticles (Fe-P NPs) sample lack distinct diffraction peaks (no obvious characteristic peaks were observed), suggesting that the nZVI-P formed was amorphous (the absence of any ordered crystalline structure). This indicates the absence of crystalline structure of the particle in which the polyphenols are in complexes with iron. Similarly, the amorphous nature of the developed particle was reported.

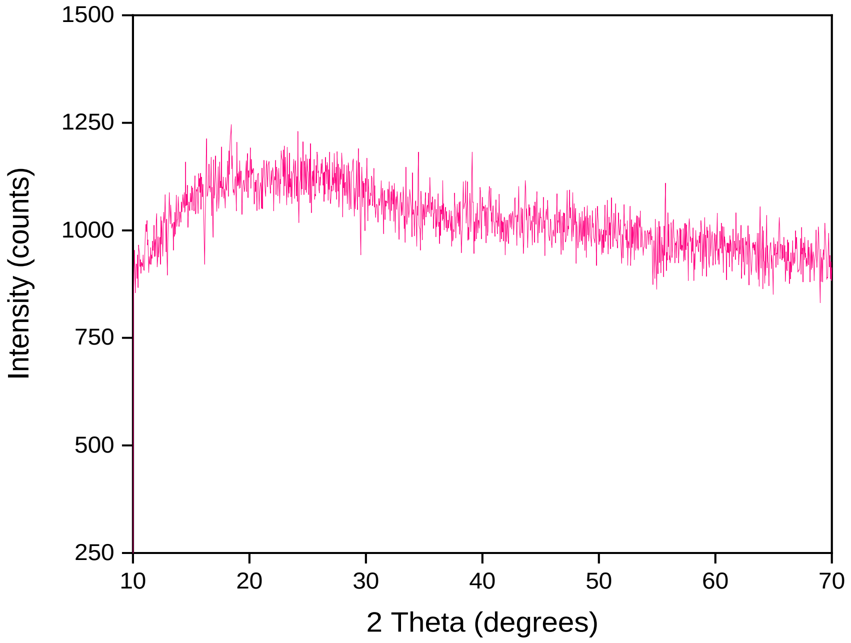


Figure 14 X-ray Diffraction pattern of formed nZVI using Polyphenol extract

4.1.3 FTIR Spectroscopy analysis of nZVI-TS

FTIR analysis provides information about vibrational state of adsorbed molecule and hence the nature of surface complexes. The technique was used to study the spectra of iron nanoparticles. Figure 15 described the FT-IR spectrum of nZVI-TS particles powder sample, revealing several peaks in the spectral range 4000-450 cm^{-1}. The strong, very broad band at 3401.75 and 3432.25 cm^{-1}, were attributed to the -OH stretching vibration of polyphenols and partial oxidation of surface iron to lepidocrocite (FeOOH). The band at 1652, 1633, 1301 and 1288.75 cm^{-1} was also assigned to stretching O-H vibrations. The peak around 2938 cm^{-1} was attributable to the stretching mode of the bulk hydroxyl groups in the goethite (α-FeOOH) structure. The peaks observed at 603 and 580.75 cm^{-1} were due to the characteristic absorption of Fe-O stretching suggesting the Fe-O bond formation in the prepared nanomaterials. Bands at 1072, 877, and 875.5 cm^{-1} were attributed to C-O stretching vibrations. The presence of magnetite nanoparticles can be seen by absorption bands at 586.32, 1623.95, 3401.75 and 3432.25 cm–1. Strong bands at < 900 cm^{-1} in the nZVI alone were attributable to iron oxides on the surface (Zhang , et al., 2011). It was concluded that the spectra show the formation of iron nanoparticles and the bands formed before adsorption and after adsorption were similar.

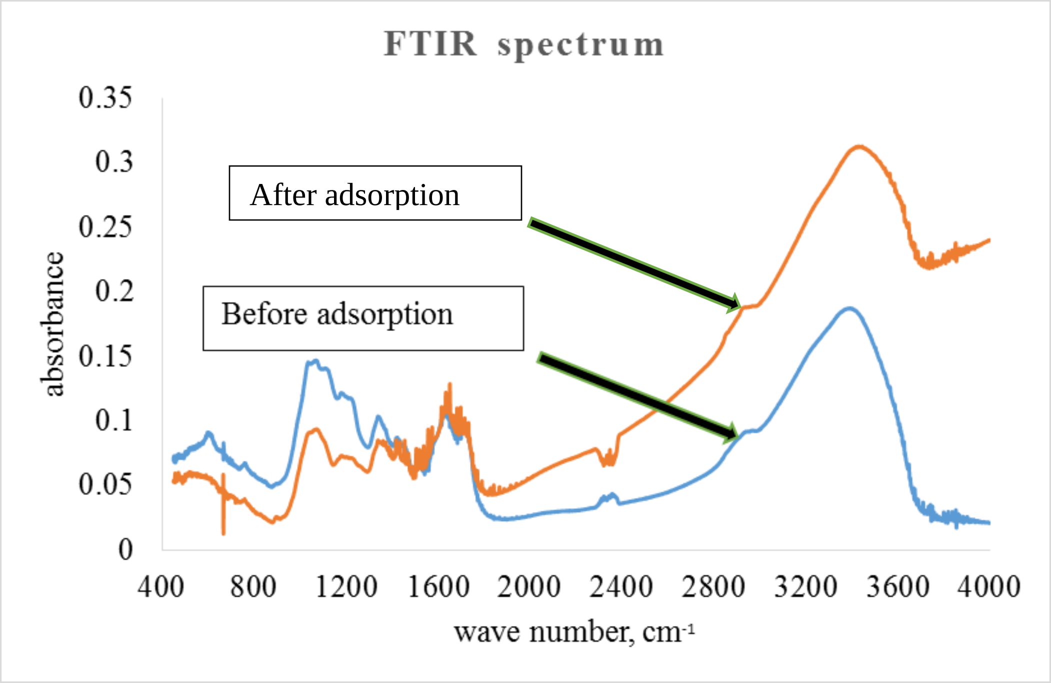


Figure 15 FT-IR spectrum of nZVI-TS particles before and after adsorption

4.2 Effects of experimental parameters on Cr(VI) removal

4.2.1 Effect of nZVI-TS dosage on Cr(VI) removal

The effect of nZVI-TS dosage on the removal of Cr(VI) by nZVI-TS was studied by altering the initial dosage (0.1,0.325 0.55, 0.775, 1.0 g/100 ml), Cr(VI) concentration (10, 15, 20, 25, 30 mg/1000 ml), in time interval (2, 5.25, 8.5, 11,75, 15 min). Figure 16 shows the percentage removal of Cr(VI) at Cr(VI) concentration of 20 mg/1000ml, contact time of 8.5 min and pH of 6.5 using nZVI-TS dosage of 0.325, 0.55 and 0.775 g/100 ml. From this graph it was discussed that the removal efficiency was increased from 99.13% to 99.79%. The relationship between both parameters shows as the amount of nZVI-TS increases the removal of Cr(VI) increases whereas other parameters are constant. As shown on experiment, the increase in Cr(VI) percentage removal is in general increased with an increasing in nZVI-TS dosage. This effect is due to the increase in surface area and adsorption sites/binding sites available for adsorption/more collision with Cr(VI) molecules. As the Fe^0 nanoparticles concentration increases the reactive ZVNI surfaces increases facilitating the Cr (VI) adsorption efficiency and adsorption efficiency reached to 98.1% (Madhavi, et al., 2013). Thus, the results reveal that the nZVI-TS particles are able to remove Cr(VI) more effectively.

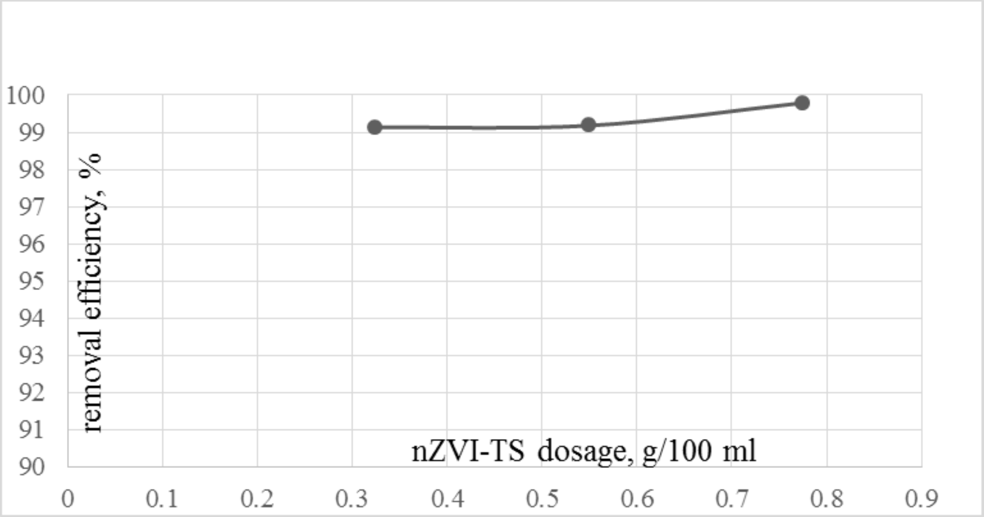


Figure 16 Graph of nZVI-TS dosage versus removal efficiency

4.2.2 Effect of concentration on Cr(VI) removal

The core work of this study was to remove Cr(VI) from aqueous solution. Since Cr(VI) is a toxic heavy metal that causes several problems, its amount should be removed completely and /or lowered in its concentration.

The effect of initial concentrations ranging from 15 to 25 mg/1000 ml, pH = 6.5 and dosage = 0.55 g/100 ml was discussed. As shown in figure 17, the removal of Cr(VI) decrease with an increase in initial concentration of Cr(VI). The result shows the removal efficiency of Cr(VI) decreased from 99.18% to 94.79%. The decrease in the removal of efficiency of Cr(VI) can be described with the reason that the adsorption has reached saturation due to a limited active sites of nZVI-TS. The work of Rahmani et al showed that the percentage removal of Cr(VI) was decreased from 99% to 71.3% as the initial concentration of Cr(VI) increased from10 to 30 mg/1000 ml (Rahmani, et al., 2011). Hence, as the initial Cr(VI) concentration increased ions of Cr(VI) were not completely adsorbed due to the saturation of active sites and the negatively charged of adsorbed Cr(VI) ions electrostatically repel the incoming sorbent ions causing the decrease in removal efficiency. These results are consistent with other researchers' reports.

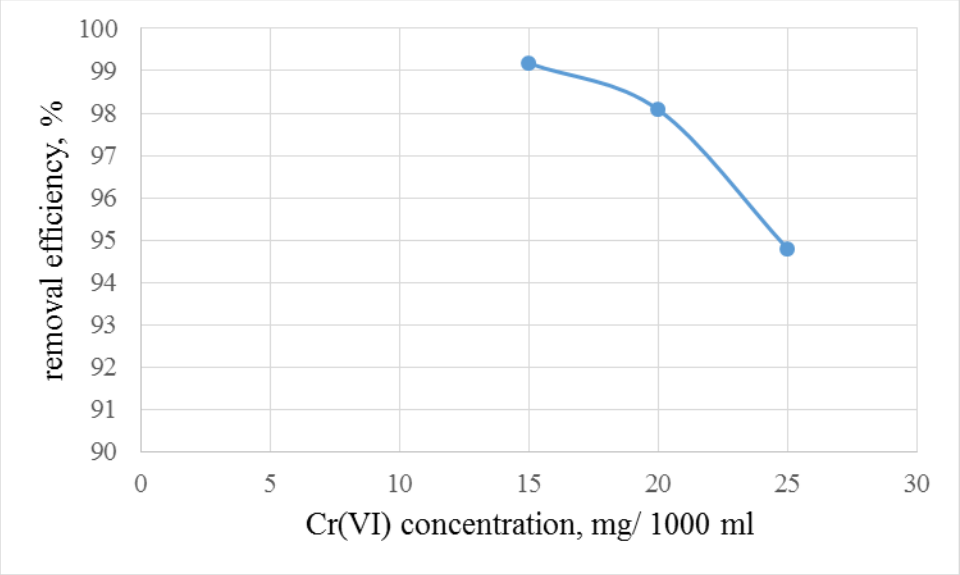


Figure 17 Graph of Cr(VI) concentrations versus removal efficiency

4.2.3 Effect of pH on Cr(VI) removal

The effect of solution pH on the removal of Cr(VI) was discussed ranging from 4.75 to 8.25, time = 8.5 min, Cr(VI) concentration = 20 mg/1000 ml, and nZVI-TS dosage = 0.55g/100 ml. The removal efficiency was increased from 96.84% to 99.79% with increasing the initial pH and decreased from 99.79% to 97.3%. The acidic pH range causes protonation of active groups in the bio-sorbent molecules, developing positive charge and attracting the Cr(VI) species that are negatively charged at that pH ($HCrO4^-$,

$Cr_2O_7^{2-}$, CrO_4^{2-}). As pH increased the $HCrO_4^-$ species shifted to other forms CrO_4^{2-} and $Cr_2O_7^{2-}$ due to the competition between Cr(VI) anions and OH^-.

According to Park et al., 2007, the Cr(VI) removal efficiency increases with the decrease in pH amounts due to the existence of CrO_4^{2-}, $HCrO_4^-$, $HCrO_4$, $HCr_2O_7^-$ or $Cr_2O_7^{2-}$ on the pH of medium in the total concentration. At lower acidic situations, a higher extent of protonated of nanoparticles surface can be formed and resulted in a strong attraction between the negatively charged complex ions and the positively charged surface (Zhang , et al., 2011). In the work of Choppala et al., 2013, low sorption of Cr(VI) anions was observed in alkaline medium. The noticeable sorption of $HCrO_4^-$ was detected but negligible sorption of CrO_4^{2-} where Cr(VI) occurs as $HCrO_4^-$ in acidic soils and as CrO_4^{2-} in alkaline soils (Griffin, et al., 1977). Thus, at lower solution pH the biosorbent functional groups become protonated and easily attract negatively charged chromium. In contrast, at high solution pH deprotonation occurs, functional groups become negatively charged, repelling negatively charged chromium.

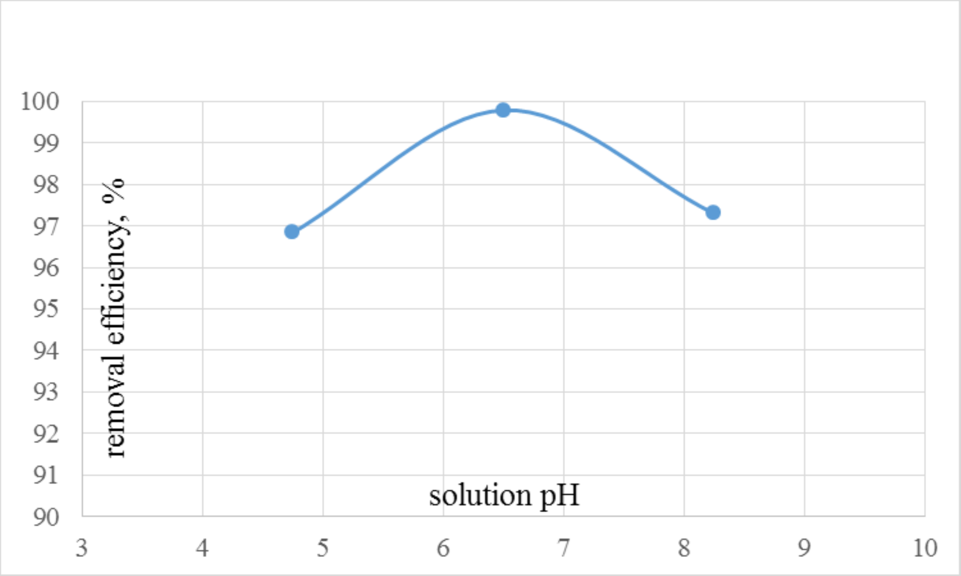


Figure 18 Graph of pH versus removal efficiency

4.2.4 Effect of contact time on Cr(VI) removal

The effect of contact time on Cr(VI) removal by nZVI-TS was discussed by ranging contact time (5.25 to 11.75 min), nZVI-TS dosage = 0.55g/100 ml, Cr(VI) concentration = 20 mg/L and pH = 6.5. As shown in figure 19, the percentage removal of Cr(VI) increased from 94.24% to 99.79% and decreased from 99.79% to 93.38%. During the process, adsorption reaches equilibrium point so that the removal of the hexavalent chromium from the aqueous solution attains its maximum efficiency. The maximum percentage removal was achieved at 8.5 minutes and the efficiency become low when exceeding the optimum contact time. Rahmani et al., 2011 reported that the removal efficiency of Cr(VI) increased as contact time increased from 20 to 120 minutes for initial Cr(VI) concentration of 20 m/L and optimal removal efficiency was resulted at 10 minutes. Therefore, rapid rate of removal efficiency at ≤ 8.5 min was due to the availability of vacant binding sites of the adsorbents for anionic Cr(VI) species in the solution.

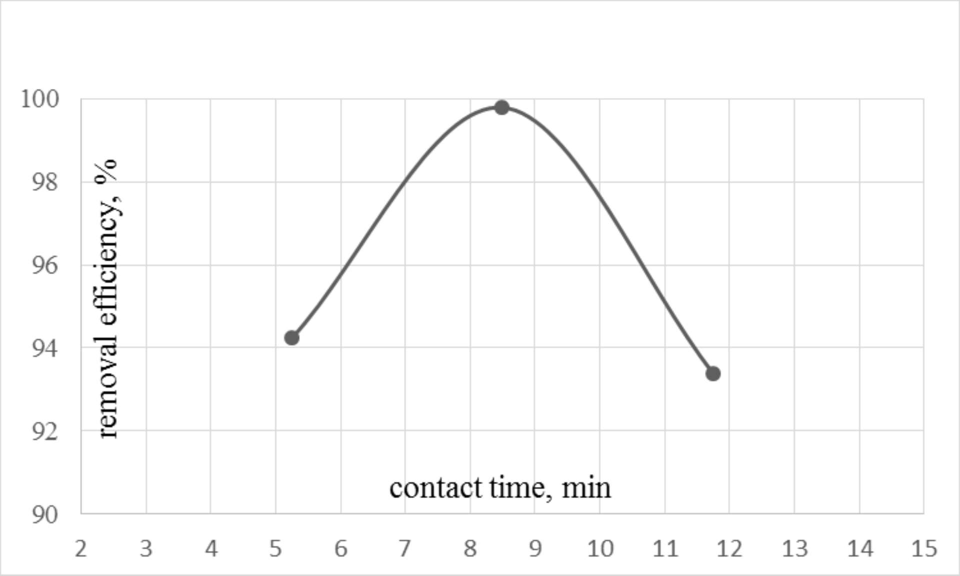


Figure 19 Graph of contact time versus removal efficiency

4.3 Adsorption Isotherms

The results obtained on the adsorption of Cr(VI) were analyzed for Langmuir and Freundlich isotherm model models that correspond to homogeneous and heterogeneous adsorbent surfaces, respectively.

A plot of Ce/qe versus Ce (Figure 20) yield a straight line for the Langmuir equation but a plot of log qe versus log Ce (figure 21) didn't yield a straight line for the Freundlich equation so that the Langmuir model give a good fit for the equilibrium data. Both models were evaluated for their correlation coefficients (R^2) for the adsorption process that give a better fit with the experimental data. As shown in Figure 20, Langmuir isotherm model able to describe the experimental data better than Freundlich isotherm model due to its higher R^2 representing the adsorption process resplendent.

As shown on Table 4, R^2 value for Langmuir model was 0.9987; the values of Langmuir parameters (b and q_{max}) for the adsorption of Cr(VI) were determined from the slope and intercept of Langmuir equation. From Freundlich model equation, R^2 was 0.9625 and the parameters (n and k_f) were determined from the slope and intercept of Freundlich equation.

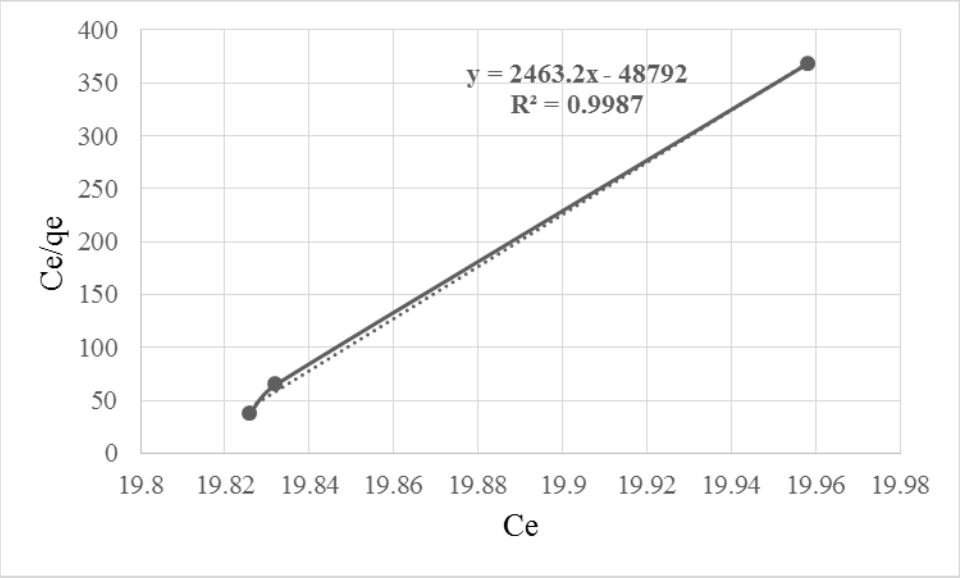


Figure 20 Langmuir isotherm model

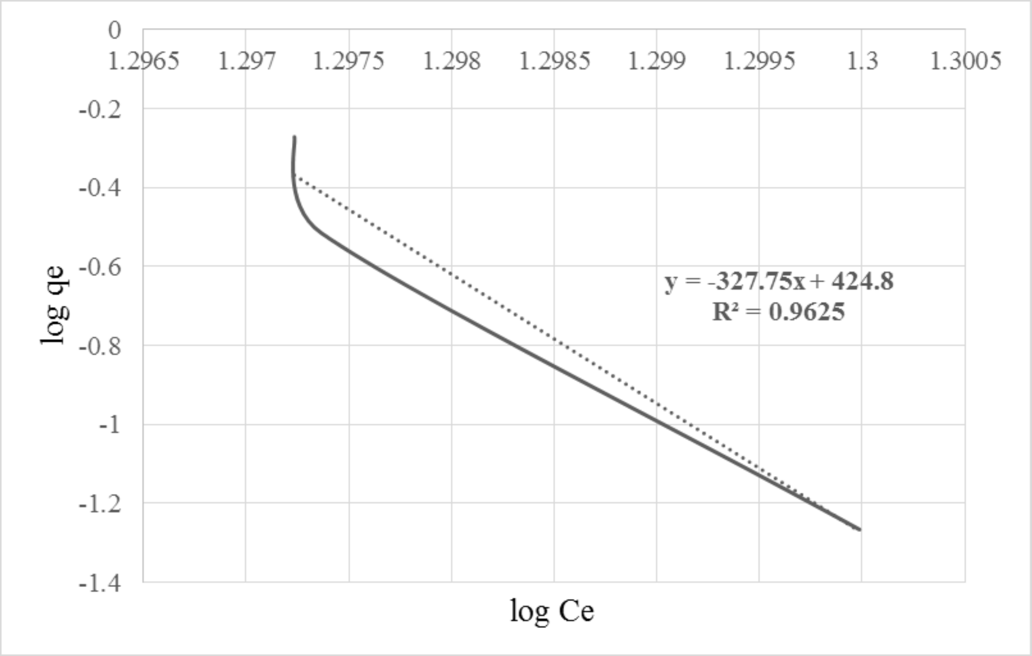


Figure 21 Freundlich isotherm model

To know the suitability of adsorbent for the adsorption i.e. the affinity between adsorbate and adsorbent, the essential feature of the Langmuir isotherm model was described in terms of separation factor, R_L. This dimensionless number/value show the conditions of the adsorption isotherm to be either favorable ($R_L < 1$), unfavorable ($R_L > 1$), linear adsorption (R=1 at b=0) or irreversible adsorption ($R_L=0$). The result obtained from the Langmuir equation $R_L=1$ indicating the adsorption of Cr(VI) on to nZVI-TS was linear and favorable.

The Freundlich parameter n gives an indication of the favorability and capacity of the adsorbent/ adsorbate system. As indicted in table, the value of n obtained from Freundlich equation for Cr(VI) adsorption was a huge number. Renge et al., 2012 reported that the values of n (that reflects the intensity of adsorption) ranging from 2 to 10 represents favorable adsorption condition (Renge, et al., 2012). Therefore, the value obtained from the equation was not consistent with the range for favorable adsorption since it was out of the range. To conclude, the study indicated that the higher value of R^2 and favorable adsorption condition for Langmuir isotherm model represent the model gave a better fit to the experimental data and a favorable adsorption process as compared to Freundlich isotherm model.

Table 4 Values of Langmuir and Freundlich adsorption isotherm parameters and coefficient of regression

Adsorption Isotherm	**Parameters**	**Values**
Langmuir Isotherm	R^2	0.9987
	b	≈0
	R_L	1
Freundlich Isotherm	R^2	0.9625
	n	≈0
	k_f	∞

4.4 Statistical experimental analysis of Cr(VI) removal using ANOVA

As previously stated, a CCD matrix was employed for conducting the experiments and data analysis. The hexavalent chromium removal percentages were measured for 30 runs and recorded in Table 5 and the values of predicted values and residuals obtained were recorded in Table 6.

Table 5 Design (actual) data for ANOVA

Std	Run	Factor 1 A: nZVI-TS dosage g/100 ml	Factor 2 B: Cr(VI) concentration mg/1000 ml	Factor 3 C:pH	Factor 4 D: Contact time min	Response 1 Removal efficiency %
1	15	0.1	10	3	2	88.58
2	23	1	10	3	2	87.58
3	1	0.1	30	3	2	74.61
4	17	1	30	3	2	71.95
5	22	0.1	10	10	2	85.48
6	3	1	10	10	2	89
7	2	0.1	30	10	2	78.09
8	4	1	30	10	2	80.43
9	9	0.1	10	3	15	83.7
10	8	1	10	3	15	83.76
11	21	0.1	30	3	15	75.29
12	20	1	30	3	15	74.86
13	27	0.1	10	10	15	79.67
14	16	1	10	10	15	84.13
15	30	0.1	30	10	15	78.16
16	6	1	30	10	15	81.98
17	25	0.325	20	6.5	8.5	99.13
18	13	0.775	20	6.5	8.5	99.79
19	28	0.55	15	6.5	8.5	99.18
20	11	0.55	25	6.5	8.5	94.79
21	14	0.55	20	4.75	8.5	96.84
22	12	0.55	20	8.25	8.5	97.3
23	24	0.55	20	6.5	5.25	94.24
24	19	0.55	20	6.5	11.75	93.38
25	29	0.55	20	6.5	8.5	98.7
26	18	0.55	20	6.5	8.5	98.9
27	7	0.55	20	6.5	8.5	98.08
28	26	0.55	20	6.5	8.5	98.43
29	5	0.55	20	6.5	8.5	98.76
30	10	0.55	20	6.5	8.5	99.16

Table 6 Central Composite design matrix in coded terms with experimental and predicted values removal efficiency %

Run Order	**Coded factor**				**Removal efficiency (%)**		**Residual**
	A g/100 ml	**B mg/1000 ml**	**C**	**D min**	**Actual value**	**Predicted value**	
1	1	10	3	2	87.58	87.48	0.0979
2	0.55	20	6.5	5.25	94.24	94.59	-0.3533
3	1	30	10	15	81.98	81.91	0.0679
4	1	30	10	2	80.43	80.39	0.0420
5	0.1	10	10	2	85.48	85.56	-0.0779
6	0.55	25	6.5	8.5	94.79	95.24	-0.4533
7	1	10	3	15	83.76	83.85	-0.0861
8	0.1	10	10	15	79.67	79.51	0.1631
9	0.55	20	6.5	8.5	98.43	98.25	0.1844
10	0.1	30	10	2	78.09	78.06	0.0287
11	0.55	20	6.5	8.5	98.9	98.25	0.6544
12	0.55	20	6.5	8.5	99.16	98.25	0.9144
13	0.55	20	4.75	8.5	96.84	96.90	-0.0605
14	1	10	10	15	84.13	84.25	-0.1236
15	1	30	3	2	71.95	72.17	-0.2205
16	0.55	20	6.5	11.75	93.38	93.71	-0.3284
17	1	30	3	15	74.86	74.68	0.1779
18	0.55	20	6.5	8.5	98.08	98.25	-0.1656
19	0.1	10	3	2	88.58	88.71	-0.1254
20	0.55	20	6.5	8.5	98.76	98.25	0.5144
21	0.325	20	6.5	8.5	99.13	99.48	-0.3545
22	1	10	10	2	89	88.88	0.1229
23	0.1	30	3	15	75.29	75.47	-0.1804
24	0.1	30	3	2	74.61	74.39	0.2237
25	0.775	20	6.5	8.5	99.79	100.12	-0.3272
26	0.55	15	6.5	8.5	99.18	99.41	-0.2284
27	0.1	10	3	15	83.7	83.64	0.0581
28	0.55	20	8.25	8.5	97.3	97.92	-0.6211
29	0.55	20	6.5	8.5	98.7	98.25	0.4544
30	0.1	30	10	15	78.16	78.16	0.0021

4.4.1 Analysis of Variances (ANOVA)

The absorption values obtained from experiments using UV-vis spectrophotometer at wavelength of 540 nm were analyzed to evaluate the removal of the Cr(VI) from the aqueous solution. The analysis was done with four factors and three levels of experiments using Central Composite Design. The design provided 30 experiments for which 6 center points were used to increase the accuracy of results obtained and reduce the load of conducting many experiments. As a result, the model provided the effects of the parameters a shown in Table 7.

Table 7 ANOVA for Quadratic model

Response 1: Removal efficiency

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	2516.59	14	179.76	848.35	< 0.0001	**significant**
A-nZVI-TS dosage	6.61	1	6.61	31.18	< 0.0001	
B-Cr(VI) concentration	286.25	1	286.25	1350.95	< 0.0001	
C-pH	17.19	1	17.19	81.11	< 0.0001	
D-Contact time	12.92	1	12.92	60.97	< 0.0001	
AB	0.9851	1	0.9851	4.65	0.0477	
AC	20.63	1	20.63	97.38	< 0.0001	
AD	2.04	1	2.04	9.62	0.0073	
BC	46.55	1	46.55	219.67	< 0.0001	
BD	37.79	1	37.79	178.36	< 0.0001	
CD	0.9752	1	0.9752	4.60	0.0487	
A^2	6.44	1	6.44	30.39	< 0.0001	
B^2	2.25	1	2.25	10.63	0.0053	
C^2	1.86	1	1.86	8.76	0.0097	
D^2	44.65	1	44.65	210.71	< 0.0001	
Residual	3.18	15	0.2119			
Lack of Fit	2.47	10	0.2471	1.75	0.2799	**not significant**
Pure Error	0.7077	5	0.1415			
Cor Total	2519.76	29				

From Table 7 the analysis of variance indicated that the **Model F-value** of 848.35 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. **P-values** less than 0.0500 indicate model terms are significant. In this case A, B, C, D, AC, AB, AD, BC, BD, A^2, B^2, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Fit Statistics

Table 8 Model adequacy measures

Std. Dev.	0.4603	**R^2**	0.9987
Mean	88.80	**Adjusted R^2**	0.9976
C.V. %	0.5184	**Predicted R^2**	0.9966
		Adeq Precision	85.8600

The **Predicted R^2** of 0.9966 is in reasonable agreement with the **Adjusted R^2** of 0.9976; i.e. the difference is less than 0.2. The regression coefficient (R^2) quantitatively evaluates the correlation between the experimental data and predicted response. Since the value of R^2 is closely related to 1, the regression line is perfectly fitted the data of the experiment. From this value it was suggested that only 99.87% of the total variance was described by the developed regression model. Therefore, the obtained correlation coefficient (R^2) from the quadratic model able to represent in the actual laboratory results over 95% confident interval suggests a good adjustment to the experimental results.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable and a ratio of 85.86 indicated an adequate signal. The Lack of Fit F-value of 1.75 implies the Lack of Fit is not significant relative to the pure error. There is a 27.99% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

4.4.2 Regression model equation development

Polynomial regression analyses resulted in a quadratic equation as the best response surface model for explaining the interaction between factors with the response variables in the Cr(VI) removal process. The quadratic model in terms of the coded factor along with the statistics is explained as follows:

Table 9 Coefficients in Terms of Coded Factors

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	98.25	1	0.1276	97.97	98.52	
A-nZVI-TS dosage	0.6327	1	0.1133	0.3912	0.8743	1.0000
B-Cr(VI) concentration	-4.17	1	0.1133	-4.41	-3.92	1.0000
C-pH	1.02	1	0.1133	0.7791	1.26	1.0000
D-Contact time	-0.8848	1	0.1133	-1.13	-0.6433	1.0000
AB	-0.2481	1	0.1151	-0.4934	-0.0028	1.0000
AC	1.14	1	0.1151	0.8903	1.38	1.0000
AD	0.3569	1	0.1151	0.1116	0.6022	1.0000
BC	1.71	1	0.1151	1.46	1.95	1.0000
BD	1.54	1	0.1151	1.29	1.78	1.0000
CD	-0.2469	1	0.1151	-0.4922	-0.0016	1.0000
A^2	6.22	1	1.13	3.82	8.63	42.36
B^2	-3.68	1	1.13	-6.08	-1.27	42.36
C^2	-3.34	1	1.13	-5.74	-0.9341	42.36
D^2	-16.38	1	1.13	-18.78	-13.97	42.36

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-colinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable.

The model equation in terms of coded factors

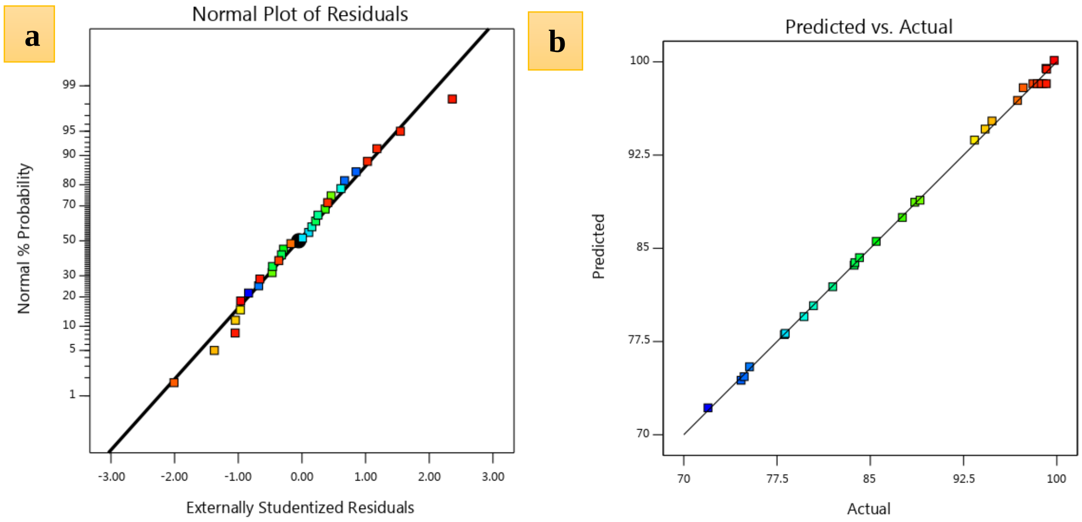
Removal efficiency = $+98.2456 + 0.632727 * A - 4.16515 * B + 1.02061 * C -0.884848 * D - 0.248125 * AB + 1.13563 * AC + 0.356875 * AD + 1.70563 * BC + 1.53688 * BD - 0.246875 * CD + 6.22077 * A^2 - 3.67923 * B^2 - 3.33923 * C^2 -16.3792 * D^2$ **(4.1)**

Where, A is nZVI-TS dosage (g/100 ml); B is initial Cr(VI) concentration (mg/1000 ml); C is solution pH and D is contact time (min).

In this model, the positive signs indicate the positive effects of the factor for an increase in the response and the negative signs indicate the decreasing effect of independent parameters on hexavalent chromium adsorption efficiency. Thus, the equation in terms of coded factors is important to determine the relative influence of process variables by comparing the coefficients of the variables.

4.4.3 Graphical analysis

The figure 22a showed that the normal probability plot indicates the distribution of experimental values were fitted to the straight line and the model satisfies the asumptions in ANOVA which is the errors are approximately normally distributed with constant variance. In figure 22b, the plot of predicted versus actual values indicate that they are approximately related and their ditribution was fitted to straight line which confirms the ANOVA model as it satisfies the assumptions i.e errors are approximately normally distributed with constant variance. From the figure 22c, the plot indicates the residuals and predicted responses have no specific structure i.e. the values of the response were randomly scattered. A plot shows the residuals were fitted with predicted values with the assumption of constant variance and the random scatter justifies that there is no need of alteration to minimize personal error. As shown in figure 22d, the residualas are randomly scattered indicating that the the effects were distributed over all runs.



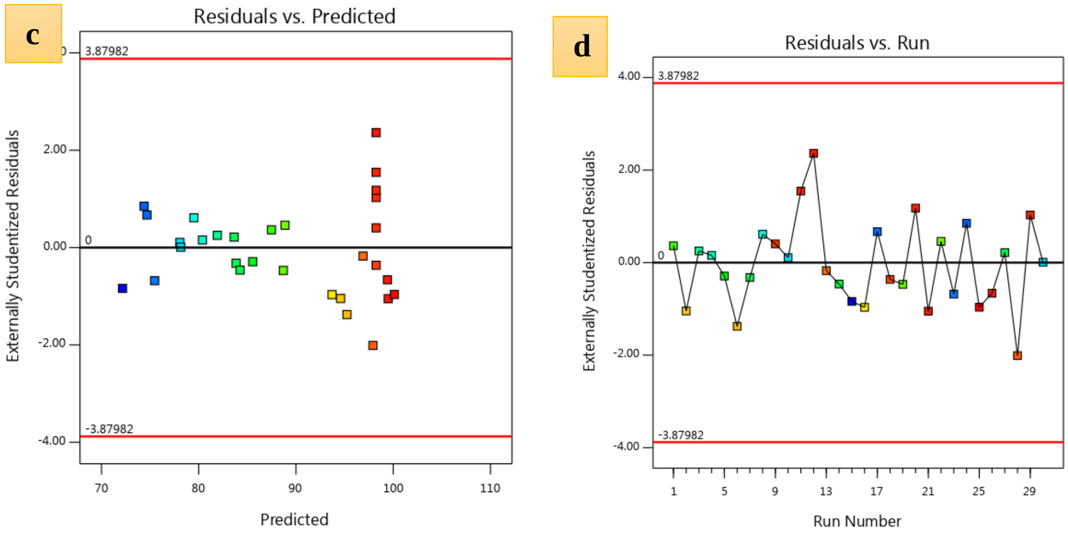


Figure 22 Graphs describing diagnostics of model factors

4.4.4 Effect of model parameters on hexavalent chromium removal efficiency

According to ANOVA result shown in Table 7 and Figure 23, all first-order terms of A, B, C, and D and second-order terms of A^2, B^2, C^2, and D^2 were highly significant to the response variable with a confidence of 99.87%. In addition, the two-factor interaction terms of AC, AB, AD, BC, and BD demonstrated significant effects on the hexavalent chromium removal efficiency Each factors evaluated as their individual effect shows parabolic relation with the response i.e. removal efficiency. The effect of nZVI-TS on removal efficiency shows upward curve and the effect of initial Cr(VI) concentration, solution pH, and contact time show downward curve shape. The perturbation curve shows the trends of all the factors effects n removal efficiency.

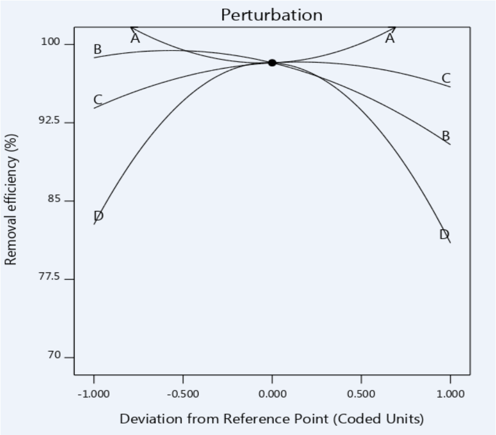


Figure 23 Perturbation curve of process factors

In Figure 24, the ANOVA result shows the contour plots of all factors that represent the effect of interaction between two process variables on removal efficiency. The effect of interaction between nZVI-TS and initial Cr(VI) concentration indicated that removal efficiency was high when initial Cr(VI) concentration is between 15 and 25 mg/L and nZVI-TS dosage is ≤ 0.775 g/100 ml. Higher removal efficiency was observed when solution pH is less than 9 and initial Cr(VI) concentration is less than 25 mg/L and their interaction is significantly affect the efficiency. When the dosage of nZVI-TS is less than 0.4 g/100 ml and greater than 0.7 g/100 ml, and solution pH is less than 7, higher removal efficiency was obtained. At initial Cr(VI) concentration is less than 25 mg/L and contact time is between 5 and 12 minutes, maximum removal efficiency was attained. It was found that higher removal efficiency was attained when dosage of nZVI-TS is less than 0.4 g/100 ml and greater than 0.7 g/100 ml and contact time is between 5 and 12 minutes. The maximum removal efficiency was obtained for the solution pH varies from 5-9 and contact time varies from 5-12 minutes.

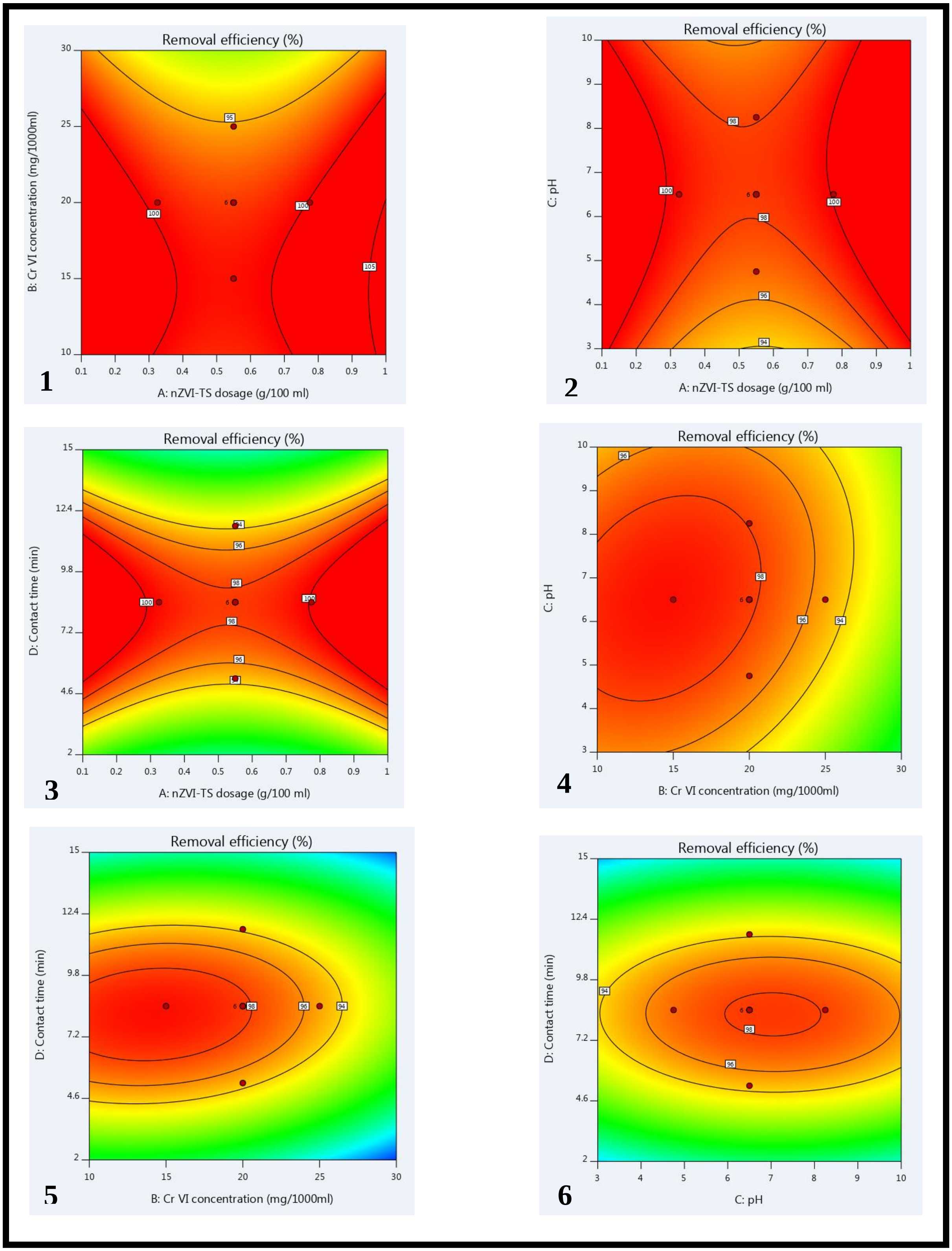
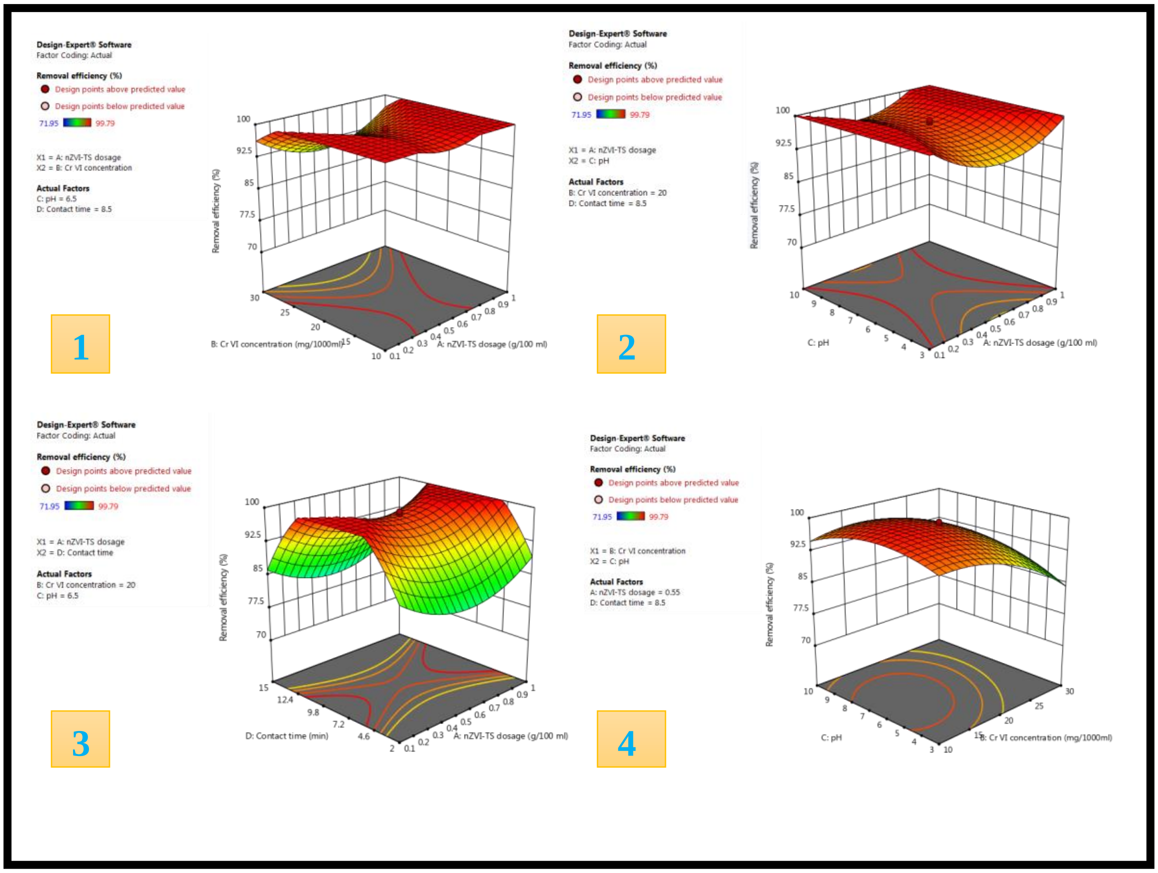


Figure 24 Contour plots of process factors

In addition, Figure 25 shows the 3D plots of all factors that represent the effect of interaction between two process variables on removal efficiency and Figure 26 shows the cube plots of the interaction of nZVI-TS dosage, initial Cr(VI) concentration, and contact time at solution pH of 6.5 on removal efficiency. The effects of the process variables illustrated on these figures confirm the effects illustrated on contour plots.



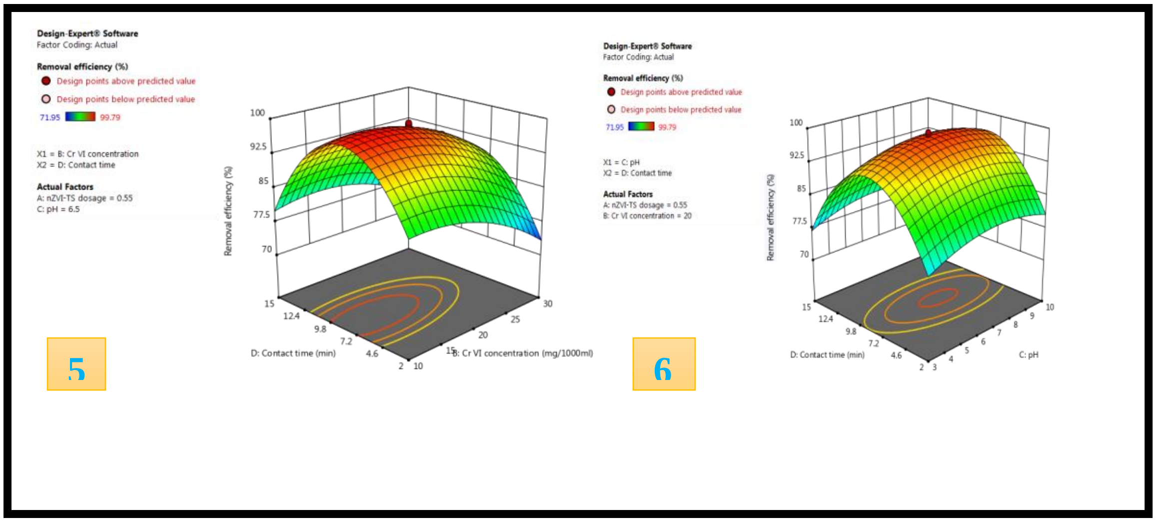


Figure 25 3D plots of process factors

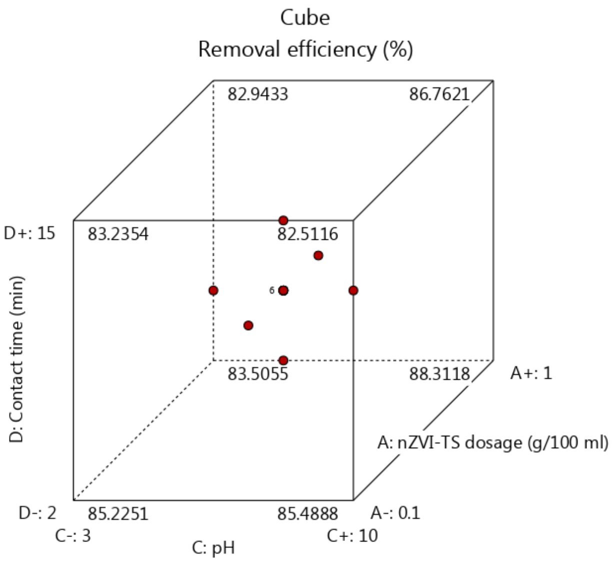


Figure 26 Cube plots of process factors

4.5 Parameters optimization for Cr(VI) removal by nZVI-TS

The experiment of adsorption process for the removal of Cr(VI) from the aqueous solution was done using the parameters such as nZVI-TS dosage, initial Cr(VI) concentration, solution pH, and contact time influencing the experimental process. This experiment involved the interaction of all the parameters to study their effects in order to observe their capability of removal efficiency. But studying all the interaction effects between parameters and analyzing each and every effect is too cost, quiet tedious and time consuming. Thus, a RSM using CCD was able to reduce the difficulties of assignment by optimizing all the parameters influencing the adsorption process within a short period of time.

CCD model gives a greater precision in estimating the overall effects and interactions of the parameters. The model assumes center points and distributes their effects over the other levels instead of replicating the experiments. CCD was employed to reduce the total number of experiments to attain the best overall process optimization. The design model evaluates the interaction of each parameter/factor on response as well as how could the interaction of each parameter alters with the change in the level of the other parameters so that the effects of the parameters interaction could be determined using design of experiments only. The optimization of adsorption parameters for the Cr(VI) adsorption by nZVI-TS were summarized as follows:

Table 10 Constraints of parameters for the optimal Cr(VI) adsorption removal efficiency

Name	Goal	Lower Limit	Upper Limit
A:nZVI-TS dosage	is in range	0.1	1
B:Initial Cr(VI) concentration	is in range	10	30
C:pH	is in range	3	10
D:Contact time	is in range	2	15
Removal efficiency	maximize	71.95	99.79

Adsorption efficiency (removal efficiency) of Hexavalent Chromium was taken as a dependent variable in an optimization process.

Objective function:

$Y = f(A, B, C, \text{and } D) + \varepsilon$

Where Y is dependent variable (removal efficiency) and independent variables: nZVI-TS dosage, Initial Cr(VI) concentration, solution pH, and Contact time were coded as A, B, C, and D respectively. Therefore, final equation in terms of coded factors was taken as an objective function.

Removal efficiency = $+98.2456 + 0.632727 * A - 4.16515 * B + 1.02061 * C - 0.884848 * D - 0.248125 * AB + 1.13563 * AC + 0.356875 * AD + 1.70563 * BC + 1.53688 * BD - 0.246875 * CD + 6.22077 * A^2 - 3.67923 * B^2 - 3.33923 * C^2 - 16.3792 * D^2$ **(4.2)**

As shown in Table 11, optimum conditions of hexavalent chromium adsorption using zero valent iron nanoparticles supported by Teff straw was obtained by selecting from 20 optional number of solutions. Based on this, maximum removal efficiency 99.984% was selected.

Table 11 Optimal possible solution of RSM

Number	nZVI-TS dosage	Cr(VI) concentration	pH	Contact time	Removal efficiency	Desirability	
1	**0.972**	**21.034**	**4.166**	**6.990**	**99.984**	**1.000**	**Selected**

The optimal conditions selected were illustrated on ramps in Figure 27. Optimal points responsible for optimum removal efficiency were indicated on the ramps that connect the values of the process variables. Thus, optimal removal efficiency indicted on ramps was obtained at optimal parameters where nZVI-TS is 0.972 g/100ml; initial Cr(VI) concentration is 21.034 mg/1000 ml; solution pH is 4.166 and contact time is 7 min.

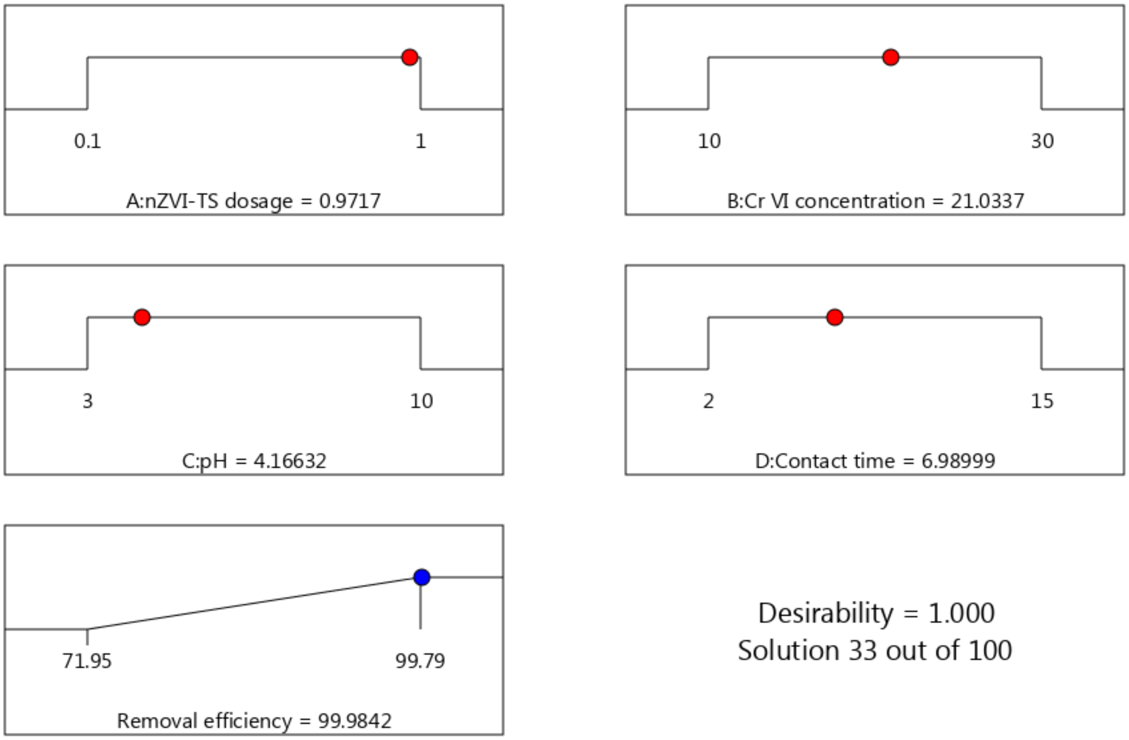


Figure 27 Optimal conditions by ramps

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The study of green synthesis method for the preparation of zero valent iron nanoparticles using Eucalyptus Camaldulensis leaves extract was successful. The use of distilled water as a solvent for the extraction of Polyphenol from Eucalyptus Camaldulensis leaves has given sufficient amount of extract. The Polyphenol extracted was a strong reducing agent and not resulted in loss of reduction power in water. An adsorption of hexavalent chromium (Cr(VI)) by nZVI-TS was analyzed by Potassium dichromate ($K_2Cr_2O_7$) as a model synthetic contaminant in aqueous solution/waste water. The absorbance peak analyzed using UV visible spectrophotometer confirmed the reduction of Ferrous Sulphate solution into zero valent iron and the formation of iron nanoparticles. Zero valent iron nanoparticles synthesized by Polyphenol extract exhibited amorphous structure and the peaks observed on FTIR spectroscopy also sufficiently confirmed the formation of zero valent nanoparticles and existence of surface functional groups in it.

The adsorption process experiment was significantly affected by dosage of zero valent iron nanoparticles, concentration of Cr(VI), solution pH and contact time. Removal efficiency in adsorption process was increased as initial Cr(VI) concentration was decreased indicating that the availability of adsorption sites was limited at fixed amount of adsorbent, hence, leading to percentage removal of Cr(VI) concentration. The percentage removal of Cr(VI) concentration was high at lower to moderate pH of the solution. As a result, the maximum amount of Cr(VI) concentration removed was found 0.042 mg/L. From the adsorption isotherm evaluation, the equilibrium data was fitted better using Langmuir isotherm better than Freundlich isotherm. In addition, statistical experimental analysis tool used was able to analyze all the interaction of the process parameters to study their effect and reduce the work load, hence, minimize the cost of experiments. The optimum removal efficiency which is 99.984% was obtained at optimum values of nZVI-TS dosage of 0.972 g/100 ml, initial Cr(VI) concentration of 21.034 mg/1000 ml, pH of 4.166, and contact time of 6.99 min.

Finally, the results show that the synthesis of zero valent iron nanoparticles supported by Teff straw for the removal of hexavalent chromium from aqueous are effective. The addition of porous biomass as a support overcome instability of iron nanoparticles synthesized, increase removal efficiency and helped to produce low cost and environmentally friendly nanomaterial for the removal of hexavalent chromium from aqueous solution.

5.2 Recommendations

This paper work tried to ground its allotment in synthesizing zero valent iron nanoparticles supported by Teff straw using polyphenol extract for the removal of hexavalent chromium from aqueous solution. For its further study and possibility of commercial application, the following further investigations are recommended.

1. Before practical and commercial applications, the physicochemical interfaces of synthesized iron nanoparticles with environmental media should be studied in detail.
2. The magnetic property, surface area and porosity of synthesized iron nanoparticles should be clearly studied for the enhancement of adsorption efficiency.
3. Thermodynamic parameters and kinetic model should be studied to analyze adsorption mechanism.
4. The use of porous biomass should be promoted for the economic use and environmental protection.

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APPENDIX A

A-1. Extraction of polyphenol

Figure A-1 Production process of polyphenol extract

A-2. Preparation of Teff straw

Figure A-2 Preparation process of Teff straw powder as a support

A-3. Synthesis of zero valent iron nanoparticles

Figure A-3 Synthesize of nZVI using polyphenol extract

A-4. Characterization of synthesized iron nanoparticles

Figure A-4 UV visible analysis for absorbance of nZVI

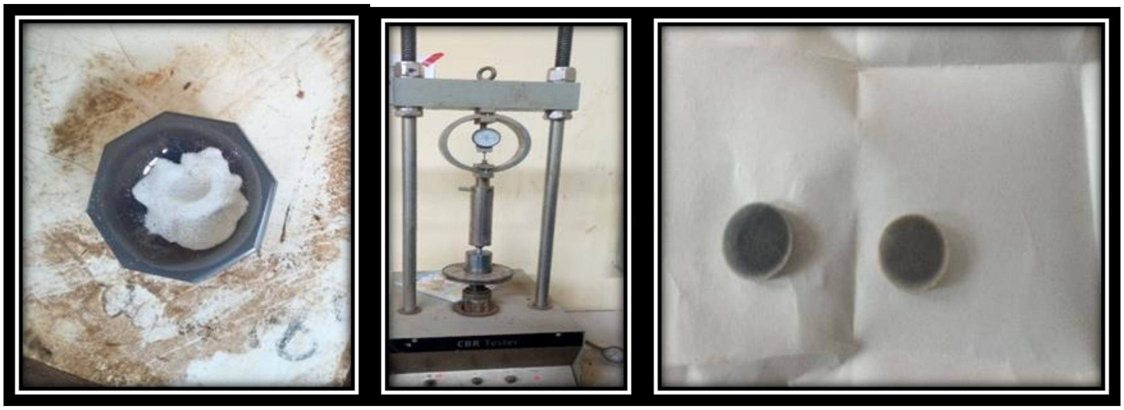


Figure A-5 Preparation of nZVI pellet for FT-IR analysis

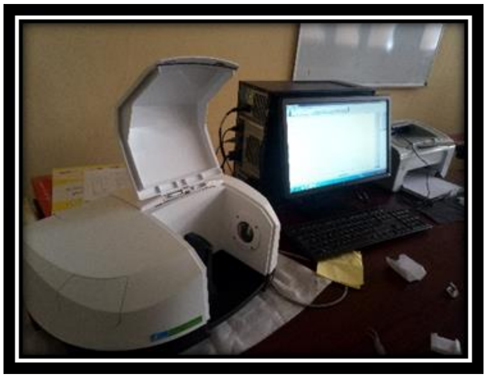


Figure A-6 FT-IR analysis process for nZVI

A-5. Adsorption experiments

Figure A-7 Adsorption of Cr(VI)

APPENDIX B

Table B-1 Final concentration data after adsorption

Std	Run	Factor 1 A: nZVI-TS dosage g/100 ml	Factor 2 B: initial Cr(VI) concentration mg/1000 ml	Factor 3 C:pH	Factor 4 D: contact time min	Response 1 removal efficiency %	Final concentration g/L
1	2	0.1	10	3	2	88.58	0.001142
2	29	1	10	3	2	87.58	0.001242
3	15	0.1	30	3	2	74.61	0.007617
4	17	1	30	3	2	72.28	0.008316
5	25	0.1	10	10	2	85.48	0.001452
6	18	1	10	10	2	89	0.001100
7	8	0.1	30	10	2	78.09	0.006573
8	22	1	30	10	2	80.43	0.005871
9	6	0.1	10	3	15	83.7	0.001630
10	1	1	10	3	15	83.76	0.001624
11	11	0.1	30	3	15	75.29	0.007413
12	7	1	30	3	15	74.86	0.007542
13	5	0.1	10	10	15	79.67	0.002033
14	14	1	10	10	15	84.13	0.001587
15	9	0.1	30	10	15	78.16	0.006552
16	19	1	30	10	15	81.98	0.005406
17	28	0.325	20	6.5	8.5	99.13	0.000174
18	21	0.775	20	6.5	8.5	99.76	0.000048
19	20	0.55	15	6.5	8.5	99.18	0.000123
20	26	0.55	25	6.5	8.5	94.79	0.001302
21	12	0.55	20	4.75	8.5	96.84	0.000632
22	10	0.55	20	8.25	8.5	97.3	0.000540
23	13	0.55	20	6.5	5.25	94.24	0.001152
24	27	0.55	20	6.5	11.75	93.38	0.001324
25	30	0.55	20	6.5	8.5	98.43	0.000314
26	3	0.55	20	6.5	8.5	98.9	0.000220
27	16	0.55	20	6.5	8.5	98.96	0.000208
28	24	0.55	20	6.5	8.5	98.08	0.000384
29	4	0.55	20	6.5	8.5	99.16	0.000168
30	23	0.55	20	6.5	8.5	98.7	0.000260

For Co= 20 mg/L and Ce=19.958 mg/L, $E_{removal} = 1 - \frac{C_e}{C_o} * 100 = 1 - \frac{19.958}{20} = 99.79\%$

Final concentration = (20-19.958) mg/L= 0.042 mg/L

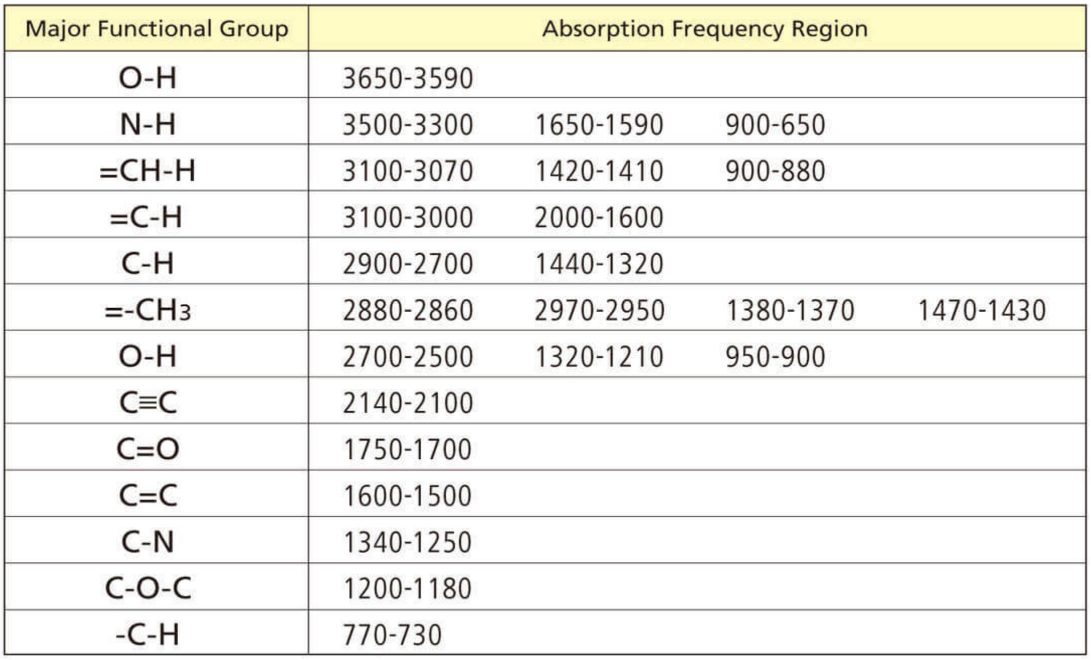
Table B-2 Data used for analysis of Freundlich isotherm model

Dosage (mg/ml)	**Ce** (mg/ml)	**Co-C=X** (mg/ml)	**X/M=q**	**log Ce**	**log qe**
0.325	19.826	0.174	0.535385	1.297235	-0.27133
0.55	19.832	0.168	0.305455	1.297367	-0.51505
0.775	19.958	0.042	0.054194	1.300117	-1.26605

Table B-3 Data used for analysis of Langmuir isotherm model

Dosage (mg/ml)	**Ce** (mg/ml)	**Co-C=X** (mg/ml)	**X/M=q**	**Ce/qe**
0.325	19.826	0.174	0.535385	37.03132
0.55	19.832	0.168	0.305455	64.92619
0.775	19.958	0.042	0.054194	368.2726

Table B-4 Functional groups and their absorption frequency region



Major Functional Group	Absorption Frequency Region			
O-H	3650-3590			
N-H	3500-3300	1650-1590	900-650	
=CH-H	3100-3070	1420-1410	900-880	
=C-H	3100-3000	2000-1600		
C-H	2900-2700	1440-1320		
$=-CH_3$	2880-2860	2970-2950	1380-1370	1470-1430
O-H	2700-2500	1320-1210	950-900	
C≡C	2140-2100			
C=O	1750-1700			
C=C	1600-1500			
C-N	1340-1250			
C-O-C	1200-1180			
-C-H	770-730			

Source:www.chromatographytechniques.com/sites/chromatographytechniques.com/files/legacyimages/Table-2.jpg

Table B-5 Build information from ANOVA

Factor	Name	Units	Type	Min	Max	Coded Low	Coded High	Mean	Std. Dev.
A	nZVI-TS dosage	g/100 ml	Numeric	0.1000	1.0000	-1 ↔ 0.10	+1 ↔ 1.00	0.5500	0.3394
B	Cr VI concentration	mg/1000ml	Numeric	10.00	30.00	-1 ↔ 10.00	+1 ↔ 30.00	20.00	7.54
C	pH		Numeric	3.00	10.00	-1 ↔ 3.00	+1 ↔ 10.00	6.50	2.64
D	Contact time	min	Numeric	2.00	15.00	-1 ↔ 2.00	+1 ↔ 15.00	8.50	4.90

Table B-5 Model Comparison Statistics

PRESS	8.52
-2 Log Likelihood	17.79
BIC	68.81
AICc	82.08

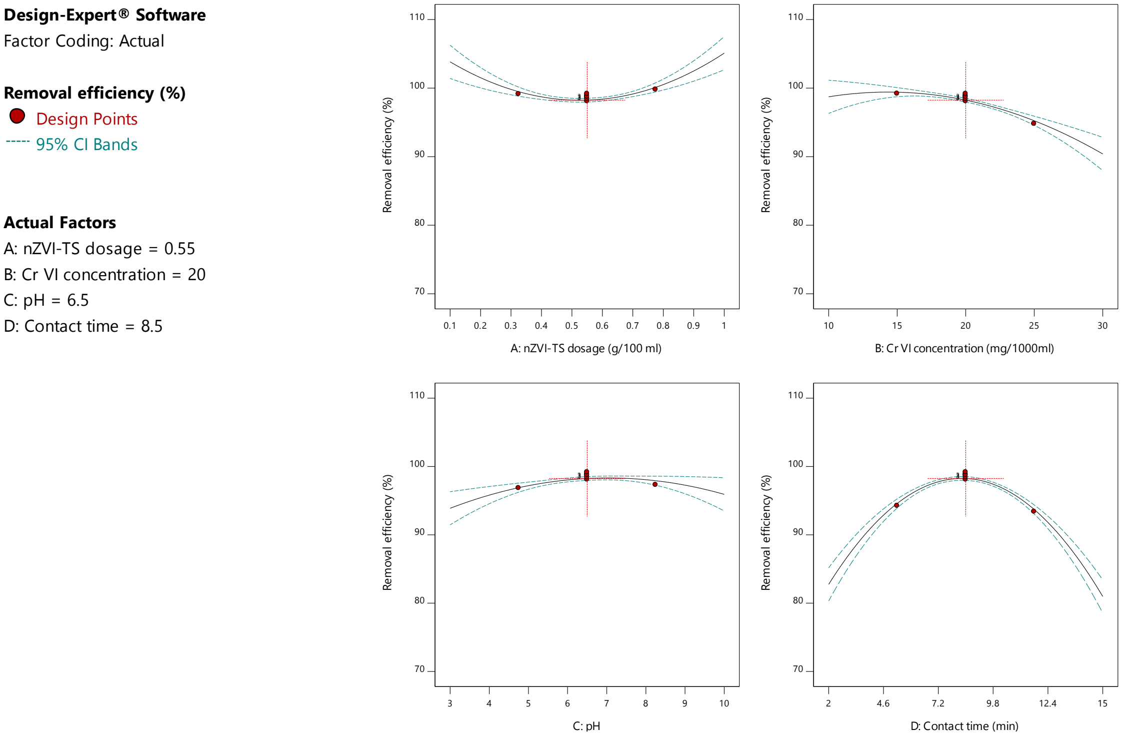


Figure B-1 One factor effect on removal efficiency

Table B-6 Fit Summary from ANOVA

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.4685	< 0.0001	-0.0113	-0.2931	
2FI	0.9830	< 0.0001	-0.2647	-2.5919	
Quadratic	**< 0.0001**	**0.2799**	**0.9976**	**0.9966**	**Suggested**
Cubic	0.9943	0.0335	0.9955	0.8849	Aliased

Table B-7 Lack of fit tests

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Linear	2196.09	20	109.80	775.80	< 0.0001	
2FI	2087.12	14	149.08	1053.30	< 0.0001	
Quadratic	**2.47**	**10**	**0.2471**	**1.75**	**0.2799**	**Suggested**
Cubic	2.04	2	1.02	7.22	0.0335	Aliased
Pure Error	0.7077	5	0.1415			